INTERNATIONAL ASSOCIATION
OF GEOCHEMISTRY AND COSMOCHEMISTRY

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OF EXPLORATION GEOCHEMISTS

EXPLORATION GEOCHEMISTRY 1990

PROCEEDINGS OF THE THIRD INTERNATIONAL
JOINT SYMPOSIUM OF THE IAGC AND THE AEC,
PRAGUE, CZECHOSLOVAKIA 1990

EDITOR: F. MRŇA

Geological Survey, Prague
and Czech Academy of Sciences,
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PREFACE

The Third International Joint Symposium of the Association of Exploration Geochemists and the Working Group for Geochemical Exploration of the International Association for Geochemistry and Cosmochemistry was simultaneously the 5th Symposium of the Working Group and the 14th Symposium of AEG. It was also the first international Symposium on Geochemical Exploration held under new conditions in international relations facilitating contacts among specialists from various countries. This was fully proved by the presence of numerous geochemists who attended such international gathering for the first time.

Another important feature which influenced the program of the Symposium was a basic and long-term change in work objectives of many exploration geochemists who converted from search for new mineral resources to solving a wider range of problems associated with applied geochemistry and particularly with geochemical problems of the environment. This increasingly pronounced trend has two major reasons:

1. More rational and efficient exploitation of mineral resources reduces their relative consumption at a simultaneous growth of the world production. Changes in the political climate in the world removed many barriers which hindered the development of the world mineral market and thus reduced the pressure put upon search for new deposits in various parts of the world;

2. More attention is rightfully given to acute problems of preserving and forming an optimal environment. Geochemistry plays an irreplaceable role because changes in concentrations and cycles of individual elements and compounds studied by geochemistry are also connected with numerous anthropogenic alterations of natural conditions and have á negative impact on the development of the biosphere including man.

As joint international conferences organized by IAGC and AEG are attended by exploration geochemists from all over the world, it is possible to asses periodically the trends in exploration geochemistry assuming from the orientation and subjects of given papers. Some fundamental changes can be recognized since the last joint Symposium held in Orléans, France in April 1987. These changes are considered to be very useful for further development and advances in applied geochemistry. Let me summarize some of these trends.

1. Much more attention apeears to be paid to geochemical survey at various scales and in diverse climatic and morphological conditions. This geochemical mapping allows to apply methods and works for solving a great variety of heterogeneous problems which can be characterized as follows:
   - a/ utilization of results of geochemical survey to solve geochemical and metallogenic problems, to study geochemical evolution of certain examined region or a given geological object;
   - b/ acquisition of valuable data to be used in preparation of prognostic studies for certain areas from the viewpoint of mineral potential, for the occurrence of individual minerals or the evidence of genetically different deposits;
   - c/ geochemical survey brings fundamental geochemical parameters for a certain region /e.g. geochemical background values, variation in geochemical field, etc./ which are of great importance when designing more detailed geochemical prospecting, follow-up programs or exploration

works. They also facilitate selection of pathfinder elements, prospecting grid with respect to the manifestation of local metallogenic processes in the primary geochemical environment and with regard to the origin of secondary geochemical anomalies.

d/ very promising and prospective is the application of geochemical survey in enviromental studies of individual regions, to recognize and identify major pollutants, their source and behavior in certain geochemical environment.

So far, the contents and methods of geochemical mapping were rather dissipated than unified. Even though the diversity of geochemical survey, its objectives and various conditions under which it is applied deserve modifications in methods, on the other hand any trends towards unification of methods or procedures, whenever it is possible and useful, are to be welcomed. These trends which, thanks to A. G. Darnley, the Project Manager of IGCP project no. 259 "International geochemical mapping" and his collaborators, are of greate importance in helping to compile international geochemical maps and atlases and eventually to compile the geochemical atlas of the world.

Numerous excellent papers dealing with these subjects are published in Extended Abstracts of the Symposium. The contributions of P. Eden and A. Bjorklund /Finland/, L.S. Galetskij, B.A. Gorlitskiy and V.I. Pokhtarenko /USSR/, P.V. Koval /USSR/ are examples of papers devoted to these topics and which are published in Proceedings of the Symposium.

Many papers dealing with the application of geochemical survey in enviromental studies are also given in Extended Abstracts. The Proceedings are reserved for fundamental and comprehensive papers related to the environmnet. Among them the follwong are to be mentioned: V.K. Lukashev /USSR/ on geochemistry of technosphere, O. Weinzierl /Austria/ on methods distinguishing natural and man coused geochemical anomalies, V. Cílek, F. Mrňa, M. Žežulka /CSFR/ on geochemical investigation of metallurgical waste, I. K. Nezhdanova, I.P. Suetin /USSR/ on geochemical survey of urban agglomerations and P.W. Lahermo /Finland/ on the application of regional geochemical maps for environmental studies.

2. Geochemistry can provide objective data for the investigation of processes of the Earth crustal evolution which occurred during geological history as well as in recent or present times. The paper of J.A.C. Fortescue and E.A. Vide /Canada/ on geochemical variation in lacustrine sediments in Ontario may serve as an excellent example of such studies.

3. The majority of given papers and published articles both in Extended Abstracts and Proceedings shows considerable extention of the scope which more often exceed the frame of classical exploration geochemistry. These studies are focused on prognostication of mineral deposits based on geochemical data /e.g. D.A. Dodin - USSR, Y.I. Chetvertkov - USSR, V.D. Kozlov, L.N. Svadkovskaya - USSR, N.P. Piskorsky - USSR and others/, on relation between ore-bearing geological complexes and the location of metallic mineral deposits /K. Breiter - CSFR/, on modelling of ore processes and ore fields /e.g.D.A. Dodin, M.A. Sadikov, I.I. Sidorov, N.A. Durasova et al, A.I. Grabezhev, M.A. Kukulian, M. Voitsekhovskaya - all from USSR/.

4. A progress in developing individual prospecting methods can be also observed. Interesting papers dealing with heavy mineral survey are published in Extended

Abstracts /e.g. Y.T. Maurice - Canada, N.G. Patyk-Kara-USSR, J. Simek - CSFR, T. Alapieti et al. - Finland, M. Viladevall et al. - Spain, and some others/. Only few papers published in Proceedings deal with this subject /V.Y. Zagosky et al. - USSR and V. Peuraniemi - Finland/.

Very interesting papers from the viewpoint of methodology are devoted to biogeochemical procedures in exploration geochemistry. A.L. Kovalevskyi concentrated on basic principles of biogeochemistry whereas B.A. Kolotov et al., A.L. Kovalevskyi O.J. Kovalevskaya /USSR/ are focused on the application of biogeochemical methods. V.A. Zagoskin /USSR/ employs microbiogeochemical methods in search for deap seated mineral deposits. Boiogeochemical methods are widely represented in Extended Abstracts /e.g. C.E. Dunn - Canada, G. Camacho et al. - Spain, Ping Gao -China, H. Neybergh et al. - Belgium, P.V. Ivashov and M.G. Opekunova - USSR/. These papers demostrate results of biogeochemical methods of prospecting in various environment /permafrost, loess/ as well as their application in search for diverse types of mineralization /precious metals, base metals, etc./.

Many papers are devoted to improving the efficiency of geochemical prospecting in desert areas /V.A. Bugrov - USSR, R. Marmi - Algeria, B. Murrel - Australia, M. Shirav et al. - Israel/.

5. Long-term trends in more complex investigation of geochemical samples could have been observed even in papers presented at the Symposium´s sessions. The contribution of L.V. Barsukov et al. /USSR/ on methods and character of ammonia halos around gold deposits and the paper of A.A. Ganeyev et al. /USSR/ on improvement of analytical determination of Hg in various types of geochemical samples may serve as an example of lectures dealing with this topic. Some other papers of this kind are published in Extended Abstracts.

Very important papers are those devoted to the mode of occurrence of individual elements in geochemical samples. The paper of V. Peuraniemi /Finland/ on the distribution of zinc in glacial deposits may belong to this group of topics.

I assume this particular subject to be of utmost significance for further development and advances of applied geochemistry. It appears to be neccessary to pay much more attention to this field. Consequently, the mode of occurrence of elements controls their behavior during weathering processes, their migration mobility, their interaction with individual compouds of the biosphere and eventually controls their share during the origin of genetically different types of geochemical anomalies. Consequently, when knowing the mode of occurrence of an element, the character of geochemical processes leading to its manifestation in primary or secondary environment can be more easily decoded and interpreted.

The investigation of geochemical parameters of the environment, geomedicine and agrogeochemistry are the fields shere our knowledge of interactions of elements or compounds in diverse environment, the origin, existence and decomposition of complex compounds, colloids and suspensions, is limited. These subjects, however, obviously deserve to be given more attention.

It would be also useful to follow-up already classical investigation of stability of a given element in geochemical sample or to what extent it can be extracted or recovered using various methods of decomposition. The standard ratio cxMe:hxMe can be followed in this kind of investigation /i.e. what portion of an element can be extracted using weak acid attack without breaking down the mineral vs. stronger attacks like hot extraction of fusion of fusion, etc./.

There is no doubt that atlases of the environment compiled on this ground would show elements and their behavior from a different angle. They will show to what extent the elements are "available" for the biosphere that would further positively affect geomedicinal and agrogeochemical studies, to make them more specific and efficient.

6. Lower detection limits and higher reliability of analytical methods will improve the interpretation of geochemical anomalies including yet neglected negative anomalies. The investigation of processes of leaching of some elements, their removal or redistribution is to provide new ideas on the origin of some mineral deposits, on the origin of primary geochemical haloes, etc. It will also contribute to a new identification of promising areas for the occurrence of mineral deposits just on the ground of cheap reinterpretation of already existing geochemical data. Systematic studies of negative anomalies will contribute to decipherment of basic criteria for recognition or distinction of significant from unimportant anomalies and to understand their origin. Not too much attention has been paid yet to this subject in general including this Symposium.

7. Exploration geochemistry tends more often to deal with problems that by far exceed its own subject and scope. New inter-science trends led to creation of such branches like agrogeochemistry, geomedicine, technogeochemistry and others. It is obvious that exploration geochemistry has its share in their origin. It provides methods, procedures, experience and particularly a vast amount of data that has been yet collected. Multipurpose and multiple application of geochemical information leads consequently to a relative reduction of costs of geochemical works, to putting pressure on getting more complex data and to having better access to geochemical data bases, their exchange and eventually may contribute to the establishment of international data bases. If these trends are to happen, then the exploration geochemistry and geochemistry as a whole will benefit from this development. New ideas will be certainly gained and neš possibilities for its application will be opened.

8. Transition from analysis of limited number of elements to larger sets of elements in geochemical samples is associated with a substantial increase of geochemical information. This quantitative increase of data, however, has no adequate reaction in a new approach towards compilation and plotting of geochemical maps. It may be useful to switch from monoelemental maps to a suitable selection of element associations which would facilitate the determination of the treshold of a geochemical anomaly and the discrimination of positive and negative anomalies from the viewpoint of their importance for a follow-up exporation program. Similarly, when using geochemical data for other purpose it would be essential to know if, for instance, the biological reactivity of a certain element is reduced or strenghtened by the presence of other elements or complex compounds which is to be taken into consideration when doing interpretation.

The proceedings which summarize the main ideas and trends presented at the Symposium illustrate both these facts by presenting various geochemical schools from more than 40 countries all over the world as well as by the wide range of discussed problems. We seem to be shifting from genuine exploration geochemistry to applied geochemistry, to solving the prognostication of regional mineral potential and to topical problems of methodology for compiling international geochemical maps and eventually a geochemical atlas of the world.

When selecting papers for Symposium Proceedings and Extended Abstracts, an effort has been made to include also contributions which were not directly connected with the field of exploration geochemistry, but which brought new ideas and topics assumed to be very useful for futher developments and advances in exploration geochemistry and for employment of their methods in other scientific and practical fields.

Already mentioned diversity of papers led us to arrange them in alphabetical order instead of following the subject arrangement. As we tried to speed up the printing of submitted paper to make them available for geochemists as soon as possible, the articles are published in the original form with almost no language corretion. Consequently, the autors are fully responsible for their contents and understability.

As mentioned before, a substantial part of materials which conveniently supplie these Proceedings, has been already (in a short version) published in Extended Abstracts. They have 262 pages of big format and contain 212 papers of geochemists from 34 countries.

Prague, June 1991.

FFrantišek Mrňa,
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GEOCHEMISTRY OF QUARTZ-ADULARIA METASOMATITES FROM THE MADZHAROVO TERTIARY POLYMETAL Au-Ag DEPOSITS, THE EAST RHODOPES

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Madzharovo polymetal deposit (main minerals: Pb, Zn, Cu, with an increased content of Ag and Au) is medium up to low-temperature one: 270-260 to 230°C for quartz-sulphide paragenesis and 220-180°C for quartz±chalcedony-barite paragenesis (Петров, Бресковска, 1982). The idealized vertical zonality (Velinov et al., in press) of mineralization is: 1) near surface quartz-barite zone (quartz, chalcedony, quartzite, barite, adularia, poor sulphide mineralization) with increased contents of Au and Ag; 2) zone of galena-sphalerite ores; the galena predominating and the contents of Au and Ag being increased; 3) zone of sphalerite-galena ores with an equal amounts of sphalerite and galena; 4) zone of chalcopyrite-sphalerite-galena ores, the amount of chalcopyrite being increased. Pyrite is found in all zones. The deposit is located within the range of a paleovolcano of the same name, which lies in the zone of crossing of regional fault systems different by nature. The main one is of an orientation of 130° (Велинов et al., 1977). The paleovolcano consists of several lava sheets interbedded by pyroclastic volcanogenetic-terrigenous rocks. Lava is presented by shoshonites, latites, trachytes, quartz-trachytes up to potassium rhyolites. With respect to petrochemistry the rocks are characterized by: variations of SiO_2 of 53 up to 73 %, high ratio of K_2O/Na_2O ($\geqslant 1$) and Fe_2O_3/FeO (from 1.3 up to 6.7); high content of Al_2O_3 and P_2O_5; low content of TiO_2 ($\leqslant 1$); high concentrations of "incompatible" elements, particularly those of long ion radii: Rb, Ba, Cs; content of "compatible" elements (Cr, V, Co, Ni, Sr), which are close to those of the andesite series. The K/Ar age of the volcanic rocks is 33.5-31.5 Ma (Lilov et al., 1987).

The hydrothermal metasomatic medium to low-temperature alterations of the Madzharovo volcanic rocks are regarded as a "prefault type" (Radonova, Velinov, 1970). Propylites are the best manifested, in the sense implied by Nakovnik (1968), as well as the secondary quartzites and quartz-adularizites. The quartz-adularia mineralization is clearly overprinted on the regional propylites and secondary quartzites. It is of a vast area spread. The most intensive and best defined zones (K/Ag age - 32-33 Ma) are mainly located along faults orientated at 130°. Their thickness is 3-4 up to 70 m (Velinov et al., in press).

The adularized rocks are white up to light-gray or pale pink up to pinkish-brown. The contacts with the propylitic rocks are gradual, and towards them the content of adularia and the degree of mineralization decrease. The less altered rocks are of a conserved porphyry structure over plagioclase and mafic minerals. Plagioclase phenocrysts are substituted, to a different degree, by sericite and adularia, rarely by quartz and epidote, quartz, ore minerals, leucoxene, and more rarely by chlorite and carbonate. In the strongly altered rocks the groundmass is fine-grained or trachitic with microlites of potassium feldspar (the content of K_2O in them is from 7.5 up to 15.0 %). At an advanced adularization the rocks are transformed into a cryptograined aggregate mainly consisting of quartz and adularia.

Besides pseudomorphs along the plagioclase, adularia fills in amygdules together with quartz or forms quartz-adularia veinlets ± ore minerals (pyrite, sphalerite, chalcopyrite, galena, molybdenite, and sulphosalts). The adularia in the caves is represented by well formed, consisting of m $\{110\}$, c $\{001\}$, x $\{101\}$ white, semitransparent up to transparent crystals measuring up to 1.5-2 mm. The X-ray studies characterize adularia as a low sanidine with a transition to orthoclase (Al occupancy of tetrahedral position - $2T_1$ - 0.68-0.75). The average chemical composition (23 analyses) is: $Or_{97.4}Ab_{2.3}Cn_{0.3}$.

During the process of adularization mainly K_2O and SiO_2 are supplied; Al_2O_3 is comparatively inert; Na_2O, CaO, FeO, Fe_2O, MnO, MgO are removed to a different degree depending on the intensity of the alterations.

Increasing the potassium activity, considerable alterations in the distribution of a number of elements-admixtures occur.

Rubidium. In the unaltered volcanites the content of Rb varies from 142 up to 400 ppm, an average content of 260 ppm.When K_2O varies from 3.3 up to 6.3 %, the ratio K_2O/Rb varies from 80 to 260 ppm, an average - 180 ppm. In the rocks adularized the content of Rb varies from 165 up to 775 ppm, an average content of 400 ppm; K_2O/Rb - 150-410 ppm, an average of 250 ppm. A tendency towards a more rapid increase of the content of K to that of Rb is established.

Barium. Its content in the unaltered volcanites is between 1060 and 1950 ppm, mean value of 1500 ppm; K_2O/Ba - 24-38, mean value of 28 - almost equal for each petrographic variety. The variations of Ba in the quartz-adularia metasomatites are considerable - 915-5255 ppm at K_2O/Ba - 13-64. In spite of the considerable increase of the content of Ba towards the adularized zones, as well as in the case of Rb, a relatively more rapid increase of K_2O concentrations in the same direction is established. The variations in the Ba content to a considerable extent are due to the frequent presence of baryte in the minetalized quartz-adularia metasomatites and due to late leaching.

Comparing of data on the distribution of ore elements-admixtures (Pb,Zn,Cu,Mo) is impeded by superimposed hydrothermal mineralizations within the zones of adularization.

Lead. Its content in the unaltered magmatic rocks is 31-72 ppm, on the average - 41 ppm. It is higher than the clarke for similar rocks (18 ppm). A slight tendency towards an increase of Pb in the more alkaline, richer in K rock varieties, is observed. The content of Pb in the quartz-adularia metasomatites varies within the limits of 10-150 ppm, in individual samples - up to 1000 ppm. The high concentrations are due to the presence of a superimposed sulphide mineralization. The phase composition of Pb (Σ Pb), at which two phases are distinguished - "silicate lead" (Pb_{Si}) (which is assumed to be bound in the framework of the silicate minerals - mainly feldspars) and lead of the "mineral microadmixtures" (Pb_{Sf}) - sulphides, sulphates, carbonates (Арнаудов, Павлова, 1969), shows that the increased contents of Pb in the adularized zones are caused by mineral admixtures (up to 85 % Σ Pb). Comparing the so-called Pb_{Si}, in the unaltered magmatic rocks, and the quartz-adularia metasomatites developed over them, shows that during adularization there is no increase of the content of Pb occurring parallelly with the increase of the K content.

Copper and Zinc. The unaltered volcanites contain about 40 ppm of Cu and 80 ppm of Zn on the average. In some samples the concentration of either elements is considerably higher, but in these cases sulphides are found to be present (chalcopyrite, sphalerite, pyrite, etc.). However, in the quartz-adularia zones,where sulphides are not found, the content of Cu and Zn is considerably lower than that of the unaltered rocks, 27 ppm and 52 ppm correspondingly. Hence, during adularization in the effusive rocks studied, the alteration of the mafic minerals, which are the main carriers of Cu and Zn, causes a considerable removal of these elements.

Molybdenum. In the volcanites unaltered, the content of Mo is considerably higher than the clarke one - 2-7 ppm. It varies within a vast interval in quartz-adularia rocks-1-4000 ppm. The contents within the limits of 10-20 ppm are predominating. The phase analysis on the samples of deep mining levels shows that 15-23 % Mo are bound in molybdates, 57-70 % - in the form of molybdenite, and 5-11 % are probably bound in the form of an isomorphic admixture (Бояджиева, Арнаудов, 1986). In the surface outcrops of the quartz-adularia zones, the oxide form is predominant - molybdites and ferro-molybdite ($\sim$ 85%), while molybdenite is 12-15 %. The high concentrations of Mo are probably related to the process of generating and migrating of solutions rich in K. In the deeper levels of the quartz-adularia metasomatites molybdenite is predominantly deposited, while in the near-surface parts - oxide molybdenum compounds.

Gold and silver. The content of Au in the unaltered magmatic rocks varies from $<$ 0.01 ppm up to 0.07 ppm, while in quartz-adulariametasomatites - from $<$ 0.01 up to 12 ppm. In 60 % of the analysed 160 samples of metasomatites, the content of Au is higher than 0.02 ppm, on the average - 0.53 ppm. The content of Ag in the unaltered volcanites varies within the limits of 0.3 and 99 ppm. In 65 % of the studied 370 quartz-adularia samples the content of Ag is higher than 0.3 ppm, the average content being 2.5 ppm. The distribution of Au and Ag is uneven, without showing any dependence on the content of the main petrogenic elements in the quartz-adularia metasomatites. Increased, super-clarke contents of Au and Ag are mainly established in the near-surface zones of a poor intervein-injected polymetal mineralization. Gold is deposited in a virgin fine-dispersed form. The main carriers are: chalcedony-like striated quartz, fine-grained pyrite, and porous hematite. Silver is mainly related to sulphides and sulpho-salts. A regular change of the concentrations of Au and Ag, parallelly with that of Cu and Bi, is established in the intervein-injected mineralizations.

Au is considered to be transferred by acid chloride solutions and is deposited when they are neutralized. Such a kind of mechanism explains the characteristic relation of Au mineralization with adularization. The adularia zones, having been formed prior the main polymetal mineralization turn out to be a favourable medium, which on its part facilitates alkalization and deposition of ore components and gold.

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THE INVESTIGATION TECHNIQUE AND NATURE OF AMMONIUM HALOES ON GOLD DEPOSITS

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Nitrogen as well as its reduced form ammonium ion is considered as a common part of hydrothermal solutions. The fluid inclusions analysis have developed ammonium ion in quartz in a number of gold-silver deposits (Moiseenko V.G., Malachov V.V. 1979, Volynets V.F, Sushevskaya T.M. 1972). Nitrogen was detected in inclusions in native gold. Hydrothermally altered rocks on some deposits generally contain ammonium-bearing minerals. Ammonium substitutes for potassium ot other alkali cation within the crystal structure of some silicates, such as K-feldspars (buddingtonite), micas (tobelite), illite and others (Hallam M., Lugster 1976, Sterne E., Zantop H., Reynolds 1984).

Experimental investigations of the solubility of gold under the conditions of natural hydrothermal solutions established a significant role of the redox reactions in the transportations and deposition of gold (Zotov A.V.,Baranova N.N. et al., 1990). On this base the assumption was made that reducing conditions which corresponds to deposition of gold would result in the appearance of considerable amounts of ammonium ion in hydrothermal solutions and the formation of ammonium haloes in gold deposits (Barsukov V.L. 1982). The development of ammonium-bearing potassium feldspars and micas in the near-to-ore alteration zones of gold-silver deposits (Barsukov V.L., Akhmanova M.V. et al. 1980), as well as the development of the ammonium haloes in gold deposits (Blomstein E.J. 1984, Kydd R.A., Levinson A.A. 1986, Krohn M.D., Altaner S.P. 1987) confirm that assumption. It is reasonable to study the entire succession of the following interconnected processes: the appearance of the ammonium-bearing mineral phases,the formation of ammonium haloes, the evolution of the organic matter within the hydrothermal systems.

The study of distribution of ammonium in the hydrothermal systems is accompanied by considerable analytical difficulties, caused by a low content of ammonium and relatively high content of total nitrogen in the objects of study. There is no analytical technique which allows to determine nitrogen in a great variety of natural samples and in various degrees of oxidation. The necessity of determination of both the total content of nitrogen and its reduced form (ammonium) as well as a great variability of the objects of study from fluid inclusions in quartz up to the sedimentary and metamorphic rocks requires the use of a set of techniques, which includes the spectrophotometric technique, IR-spectroscopic determination of ammonium ion in micas, EPR investigation of potassium feldspars, C-H-N analysis.

The IR-spectrum of absorption of micas is obtained by means of the "Specord-75" instrument (fig. 1).An absorption band having a frequency of 1400 cm^{-1} was used as an analytical one (Shigorova T., Kotov N.V. 1981). The ammonium content was evaluated in accordance with a graph plotted by means of standard points for which ammonium content was determined by spectrophotometric technique. The lower limit for the ammonium detection is 0.01% by weight accuracy ± 10 %.

The electron paramagnetic resonance technique was used for investigation of the distribution of nitrogen and ammonium ion in potassium feldspars (Mathyah I.V., Bagmut N.N. et al. 1982). Ammonium could be detected by this technique directly, but we could transform the ammonium ion into nitrogen-containing paramagnetic centers using gamma-radiation:

$$NH_4^+ + \text{gamma} = NH_3^+ + H^0 .$$

Samples of potassium feldspars were subjected to gamma-radiation using Co^{60} as a source at room temperature. EPR-spectra were recorded by $SE_x - 2544$ "Radioplan" (Poland). The typical spectrum of nitrogen containing paramagnetic centers in feldspars is shown on fig. 2

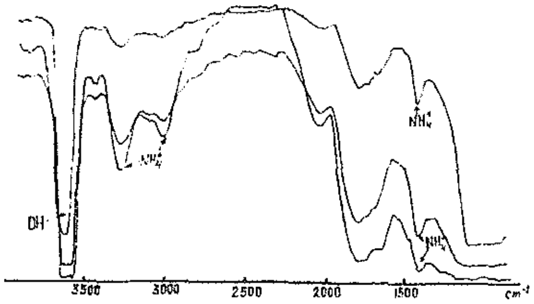

Fig. 1 - IR-spectrum of ammonium-bearing micas

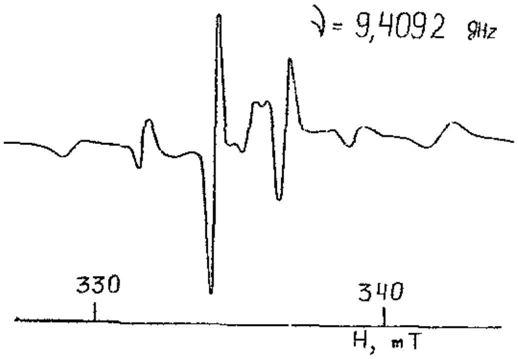

Fig. 2 -EPR-spectrum of nitrogen containing paramagnetic centers in K-feldspars

It represents the combination of signal from two nitrogen-containing paramagnetic centers in feldspars (NH_3^+ and N_2^-). Annealing at 900 °C causes a disappearance of the signal. After annealing and subsequent repeat gamma-radiation of thesample new nitrogen containing paramagnetic centers appears. The combination of gamma-radiation and annealing provide the quantitative determination of nitrogen in potassium feldspars.The dependence of EPR signal intensity from containing ammonium in potassium feldspars ispresented on fig. 3.

This technique has a considerable edge over the chemical one, because it facilitates a simultaneous determination of nitrogen at various degrees of oxidation and it is very sensible.

The basic techniques for routine analysis for studying the distribution of nitrogen within ore zones is presented with the C-H-N analysis. The determination was conducted at 600 and 900 °C. Nitrogen which is determined at 600 °C correspond to nitrogen of an organic matter, but the "high temperature form", in general, correspond to the NH_4^+ ion in the crystal lattice of mica and potassium feldspars.

The combination of the C-H-N analysis, spectrographic determination of the ammonium ion, IR-spectrometry, EPR determination obtains maximal information regarding the distribution of nitrogen (ammonium) within the ore-metasomatic zones.

The data on the ammonium content in the fluid inclusions in quartz of ore bodies were obtained. Great variety of the ammonium contents from 0.42 up to 0.07 $mol.kg^{-1}$ H_2O were detected.Maximal concentrations were found in quartz of the productive quartz-feldspar mineral association (appr. 0.26 $mol.kg^{-1}$). The values in the quartz-sulphide associations are found to be 2-3 times lower. The data analysis as to the distribution of ammonium in fluid inclusions revealed a connection between the higher concentration of ammonium in fluid inclusions in quartz and the productive gold mineralization.

The organic matter of host rock and ore-nearby metasomatites was subjected to a study. Bitumoid contents in the samples vary within 0.1 to 0.04%. The composition of the studied bitumoids includes hydrocarbons (73 to 87%). The nature of chromatograms of the hexan fraction, as well as the values of pyrometric parameters claim a high degree of transformation of the bitumoid matter and its migration origin, and suggest that the matter was transported into the ore field from the zones showing a higher degree of metamorphism. Results of the elemental analysis indicate, that metamorphogenic transformation of the organic matter was accompanied by a minor decrease of the nitrogen content. However the content of nitrogen in micas considerably increased, i.e. nitrogen was redistributed between the organic and mineral components of the rocks. Simultaneously with hydrothermal alteration developing in the near-to-ore metasomatites a considerable growth of oxidation degree of the organic matter and low nitrogen is noticed.

Infrared spectra of chloroform extracts from samples representing main mineral associations of gold deposit show that organic matter of the productive association is more oxidated. This conclusion was based on the comparison of absorption band intensity within 1720 - 1740 cm^{-1} range (fig. 4).

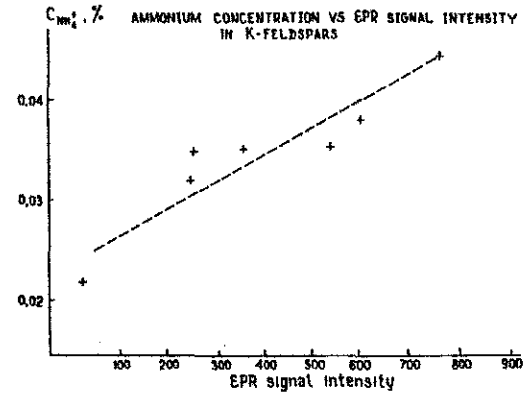

Fig. 3 - EPR signal intensity vs NH_4^+ content in K-feldspars

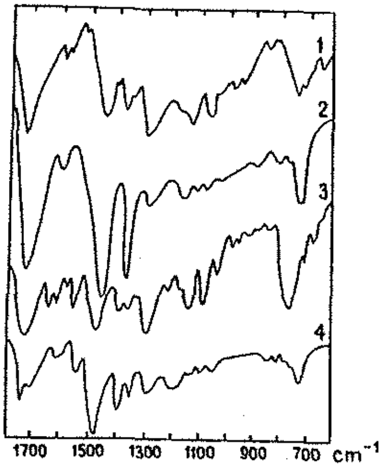

Fig. 4 - IR-spectra of chloroform extracts. 1. Early association, 2., 3. Productive association, 4. Post ore association.

Fig. 5 represent the data on investigation of organic matter, distribution of nitrogen in organic matter and the data on determination of ammonium in fluid inclusion solutions in quartz. From the data on fig. 5 we find that in a productive mineral association simultaneously takes place: increase of oxidation degree of organic matter; decrease of nitrogen content in organic matter and increase of ammonium content in fluid inclusion solutions. Permanent character of the mentioned phenomena makes possible to suppose that the basic source of nitrogen in the hydrothermal system is the organic matter of the host rocks and ore-nearby metasomatites.

The distribution of ammonium in the ore zones has been studied. It is confirmed that there are haloes of ammonium of a length from 2-3 to 30-50 m around the ore zones with gold mineralization (fig. 6,7). Inside the haloes, the ammonium ion contents grow from 3 up to 20-30 times as compared with background values. More vivid and longer haloes are developed around the ore bodies in terrigennous rocks. The haloes are getting sufficiently longer in the upper level of the ore bodies.

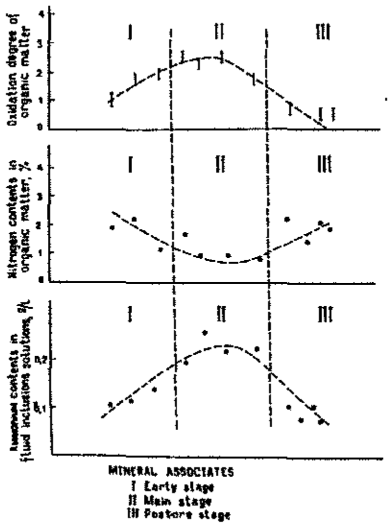

fig. 5 - The data of investigation of organic matter of the ore bodies and fluid inclusions in quartz

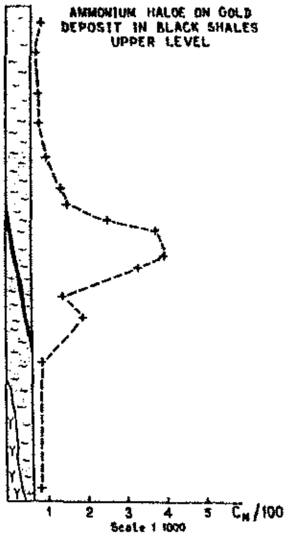

fig. 6 - Ammonium halo on gold deposit in black shales. Upper level.

Thus, we came to conclusion that ammonium haloes found on gold deposits and locatedaround the ore bodies are genetically linked with the transformation of the organic matter in a hydrothermal system. The presence of NH_4 ion disclosed in mineral of wall-rock metasomatites (micas, feldspars, illites, montmorillonites) can be sufficiently reliable criterion of deep-seated intense oxidation of the organic matter in the redox potential range providing for the reduction and precipitation of gold, silver and a number of ore elements.

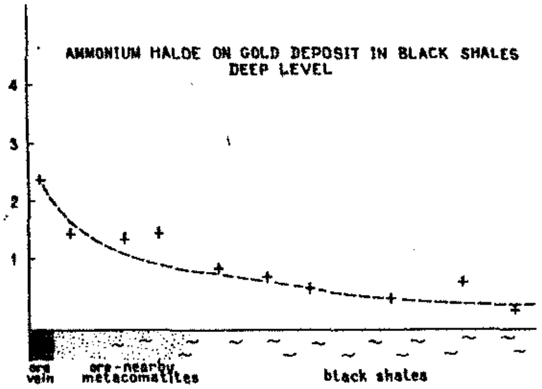

fig. 7 - Ammonium halo on gold deposit in black shales. Deep level-

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THE USE OF STREAM SEDIMENTS FOR FORECAST GEOCHEMICAL MAPS

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The range of using the stream sediments for forecast widens at present. This method is applied for geochemical and geological mapping, aimed at the control of the environment. But the main task of this approach is the prospecting of ore deposits. It is the only effective method of prospecting ore deposits, which are overlapped by the loose sediments, in low-mountain taiga landscape.

The article consideres the possibilities to use the forecast geochemical maps from the stream sediments, based on one of the gold-bearing regions of Siberia, which is overlapped by the loose sediments, in the low-mountain taiga landscape.

The region under study is composed of the Proterosoic rocks, metamorphized to different extent.The rocks are broken by the granitoid intrusion in the western part, Fig.1.

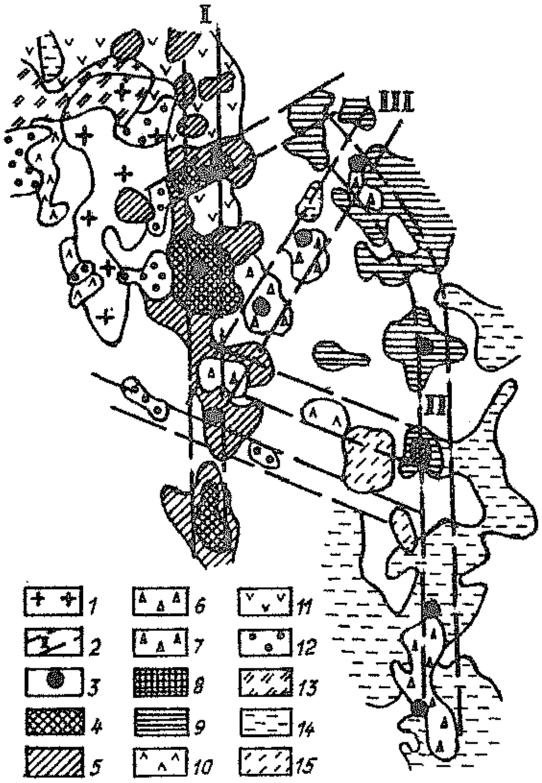

Fig.1. Polyelement geochemical map

1 - granitoid intrusion; 2 - tectonic dislocations; 3 - ore objects; 4-15 - geochemical classes.

4 $\frac{\text{Au}}{90\text{-}30}$; $\frac{\text{Mo Ag Cu}}{2,5}$; $\left(\frac{\text{Ni Co}}{1,9}\right)$ veinlet-dissiminated gold-sulphide type

5 $\frac{\text{Au}}{40\text{-}10}$; $\frac{\text{Mo Ag Cu}}{2,5\text{-}1,9}$; $\left(\frac{\text{Ni Co}}{1,9}\right)$

6 $\frac{\text{Au}}{91\text{-}15}$; $\frac{\text{As}}{10\text{-}50}$; $\frac{\text{B}}{4,0}$; $\left(\frac{\text{ZnPb Mn Li CrSb}}{2.0\text{- }1,8}\right)$ gold-quartz-sulphide

7 $\frac{\text{Sb}}{16\text{-}8,0}$; $\frac{\text{Au}}{14\text{-}3,0}$; $\frac{\text{B}}{3,0\text{-}2,0}$; $\frac{\text{ZnPbAsCrMnLi}}{3,4\text{-}1,6}$ gold-sulphide antimonial

8 $\frac{\text{Au}}{90}$; $\left(\frac{\text{Mn B Cr Li Y Cu}}{3,0\text{-}1,8}\right)$

9 $\frac{\text{Au}}{10}$; $\left(\frac{\text{Mn B, Cr Li Y Cu}}{3,0\text{-}1,8}\right)$ gold-quartz type

10 $\frac{\text{Ag}}{6,0\text{-}2,7}$; $\frac{\text{Zn Pb Cu Y Cr}}{2,5\text{-}1,9}$ anomalies, connected with central and exocontact zone of the granitoid massif

11 $\frac{\text{Mo}}{2,5\text{-}1,9}$; $\frac{\text{Ag Cu Zn Pb Ni Co Sc}}{2,3\text{-}1,8}$

12 $\frac{\text{W}}{40,0\text{-}7,0}$ $\frac{\text{Mo Pb Co V}}{2,5\text{-}1,9}$

13 $\frac{\text{Nb}}{10,0\text{-}3,5}$; $\frac{\text{Sc}}{3,3}$; $\frac{\text{Ag Mo}}{2,5\text{-}2,0}$

14 $\frac{\text{Y}}{3,0}$; $\frac{\text{La}}{2,0}$; $\frac{\text{Zr}}{2,0}$; $\frac{\text{Mn}}{1,5}$ above-intrusion anomalies

15 $\frac{\text{Zr}}{14,0\text{-}8,0}$; $\frac{\text{Au}}{3,0}$

The granitoid intrusion is surrounded by the matabasite bodies, which occur among highly metamorphized marbled limestones, amphibolites, quartzites and black schists.

The aleurite-clayey sequences and interbeds of quartz-like sandstones, tuffites and porphyrites are distributed in the central part. The rocks of this series are metamorphized to greenschist facies of metamorphism.

The eastern part contains weakly-metamorphized limestone-clayey schists.

The region possess the block structure, caused by the system of fractures of different directions. The eastern and western zones of submeridional fractures I and II, distinguished as the fragments of the regional deep fault,are the largest zones. The zone of heightened rock jointing of north-east direction is observed in the central part. A number of inner block faults are avialable.

Geochemical survey from stream sediments was done over the area of 3000 sq.km. Sampling density corresponded to the scale 1:200000. The samples of silt-clay material was collected over 500 m, the 1 mm fraction was analyzed. Monoelement and polyelement geochemical maps were compiled via the method of multi-dimensional field, using survey data (Evdokimova, 1978).

The polyelement map (Fig.1) shows the element combination in anomalies as the geochemical classes, which indicate the primary composition of the element associations. Each geochemical class is characterized by the formula. The elements are arranged in the formula according to the decrease of contrast coefficients. The main elements are given in the formula at the beginning and the associated elements (in brackets) are given at the end of this formula. The associated elements are not distributed everywhere and they possess low contrast coefficients.

The gold metamorphogenetic-hydrothermal mineralization id widely distributed in the region. The temporal and spatial ratio of different formation types of this mineralization is established. The veinlet-disseminated gold-sulphide type, which occur at the basement of ore system, gold-sulphide,occurring in the upper horizons and the quartz-veined which occupy the intermidiate position. Gold mineralization of this type may occur in the vertical section up to 3 km.

Gold mineralization in the region is found in tectonic dislocations. It is clearly seen from the gold stream sediments.

Within the western submeridional zone I, the veilet-disseminated gold-sulphide mineralization with chalcopyrite-pyrrhotite-pyrite associations, common to low levels, is available This zone is characterized by the association of gold, molybdenum, copper and silver.

The monoelement gold anomalies with the markedly decreased concentrations of other elements are distributed in the northern and central parts of the zone II. The gold mineralization of the quartz-veined type is common to these regions.

The zone III is marked mainly by the gold-quartz-sulphide mineralization type with the significant distribution of arsenopyrite-pyrite and pyrite-fahlore associations, which occur in the upper levels of the ore-bearing zones. The gold-antimonial mineralization is superimposed to the gold-quartz-sulphide mineralization type. In this case, besides gold, arsenic, antimony, lead and zinc are available in the heightened concentrations. It should be noted, that the lithophile elements (boron, lithium, manganese and chrome) surve as the elements, which form stable extensive anomalies. The position of these elements in the zonation series is caused by the fact that they leach from the lower parts of the mineralization zones and deposit in the upper levels, forming the above-ore haloes. The haloes are reflected by the stream sediments.

The element composition in the associations markedly changes around the granitoid massif. The elements of rare-metal character, such as tungsten, niobium which are associated with the scheelite mineralization appear here and some anomalies indicate the presence of the unknown ore bodies of rare-metal composition. Anomalies of rare-earth composition (yttrium, lanthanum etc.), which are concentrated in the south-eastern part, are probably the above-intrusion halo, for according to geophisical data the intrusive massif is evident on the depth in this region. The data indicate, that the stream sediments reflect the differences in the occurrence of ore mineralization. They can be used for the preliminary assessment of the formation type and the level of the erosion shear in ore-bearing zones and individual occurrences.

Each stage of the prospecting works should be terminated by the forecast of mineralization. It is supposed, that the concentrations of chemical elements in the fraction of channel stream sediments indicate the potentials of the anomalies from the stream sediments. But it is not a right approach, because of the complicated behaviour of elements, which depends on a number of processes, occuring here. Thus , the quantitative assessment of mineralization from the stream sediments is very important. It can be solved via the mathematical modelling of the processes, which take place under the formation of stream sediments. The present article consideres the quantitative assessment, based on the mathematical model of the stream sediment, proposed by V.V. Polikarpochkin (1981). Figure 2 represents the graphic model of the stream sedimant. The river, as well as the alluvial deposits, which are formed by it, and the waters in the deposits refer to the river system. The stream sediment. is formed from the substance supply into the river, which may occur in the solid and liquid phases, as well as the substance transportation afloat. The reduction in sizes, sorting and leaching of the transported material as well as the phase substance transitions, which are common for the stream sediments are significant.

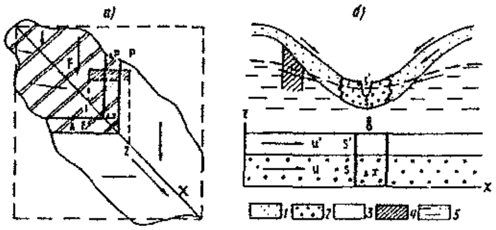

Fig.2. The stream sediment scheme

a - plan, b - transversal and c - longitudinal

1 - loose slope sediments, 2 - alluvial sediments, 3 - bedrocks, 4 - ore body, 5 - underground waters.

The mathematical equation, which represents the model, is made as the mass balance for elementary volume I. This volume is seen on Fig.2. For the solid phase the equation is:

$$\frac{\Delta(\bar{u}'s'\bar{c}')}{\Delta x} + \frac{\Delta(\bar{u}\ s\ \bar{c})}{\Delta x} - \varphi' s'\ \bar{c}' - \varphi s\bar{c} + \frac{\Delta(s'\bar{C}')}{\Delta t} + \frac{\Delta(s\bar{c})}{\Delta t} - m\Delta H\ \frac{\Delta P}{\Delta x} = 0 \quad (1)$$

where s, s' - areas of the transversal section of the fluvial and underfluvial streams; u,u' - rate of their current, correspondingly; $\bar{u}$,$\bar{u}'$ - average values of the rates along the transversal section; c,c' - volumetric substance concentrations; $\bar{c}$,$\bar{c}'$ - average concentrations; Δx,Δt - stream interval and time; ΔP - deposit productivity increment per unit of the depth on the interval; m - ore substance share, dupplying into the channel in the given phase; ΔH - denudation rate; φ, φ' - coefficients of phase transitions.

Equation (1) may be applied for the solid phase as well as for any other phases and for different granulometric fractions. It is appropriate for the valley interval, where the supply of substance from the source takes place (the present interval is called the head part or the head of the stream sediment) and for the underlying interval (trail).

The first member of the equation shows the transporting activity of the river. The second one indicates the same for underchannel stream. In general, two first members represent the varieties between the substance amount, supplied and removed by the channel and under-channel streams on the single river interval.

The following two members show the substance transition between phases and fractions. The fifth and sixth members consider the change of substance quantity in the channel and under-channel streams per time unity and reflect the accumulation process of alluvial deposits. The last member of the equation shows the substance quantity, supplied on this interval from the source (deposit).

The equation may be used for investigation of specific features of the stream sediment and quantitative estimation via the computer.

Making some assumptions (the main one is the substance concentrations in the deposit (c) and in streams are supposed to be proportional to each other, and the regime of the stream is characterized by the constant cross-sections and substance concentration in each given point, i.e. $\Delta(s'\bar{c}')/\Delta t = 0$) the equation (1) may be simplified as:

$$1/k'\ \Delta P = \Delta P' + g(c - c_{\text{ф}})\Delta x \quad (2)$$

where $\Delta P'$ is increment ofstream sediment productivity on the interval; ΔP - deposit productivity increment; K' - propotional coefficient between stream sediment productivity and deposit productivity; g - coefficient consideres river dynamics and phase substance transitions , c_{φ} - background concentration.

The first assessment of the deposits from the stream sediments was proposed by A.P. Solovov (1959) in the form of the expression:

$$P = k'P' \quad (3)$$

According to this formula, it is suppoced, that on deposit region i.e. in the stream head, the stream productivity (P') increase directly proportionally(k' coefficient) to the deposit productivity, and in the trail it is constant and correspond to the total productivity of the above-located deposit. But at the same time, this formula cannot be applied, for the stream productivity in the trail is not a constant value. In some regions it is explained by the influence of the nearset slopes or by the dynamic factor. The values of phase transition of the substance are not less, even in most cases, they are larger, because the samples are collected not from the whole deposit mass or the whole material, which moves in the stream, but only from some or other fraction. The correction for these factors is necessary. In the derived formula (2) this correction is given via phase-dynamic coefficient g.

At $g = 0$ the formula (2) has the form: $P = k'P'$, i.e. the expression(3) is the particular cese of the formula (2). The value of g coefficient may be determined in the stream trail, for which the condition $\Delta P = 0$ is true. In this case, it follows from the formula (2) that:

$$g = -\frac{\Delta P'}{(c - c_{\varphi})\,\Delta x} \qquad (4)$$

The g determination should be started from the low points of the stream sediment and continued untill the obtained values stop to conform to the regularity of g change. It is the sign which indicates the end of the stream trail and the beginning of the head. In the head part the formula (4) cannot be applied, for $\Delta P' \neq 0$ here. The g value is determined via the extrapolation from the trail, considering the regularity of g value change. In the point of the line break on the plot, on the boundary between the trail and the head g is determined precisely. It is very important for the assessment. Putting the obtained value in the formula (2), and knowing all the rest members of the right part the value $1/k'\Delta P$ i.e. the value which is proportional to increase productivity of the deposit on the calculated interval, may be determined. We call this expression the increase of the conventional deposit productivity. Thus it follows from the formula (2) :

$$\Delta P_{\text{conv.}} = \Delta P' + g(c - c_{\varphi})\cdot\Delta x \quad , \qquad (5)$$

where $\Delta P_{\text{conv.}} = 1/k'\Delta P$. The total deposit productivity is determined through the obtained values of its increase.

If we consider the k'value to be constant, the total deposit productivity may be estimated as the sum of productivities on the calculated intervals:

$$P_{\text{conv.}} = \frac{1}{k'}\cdot\sum_{i=1}^{n}\Delta P_i \quad , \qquad (6)$$

where n is the number of the calculated intervals. The obtained productivity is expressed in conventional units. The P value in absolute units may be estimated from the condition:

$$P = k'P_{\text{conv.}} \qquad (6')$$

The k'value depends on the chemical element, for it is dependent on its properties and behaviour in the hypergenesis. It changes with deposit type, fullness of weathering, the deposit location and other conditions. The total value may be obtained via the sampling of the deposit with the certain reserves from the equation (6').

At present, the automatized processing program of the data from the stream sediments is compiled via computer.This program provides for compiling the map of ore productivity. The example of such map is given on Fig.3. The map represents the data of quantitative estimation, calculated in the form of ore productivities per area unit and forecast metal reserves from the anomalies on the whole.

The obtained estimation is different from the one, which may be derived from the concentration map. Each anomaly (Fig.3) is estimated in comparison with the anomaly I, which corresponds to the prospected region and surves as the standard.

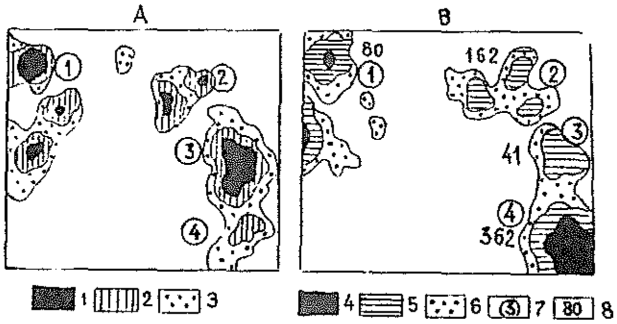

Fig.3. The map of metal concentrations from the stream sediments (A) and ore productivity in the original bedding(B).
Metal concentrations in anomalies: 1 - high, 2 - average, 3 - low; productivity values: 4 - high, 5 - average , 6 - low; 7 - number of the anomalies; 8 - the total productivities in anomalies.

So, the anomaly 3, is seen on the map as the potential anomaly, but in reality it is not so(Fig.3, A,B). At the same time more potential anomaly 4 is distinguished in the southern part. Thus, the obtained data show that the proposed procedure permits the forecast of reserves from different regions to be estimated as well as the areas for prospecting works to be recognized.

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GEOCHEMICAL PROSPECTING IN STRATA-BOUND Pb-Zn ORE DEPOSITS FROM CANTABRIA (SPAIN).

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I. INTRODUCTION

Strata-bound Pb-Zn sulfide deposits in carbonated rocks of Lower Cretaceous from Cantabria (North of Spain) have been mined since the middle of the nineteenth century.

In four areas -La Florida, Novales, Reocin and Santander- included in the mining district, have been studied the geochemical and microscopical characteristics of samples from carbonated rocks enclosing the Pb-Zn mineralizations, with the aim to know the dispersion and the distribution of some elements (Fe, Mn, Sr, Pb, Zn and Cu) in the rocks, in order to stablish the geochemical characteristics of these rocks, and the possibility to use these characteristics in geochemical prospection.

II. SAMPLING AND ANALYTICAL PROCEDURES

In the four areas, 582 samples of Lower Cretaceous (Aptian-Albian age) carbonated rocks have been studied. These samples correspond to the enclosing rocks of important strata-bound Pb-Zn ore deposits, with actual mining works in the area of Reocin.

Novales and Reocin are the areas where Pb-Zn mineralizations are more importants. The number of samples are distributed as follow in the different areas: 126 from La Florida, 53 from Novales, 311 from Reocin and 92 from Santander. The great majority of these samples are from drill holes, and in smaller number from surface outcrops.

The chemical analyses of these samples have been realized by atomic absorption spectrometry.

III. DATA DESCRIPTION AND INTERPRETATION

Table I shows the average content of the analysed elements in the carbonated rocks -limestones and dolomites- (Bravo et al., 1989). Pb-Zn ore deposits are mainly related to the dolomite levels, whereas the limestone levels are practically steriles.

In general, on the four areas, it is observed that Fe, Mn and Zn contents are higher in dolomites than in limestones, whereas Sr content is higher in limestones than in dolomites (Bravo, 1987), and this low Sr content in dolomites can be frequently related to late dolomitization processes, which are in agreement with the clear structural controls of the dolomitization observed in some areas.

AREA	LIMESTONE					DOLOMITE				
	Sr	Fe	Mn	Pb	Zn	Sr	Fe	Mn	Pb	Zn
LA FLORIDA	321	7162	265	72	46	41	16132	330	55	87
NOVALES	272	3680	48	108	80	45	266666	1326	100	183
REOCIN	251	4212	100	81	46	40	22818	868	59	124
SANTANDER	384	963	342	36	33	67	11500	490	18	96

TABLE I: Average contents in p.p.m. of Sr, Fe, Mn, Pb and Zn, in the enclosing rocks of Pb-Zn mineralizations.

The regional geochemical background values of Fe in dolomites from the areas of Novales and Reocin are higher than the usual values of Fe in these type of rocks (Rose et al., 1979, indicate 13000g/t as average values of Fe in dolomites).

Mn contents are importants too, but considering values of 1000 g/t (Rose et al., 1979) as usual Mn contents in dolomites, only Novales area shows values higher than this one.

Pb regional geochemical background values in Novales and Reocin areas are higher than values given for Pb in carbonated rocks by authors. Limestones show higher Pb content than dolomites.

Against Pb behaviour, Zn content is higher in dolomites than in limestones, and the areas of Novales and Reocin show a regional geochemical background value higher to the usual value of Zn in carbonated rocks.

Cu content is not significatively important in the four areas, and their values can be considered as usual in carbonated rocks.

The high contents of Fe, Mn, Pb and Zn can be interpreted as geochemical anomalies in the carbonated rocks from Novales and Reocin areas, and from the geochemical data it is possible to deduce too a predominance of Zn over Pb on dolomites.

Fe and Mn are very dependent variables in these areas (Fig.1). Usually, whereas the limestones show low content in Fe and Mn, the dolomites show high Fe and Mn contents. These dolomites present a Fe/Mg molar relation of 1/4, from what they correspond to ferriferous dolomite type.

In a parallel way to the increasing of Mn and Fe contents in dolomites, a decrease of Sr in dolomites is observed (Fig.2).

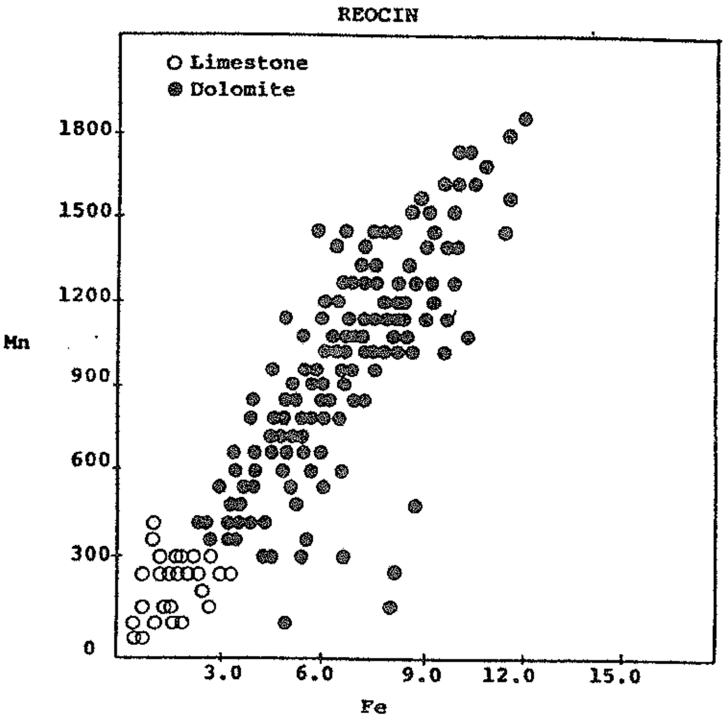

FIG.1: Relationship between Fe and Mn contents in the enclosing rocks of Pb-Zn mineralizations (Reocin area).

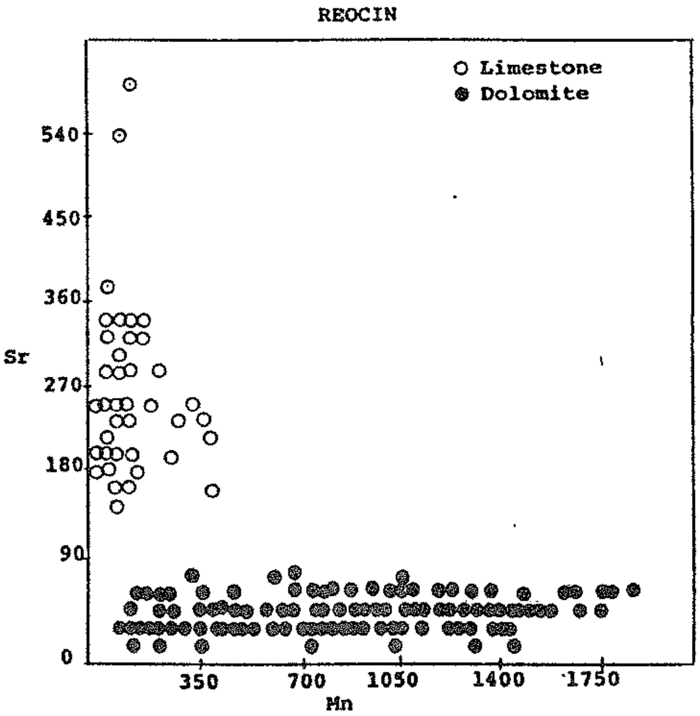

FIG.2: Relationship between Sr and Mn contents in the enclosing rocks of Pb-Zn mineralizations (Reocin area).

In the ferriferous dolomites there are a considerable increase of Zn content, from what can be deduced that Zn appears as related to Fe and Mn (high correlation between Fe, Mn and Zn) (Fig.3)

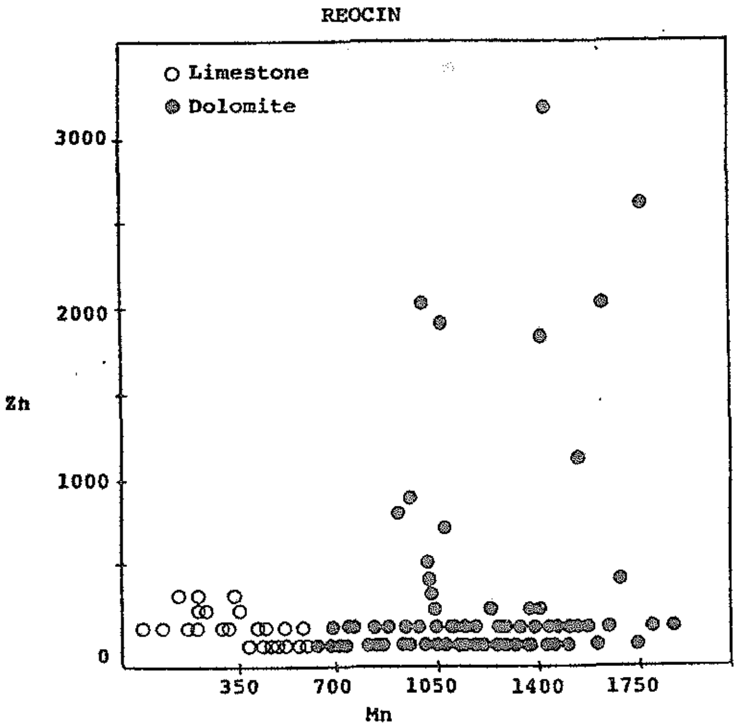

FIG.3: Relationship between Zn and Mn contents in the enclosing rocks of Pb-Zn mineralizations (Reocin area).

The increasing of Zn content in the carbonated rocks from these areas can be supposed closely associated to the dolomitization processes, in addition to Fe enrichment (formation of ferriferous dolomites). Authors suggest that the position of iron inside the crystal lattice of carbonates can be result of a later transformation process over previous non ferriferous dolomites (Vadala et al., 1981; Barbanson et al., 1983).

The high Fe content of carbonated rocks of these areas is an important and characteristic factor in relation to the Pb-Zn mineralizations, provided that an important part of the ore deposits of these areas are related to dolomites with high Fe contents.

IV. CONCLUSIONS

Novales and Reocin areas are geochemicaly similars, whereas La Florida and Santander areas have some different characteristics and they are geochemicaly less developed and their metallogenetic interest is lower.

As results of the geochemical studies over the samples from the four areas, can be stablish that the carbonated rocks from Novales and Reocin indicate that on a high regional geochemical background there is in these areas an important enrichment in Zn, Fe and Mn in the dolomites, in proximity the Pb-Zn mineralizations, and this enrichment is in correspondence with a negative anomaly in Sr. A ferriferous envelopment to the Pb-Zn mineralizations can be defined.

Fe and Mn contents in dolomites could be related to phases inmediately afterwards the dolomitization, in relation with areas of high porosity given rise to ferriferous dolomites. These dolomites, which show a bigger porosity and a better conditions to fluid circulation, present high Zn contents and they constitute the most favourable rocks to prospect Pb-Zn mineralizations in these areas.

The results on geochemical data for these areas are in agreement with a genetic model related to late processes where the enrichment of the enclosing rocks in Zn, Pb, Fe and Mn is later than the dolomitization, and the source of these metals is away from the enclosing rocks.

Finally, in relation to the utilization of these data in similar geological contexts, it is deduced that Fe, Mn and Sr can be indicator elements of hydrothermal processes in dolomites, and therefore they can be used as geochemical guides in the determination of favourable zones.

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Connection of tin ores with granite of the Njedek massif /Ore Mountains, Czechoslovakia/

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Geology

The Krušné hory - Erzgebirge Mts. is the clasical central European tin mining district with greisen deposits in the Hercynian granite massifs. Most attractive is the Nejdek massif, the largest granite outcrop of the area. The Nejdek massif is a complicated body composed of numerous intrusions and petrographical facies. Here two major granite types were distinguished more than one hundred years ago /Laube 1876/; The older, unmineralized "mountain granite" /Gebirgsgranit/, nowadays often termed "older intrusive complex" /Carboniferous/, and the younger, ore bearing "Krušné hory granites" /Erzgebirgsgranit/ now classified as "younger intrusive complex" /Permian in age/. Only recently, the "transitional granites" /formerly discovered in the Slavkovský les area by Fiala 1968/ and the youngest "lithium granites" have been recognized in the Nejdek massif, too. In wiew of gravitational and seismic inhomogenities inside the massif we incline to the image of the board-like character of the massif, with the root zone in the east in the Jáchymov deep fault zone /Pokorný 1985/. The mantle of the granite Nejdek massif is buildl by Cambrian mica schists and micaceous gneisses with amphibolites /Jáchymov group/, and by Ordovician chlorite-sericite phyllites with quartzites and metabazites /Phyllite group/.

Chemical types of granites

On the basis of statistical processing of more than 200 chemical analyses there were established 4 basic chemical types of granites in the Nejdek massif. /Fig. 1/:

1. Mountain granite /Laube 1876/ This is a coarse - to medium-grained biotite monzogranite. This granite built two large outcrops in the E and SW parts of the massif.

2. Transitional granite /Fiala 1968/ - defined formerly in the Slavkovský les region, now found also in the Nejdek massif, Mostly fine-grained porphyritic two-mica granites. Locally, big blocks of this type of granite are being found in the younger type 3 bodies; this can be observed at a very impressive locality called Bílá skála /White rock/. This is another name sometimes used for the type 2 granite.

3. Krušné hory granite /Laube 1876/ These are mostly coarse-grained biotitic syenogranites with a characteristic topaz content, but they include appreciable chemical variations. The dome of Blatná, for instance, is formed by a late phase of this type. Type 3 granites occur mainly in the central part of the Nejdek massif and underlie the phyllites in the NE surroundings of the massif.

4. Lithium granites are the youngest, most differentiated granites in the Krušné hory Mts. The rocks are fine-grained, rarely medium-grained albite-topaz-zinnwaldite granites. They form small intrusive bodies, stock and dykes. Cupolas of these granites are often rimmed by marginal pegmatites /Stockscheider/, greisenization is very frequent. The character of these granites suggests a rapid ascent to shallow depths /Škvor 1986/.

The granite types 1, 2 and 4 are accompanied by vein suites which chemically correspond with the respective group. Granite porphyries typically surround, the bodies of types 1 a 2 to a considerable distance, while topaz aplites originationg from Li-granites are only found within a zone of a few hundred meters from the stocks. These topaz aplites are in many respects similar to ongonites of the Bajkal area USSR and Mongolia /Kovalenko and Kovalenko 1976/. They are good prospecting guides for hidden Li-granites with potential Sn-W mineralization.

Geochemical characteristic

All granites of the Nejdek massif are peraluminous and can be compared to plumasitic granites /Tauson 1977/, Li-F granites /Kovalenko 1977/ of I_{kk}-granites /Tischendorf, Palchen 1985/. The I- and S- type classification proposed by Chappel and White /1974/, however, cannot be applied here since individual criteria are controversial. Furthermore, the Nejdek massif granites are certainly not anorogenic A-types, but postorogenic, originating from crustal melting well after termination of the Hercynian metamorphism.

During magmatic evolution by differentiation, marked changes of compatible and uncompatible elements occurred. This can be illustrated by a Sr/Rb plot /Fig. 1/, which delineates the early loss of compatible elements /here Sr, but Mg, REE and Zr behave similarly/, and following enrichment of lithophile elements /Rb, and Li, Cs, F/.

The REE distribution in the Nejdek massif is comparable to other leucocratic, strongly differentiated granite suits. Starting from a marked LREE enrichment relative to HREE follows a progressive decrease of total REE and of the Ce/Yb_{cn} ratio accompanied by EU-anomaly during differentiation. Main REE concentrating phases are here monazite and apatite.

Mineralization

Several types of tin and tungsten mineralization in granites of the Nejdek massif and its phyllite mantle can be distinguished:

Peri-contact greisens - flat bodies of greisens in the elevation structures of granites, W-mineralization prevails;

a, quartz-topaz-zinnwaldite greisens in Li-granites /Podlesí/;

b, quartz-topaz-muscovite greisens in biotitic granites /Hubertky, Vykmanov/.

Vein greisens, typical of the Nejdek massif. Quartz-muscovite /sericite/+topaz greisens associated with fracture zones in biotitic granites. Zones of greisenization are uniformly oriented /Rolava, Přebuz/ or of all directions /Horní Blatná surroundings/. Sn mineralization strongly prevails over the W.

Mineralization of the phyllite mantle of the massif, exclusively tin-bearing

a, zones of tourmalinization with cassiterite conditioned by E-W tectonics;

b, "skarns" - metasomatically altered lenses of metabasites on the deposit Kaff by Zlatý Kopec. Magnetite /older than Sn/, sphalerite and chalcopyrite are present in addition to cassiterite;

Quartz veins with wolframite in the mountain type granites /Rotava/.

Soutline of the genetic model of the Sn mineralization

The following model of Sn-W mineralization formation can be composed with high probability, based on the investigation of the Blatná massif /Breiter 1985, Lhotský et al. 1988, Breiter 1987/ and making use of all the older works /Janečka et al. 1973/:

1. Variscan regional metamorphism and folding, compression in the NE-SW direction and formation of faults of the NW-SE direction /Jáchymov deep fault, Horní Slavkov deep fault e.o./;

2. Intrusion of granitoids of the mountain, transitional and Krušné hory Mts. types, younger intrusions penetrated into zones of lower pressure, ascended more rapidly, because of the presentation of internal heat they could move closer to the earth surface /Škvor 1986/. Intrusions were of laccolith shape, with roots in the Jáchymov deep fault zone, intrusions of granites were accompanied by veins of granite porphyries, firstly of NW-SE and later E-W and N-S directions. Phyllites suffered a contact metamorphism, doming, folding, and formation of joints occurred above the granite elevations. Albite, biotite, quartz and dark tourmaline were formed in zones of E-W fracturing. Fluids released in the lower parts of the last Krušné hory Mts. type intrusions moved upwards, and small deposits of peri-contact greisens with prevalence of W over Sn could have developed in optimal conditions /dep. Hubertky /Absolonová, Pokorný 1983/, Vykmanov /Štemprok 1984/.

3. Intrusions of Li-granites forming minor stocks or ridges of NW-Se direction, with an aureole of aplites rich in topaz. These occurrences indicate the root zone of the massif. Li-granites caused doming of the mantle of the biotitic Krušné hory Mts. granites at their ascent, in phylites also local contact metamorphism to zwitterization. In the Li-granite elevations, pegmatite rims at the contact are frequent. This pegmatite type has granitic composition and formed by crystallization from the melt. Small folds or brecciation occurred in phyllites above the Li-granite copulas. Steep fractures of all the directions formed and the dip of flat L-joints changed in biotitic granites above the copulas. Solutions released during the crystallization of deeper parts of intrusions contained sufficient amount of F /1-2%/ for the transition of tin and tungsten. These solutions were accumulated in dome structures, where the flat greisen bodies - sometimes again with pegmatitic rims /this time of metasomatic origin/ at the upper contact were formed. Solutions migrated along steep fracture systems into the overlying biotitic granites. Here, several hundreds meters above the contact, in the zone of only brittle deformation, where the fractures were open, the "vein greisens" developed. Productive zone of vein greisens continued to the contact of biotitic granite and phyllite. Partial alternation in the fractures direction and dispersion of the solutions takes place at the transition of structures into phyllites. This way, the irregular bodies of peri-contact mineralization formed - it is of small extent, but it was mined in the old times in Jelení vrch hill. Hydrothermal solutions caused redeposition of the blue tourmaline II and formations of cassiterite in the overlying phyllites. Metasomatism of all the rock volume and development of the "tin-bearing skarns" occurred in places shere the feeding channels of the solutions crosscut the metabasite lenses.

Conclusion for prospecting

Further exploration and prospecting are recommended to concentrate on detection of buried elevation and ridges of the lithium granite with flat peri-contact greisens, especially beneath the largest so far known nodes of vein greisens. For this purpose lithogeochemistry at least on the scale of 1:10 000 should be used togethet with a detailed structural analysis. In justifiable cases reflection seismics may be applied in observation of hidden rock boundaries.

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Average content of elements in granites of Nejdek massif

Type	Mountain granite	Transitional granite	Krušné hory Mts. granite	Lithium granite
SiO_2	68.9	74.2	75.1	72.6
TiO_2	0.6	0.2	0.1	0.05
Al_2O_3	15.1	13.8	13.2	15.2
Fe_2O_3	0.5	0.4	0.3	0.2
FeO	2.3	1.0	1.1	0.9
MnO	0.05	0.03	0.03	0.04
MgO	1.2	0.3	0.15	0.07
CaO	1.7	0.6	0.4	0.3
Li_2O	0.02	0.03	0.07	0.18
Na_2O	3.3	3.1	3.1	3.9
K_2O	4.6	5.0	4.8	4.4
P_2O_5	0.3	0.2	0.26	0.45
H_2O	1.0	1.0	0.9	0.9
F	0.1	0.1	0.4	1.1
Rb	214	341	656	1360
Sr	225	57	26	16
Nb	17	14	19	38
Zr	254	119	80	30
Hf	8	4	3	2
Y	28	44	23	11
Sc	9	4	3.5	4
La	69	27	13	5
Ce	112	47	29	12
Sm	7	4	3	2
Eu	1.1	0.43	0.17	0.13
Yb	2.5	2.0	2.3	2.4
Lu	0.3	0.2	0.2	0.2
Sn	9	13	17	41
Be	6	8	16	11
B	37	62	79	97
Zn	63	49	51	53
Ni	9	8	9	13
Cr	23	14	12	14

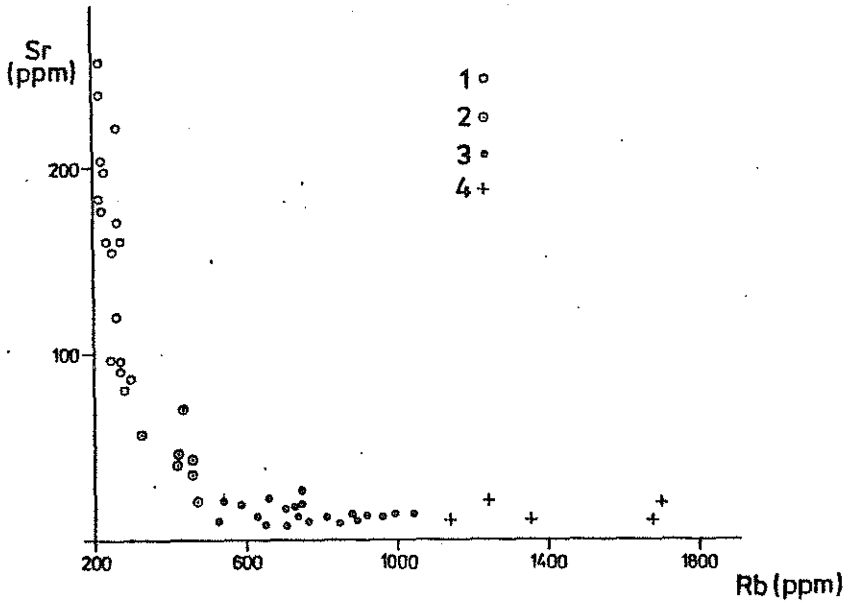

Fig. 1 Sr/Rb-plot examplifying behaviour of compatible and uncompatible elements during evolutin of the Nejdek massif. L-Mountain-type granites; 2-Transitional-type granites; 3-Krušné hory Mts.-type granites; 4-Lithium-granites.

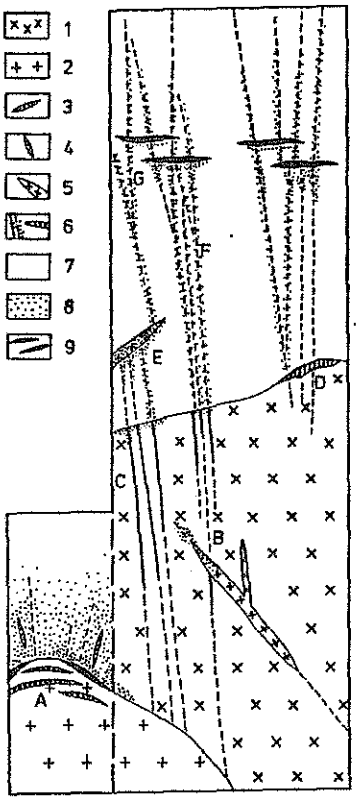

Fig. 2 Idealized vertical zonality of the tin mineralization. 1-biotite granite; 2-lithium granite; 3-border pegmatite; 4-aplite; 5-granite porphyry; 6-greisens, disseminated greisenisation; 7-phyllites; 8-strong altered phyllites, tourmalinisation, zwitterisation; 9-skarns, amphybolites.
Deposits: A-Podlesí; B-Jelení vrch; C-Hřebečná; D-Hubertky; E-Stráň; F-Glucksburg; G-Zlatý Kopec-Kaff.

SELECTION OF THE SAMPLING SIZE FRACTION IN GEOCHEMICAL EXPLORATIONS FOR MINERAL DEPOSITS BY SECONDARY AUREOLES AND DISPERSION TRAINS

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INTRODUCTION

Modern geochemical surveys by secondary aureoles and dispersion trains allow to solve the following tasks of prospecting:

- revealing of promising areas and structures;
- discovery of new mineral deposits, their tracing along the strike and delimiting;
- revealing or refining prospecting geochemical criteria and indications of mineral deposits;
- geochemical assessment of geological targets and known geophysical anomalies;
- verification and closer definition of geochemical and metallogenic specialization of studied areas and establishing, through related anomalies, the regularities in distribution of mineral deposits;
- outlining anomalies corresponded to known deposits which is assential for justification of efficiency of a sampling method applied;
- comparison of discovered mineral deposits and associated anomalies with studied economic targets, with the view of refining the criteria of outlining of such targets;
- quantitative evaluation of geochemical anomalies and occurences with calculation of prognostic resources, and determination of the potential and priorities for their further study;
- justification of follow-up prospecting programmes.

Successful solution of these tasks depends, to a considerable extent, on the dimentions and contrast of the revealed hypergene anomalies resulted from the eroded mineral deposits and their primary haloes, on the one hand, and on the correct selection of the technique of loose sediment sampling, including the choice of the size fraction of the sampling material, on the other hand. This is especially true of the areas where exploration is difficult to conduct: arid areas with eolian contamination of the loose sediments to be sampled and areas of humid tropics and subtropics with laterite duricrust (areas overlain by tills are not treated here).

The review of pertaining publications show that a considerable effort is made annually throughout the world in orientation surveys aimed at selection of the "optimum" size fraction. Moreover, contradictory conclusions and recommendations often are given even for areas of similar landscape-geochemical conditions. Therefore, systematization of approaches and determination of the main principles of selection of the sampling size fraction is one of the very important tasks in refining the methods of geochemical exploration.

SOME BASIC PRINCIPLES

Improvement of the methods and techniques of geochemical exploration with the view of increasing its reliability, informativeness, effectiveness and economic efficiency is known to be the principal tasks of the orientation surveys. The selection of the optimum size fraction is an important integral part of such experiments. The basis of success in achieving of the goals set is fostered even at the stage of the planning the orientation survey and exploration work by secondary aureoles and dispersion trains. Therefore, the following should be analyzed and taken into account prior to beginning of work:

- tasks of the exploration programme with close relation to the scale of work (reconnaissance, regional, detailed);
- available results of the previous geological, geophysical and geochemical work and data on the landscape-geochemical peculiarities to be expected during geochemical exploration in a specific area;
- expected types of mineral deposits and possible mineral forms of ore-forming chemical elements and indicator-elements of such deposits;
- the factors affecting the hypergene migration of elements and formation conditions of secondary haloes and dispersion trains under specific geochemical landscapes including the character of leaching and depletion of corresponding anomalies in paleo- and present-day environments;
- methods of geochemical samples analysis to be used to programme.

First of all, such a preparation allows to determine the availability or the lack of complications expected during prospection, what should be taken into account during orientation surveys. Therefore, in addition to the above mentioned principal tasks to be solved, the clear understanding of physico-chemical and geological nature of processes controlling the selection of geochemical prospecting technique in a specific area is needed.

Methods and principles of comparison between results obtained for each size fraction studied is of great importance in obtaining correct and reliable choice of the optimum size fraction. Many publications are still found to contain a description of the selection of such fraction based on the comparison of certain chemical element in different size fractions using the "more - less" principle. The other principle is based on comparison between graphs of frequency distribution of chemical element in different size fractions of the sampled material and their geometric (arithmetic) means.

Such principles of the selection of the optimum size fraction undoubtedly produce good results for investigators. However, it is advisable to apply more accurate principles of comparison between study results of the various size fractions, which have successfully tested by Soviet geochemists. The proposed principles are based on the comparison between studied size fractions, using parameters of local geochemical background, contrast indexes and dimentions of the revealed anomalies.

Dimentions and contrast of hypergene anomalies are intemately connected with the parameters of background which is described by two values: by background value of the element ($\tilde{B}$) and by standard factor (ε) for lognormal distribution, or standard deviation (s) for normal distribution. Therefore, the study of the local distribution of chemical elements at the "background" localities is obligatory.

In practice, the contrast index is confused with the C_{max}/B ratio. However, the correct evaluation of the contrast index (γ) demands to compare anomalies not only with the level of the background but also with its consistency of which the standard deviation $\underline{s}$ (or ε) is the mesure. In other words, the contrast index is provided by "signal-to-noise" ratio, i.e. relation of the geochemical anomaly amplitude C_{max} minus the background value to the magnitude of the standard deviation (Solovov, 1987).

Thus, the contrast index is founds as follows: $\gamma = \frac{C_{max} - \bar{x}_b}{s}$; for normal distribution, and $\gamma = \frac{\lg C_{max} - \lg \tilde{B}}{s_{\lg}} = \frac{1}{\lg \varepsilon} \cdot \lg \frac{C_{max}}{B}$; for lognormal distribution, where: $\bar{x}_b$-is average arithmetical content, $\tilde{B}$-is average geometrical content.

To define the dimentions of the revealed anomalies it is advisable to employ a notion of their "effective dimentions", which are not the properties of chemical elements but have an important technical implication since the dimentions of anomalies increases with the increase in accuracy of geochemical investigations and decrease in C_A (Solovov, 1987). This is very important for discovery of relatively weak anomalies, especially during geochemical exploration by dispersion trains with low sampling density.

Generally accepted the lowest anomalous element content found as $C_A = \tilde{B} \cdot \varepsilon^3$ or $C_A = \bar{x} + 3s$ ensures the outlining of anomalies and determination of their effective dimentions by uniform criteria. To outline weak anomalies, including those detected under complicated exploration conditions, the lowering of the threshold value is practiced according to the criterion: $C_A = \tilde{B} \cdot \varepsilon^{3/\sqrt{m}}$ or $C_A = \bar{x}_b + 3s/\sqrt{m}$, where m= 2, 3, 4,...9 is the number of sampling points allowing their jointing on the geological map into one common anomalous contour, i.e. forming the groups of geologically correlated points with common outlines (Solovov, 1987).

Thus, the sufficiently strict principles of the optimum size fracrion selections lie in comparison of the local geochemical background parameters and effective dimentions of anomalies for each chemical element of interest by each studed size fraction of the sampled material.

Summary of the collective experience in selection of the optimum size fraction allows to single out a number of tasks to be taken into account as early as the planning stage of orientation survey and exploration work. The major tasks are:

- discovery anomalies of maximum effective dimentions at a possibly high contrast, which allows to reduce labour cost of sampling due to decrease in sampling density;
- achieving a preset probability of discovery of mineral deposits which are goals of explora-

tion programme in a specific area;

- ensuring a good reproducibility of the samping data;
- solution of the tasks of obtaining objective data reflecting the natural distribution of chemical elements in the anomalies associated with mineral deposits and in the accumulative anomalies formed at different geochemical barriers;
- ensuring the possibility of quantitative evaluation of the secondary haloes and dispersion trains with calculation of productivity and prognostic resources of metals in the expected targets, which also related to the choice of corresponding method of samples analysis.

Determination of productivity and prognostic resources by geochemical data is an important integral part of prospecting since this allows to quantitatively sort out the revealed anomalies and to select targets to be involved in follow-up programmes.

Thus, in exploration for mineral deposits by secondary haloes and dispersion trains the choice of optimum size fraction of the sampling plays a rather important part in achieving the objective of the prospecting programme since such a choice bears on the whole system of interrelated actions and their results. This system is aligned as follows:

- choice of the sampling size fraction based on the orientation survey results and choice of the method of samples analysis →
- determination of the effective dimentions and the contrast of geochemical anomalies formed on the account of mineral deposits which are the targets of prospecting →
- selection of the sampling density (sampling grid) ensuring a reliable solution of the prospecting tasks →
- revealing the anomalies with the probability not lower than the present one →
- application of the method of quantitative interpretation of geochemical anomalies →
- choice of targets to be involved in the follow-up programme.

Naturally, this system can effectively work only with due account of the most important lanscape-geochemical peculiarities of each specific area involved into geochemical survey and, above all, with due account of the complications affecting this survey.

HOT DESERTS

The lanscapes of hot deserts are characterized by the excess solar energy, great prevealence of vaporability over the precipitation, very poor vegitation, weak influence of living matter on the water migration of chemical elements, lack of developed soils and by a good exposure of bedrock. All this leads to mostly mechanical migration of mineral compounds in the present-day desert landscapes. Such a migration is also activated by strong wind erosion (deflation) and intense wash-off of the weathered products during rare rain periods.

The prevealence of the mechanical transport of mineral compounds in deserts suggests (and this has been confirmed by practice) that under such conditions the relatively coarse size fractions of the loose material are more representative than fine size fracrions. And if young loose sediments of the study area diluted by admixture of eolian material (usually fine enough), the representativity of the fine size fraction becomes even lower. In such a case, a problem arises to remuve the deluting effect of eolian material, transported by winds.

In the course of establishing the fact of eolian contamination of loose sediments, the character of processes of oxidation and transportation of "ore" material is studied as are the data by investigators-geographers on granulometric composition of eolian material from different deserts of the world and its dependence on the velocity of the dominating winds. Then the data of local meteorological stations on the velocities of the dominating winds are gathered. This forms the basis for planning and carrying-out the orientation surveys in selection of the sampling size fraction.

When geochemical survey is planned on a new, inadequately studied area characterized by eolian contamination of loose sediments to be sampled and by limited initial data needed for orientation survey, the prospecting programme can be started right away with the following idea in mind: the solution of the problem of elimination the eolian admixtures from the samples lies in determination of the prevealing size of wind-blown particles and their removal from the sample. In such cases, data by geographers who have studied the granulometric size distribution in eolian material from the different deserts of the world long ago, can be tentatively applied. Summary of such data shows that practically in all deserts of the world (except Atakama) from 70% to 100% of wind-blown material have a size particle under 0.25 mm. Therefore, in a new or any other area with unknown targets to be involved into orientation survey for selection of the size fraction, the prospecting by secondary haloes and dispersion trains can be carried out with the use of the fraction -1 +0.25 mm (Bugrov, 1983). Subsequently, after revealing of the ore target, the selection of the size fraction can be redetermined with the aid of orientation survey.

When such targets are avaliable the issue of selection of the optimum size fraction is solved on the basis of the orientation survey results. But planning and conducting of work is implemented with due account of the above principles. However, in practice one can, until now, run across the fact of inadequately prepared orientation surveys, for instance, by dispersion trains. Some investigators study distributions of chemical elements in fine fractions (under 70-80 mesh) dispite the presence of eolian admixtures in the stream sediments sampled. Others start by sieving-off only coarse (over 10 mesh) size fractions. Still others carry out orientation surveys by individual profiles (2-3) across a dry valleys with samples taking every 10-20 m along the profiles spaced 100-200 m apart and lain out 300-500 m from the ore occurence.

Such experiments fail to take into account the important fact that fine size fractions of bottom sediments are, as a rule, contaminated by eolian admixtures and, in sampling coarse size fractions, the reproducibility of the data obtained decreases; besides, the dispersion trains are linear targets which should be studied along the streams draining the ore occurence.

In addition, prospecting method by dispersion trains is chiefly used during reconnaissance or regional study of the vast territories where mineral deposits of various genetic types can be present. Therefore, the sampling procedure and choice of the method of sample analysis should be optomized with the view of obtaining reliable information on the maximum amount of the expected chemical elements. It is known, that the employment of the fine size fractions (-80 or -200 mesh) as the basis for prospecting with the use of cold extraction of base metals leads to the loss of information on rare and rare-earth elements.

The use of prospecring method by secondary dispersion haloes in desert regions has some limitations. They arise from inadequate development of soils and scare eluvial-deluvial fractions suitable for sampling. Eventhough such a material cannot be entirely used for geochemical sampling, for example, in search for an ores represented by minerals resistant to oxidation and mechanical dectruction. This is due to the fact that under such conditions very high concentrations of these minerals are formed eventhough the parent rocks contain them as accessory constitutients. Therefore, the exploration for certain rare and trace elements by their secondary haloes (or dispersion trains) may result in disclosing the accumulative anomalies pointing out, at best, to the zones of lean mineralization.

HUMID TROPICS

In such areas, the important features uniting the landscapes of constantly and seasonally wet forests, humid savannahs and savannah forests of equatorial, tropical and subtropical belts are the following:

- vigorous biological rotation of chemical elements due to abundance of heat and moisture, prevalence of chemical weathering of rocks and ores and a rapid progress of these processes;
- very rapid disintegration of dead vegetation with vigrous activity of microorganisms accelerating the rotation of chemical elements;
- extraction from soils and atmosphere of a great amount of chemical elements with passage of oraganic matter of the dead organismus into mineral state in the course of interchange of substances (Perel'man, 1979).

All this favours the formation of the secondary haloes and dispersion trains of considarable dimentions and aid in search for mineral deposits. Nevertheless, the selection of the optimum size fraction of sampling is of a great importance for obtaining reliable results during geochemical exploration in such areas.

Thus, the prospecting by secondary haloes and dispersion trains with collection of -80 mesh fraction and application of colorimetric analyses and methods of partial extraction of metals (for example, the method of cold extraction) on 3-5 chemical elements (Webb, 1958; Haweks, Webb, 1962) became a common practice in 1950s-1960s in the regions of humid tropics of Africa for discovery of deposits of a limited amount of metals. Such technique of prospecting proved to be payable since it allowed to conduct analyses immediately in the field camp to make work fast and cheap. However, the limited amount of the elements analysed rendered the data obtained incomplete. The other deficiency of this technique consisted in impossibility to use the data obtained for quantitative evaluation of the geochemical anomalies.

Nevertheless, many investigators transfer the experience of the -80 mesh sampling to other regions with employment of spectrographic analyses of samples for obtaining information on 30-40 chemical elements. Frequently, this leads to the methodical errors and unfavourable results of prospecting for mineral deposits by secondary aureoles and dispersion trains. Thus, in the Madhya Pradesh State (India), in the area containing tin-bearing pegmatites with coarsely crystalline cassiterite, more than 90% of tin is detected in the size fraction over 70 mesh. But initially the field programme was carried out with sampling of the -80 mesh fraction, and dispite the presence of visible fragments of cassiterite in the sampled surfical material, a negative results for tin was obtained. Subsequent work indicated that 93.7% of the tin amount is concentrated in the -10 +70 mesh size fraction comprising only 39.4% of the loose material mass, while the -80 mesh fraction comprizes less than 1% of the overall amount of tin, although it makes up 45% of the loose material mass. That is why the tin contents are detected with great difficulty in it. This points to necessity of taking into account all geological and geochemical data while selecting the optimum size fraction of sampling and calls for a great caution in applying the experience of different investigators to other regions.

The experience available (Levinson, 1980) shows that in other cases, for example, in areas where duricrust is available, the most contrast anomalies of considerable dimentions, for some chemical elements of good mobility in water, can be obtained by sampling a coarse soil fraction (+1 mm) or fragments of the duricrust. Many other examples may be given, but it is already clear enough that the correct selection of the "representative" sampling fraction plays an important part in successful solution of prospecting tasks during geochemical surveys.

CONCLUSION

The need for effective and reliable solution of prospecting tasks facing the geochemical surveys by secondary aureoles and dispersion trains necessitates the application of stricter methods and principles of selection of the optimum size fraction of loose material sampling than those frequently in use. It is especially true of geochemical surveys conducted in the areas under complicated prospecting conditions.

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GEOCHEMICAL MAPPING IN THE USSR

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INTRODUCTION

In our country, the idea of the International geochemical mapping came to mind of scientists in the 20s of this century. V.I.Vernadsky was the first to put forward the proposal to create a radioactive map of the Earth's crust. This map was intended at representing the distribution of radioactive elements and corresponding change of thermal effect (Vernadsky, 1983). In the 30s A.E.Fersman (1931) proposed the principal grounds of geochemical mapping in connection with the problem of geochemical zoning of the Earth (recognition of geochemical provinces) and search for useful minerals.

A systematic geochemical mapping of the country was started since the 50s. It mainly involves works conducted along with compiling state geological maps of 1:200000 scale. They cover over 50% of the country territory. A number of establishments compiled specialized geochemical maps aimed at solving the problems of prospecting, general geochemistry and ecology. Some characteristic features typical for our country should be considered in executing regional geochemical works similar to IGCP Project 259. These are:

1. Huge dimensions of the territory (1/7 of the whole globe land area);

2. Landscape and geological diversity;

3. Continuous period of work (50 yrs)which provided a great deal of information nonuniform in methodology, sampling media, number of elements and quality of analyses.

4. Dissimination of information amongst a big number of producers both regional and bureaucratic;

5. Varying administrative and economic situation.

Considering the above features in compiling transregional geochemical maps it should be stated that the main difficulties are the same as for "International Geochemical Mapping" Project on the whole. They imply compatibility of results of different regional surveys, financing and organization. In addition there is a problem of huge nonuniform previously collected information and the lack of modern analytical equipment.

Below the main types of regional geochemical maps being compiled in the USSR are briefly described. Considering the objectives and scale of the maps they are divided into three groups: (i) geochemical maps of common use, (ii) special-purpose (specialized) and (iii) review maps.

Middle-scale geochemical maps for common use

The maps of this group comprise the main bulk of available geochemical information in the country. The mapping is as a rule conducted jointly with the state geological surveys of 1:200000 scale. It was mainly made from secondary media (soils, bottom, sediments, more rarely water and vegetation) based on semi-quantitative optical emission spectroscopy and predominantly aimed at solving prospecting targets. They were recently supplemented with the ecological problem.

The works are normally conducted according to unified techniques which are regularly supplemented by new manuals and directions, confirmed by the Ministry of Geology of the USSR. The latest directions of this kind were published in 1983.

A number of computerized systems developed by different regional establishments (Evdokimova, 1978; Kogan et al., 1988) are used to handle the results. One of these is "Geoscan-200" system which may be used both for processing a homogeneous information and for summerizing data of different surveys carried out on different media. According to this approach a map of anomalies in the regions of BAM zone was produced. It combines the results of surveys made from stream sediments, soils, water and bedrocks. The principal results of this work consist in the evaluation of the situation from old data in order to choose the direction of further works.

The state geochemical surveys of 1:200000 scale made it possible to create a set of single-element and complex forecast-geochemical maps. They are as a rule complemented by additional maps of geochemical enventory and landscape-geochemical regionalization. The latter demonstrate classification of areas according to main parameters which define conditions of application of different geochemical methods: geological structure, relief, climate, etc. The theoretical grounds of landscape-geochemical zoning are elaborated in a number of works of the Soviet authors (e.g. Glazovskaya, 1967; Mitskevich, Suschik,1981). For routine geochemical surveys various methodological manuals are used in order to compile the landscape-geochemical maps (e.g. Methodological recommendations, 1989). Such maps provide the possibility to choose appropriate sets of optimal geochemical approaches and to estimate the results of previous studies for recent works.

An experience of small-scale landscape-geochemical zoning (e.g. Perelman, 1964) is undoubtedly useful for realization of the project "International geochemical mapping" and compilation of the Geochemical Atlas of the Earth.

Specialized geochemical maps

Such maps are compiled for solving prospecting, ecological, scientific and methodological problems. These are maps of ecological risk, sick rate, snow-geochemical, atmo-geochemical, etc. The scales vary from 1:1000000 to 1:10000 and more. The most common scales are 1:50000 and 1:200000. The contents of some specialized maps are illustrated in Figs. 1-3 which present twice-reduced black-and-white copies of some colour maps from the "Ecological Atlas of Moscow".

The compilation of specialized geochemical maps is getting particularly important in connection with ecological problems. At the moment, the geochemical atlases or sets of specialized geochemical maps are being constructed for over 200 cities of the country. A special system "ECO-SCAN" is developed for the purpose of ecologo-geochemical monitoring of the environment. It allows to find out the degree, specific features and spatial localization of anthropogenic pollution. The system "Multi-dimensional geochemical field"is also improved.

Review geochemical maps

The compilation of such general geochemical maps for the whole country or its largest part is normally carried out on 1:000000-1:10000000 scales and more rarely 1:500000. Their major goal is geochemical zoning of territories, i.e. to distinguish the geochemical territorial units of different ranks (megaprovinces, zones, provinces, regions, etc.). Such a zoning is rather useful for solving the problems of forecast and search for mineralization, environmental protection, medical-geochemical evaluation of the territory and other problems. In constructing regional geochemical maps different media are used, e.g. bedrocks, stream sediments, biological objects.

The maps constructed for bedrocks normally show the geochemical characteristics of different systems: structural-formational zones and geological complexes or geochemical types of rocks (Geochemical map..., 1982; Geochemical map..., 1984; Geochemical map..., 1979, etc.). They are as a rule supplied by the schemes of geochemical regionalization demonstrating geochemical provinces and zones, deep faults, types of epigenetic processes.

The examples of review maps of secondary media are "Hydrogeochemical map of the USSR of 1:10000000 (VSEGEI) and landscape-geochemical maps of Nizhniy Don and North Caucasus of 1:50000 scale compiled by Alexeenko V.A. et al. (1986).

CONCLUSIONS

In the USSR the idea of geochemical mapping arose in the 20s of the present century when V.I.Vernadsky and A.E.Fersman posed the problem of geochemical mapping and zoning and proposed the approaches to solve.

Within the time span from the 50s to the 80s the geochemical surveys covered over 50% of the country territory. A huge bulk of nonuniform geochemical materials have been collected, their informative capacity still not completely used. This fact necessitates, along with new surveys, the evaluation of geochemical information of previous works and resampling of some territories in accordance with new tasks and methodological level of modern geochemical mapping.

Despite the difficulties of the last years, the projects of comprehensive multi-aim geochemical surveys of average

(1:200000) and small scales (1:1000000) using primarily secondary media (region adjoining Chernobyl, Uzbekistan, South Siberia) have been elaborated. The projects of compilation of geochemical enventory maps of the USSR, multi-aim geochemical maps of the USSR (1:1000000), individual regions (1:200000) and regions (1:50000) have been developed.

The experience of geochemical mapping in the USSR shows that to accomplish the idea of "International geochemical mapping" jointly with independent international projects it is important to involve sufficiently large national and regional projects as well as creation of geochemical polygons similar to those in the Caucasus and Trans-Baikal are in order to master coordinated methodological approaches.

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FIGURE CAPTIONS

Fig. 1. The average daily fall-out of the heavy metals with dust.

1 - the reference fall-out level corresponding to a low pollution typical for nonindustrial settlements;
2 - middle level (5-10 times higher than reference one);
3 - high level (10-50 times higher than reference one;
4 - very high level (50-100 times higher than reference one). The main transport roads are shown by solid lines, the main rivers by thin lines.

Fig. 2. The heavy metals pollution of the city soils.
1 - the natural level corresponding to the pure territories (summary index is taken as 1; 2 - low level (total pollution level is 8-16 times higher than natural level); 3 - middle level (16-32 times higher than natural one); 4 - high level (32 times and more higher than natural one). Other signs are the same as in Fig. 1.

Fig. 3. The city regionalization according to he heavy metal pollution.
1 - pollution is practically absent; 2 - remainder pollution (accumulation of heavy metals in soils, the level of the recent fall-out is not high; 3 - recent pollution (the heavy metals accumulation is found in the snow, the pollution level is not high); 4 - both the remainder pollution and the recent one; 5 - typical associations of the pollutant elements and their concentrations normalized to the natural level in the snow cover (above the line) and in the soils (under the line):

1 $$\frac{W_{136}\ Mo_{125}\ Ni_{88}\ Co_{57}\ Cr_{19}\ Zn_{14}\ Cu_{9}\ Be_{8}\ Pb_{7}\ Ag_{6}}{As_{17}\ W_{10}\ Zn_{8}\ Ag_{7}\ Mo_{7}}$$

2 $$\frac{Cd_{123}\ W_{25}\ Sb_{23}\ Ag_{8}\ Be_{8}\ Pb_{7}\ Cu_{6}\ Co_{5}.}{}$$

3 $$\frac{W_{300}\ Zn_{20}\ Mo_{19}\ Cr_{13}\ Cu_{11}\ Pb_{11}\ Ni_{10}\ Ag_{8}\ Be_{7}Sn_{7}\ Co_{6}\ Se_{5}}{Ag_{50}\ Zn_{32}\ Sb_{20}\ As_{17}\ Cd_{16}\ Pb_{15}\ W_{11}\ Cu_{9}\ Sn_{8}\ Bi_{6}}$$

4 $$\frac{W_{38}\ Ni_{13}\ Zn_{11}\ Sn_{11}\ Ag_{10}\ Be_{10}\ Cu_{7}\ Pb_{6}\ Co_{5}\ Mo_{5}\ Ba_{5}}{Be_{33}\ Ag_{28}\ Pb_{10}\ Zn_{10}\ W_{9}\ Bi_{7}\ Ni_{5}}$$

5 W_{30} Ni_{10} Zn_{10} Ag_{10} Sr_{9} Be_{8} Cu_{7} Pb_{6} Co_{5} Mo_{5}

Ag_{167} Mo_{38} Zn_{19} Pb_{11} W_{10} Cu_{7} P_{5}

6 W_{23} Zn_{18} Ag_{15} Cu_{11} Be_{10} Ni_{8} Cr_{7} Pb_{7} Mo_{5}

7

Zn_{53} Sb_{45} Ag_{28} Cd_{17} W_{8} Pb_{7} Cu_{7} Sn_{5}

8 W_{23} Zn_{18} Ag_{15} Cu_{11} Be_{10} Cr_{7} Pb_{7} Mo_{5}

As_{43} Pb_{37} Zn_{21} Ag_{14} Sn_{13} Cr_{11} V_{6} Bi_{5}

9

Ag_{50} Zn_{25} Cd_{16} W_{11} Cu_{10} Bi_{6} Pb_{6} Sn_{6} Mo_{5}

10 Ag_{14} Zn_{12} Sn_{9} W_{8} Pb_{6} Cu_{6} Mo_{5}

Sb_{22} Cd_{17} Zn_{16} W_{8} Cu_{6} Sn_{6} Bi_{5} Pb_{5} Mo_{5}

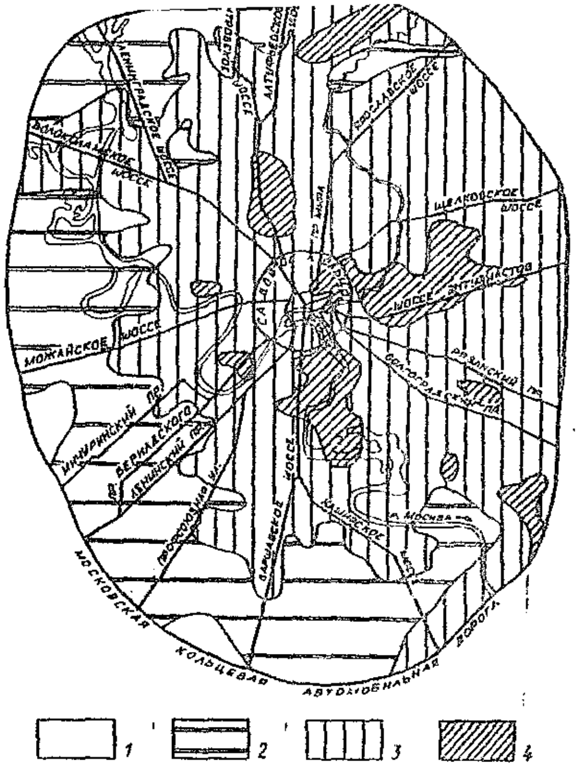
11

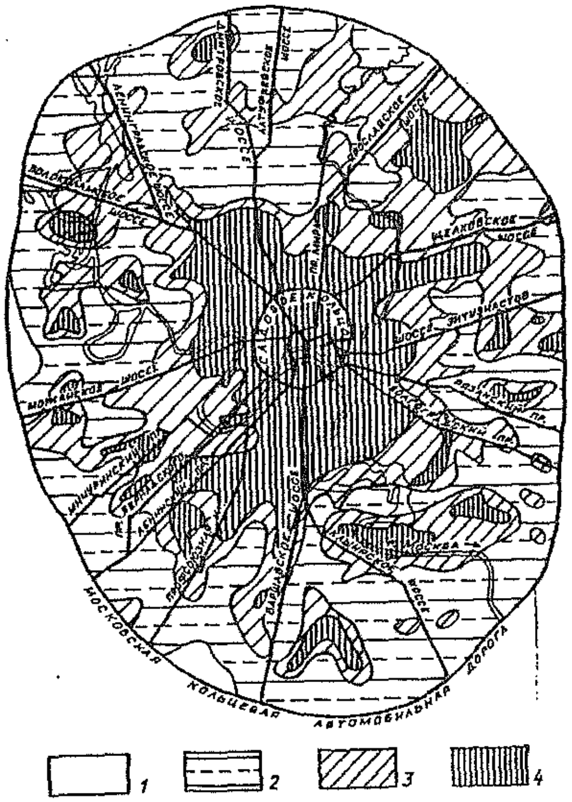
Zn_{36} Cd_{17} Ag_{15} Sb_{15} W_{15} Pb_{5}

12

Cd_{15} Zn_{8} Ag_{7} W_{5}

Figure 1.





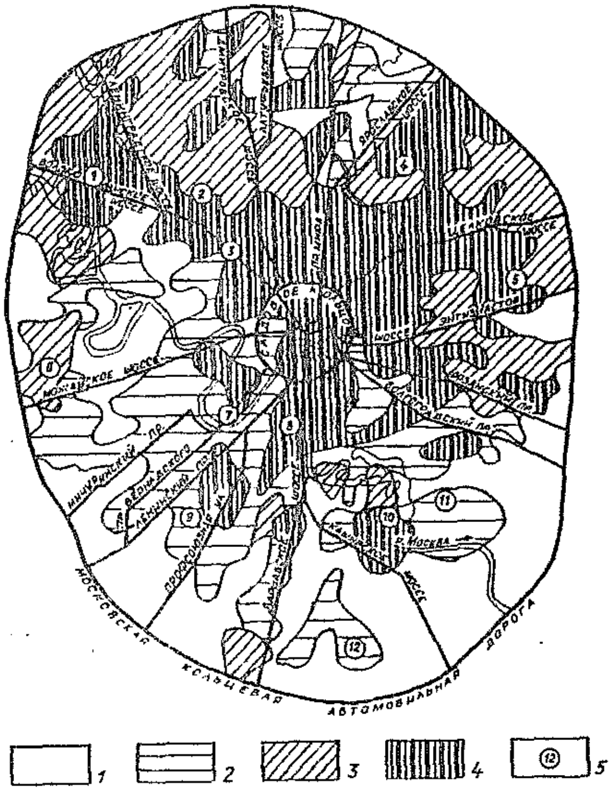


Figure 2.

Figure 3.

GEOCHEMICAL AND TECHNOLOGICAL RESEARCH OF METALLURGY WASTES IN POLDI KLADNO STEEL-WORKS NEAR PRAGUE

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1. Introduction

The resources of the raw materials of Czechoslovakia are limited. That is why the Geological Survey are passing also to non traditional resources, which have not been exploated till now. We are looking for them especially in industrial wastes using new technologies. An other important reason is the negative impact of wastes into an environment.

The research methods of wastes and secondary metall content raw materials from wastes are not so different from natural deposits on which the classical geological, geochemical, geophysical and technological methods are used. We used the experience on some project dealing with these problems during last years - as for exemple - possibility of utilization of neutralization and grinding sludges from glass industry, extraction possibillity of some metalls from galvanic process waste and others.

The most extensive project is the technological and ecological study of waste deposit of Poldi Kladno steel-works near Prague.

The dupm body is situated on the outskirts of Kladno town about 10 kilometres west from Prague. It covers the area of 50 hectares and it's hight reaches up to 70 metres. The materials of this dump represent a real danger for its surroundings - especially through the outflows of highly contaminated waters or through the out let of dust and ash. The Kladno steel-works has no other areas where to deposit a new incoming wastes and actual capacity of this dump area is sufficient for two years only.

This dump represent about 20 millions tons of different materials, which could become an interesting source of secondary raw material comparable with classical natural deposit. The results of research can be used for another dumps of this type in Czéchoslovakia.

2. Research methodology

The first stage of research took place in 1988 and 1989 with the aim to explore the proper dump deposit, its surroundings and the influence of dump wastes on the local exological system. Following complex methods have been used:

- geological and engineering mapping
- geophysical and geochemical research
- laboratory and technological tests.

2.1. Geological and engineering research

The following research was carried out:

a) detailled geological mapping of dump surroundings;

b) preparation of schematic map of the waste material;

c) sampling and laboratory evaluation of the waste material.

The underlying rocks are represented by Upper Proterozoic slates with low degree of permeability. Small part of territory is built by sediments of Upper Carboniferous and the biggest part is covered by Cretaceous sediments with fracture permeability.

The beginning of waste deposition started in 1951 and about 24 millions tons of material has been placed there up to date. The surface geological mapping was only used because the drilling of boreholes is almost impossible as it was tested in several metallurgical dumps in the past.

A part of this study was the evaluation of archive data and the analyses of historical production in Kladno steel-works. In first stage, the blast furnace slags and slush have been there deposited. After 1975, when the blast furnaces stopped the production, steel slags from the martin and electrical furnaces were dumped.

Other waste products are represented by steel-works slush, energetical wastes as for exemple cinder and ash.

The composition of waste products is very important for the technology of their transformation into the secondary raw material. The research indicated that the position of metallurgical and energetical waste within the dump body is very complicated - some of them are mixed together and especially during the last ten years almost chaotic deposition took place and what is the most serious - even toxic material has been found (the eastern margin of the dump).

Despite this facts, in the combination of all research, we succeded in the location of the main types of waste materials with cheap and rapid methods.

2.2. Geophysical research

The aim of the geophysical measurements was to assume if the body of the dump represent an physical anomalies with regard to the surroundings and to try to differentiate the waste materials within the body.

Several methods have been chosen to obtain a complex geophysical picture of the dump data:

a) temperatures in the deepth of 0,8 metres;

b) the intensity of magnetic field;

c) natural gamma activity (K, U, Th content);

d) radon level in soil.

The results of temperature measurements indicate the body of waste dump as distinctly positive anomaly. The average temperature is about 25°C, locally even 60°C and in the depth of 3 metres until 240°C.

The areas of increased temperature correspond to the extension of slag layers. Presently these areas are checked for the use of the slag's heat potential for industrial purposes.

The results of magnetic field intensity and magnetic susceptibility can be used for indication of these anomalies with higher content of ferro-magnetic i.e. layers of Fe-slags.

The measurement of gama activity has shown several times higher level in the dump than on the surroundings. The beds of ash from power plant and cinder are the most radioactive.

The radon content in soil atmosphere is also much higher - ten to twenty times more than the value of normal background. From the ecological stand point the radon content is rather insignificant, it quickly dissolutes in the air.

The U and Th content in cinder and ash and their daughter products on the other hand could substantially hinder the use of these materials as building products purposes.

Generally the geophysical methods applied during the research have shown good results - they supplied the cheap, simple and valuable information.

2.3. Geochemical research

It took place simultaneously with other activities and was undertaken in several directions:

- research of waste composition;
- detailed investigation and ecological evaluation of ecological impact of dump on the surroundings:

a) study of heavy metals content in water;
b) study of gas exhalation above the dump;
c) estimation of fall down of dust from dump deposited on the nearby fields.

The main aim was concentrated to distinguish the degree of the pollution of the environment within the studied area produced by the dump or by the whole Kladno industrial complex.

The stream cutting through the industrial area are strongly enriched by heavy metals - mainly by Fe, Mn, Zn, Cr and the group Cu - Mo - Ni. High content of sulphates and chlorides was also detected. Special attention was paid to presence of the cyanides. The degree of pollution of stream waters is generally very high.

The contamination of agricultural soil in the neighbourhood of dump was measured on several profiles. The content of the most harmful toxic elements (Cadmium and Arsenik) in all analysed samples is lower than detection limit of the analytical methods. Other element content in top soil in the fields in the vicinity of dump is much higher comparying to the area outside the reach of the dust falldown from the dump.

High contents of heavy metals and Cadmium was confirmed in the sediment from waste water treatment station.

2.4. Technological research and evaluation of reserves

The investigation of typical samples was completed by the semiindustrial technological research. Two trenches were made across the dump for mapping the composition of waste materials and the technological sampling.

Preliminary calculation indicate, that the dump could represent an important source of secondary materials:

- about 5 millions tons of steelwork slug for use as building material, 700 000 tons of bound Iron and about 300 000 tons of metallic Iron; 200 000 tons of Manganeese and 50 000 tons of Chromium;
- there is deposited about 3,4 millions tons of blast furnace slug supposed to be used as a fertiliser in agriculture and/or in building industry;
- important is the presence of about 1.8 million tons of blast-

furnace slush with composition 38-40 % Fe, 0.8 - 1.2 % Zn, 0.2 - 0.5 % Pb and 0.02 - 0.07 % Cu.

3. Conclusion

Geological, geophysical, geochemical and technological research of industrial waste can be useful for ecology and for the supplies of secondary raw materials.

IMAGE-PROCESSING OF GEOCHEMICAL DATA TO MAP GEOLOGICAL STRUCTURES AND ALTERATION ZONES

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INTRODUCTION

To fully utilize all the intrinsic information in spatially referenced geoscientific data they must be portrayed in a way that can be clearly and quickly understood, without the introduction of artifacts during data processing. This requires an understanding of both the data and their application, and is greatly facilitated using image processing techniques recently developed for microcomputers. Geochemical surveys that are designed to map element distribution patterns define chemical surfaces that resemble topographic surfaces or geophysical potential fields (e.g. from aeromagnetic surveys). Traditionally, these types of spatial data have been displayed as contour maps. Enhancement techniques such as the creation of shaded-relief maps have dramatically improved the clarity and impact of topographic and magnetic data and, perhaps more importantly, have revealed subtle patterns that were overlooked before. When applied to geochemical data these techniques provide similar improvements in the clarity and resolution of subtle features, especially linear and curvilinear features that are related to bedrock structures. These linear features arise in three main ways: 1) the juxtaposition of two geological units of contrasting composition (e.g. along an intrusive or faulted contact); 2) alteration along a linear zone (commonly fault-controlled); and 3) the offset of continuous geological units along a fault.

DATA PREPARATION

Although raster images and more conventional contour maps and symbol plots of geochemical data can be produced without regard to the characteristics of the data, the resulting images or maps made in this way are seldom satisfactory. Shaded-relief images created using poorly chosen gridding and contouring parameters tend to highlight the defects of the image design rather than geochemical patterns. When the characteristics of the data are determined and taken into account, the images are usually acceptable with only minor fine tuning, and, moreover, the data analysis will suggest which parameters should be adjusted. The following steps are recommended to determine the gridding and contouring parameters appropriate for each element in a geochemical dataset.

1 Data Evaluation

1.1 Examination of element frequency distributions. This is accomplished through the calculation of basic statistics (mean, median, standard deviation, coefficient of variation and range) and probability plots (Sinclair, 1976). For elements that are clearly not normally distributed a transformation is recommended. Usually a log transformation is used for trace elements having a high coefficient of variation ($>>0.5$). Outliers and major populations are also identified at this stage. Outliers can be removed, although with the use of robust filters (Chork and Mazzucchelli, 1989) in subsequent processing this may not be requried. The identification of any major, distinct populations may aid later interpretation of the enhanced images. Contour levels are chosen from the probability plot, using either the approach of Sinclair (1976) or on a percentile-based scheme.

1.2 Evaluation of data quality and sources of error. Where available, data from site duplicates should be used to obtain for each element an indication of data reproducibility with respect to the overall range of the data through a simple analysis-of-variance approach (Garrett, 1973). If the results are available from more complex nested sampling designs (e.g. Garrett and Goss, 1980) that permit variance to be measured at more levels (laboratory, site, sample cell, etc.), this information should be evaluated too, but the most important level is at the sample site.

1.3 Examination of the spatial distribution of the data. A custom-written program (GRIDVIEW) is used to determine an appropriate grid cell size for the initial interpolation of the data from the irregularly distributed sample sites to a regular grid. An efficient cell size is one where the number of cells containing a single site is a maximum, while the number of cells multiple sites is a minimum. GRIDVIEW allows the cell size to be altered interactively, and calculates a histogram of the number of sites per cell for each cell size chosen. The program also displays the grid and the sample sites on the screen so that the uniformity of the sample coverage can be assessed visually. The data used here have a uniform random distribution, allowing the use of standard random gridding techniques to prepare a gridded data set. If the sample site distribution is quite uneven, alternative gridding methods may be required.

2 Image Creation

2.1 Initial gridding. This is carried out on the data, log-transformed as appropriate (step 1.1) using a grid cell size indicated at step 1.3. At this stage as much of the original character of the data as possible is conserved (including noise) by interpolating the value at each grid node from up to four nearest points lying within 2.5 times the length of the grid cell side, and giving more weight to values from nearer points than more distant points (typically an inverse of the distance squared is used as the weighting factor). For screen display the grid size is reduced if necessary by linear interpolation so that the image will fill the display screen. All the illustrations here have a pixel size of 1.1 x 1.1 km.

2.2 Initial image assessment. Shaded-relief images are created from the regridded data using a custom-written program (DISPLAY), which permits the gridded data to be rapidly displayed on microcomputer with a VGA monitor. DISPLAY, which adds colour capability to a grey-scale program by Teskey and Broome (1984), offers several options interactively, including: choice of colour or grey shades, inclination and declination of illumination, windowing (through decimation), and the possibility of displaying two images side by side, with independent display parameters. The image is evaluated subjectively for the clarity with which it shows geochemical features. The image at this stage usually contains a good deal of local variation which gives it a 'pockmarked' appearance that obscures the more continuous geochemical features (Fig. 1). The degree of this local variation (or noise) varies from element to element and is usually least noticable for elements whose variance at the sample site level is small compared with their overall variance (step 1.2). It also varies with shading direction, and is least noticeable when illumination is perpendicular to the main structural grain.

2.3 Smoothing and filtering. Much of the noise in the images at this stage is a result of the parameters deliberately chosen in the initial gridding (step 2.1). Changing the parameters at the initial gridding stage to increase the amount of averaging (e.g. by increasing the search radius, including a larger number of sites, changing the weighting factor to the inverse distance) will help smooth the data, and for many elements will produce a more satisfactory image. It is impossible, however, to choose a single set of initial gridding parameters appropriate for all elements. The alternative, outlined here, is to produce the initial grid that involves only a slight modification of the original data (a basic gridded data file that can be used for other purposes, such as inclusion in a GIS), and optimally smooth each element by filtering.

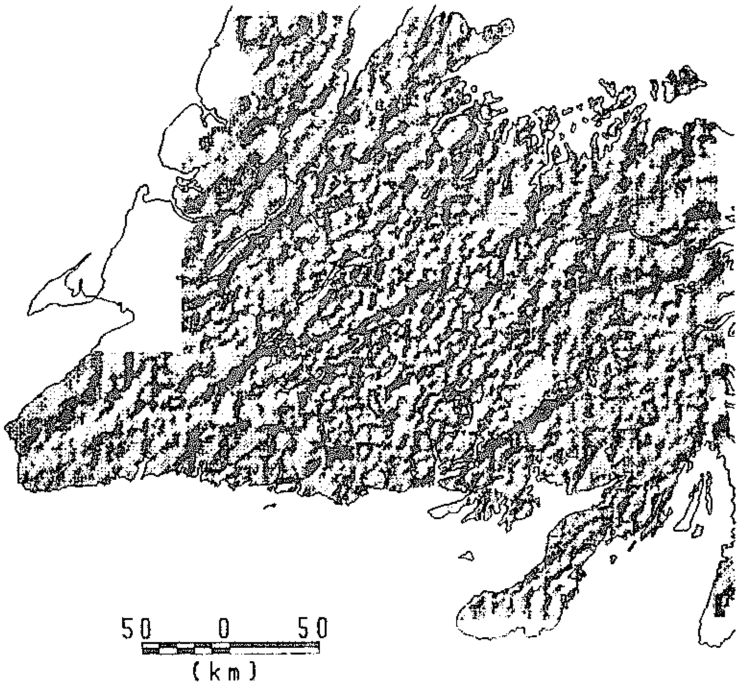

Figure 1. Initial shaded relief image of Sb in lake sediment in Newfoundland displayed as a greytone image. Grainy appearance is due to residual local noise.

Several methods for filtering geochemical data have been described. The simplest in concept is a moving average type (Howarth, 1983, chap. 5), using an n x n pixel window that is passed over the data one or more times. The degree of smoothing increases as n increases, and with the number of passes of the filter over the data. Robust alternatives are the Median filter and the Adaptive Trimmed Mean (ATM) filter (Chork and Mazzucchelli, 1989). The latter has been found to afford a robust and effective approach to smoothing regional geochemical data. To produce a satisfactory image, the various sizes of filter are tried and the results displayed and evaluated subjectively. With practice the number of trials can be greatly reduced. The results of using a 5 x 5 cell ATM filter (representing a 10 x 10 km window) on Sb are shown in Fig. 2. This image is still somewhat grainy and this graininess can be diminished using a moving average filter. This approach works well even for an element such as Au, where over 80% of the values are below the analytical detection limit, and the higher values are noisy (Fig. 3).

An alternative approach is recommended for summarizing data from large sample sets as small scale maps. An initial block averaging step is employed instead of step 2.1, where the original site data (log-transformed as appropriate) is averaged into square cells 5-10 times the average sample spacing. The cell averages are then gridded as in step 2.1, using a search radius large enough to include the four nearest grid nodes, followed by secondary gridding to a finer grid (Fig. 4). More smoothing can be achieved by adjusting the cell size used for the initial block averaging. The highly smoothed image retains a surprising amount of finer detail.

During smoothing by either method the variance of the data is reduced. Typically, however, there is a proportionally greater reduction in the noise component than the significant geochemical patterns, resulting in a better signal to noise ratio. The random noise tends to cancel, whereas the non-random geochemical signals tend to reinforce. To display subtle features after filtering it is advantageous to stretch the range of residual values to utilize the full colour range available on the image display system, a featured offered by DISPLAY, and most commercial programs. Final images are best displayed on a monitor with higher resolution than a VGA screen.

DISCUSSION

The choice of parameters used to produce shaded-relief images of geochemical dataset are dictated ultimately by the resolution of the survey itself. The term resolution as applied to a geochemical survey has not been defined clearly, but implicitly it refers to the subtlest geochemical feature that could be detected with some specified degree of confidence. The subtlety could be due to either the size of the feature (in which case sample spacing and the representivity of the sample medium would be the limiting factors on resolution) or its geochemical contrast (where data quality would be the more important factor). Sample spacing is fixed during survey design and is common for all elements, but representivity and quality will vary from element to element (representivity varying with the mobility of the various elements). Data quality can be measured from site duplicate samples, and representivity can be estimated in relative terms

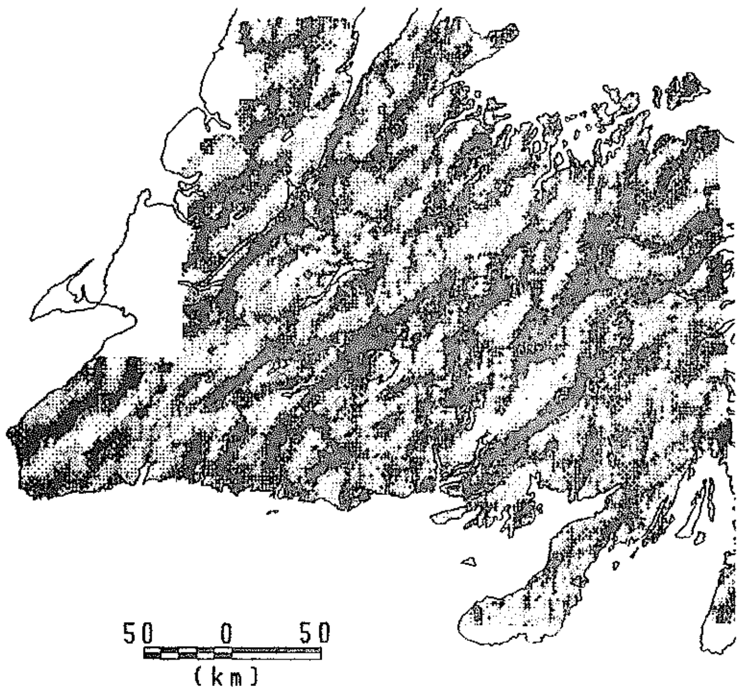

Figure 2. Greytone shaded image of Sb in lake sediment in Newfoundland after filtering using a 5 x 5 cell ATM filter.

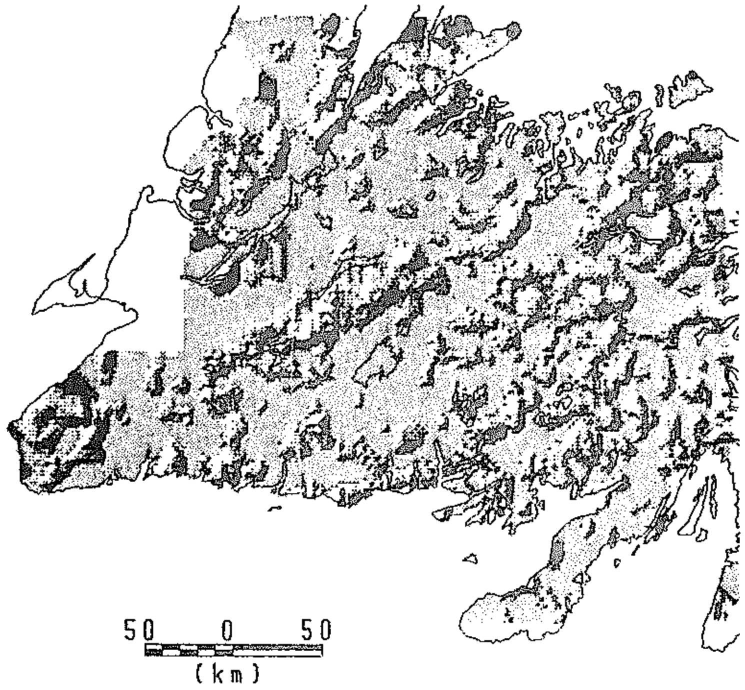

Figure 3. Greytone image of Au in lake sediment in Newfoundland after filtering using a 5 x 5 cell ATM filter.

from a nested sampling design or variograms, but the resolution cannot be exactly quantified because of the size-contrast ambiguity. The resolution of geochemical surveys for a geochemical feature of specified size and contrast is a function of both sample spacing and representivity (Fig. 5). Thus for a given survey, resolution varies from element to element, being a function of the different element representivities, or, to look at it from a different perspective, the resolution of a low density survey for Ni (one site per 200–400 km²) is roughly equivalent to the resolution for Au in a much higher density survey (one site per 7 km²) using the same sample medium (lake sediment). Other elements are intermediate between Ni and Au (e.g. Sb), and a rough guide to the relative order of resolution in a survey is given by the ratios of total data variance to within-site variance.

CONCLUSION

These differences in resolution for the different elements in a survey necessitate a flexible approach for producing images of maximum clarity for each element. Smoothing by filtering should aim for the best signal to noise ratio. The portrayal of data as carefully prepared images greatly increases their impact and the amount of useful information conveyed. Although some time and effort must be made for effective data presentation, the resources needed are minor compared with those expended on sample collection and analysis, and add a great deal to the overall impact of geochemical surveys. The linear features revealed by shaded-relief maps of elements such as Sb (Figs. 2 and 4) provide new insight into the structural control of hydrothermal systems in Newfoundland.

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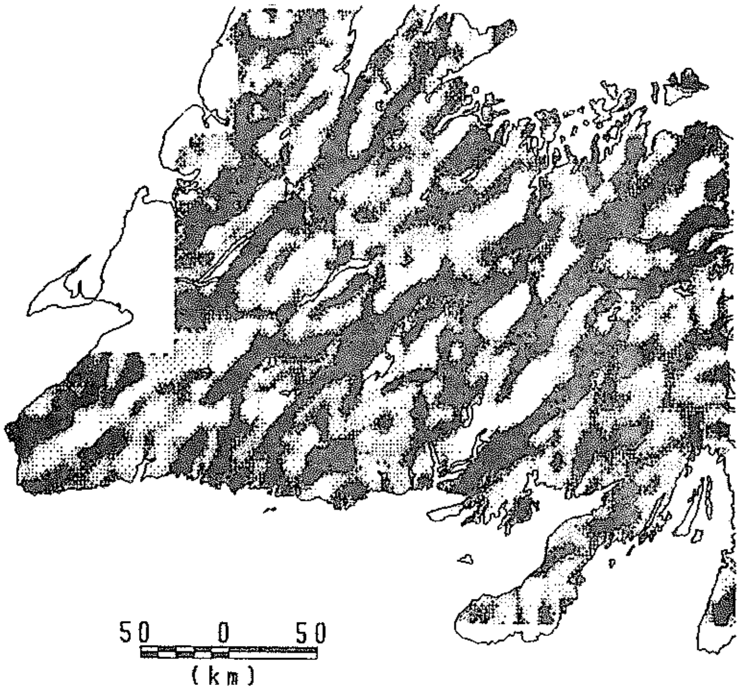

Figure 4. Greytone image of Sb in lake sediment in Newfoundland after block-averaging of individual values (log-transformed) within 7 x 7 km cells, and the random gridding of cell means to a 1.1 x 1.1 km grid.

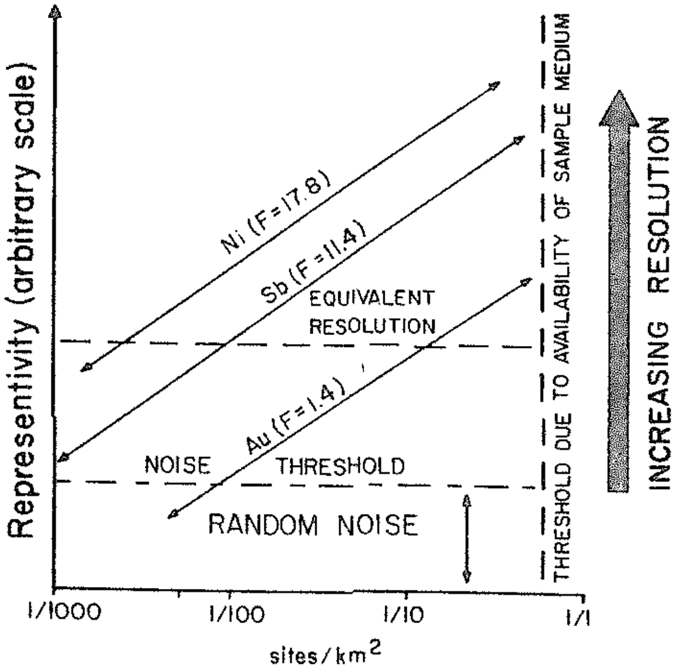

Figure 5. Schematic depiction of the relationship between sample density and element representivity in lake sediment data from Newfoundland. Representivity is approximated by the ratio of the total data variance to the within site variance (F values).

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Geochemistry of sulfide-nickeliferous ore-magmatic systems: a new approach to prediction and prospecting for deep seated deposits.

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The transition in a developed country during the last 30 years from the forecast and prospecting for exposed and near-surface deposits to unexposed, hidden and deep-seated deposits stresses an importance of techniques used in applied geochemistry, mineralogy, geophysics, and geology which is an absolutely essential pre-condition for the progress of geological sciences at the present stage.

However, today's constantly growing social-economic requirements: necessity to increase resources of mostly rich ores occuring in industrial ore fields, clusters and areas at great depth increases the importance of characteristic features of unexposed and deep-seated bodies, ores and ore fields, i.e. anomalous geological, mineralogical, geochemical and geophysical fields less characteristic and providing high resolution not always sufficient to solve a prospecting problem. Another important problem of the modern applied geology is a discovery of new ore fields in the vicinity of the old mining areas makes necessary the recognition of geochemically homogenous belts, provinces, and zones irrespective of their internal petrogenetic and metalogenetic heterogeneity. And the third probably the most important problem of the modern geochemistry is the establishment of a geochemical balance of the recognized geochemically homogenous belts for the development and application waste-free technologies enabling a rational development of the earth's deep zones.

The above mentioned topics make necessary to solve atleast two main problems:
- to establish main types of sulfide-nickeliferous ore-magmatic systems (SNOMS) and to verify recognized standard types of various origin;
- to characterize geological, mineralogically, chemically and geophysically anomalous (and not anomalous) fields of individual SNOMS in certain regions and to classify them with respect to their nickel potencial.

Ore-magmatic system (OMS) are natural associations of magmatic, metasomatic and ore assemblages and their geochemical haloes which resulted from single multiple, polyphase petrogenetic processes. SNOMS can be global tectono-magmatic systems (TMS) - Yenisei-Severnaya Zemlya belt, a system of greenstone belts of Australia(, superregional (ore areas and structural-metallogenic zones - Imandra-Varzug, Norilsk-Kharaelakh etc.), districts (ore districts - Pechenga, Norilsk, Kharaelakh), and local (ore fields - Talnakh, Little Stoby, Falcon Bridge and others).

SNOMS usually occupy active marginal parts of platforms and shields marked by anomalous crustal and mantle structures and by development of differently oriented fracture zones in areas of inferred Wadati-Zavaritsky-Benioff zones (4.4.9). The characteristic features of industrial SNOMS are: high tectono-magmatic activity of the area, the presence of one or several series of structurally complex multistage ore-magmatic assemblages, wide extent of metasomatic rocks and hydrothermal alterations, geochemical haloes and dispersion flows along fracture zones (FZ). Anomalous geochemical field (AGF) and anomalous geochemical flows (AGF) reflect the entire history of the emplacement, development and extinction of SNOMS adjacent to mantle faults, i.e. zones of the mantle melt migration, solution and fluids, juvenile crustal and surface water migration. The elucidation of geochemistry of FZ and feather joints is to give insight into geodynamics and geochemistry of SNOMS, to understand laws and sequence of their formation with space and time, i.e. to simulate geodynamics and geochemistry in the SNOMS development.

The geotectonic environment in the development of the volcanic series of SNOMS as well as their structure and composition is in many respects critical for the determination of nickel content of the system. By this method, we have established the relationship between the economic nickelcontent of SNOMS of Norilsk-Talnakh type and parameters of the contrasting-differenciated volcanic series of thePermo-Triassic trap magmatism of the second phase and showed a similarity in common trends in the SNOMS evolution of Pechenga and Norilsk -Talnakh type.

SNOMS of the Taimyr - Norilsk province.

A complete ore-magmatic model analysis showing quite a new approach to forecast and search for deep-seated copper-nickel deposits which can be applied to other deposits of magmatic-hydrothermal series was used by the authors for the largest nickeliferous province of the world - Taimyr - Norilsk province.

This province forms an integral part of the Yenisei - Severnaya Zemlya geochemically homogenous metallogenic ore belts of copper and precious metals. It provides an example of original geochemical inheritance of diachronic and genetically different ore assemblages which can form a mineral base for a modern regional industrial complex. The fundamental mineralogical-geochemical indicators of the belt are the follow:

- ore association, near-ore indications and haloes rich in chalcophilic elements (Cu, Mo, Ag, Au, Zn, Pb, Sn etc.);
- ore assemblage, haloes and dispersion flows are marked by a persistent chalcophilic to chalcophilic, chalcophilic to lithophilic, chalcophilic to siderophilic ratios;
- presence of concentrated haloes of chalcophilic elements forming chalcopyrite, bornite, chalcocite,sphalerite, galena, native gold and fairly peculiar accessories;
- spacial-time development of two series of ore-magmatic systems related to trap and granitoid magmatism of the mesozoic activization;
- adjacent occurence of two basic series of OMS depending on the major differenciation;
- relationship between endogenous and supergene geochemical fields (EGF and SGF) of ore areas of different origin and concentrations: large - rich continuous ore deposits; medium size - ore fields, impregnated ore deposits and haloes of rich ore bodies; small and medium size - ore zones and districts, haloes and dispersion flows of metalliferous masses and low grade ore deposits.

SNOMS of the Taimyr-Norilskprovince are associated with the mesozoic intercontinental rifting and related to marginal structure of the north-western Siberian platform marked by a high tectonic mobility not only in the Mesozoic but also in the Precambrian. The emplacement of the province at the junction of the Yenisei pericraton and Norilsk-Taimyr system of uplifts and depressions within the interferred WadatiZavaritsky-Benioff zone is determined by the position of the Taimyr-Tunguska through of the post-Karelian stabilization.

The data obtained on the content of Hg, K, H, N,He, Ar (including isotope dating) and another fluids in rocks and ores allow us to consider the major economic nickel zone as a long-functioning fluid system beneficiel for intense alkaline metasomatosis and formation of thick extensive AGF.

The discussed ore-forming system is related to the upper mantle and crust of great thickness and consists of several (usually no less thanfive) horizons. These black shale horizons are peculiar with respect to chalcophilic elements, they have a fairly thick basalt screen and are dessected by fracture zones which form a dep and elongated zone. This is a system which during the Middle of the Late Paleozoic to Mesozoic activization could have given rise to a structure of an economic nickel ore district,e.g. district SNOMS. The study of its geochemical zoning suggests an active concentration of AGF in fracture zones and anomalous geochemical flows on migration paths.

The development of the system consists of pre-magmatic, pre-ore, multiple volcanic, major intrusive and ore, main ore and innerintrusive,final intrusive and inner-ore, post-intrusive and final ore stages. The content of Cu, PGE, Au,Ag Hg,K increases as systems develops. It is due to the fact that the presence of contrasting zonal AGF and AGFl of these elements as well as metasomatic haloes of special composition and structure along with manifestations of young ore assemblages (PGE, polymetallic, As-Sb etc.) indicates the occurence of deep-seated SNOMS containing high grade ores. Mafic-ultramafic rocks are characterized by high (up to 120 cm^3/kg) water content, anomalous fluorine and nitrogen concentrations. The evolution of the SNOMS gaseous phase may be represented as the following (bases on predominant components): $CH_4 - H_2$; $H_2 - N_2$; $N_2 - N_o - CH_4$ and the evolution in the composition of water soluble fluid components: $HCO_3 - K^+$, Na^+, $Ca^{2+} - Cl^-$, SO_4^{2-}, HCO_3^- , $- Na^+$, $HCO_3^- - K^+$, Na^+, Ca^{2+}.

The estimates show that the recent notdepleted mantle was responsible for exctraction of nickel and cobalt from silicates. However, the original copper content is not sufficient enough to furnish concentrations characteristic of ore of the Norilsk-Talnakh type.

The pre-magmatic and pre-ore stage of the SNCMS development has the longest (from the Proterozoic do Upper Permian inclusive) and geologically most complex history. In Early Permian, the collision of Taimyr and the Siberian platform, its northern part, might have resulted in underthrusting of the oceanic crust. The involved oceanic sediments were the major source for water,sulphur and halogenic elements for fluid flows (which transported trace elements into AGF and AGFl) responsible for above discussed composition and changes of the paleomantle. Subduction stimulated the mantle convection and spreading and rifting processes occuping on the platform which finally caused the LatePaleozoic - Early Mesozoic trap magmatism to occur within the Siberian platform and the West Siberian plate. As a result at a depth of above 150 km there appeared melts of the contrasting heterogenous magma enriched in sulphur and chalcophilic elements; ore melts were subjected to liquation controlled by (nitrogen) - hydrogen fluids. The liquation caused separation of melts of different composition (ultramafic, mafic, intermediate) and separation of a single high sulphur liquid. In case of rifting, the layered fluid rich magma was implaced in upper part of the crust along the fracture zones.

Volcanic, major intrusive rocks and ore, and subsequent stages.

Mafic magma at the diapir top with maximal water fluid flow and high volatile contents, is formed on partial melting of the depleted mantle by the oppening of the upper parts of the chambers. The resulting magma chambers favour melting of the continental crust followed by the formation of rift systems probably underlain by the oceanic crust (Yenisei-Khatanga rift). The volcanic stage passed as mentioned earlier six phases. The parent melt of the four-stage second phase of the volcanic step is characterized by depletion towards south of the rift in Mg, K, P, S, Cr, non-ferrous and precious metals, by increase in Mn, V, persistent Fe content;as general, alkali content increases. Effusion of liquid mafic melt and ultramafic melt took place at early-final and terminal stage, respectively. i.e. the formation of contrasting series of lavas. Simultaneous intrusion of the layered mafic-ultramafic magma oversatured with sulphur and chalcophic elements marked the beginning of the emplacement of the economic nickel-bearing OMS of Norilsk-Talnakh type and the formation of intrusive chambers. Melanocratic basalts of the second and third volcanic phase are quite similar in composition and structure with basalt komatiites and it is a direct evidence for the presence of deep-seated SNOMS of economic importance. The marginal parts - "horns" and "ears" - of masses formed from a small part of a layered melt during the final stage of the third phase, are also a streight evidence for nickeliferous SNOMS. The final stage of the fourth phase witnessed the formation of ultramafic masses of Cu-Co-Ni assemblages exhibing, apart from high Mg content, also high P content, the proportion of Pt relative to Pd, Ni relative to Cu increases; AGF and AGFl are marked by low grade ore and predominance of accompanying elements over pathfinder elements. The main trend in evolution during the final phases of the volcanic stage and separate phases of later stages were the accumulation of Si, Fe and alkali metals in limited sites and extension of the anorthosite trend. Anomalous fields of peculiar composition and structure easily distinguishable on the basis of development and emplacement of OMS of a region are: related to effusives and intrusives (apart from economic nickel bearing).

The productive part of the volcanic stage of economic SNOMS shows the following series of migration mobility of elements: Co-Pb-V,Mn,Zr,Sr,Ba - Cu,Cr,Ni,Zn,Mo,Sn - Pd,Pt,Au,Ag, Sb,Bi,K (Ta),B,F,Cl. The above mentioned SNOMS in all horizons of the cover exhibit AGF of corresponding conditions of the series and distinct three-dimensional zoning. Petrogenetically, the most important phenomenon is the geochemical zoning due to mantle-crustal heterogeneites and primarily due to the presence of several regional SNOMS.

Phase IV and V of the SNOMS development may also be related to the volcanic stage whereas phase VI took place later. Phase IV marks the intrusion of a sulfide melt into bottom parts of complexes, chamber liquation and emplacement of Cu-Ni ore deposits, and formation of rhytmic stratification. The crystallization-gravity differentiation and internal ore alkaline metasomatosis (zoned continuous sulfide deposits showing pyrrhotine, cubanite, chalcopyrite, talnakhatite,moikhukite zones). They are also characteristic of phase metamorphism of primary ore, termination of the emplacement of metasomatic and exocontact ores and geochemical haloes, the formation of base metals,As-Sb, PGMs and other ore assemblages typical for the final phase. The fluid volume is the most important factor of the saturation of an intruded column in metals and SNOMS as a whole.

The multiform REE distribution characteristic of intrusion of Co-Ni-Cu subassemblage may be attributed to a complex development of a corresponding SNOMS incorporating all the above mentioned phases. However, the Tulai-Kiryaka-Taasannd and Bootankag SNOMS have not passed phase II and V . Of importance is the olivine accumulation (maximum of REE concentration) and plagioklase (europium extreme concentration) accumulation.

The petrochemical zoning is determined by three petrochemical trends indicating major regular changes in magmatite and ore composition in SNOMS (first and second trends) and in between (third trend). The first trend for the earliest economic nickelbearing trap phases (volcanic stage) is characterised by trends of acid-basic differentiation of Ca, Al, Mg, Cr - Si, Na, K, (P,Zr) (close to Bowen) in the central and upper horizons of intrusive complexes and Mg, Fe^{2+}, Fe^{3+}, Ni, Co, Cr - Al, Si, Na, Ca, (Zr, Sr) in mafic-ultramafic lower horizons and ore-metasomatic $Fe^{3+}Fe^{2+}$Ni Co Cu Mg Cr - Al Ca. The nickel bearing Triassic phase is expressed by trends Fe^{3+}Ca - Fe^{2+}Na K (volcanic rocks) and Mg Ca - Si Na; Mg Fe^{2+} - Si Na Al Ca (ultramafic and mafic intrusions of phase IV of the volcanic phase). The second interphase (innervolcanitic) tendency is indicated by a typical Skaergaaru trend Si Na K Al (Sr Zr P) - Mg Fe^{2+} (Fe^{3+}) Ni Cu Co Cr showing a general increase in ferric index of the volcanic stage. A general sequence of SNOMS development can be expressed by a trend P K Ti V Zr - Ni Cr (Pt) - Cu Cr Pd S Au Pt Cu As Sb Bi Zn Pb B F K.

The vertical geochemical zoning of the major mineralizing zone is marked by a change in the ore formation trend (Fe^{2+} Mn Al Na K - Mg Cr Ni Cu Fe^{3+}) of the economic nickel bearing OMS for the oxidized Fe trend (Fe^{2+} - Fe^{3+}K) and for nickelbearing and nickel barren OMS. This confirms a statement about the relationship between the degree of metalliferous expectations and peculiar fluid saturation of the district SNOMS occuring on the major fracture zone.

The proposed genetic model for the development of stratified intrusions in SNOMS gives insight into the mechanism of mineralized (ore-bearing) magma, melts, solutions and fluid, level of their accumulation and transport, formation of AGF and AGFl. It explains very high Cu concentrations in ores and causes responsible for emplacement of economic nickel-bearing stratified intrusions on rift limbs in the Taimayr-Norilsk province and helps to increase the reliability of metallogenic forecasts. and hence stresses the applicability of a new method for geodynamic-geochemical prediction.

Geochemical models of ore regions and fields and principles of their construction exemplified by nickeliferous province

D.A. Dodin, M.A. Sadikov, I.I. Sidorov

The principles of the geological-geochemical simulation are discussed using as an example the Taimyr-Norilsk industrial nickeliferous province forming part of the transregional Yenisei-Severnaya Zemlya precious metal-copper ore belt /1/. The latter is global polygenic and polychromatic tectono-magmatic system stretching in north-northeastern direction for more than 1600 km which is determined by the magnitude of series of heterogenous and diachronous tectonic structures superimposed by the belt. The Norilsk-Kharaelakh mantle fault is the major nickeliferous structure. It is noteworthy that the extent of another major platinum-bearing belt - the Bushveld - Great Dike related to the Orange River fracture zone, exceeds 1600 km.

The construction of the combined geological-geochemical models of individual metallogenic taxa comparable with ore-magmatic systems of different rank and particular ore subassemblages of the copper-nickel assemblage involves the classification of quantitative and qualitative data concerning features of their localization and structure; it consists of the following categories /1; 2; 3/, groups /1.1; 3.1.../, subgroups /2.1.1 - 2.1./, associations /2.1.1.1. - 2.1.1./ etc. i.e. the characters which form criteria for forecast and prospecting.

1. Factors of ore presence control: geodynamic /1.1/, structural-tectonic /1.2/, magmatic /1.3/, lithological-stratigraphic /1.4/.

2. Local criteria: geological-petrographic /2.1/ including geological-tectonic /2.1.1/, volcanic /2.1.2/, intrusive /2.1.3/ and metasomatic /2.1.4/, mineralogical /2.2/, petrochemical /2.3/, anomalous geochemical fields /AGF/ and flows /2.4/ including primary haloes /2.4.1/, secondary haloes /2.4.2/, lithogeochemical /2.4.3/, concentrate-geochemical /2.4.4/, hydrogeochemical /2,4,5/ flows; geophysical /2.5/.

3. Evaluation criteria: geological-petrographic /3.1/ including the presence and thickness of typical horizons of intrusive plutons /IP/, presence of inner intrusive and inner ore faults /3.1.2/, presence of typical xenoliths of near ore rocks /3.1.3/; mineral-geochemical: number and composition of major rock-forming minerals and accessories of IP /3.2.1/, thickness and composition of near intrusive /3.2.2/ and near ore /3.2.3./ haloes; petrochemical characters of IP, ore deposits /OD/ and their haloes including geochemical types of rocks and ores.

So, the authors have developed the geological-geochemical models for three subassemblages recognized in the sulfide copper-nickel and copper-cobalt-nickel /Fig.1/. The related endogenous /EGF/ and hypergenous /GGF/ geochemical fields /Tauson, 1983/ of intense, average and low concentrations of a wide range of indicator elements /IE/ and satellites /IS/ of copper-nickel mineralization differ with respect to the subassemblage in size, peculiar internal structure and mineral composition /list and element associations/, their vertical and horizontal zonality relative to IM and REE, type and strength of trend, petrogenetic features. These fields are very common in the central part of the province and exhibit a close relation to the above mentioned fractures and faults perpendicular to them, stability in time, predominance of their dimensions over those of IP and OD, fairly large set of EI and ES, low /rare average/ and intense levels of concentrations,

the fields are dominated by copper, nickel, cobalt, chromium, zink, silver, tin, molybdenum, mercury, platinum metals, potassium; salt and mechanic components often occur together. These geochemical fields according to the general classification /Dodin, 1985/ are placed into the ore-nickeliferous-intrusive group. Apart from this the author has considered as nickeliferous regions such groups as:
2/ nickeliferous intrusives; 3/ those occuring in zones of hydrothermally affected rupture; 4/ rocks of uncertain genesis /2/. From group 1 to group 4, erosion level being the same, the area of geochemical fields decreases, they become structurally less complex /low number of EI and ES deriving anomalies, no ash content/, contrast range and intensity drop, isotope composition of lead /wide range of ^{206}Pb/^{204}Pb ratio/, strontium /^{86}Sr^{87}Sr ratio increases/, argon /^{40}Ag/^{36}Ag ratio increases/, the REE and platinum metal distribution pattern changes as well. As a rule the area of anomalous fields increases in fracture zones and at the base of a thick succession of trap volcanites.

The data presented in the previous paper on the regular features in structure of different rank sulfide-nickeliferous ore magmatic systems /SNOMS/ and multiyear comprehensive metallogenic, petrographic, geochemical studies made possible the construction of geological-geochemical models of the province and its separate components: ore areas, zones, districts, and fields. Let us discuss briefly the princial models of two latter metallogenic taxa - the ore district /district SNOMS/ and the field /local SNOMS/.

Based on our constructions, the main model of geological-geochemical characters of the industrial-nickeliferous ore district are:

1. Their location at the wedge-like triangular intersection of fracture zones at the junction of two major rift systems in the Wadati-Zavaritsky-Benioff zone underlain by thick /12 km/ anomalous /doubling of the M discontinuity, presence of tilted mantle lenses with anomalously high /up to 8.8 cm/s velocity/ crust. Such slabs are interpreted as fragments of the Middle Paleozoic subduction zone of the West Siberian oceanic plate under the Siberian plate.

2. Concurrent occurrence with compensatory postvolcanic structures of trap trough and brachymorphic fold type.

3. The presence of a certain set of magmatic /from old to young: trachybasalt - trap - alkali-ultrabasic - granitoid/ and sedimentary /sulfate-terrigenous-carbonate - halogene - terrigenous - coal-bearing/ assemblages.

4. The formation of trough centres under conditions of intense intrusive magmatism at the intersection of old sublatitudinal and submeridinal faults to which intermediate chambers /asthenolenses of anomalous mantle/ and subvertical of intrusions main magmostructural elements of xenoliths - are related.

5. The development of a complex series of trap magmatic assemblages including industrial-nickeliferous, nickeliferous, low nickeliferous, and potentially nickeliferous ones. The representatives of the former are derivatives of picrite-like boron-fluoro-hydrogen fluid saturated magma rich in sulfur, potassium, copper, platinoids with REE noncompensated type of distribution, primitive mantle lead and having average Sr value.

6. The development of picrite, komatiite and anorthite basalts in volcanic strata; low explosiveness index, occurrence of high magnesia bodies in the intrusive facies.

7. The cellular distribution of peculiar composition and structure /multidimensional metasomatic zonality/ metasomatite fields.

8. Anomalous geochemical fields of EI and ES, zoned, highly contrasting, multistage, thick /up to 3000 m/ clamped on the axial rift zones. A peculiar structure of nickeliferous districtstrap troughs - is responsible for a lacy network of fringing AGF.

The main model characters of an industrial-nickeliferous ore field are the following:

1. The location at the intersection of the north-eastern fracture zones and north-western striking anticlines or arcuate faults.

2. A certain relation to wedge-shape transcrustal grabens.

3. The occurrence of nickeliferous xenoliths in the middle structural stage at least in two horizons exhibiting enclosure of chalcophile elements.

4. A fairly thick /no less than 500 m at the time of xenolith intrusion and 3000 m at the time of the emplacement of ore-magmatic system/ lava sheet.

5. The relation to a triple junction of differently oriented fractures at different depth of occurrence /Fig. 2/: magma- and ore-controlling /group A/, magma-and ore-enclosing /group B/ and intermediate /group C/. The junction sites of the former two groups are the localities of the magmatic potential columns of ore.

6. Distinct layering of xenoliths, wide-range /olivinite - diorite/ differentiation, structurally complex bottom, lower, and top /beds of Stillwater type/ horizons, high content of magnesian /30% fayalite/ chromium-bearing augite and chromespinellid.

7. Fairly high in nickeliferous xenoliths weighted average content of copper, sulfur, chromium, nickel, mercury, potassium and other metals at low nickel /copper, platinum, palladium, and sodium/ potassium ratio.

8. Noncompensated distribution of REE in xenoliths with europium maximum and smaller scatter of isotopes of lead /18.5/ to strontioum /0.7050-0.7054/ ratio; helium-hydrogen composition of gas and chloride-sodium liquid phase of fluids.

9. Liquation is of great importance by the emplacement of nickeliferous xenoliths showing a peculiar /Norilsk/ trend for their lower horizons.

10. Thick zoned under and above-intrusive /ore/ metamorpho-metasomatic haloes with lenses of nickel-free pyrrhotite ores with high content of native elements.

11. Zoned high contrasting, thick and extensive en-echelon primary, secondary haloes and flows of EI concentration and dispersion and ES of copper-

nickel presence of ore.

11.1. Structurally complex polyhorizontal EGF occurring at a vertical distance of 2000-3000 m from EP and OD, concurent presence of constituting OD and IP haloes, replacement of impoverishment sites by structurally complex AGF in above-limb parts of OD, original connection between separate elements and rocks of specific composition /geochemical barriers/.

11.2. The importance in EGF of thick complex anomalies of mercury and precious metals as well as potassium, boron and fluorine.

11.3. Stability of GGF and flows sith time.

The mathematical model of AGF for nickeliferous districts and fields has been developed as well.

In authors´ opinion a multistep liquation and crystal-gravity differentiation in IP chambers at high temperature gradient and boron-fluoride profile of mantle helium-hydrogen fluids contribute greatly to the formation of a group of complex geochemical fields, it is of importance for innerore in complex OD, subsequent diffusion and infiltration metasomatosis based on fluid mass transport. Apparently, migration along faults of the Norilsk - Kharaelakh rank and similar to it mantle fluids and hydrothermal solutions actively changing their composition when they pass through IP, OD, exocontact and near intrusive zones as well as through black shale horizons, cuprous sandstones blocks of Igara type and probably other old ore assemblages has determined the mechanism of the formation of AGF.

GEOCHEMICAL MODELLING OF HIGH TEMPERATURE PROCESSES OF COPPER MOBILIZATION

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A number of world regions display chalcopyrite deposits being confined to volcanogenic formations. The question of origin of copper in the deposits and their detection had been already mentioned before and is still open to discussion, since at present there are no direct methods to derive any unambiguous answer..

The present state of development of ore elements geochemistry depends on the quantitative concepts of sources of ore materials, determined by physical and chemical analysis of the ore elements behaviour. Such analysis includes experimental modelling for studying forms of the element under certain physical and chemical conditions, pressure, temperature, phase composition, oxygen fugacity. The latter is especialy important for elements of variable valency, which also include copper.

The paper evaluates considers the results of an experimental study on systems of Cu-melt, Cu-melt-crystal, Cu-melt-fluid under redox conditions typical for natural systems, as well as behaviour of copper in alumosilicate glass under changing conditions of temperature and oxidation.

Now we shall consider the results for the system of Cu-boninite-like melt. Its composition is proximal to the highly magnesium species of basaltoid within the ophiolite complex composition of Troodos /Cyprus/, with which chalcopyrite deposits are associated. A.V. Sobolev et al have determined parameters of T and O_2 formation in these rocks /1986/ which enabled us to select optimal experiment conditions: T-1380-1200°C, $f\,O_2 \geqslant f\,O_2$Ni-NiO. The methodology for the experiment was published in the Journal "Geochimija", No 7 1989. In order to analyse Cu^{+2} by the method of EPR in some tests, iron, hindering the procedure, was replaced by cobalt. According to Coon et al. /1976/ Co^{+2} behaves as Fe^{+2} and does not change the ratio of mineral phases in the magmatic systems.

The data obtained on copper distribution in pyrogenic phases olivine, orthopyroxene, plagioclase and glass synthesized at $f\,O_2$ buffer Ni-NiO testify of a low combined coefficient of copper distribution at the factual oxygen potentials for natural systems /Teble 1/. Similar phenomena take place in natural boninite-like formations, too. The increasing Mg concentration in the melt is accompanied by rising of copper content during crystallization of olivine and pyroxene /Fig. 1/. The determined Cu solubility rangesin the boninite-like melts are comparable to the solubility results in subalkaline basalt /Fig. 2/,

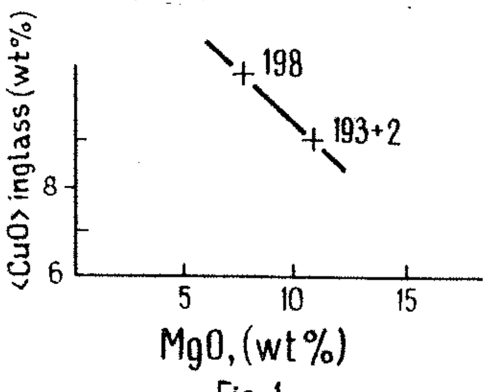

Fig. 1

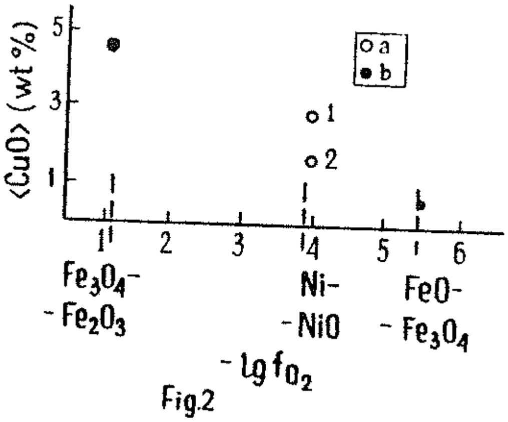

Fig.2

ten times exceeding the solubility in acid melts /Rjabchikov et al. 1984/. It is substantially higher than the average abundance Vinogradov, 1962/ which testifies of subsaturation of magmas in copper and of elements isomorphous occurence. The EPR data for glass show that Cu^{+2} compries only an insignificant copper part in the total content /0.02--0.04%/, the major part is still being contained in the lower oxidation degree species /Fig. 3/. The part of Cu^{+2} sharply increases in glasses synthesized at high fO_2 /Cu^{+2} content $\sim$ 1.5% approaching the total copper concentration in the sample/.

Solubility of CuO in magmatic phases raises and the combined distribution coefffficient increases several times resulting in some insignificant copper accumulation in the residual melt in crystallization /Table 1/.

The studies undertaken testify of accumulation of copper in the residual portions of the basic boninite-like melts crystallization with low sulphur contents /$S \leqslant 0.0N$%/, typical of natural systems oxygen potentials and temperatures, the natural formations of similar composition being undersaturated with copper appearing mainly in a singlevalency form, which generally determines the element migrations into the magmatic fluid and its behaviour at the postmagmatic stage of development.

The present data on studying the copper distribution coefficient in fluid and melt /Table 2/ show positive effects of higher Cl concentrations in the fluid, more aridic melt composition, increase of fO_2 and pressure on the copper being transfered into fluid.

In the presence of S at fO_2 of buffer Ni-NiO $C_{Cu}^{fl-melt}$ decreases by an order of magnitude due to the sulphides formation, while larger fO_2 in presence of sulphur facilitate transition of Cu into the fluid /Rjabchikov et al. 1974/.

A natural object that might be assessed for the $C_{Cu}^{fl-melt}$ of the copper mobilization degree in the magmatic phases could be a products of an actual volcanic eruption, e.g. the volcano of Eldfedl /Iceland/. The studied results on the Cu distribution in condensates and lavas show, that C_{Cu} condensate/rock $\geqslant \frac{0.05\ ppm}{44}$ 0.001, the degree of the solid component mobilization - 31000 t; by gaseous products -1.8 t /Durasova et al. 1988/. The C value gives a lower limit since it does not include the fraction of Cu, that could be mobilized by aerosols and which, according to Buat-Menard /1978/ can comprise 50%. In accordance with the previously assessed O_2 during the eruption, accounting for Fe^{+2}/Fe^{+3} in lavas and the composition of the gaseous constituents the value approaches to $fO_2Ni\text{-}NiO\text{-}SiO_2\text{-}Fe_2SiO_4\text{-}Fe_3O_4$ /Barsukov V.L. et al. 1986/; it follows from our experiment data, that under these conditions the reduced forms of copper predominate. The comparison of the copper-bearing capacity of condensates 5.10^{-6}% and the ore-bearing hydrotherms $n.\ 10^{-6} - n.10^{-4}$ /Roedder´s data, 1972/ shows, that the Cu contents are commensurable, i.e. the condensates can be of some importance in the formation of the metal-bearing solutions.

The confinement of chalcopyrite deposits to volcanogenic formations with ordinary concentrations of copper suggests probability of postmagmatic processes in the areas hosting these rocks, bringing about concentration of the elements in the ore. Skipping the details when considering the probable changing of the solutions with copper in result of the secondary hydroghermal transformation of rocks, published in the works /Kholodkevich et al., 1984/ we shall discuss our results of the copper behaviour modelled in volcanogenic glass under variable temperature and oxidization conditions, the real process in the postmagmatic history of the volcanogenic rocks existence that had not been taken into account in geochemistry of the ore elements. Why has the question become important? Let us consider the results of geological studies on location of chalcopyrites deposits and distribution character of Cu in volcanogenic formations particularly in pillow lavas of the Troodos ophiolite complex from Cyprus /Robinson et al., 1987/. The favourable factors determining the clearly defined genetic relations between these deposits and the enclosing ophiolite complex are absence of the post-volcanogenic orthogenesis and intrusive activity.

The majority of deposits occur between the upper and lower levels of the pillow lavas or on the basal level of the dyke complex. In the latter case magmatic bodies are much poorer in copper as compared to the ores in pillow lavas. The Cu contents determined in the lavas testify to the absence of copper specialization. The published Govett´s data /1983/ on copper distributed in a single pillow are very interesting, as well as the data on the isotopic oxygen characteristics of the internal and external parts of the pillow /Spooner et al., 1977/. They have noted a depletory character of copper distribution, impoverishment of the internal parts of the pillow in the ore deposits development areas /Table 3/ and great differences in $\delta^{18}O$ of the external parts as compared to unaltered marine basalts /Fig. 5/. It has made possible to suggest a higher degree of the secondary treatment of these parts by hydrothermal solutions. The depleted character of the copper distribution in this case /impoverishment of the central parts/ could have been a consequence of some other process. Such redistribution might have been caused by the heating of the pillow under oxidizating conditions.

When studying the single-valency copper containing glass with the composition Na_2O-K_2O-Al_2O_3-SiO_2, we have found that the redistribution of copper during the heating of glass in the air does not affect the macrocomposition. According to the microprobe studies the copper contents in the central parts of the heated glass were reduced by 50% /Durasova N.A. et al., 1989/. The copper spectra obtained by EPR from the initial and heated samples testified to the latter containing some increased oxidizated Cu^{+2} form in the glass. The established facts have enabled the authors to assume the following hypothetical mechanisms for the copper behaviour in the samples under study, the first of which had been previously considered in the Kamiya´s et al. works /1986/ while producing glasses with Cu-Si-Al-O composition:

$$2\,Cu^{+1}_{\text{inside glass}} + \tfrac{1}{2}\,O_2 \rightleftarrows Cu^{+2}_{\text{inside glass}} + CuO_{\text{surface}}$$

$$3\,Cu^{+1}_{\text{inside glass}} + \tfrac{1}{2}\,O_2 \rightleftarrows Cu^{+2}_{\text{inside glass}} + Cu_2O \text{ surface}$$

All the above mentioned have predetermined viability of such experimental modelling carried out on the glasses with composition approaching the natural formations, namely to the boninite-like rocks of Cyprus. Moreover we have given the data on the solubility, occurrence form and distribution coefficient of copper under conditions typical for the natural magmatic systems. The boninite-like glasses, synthesized at these parameters, without Cu^{+2} being fixed in their cobalt analogues by the EPR method, underwent heating at 500°C at fO_2 of the air and treatment by hydrochloric acid solutions. The obtained phases were analyzed by the methods of atomic absorption, quantometric and microprobe analyses, as well as by the method of electron spectroscopy for chemical analysis. As the result, the surface layer of the glass up to 60 Å depth has been investigated, determining the following: the heated glasses have this layer considerably enriched in copper, as compared to the initial samples /Table 4/. The ratio Cu_{2p}/Si_{2p} in the surface layer of the initial glasses is by several orders of magnitude smaller than that value of the heated glasses. Appearance of the divalent copper is observed

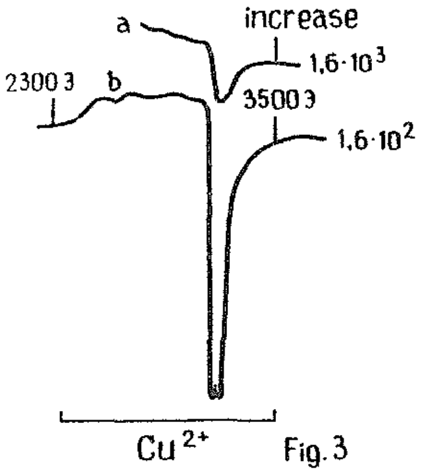

Fig.3

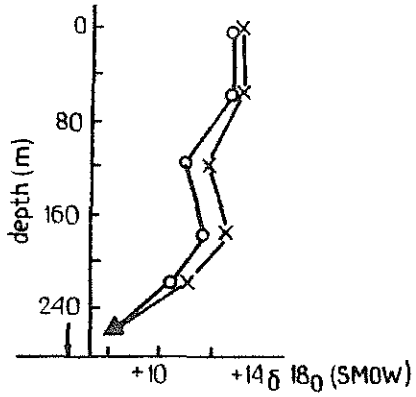

Fig. 4

as well as a substantial more than by an order mobilization of copper by hydrochloric acid solutions from the thermally treated phases, as compared to the initial ones, reaching 50% of the mobilization without any noticeable altering of the petrochemical composition of the glasses /Table 5/.

Thus the determined mechanism of the copper behaviour can cause appearance of the depleted distribution in the pillow lavas, beds, jointings with the minimum in central parts; formation of the easy soluble form on their surface. The favorable conditions for this mechanism effectiveness should be: generation of volcanogenic formations at $fO_2 \leqslant fO_2Ni - NiO$, containing Cu in a reduced form, their warming up in the presence of oxygen. Longer treatment and higher temperatures of heating, fugacity of oxygen, reduced sizes of jointings should boost the process.

Summing up the obtained results, let us enumerate the facts enhancing concentration and mobilization of copper at the magmatic stage and postmagnetic existence of the volcanogenic formations and conditioning genesis of various copper sources of the chalcopyrite deposits. The formation of magmatic rocks takes place at $fO_2 \leqslant fO_2Ni-NiO$, where copper is in the reduced form. The maximum mobilization of copper into a magmatic fluid is enhanced by high potentials of chlorineion in the system, as well as sulphur in case of highly oxidized conditions, otherwise the presence of sulphur reduces the Cu distribution coefficient between the fluid and melt.

Accounting for the data on copper solubility in melts of various composition, one has to expect higher values for C_{Cu} of fluid-melt for acid melts.

Pointing out to probable mobilization of Cu into the ore - forming solutions at the magmatic stage and in the process of hydrothermal alteration we can make conclusion about the importance of the thermal treatment of the volcanogenic rocks during the development of geological regions as an important factor in transforming the disseminated copper into a concentrated form, boosting the ore generation of volcanogenic formation regarding copper.

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CAPTIONS TO THE FIGURES

Fig. 1. Copper distributions in boninite-like glass depending on its magnesium content.

Fig. 2. Copper solubility in a boninite-like /a/ and subalcaline /b/ melts at T-1200°C and various fO_2.
1 - Fe - boninite-like glass, 2 - Co - boninite-like glass.

Fig. 3. Copper EPR spectra in cobalt-containing boninite-like glass at 77K.

a - part of the Cu^{+2} EPR spectrum, corresponding to a perpendicular orientation of the particles to the magnetic field, in a sample, synthesized at fO_2 buffer Ni-NiO,
b - the same in a sample, synthesized at air O_2.

Fig. 4. Variations of $\delta^{18}O$ in metamorphized pillows in center /O/ and on periphery /x/;
Value $\delta^{18}O$ in fresh marine basalt /+6°/OO/;
samples of a metadoleritic dyke.

Fig. 5. Part of the Cu^{+2} EPR spectrum in cobalt analogues of boninitelike glass with a perpendicular orientation of particles to the magnetic field at T-77K, sample of 40 mg.
a - initial glasses, b - warmed up in the air at 500°C.

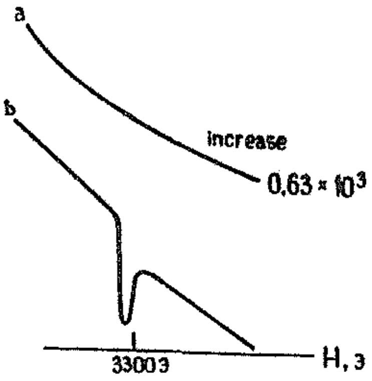

Fig. 5

Table 1

Chemical composition of the phases, mass %

Test	T °C	(h)	O_2	Phase	Na_2O	MgO	SiO_2	Al_2O_3	K_2O	CaO	TiO_2	FeO	CoO	CuO	Stand.
199	1380	5	Ni-NO	Olivine		40.5	38.7			0.3			20.7	0.0	OLC-1
				-"-		40.2	38.9			0.3			21.7	0.1	-"-
				Hyperstene		29.9	56.8	0.7		2.3			11.2	0.0	PIR
				-"-		28.9	56.4	0.7		2.6			11.2	0.1	-"-
				Glass	1.1	6.5	60.0	14.0	1.1	11.3	0.8		4.1	1.5	XF-2
				-"-	1.1	6.3	59.2	14.0	1.1	11.4	0.8		3.9	1.5	-"-
				"CuO"	0.0	0.0	0.1	0.1	0.0	0.1	0.0		1.3	18.5	-"-
197	1300	22	Ni-NiO	Olivine		39.6	39.0			0.4			21.1	0.1	OLC-1
				-"-		39.0	39.2			0.3			21.2	0.1	-"-
				Hyperstene		28.9	56.1	1.0		2.9			10.5	0.1	PIR
				-"-		29.0	56,1	1.1		3.0			10.5	0.1	-"-
				Glass	1.1	6.3	58.4	14.2	1.2	10.9	0.7		4.7	1.6	XF-2
				-"-	1.2	6.2	59.0	14.2	1.2	11.1	0.7		4.8	1.6	-"-
				"CuO"	0.0	0.0	0.1	0.2	0.0	0.1	0.0		1.6	120.1	-"-
197'	1200	48	Air	Olivine	0.1	37.4	39.9	0.2	0.0	0.4	0.0		20.6	2.0	XF-2
				-"-	0.1	37.9	39.3	0.1	0.0	0.3	0.0		20.8	1.8	-"-
				Hyperstene	0.0	25.2	56.4	1.0	0.0	3.4	0.3		12.9	2.4	-"-
			-	-"-	0.1	24.0	56.1	1.4	0.0	5.7	0.4		11.7	2.0	-"-
				Plagioclase	2.0	0.5	52.4	30.4	0.3	15.6	0.1		0.9	0.4	-"-
				-"-	2.0	0.7	53.6	28.9	0.4	15.3	0.2		1.0	0.6	-"-
				Glass	1.5	3.4	64.2	14.3	2.1	8.4	1.5		3.6	2.9	-"-
				-"-	1.6	3.4	64.8	14.1	2.1	8.2	1.3		3.4	2.9	-"-
195	1200	58		Olivine		39.8	38.9			0.3			21.4	0.2	OLC-1
				-"-		39.7	39.5			0.3			21.3	0.1	-"-
				Hyperstene		28.2	56.1	1.2		2.9			11.7	0.1	PIR
				-"-		29.1	55.8	1.0		2.9			11.0	0.0	-"-
				Glass	1.4	5.2	58.1	15.0	1.5	11.4	1.0		4.2	1.6	XF-2
				-"-	1.5	5.1	58.2	15.0	1.5	11.2	1.0		4.2	1.8	-"-
				Augite		17.0	54.2	2.0		19.7			6.3	0.2	PIR
				"CuO"	0.0	0.0	0.1	0.1	0.0	0.0	0.0		1.6	120	XF-2
198	1380	5	Ni-NiO	Hyperstene		34.6	58.1	0.6		0.9		2.3		3.9	PIR
				-"-		34.3	58.2	0.8		1.1		2.6	3.7	3.7	-"-
				Glass	0.8	8.0	56.6	10.2	0.8	7.9	0.6	6.6		9.2	XF-2
				-"-	0.9	7.9	54.5	10.5	0.9	7.8	0.6	6.7		9.5	-"-
196	1300	22	Ni-NiO	Hyperstene		33.3	56.5	1.5		2.0		5.4		0.1	PIR
				-"-		34.4	57.2	1.0		2.0		4.9		0.1	-"-
				Glass	1.0	7.0	57.5	13.2	0.9	10.3	0.7	7.0		2.6	XF-2
				-"-	0.9	6.9	57.6	13.0	1.0	10.0	0.7	6.7		2.6	-"-
				"CuO"	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1		124	-"-
194	1200	58		Hyperstene		33.0	56.5	1.0		1.9		6.6		0.1	PIR
				-"-		33.1	56.5	1.0		1.9		6.1		0.1	-"-
				Glass	1.1	6.7	56.5	13.6	1.1	10.4	0.8	6.6		2.6	XF-2
				-"-	1.1	6.6	57.3	13.7	1.2	10.0	0.8	6.5		2.8	-"-
				"CuO"	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.1		124	-"-
193-2	180	5	Ni-NiO	Glass	0.7	10.4	61.8	7.7	0.7	6.0	0.4	4.9		7.0	-"-
				-"-	0.6	11.4	59.3	8.4	0.5	6.5	0.4	5.5		7.5	-"-

Table 2.

Copper distribution coefficients between fluid and melt

distribution coefficient	fluid composition and concentration (mole/litre)	magmatic melts composition	test parameters	reference
4.5 - 5.4	1 M (NaCl+KCl)	Eldgurtite, granite	700-900 $^{\circ}$C 2 kbar	Khitarov et al. 1982
5	-"-	Non-ferrous granite	750 $^{\circ}$C, 1.5 kb buffer Ni-NiO	Rjabchikov et al. 1984
10	-"-	-"-	750 $^{\circ}$C, 1.5 kb, buffer Fe_2O_3-Fe_3O_4	-"-
9.1 ± 2.5	4.5 M (NaCl+KCl)	granite	750 $^{\circ}$C, 1.4 kb, buffer Ni-NiO	Candela, Holland 1984
6 ± 2	H_2O	basalt	1100 $^{\circ}$C, 10 kb, O_2 regon of FeO stability	

Table 3

Copper distribution in the center of the pillow from the background samples (1), 1 km removed from the mineralization (2) and 10 km removed from the ore (3). Govett 1983.

sampling site	number of samples	Cu in pillow, g/t	
		in center	phericaly
(1)	8	89	87
(2)	13	39	163
(3)	23	51	291

Table 4.

Data for boninite-like glasses (depth of the surface layer 60 Å).

element	D - 229 - 2	D - 229 - 2 - 500	
	mass %	mass %	mass%
C_{1S}	52.29	69,46	73.15
C_{1S}	24.33	19.90	21 72
Cu_{2P}	0.16	6,76	1.92
Si_{2P}	21.16	3.88	3.21
Ca_{2P}	1.28	not found	not found
Na_{1S}	1.00	not found	not found
Cu_{2P}/Si_{2P}	0.007	1.74	0.60

Analyses conducted by A.V. Shchukarev in "Mechanobr" insti- with "Kratos" spectrometer. Error of measurements - 10 %.

Table 5.

Copper contents in glasses and interreacting with them solutions before and after warming up the grains in air at T 500 ^{o}C.

Sample No	Glass composition, mass %		Glass^{xxx} warming up conditions and their interaction with 5N HCl solution			Cu in solutions contacted with glasses for 40 min, G/ml	Cu amount in glasses weight %	Evacuation of Cu from glasses by solutions, %
	oxydes	mass %	Time /h/	Weight mg	Volume of solution ml			
209-1	Na_2O	0.99	no warming up	23.60	1	0.2^{x}	0.29^{x}	0.0
	MgO	11.36						
	SiO_2	64.28						
	Al_2O_3	9.05						
	K_2O	0.45						
	CaO	7.31						
	TiO_2	0.39						
	"FeO"	6.41						
209-1	Na_2O	0.99	48	20.80	1	10.5^{x}	undetermined	17.2
	MgO	11.39						
	SiO_2	64.10						
	Al_2O_3	9.10						
	K_2O	0.46						
	CaO	7.15						
	TiO_2	0.47						
	"FeO"	6.38						
229-2	Na_2O	0.84	no warming up	40.35	2	0.5^{x}	0.29^{xx}	0.4
	MgO	10.16						
	SiO_2	65.95						
	Al_2O_3	8.83						
	K_2O	0.37						
	CaO	6.29						
	TiO_2	0.42						
	"FeO"	5.57						
229-2	Na_2O	0.84	240	41.00	2	31.0^{x}	undetermined	52.0
	MgO	11.38						
	SiO_2	66.51						
	Al_2O_3	8.76						
	K_2O	0.34						
	CaO	6.79						
	TiO_2	0.39						
	"FeO"	6.11						

x/ atomic adsorbtion method, measurements error 2 %, analysist Uchevatkina L.N.
xx/ local X-ray spectrometry, measurement error 2 %, analysist Ignatenko K.I.
xxx/ grain size 100 - 500 m

GLOBAL GEOCHEMICAL SAMPLING; A PILOT PROJECT IN FENNOSCANDIA

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INTRODUCTION

Global Geochemical Sampling (GGS) is a program under IGCP project 259, International Geochemical Mapping. The ultimate objective of the GGS is to collect large high-quality samples of different materials commonly used in geochemical mapping in different parts of the world at 3000-5000 stations distributed over the whole globe. In a first phase the GGS is carrying out pilot sampling in different global environments in order to work out procedures for the future global sampling.

One pilot project, the sampling of an area some 1 million km^2 in size for a Geochemical Atlas of Fennoscandia, was initiated in 1989 at the Åbo Akademi University in Finland. The main objectives of this project are:

- to work out procedures for sampling and analysis of very large samples
- to test the suitability of different sample types for GGS in glaciated areas
- to evaluate the cost of sampling and analysis for GGS
- to study the geochemical pattern at the scale of GGS and its correlation with geological features of the area
- to get large reference (standard) samples for future monitoring
- to produce a geochemical atlas over Finland, Norway and Sweden

GEOLOGY OF THE PROJECT AREA

Most of the bedrock in the project area consists of the Precambrian Fennoscandian Shield. The Shield shows a geochronological zonation, getting younger from northeast to southwest, a reflection of the formation of most of the crust during three major orogenic events 2900 - 2600 Ma (Lopian), 2000-1750 Ma (Svecofennian) and 1750 - 1500 Ma ago (Gothian).

The Fennoscandian Shield is divided into three domains (Fig. 1):

The **Archean Domain** in the Northeast consists of granitoids and linear greenstone belts and it is divided into two parts by the Proterozoic Lapland Granulite Belt. The Archean Domain developed into a craton, the SW margin of which was later covered by sedimentary and mafic volcanic rocks.

The early to middle Proterozoic **Svecofennian Domain** is divided into three parts; the volcanic Northern and Southern Provinces and the metasedimentary Central Province. The original relationships have been obscured by granitoid intrusions which occupy most of the Domain.

The **Southwest Scandinavian Domain** in SW Sweden and S Norway accreted to the Fennoscandian Shield during the middle Proterozoic. Volcanic-sedimentary terrains have been intruded by two generations of granitoids. Within the Domain several fault belts mark lithological discontinuities. This Domain is separated from the rest of the Fennoscandian Shield by the Transscandinavian Granite-Porphyry Belt (Gaál and Gorbatschev, 1987).

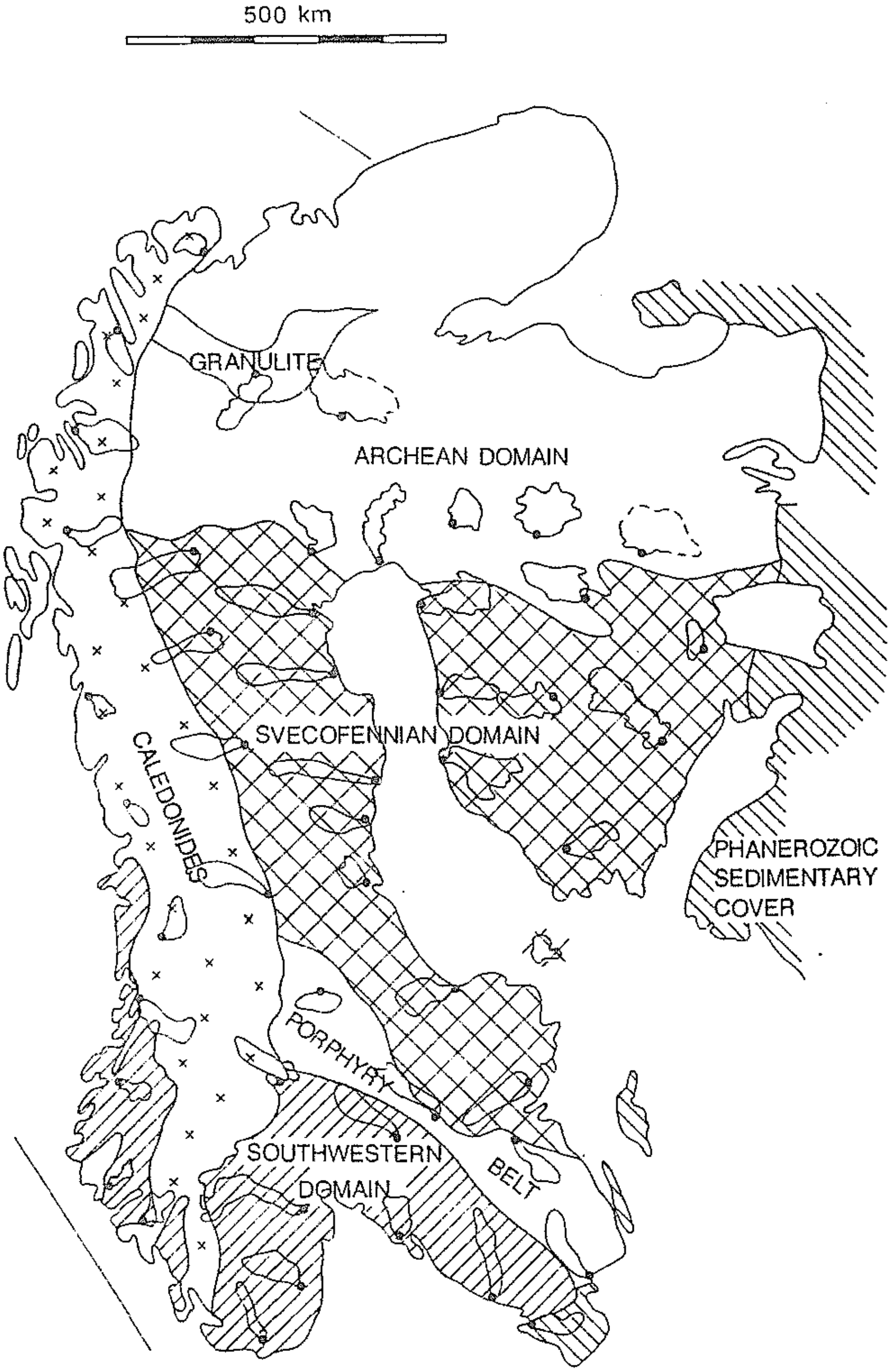

Fig. 1. Simplified geological map over Fennoscandia, with the sampled drainage areas and the mouth of these areas (●), where water and overbank sediment are sampled.

The western margin of the Shield was reworked by the Sveconorwegian-Grenvillian and Caledonian orogenies 1250 - 900 and 600 - 400 Ma ago. The **Scandinavian Caledonides** to the west of the Shield cover most of Norway and the western margin of Sweden. They are built up of a complex system of late

Precambrian-early Palaeozoic nappes thrusted over the Shield. In some places Precambrian sediments and basement are exposed (Stephens, 1988).

The Shield later developed into a peneplain, which together with the Caledonides was covered by continental ice sheets in the Pleistocene. The last deglaciation occurred 11 000 - 8 000 years ago. Extensive parts of the Shield are covered by till and glaciofluvial deposits. Postglacial Baltic seas and lakes covered the coastal areas of Finland and Sweden, leaving a thick layer of partly sulfide-rich clay and silt over some of the area. Peat covers vast areas in northern Sweden and central and northern Finland. In Norway the lowlands near the coast are also covered by clay, while the valleys and areas with moderate relief are covered by till and glaciofluvial gravels and sands.

SAMPLING

Fourtynine drainage areas, 500 - 5 000 km^2 in size, were chosen for sampling. Fifteen are situated in Finland, 19 in Sweden and 15 in Norway. They were selected to represent different bedrock-geological environments (see Fig. 1).

Initially stream water, active stream sediment, overbank stream sediment, till and humus were sampled. However, finding suitable sampling localities and sufficient amount of material for the fine fraction of active stream sediments was very time-consuming and, therefore, this sample type was abandoned in an early stage of the project. The other sample types are being sampled as follows:

Stream water: 0.5 l is sampled every month during one year at the mouth of each drainage area. The samples are frozen as such and they will be melted, combined into one composite sample for each drainage area and then refrozen. They are stored in polypropylene bottles. The samples are taken and frozen by persons (Authorities or private) living near the sampling site. In order to get some preliminary results a water sample was taken from each station when the sediment was sampled.

Overbank stream sediment: This sample type, which is thought to represent the whole drainage area, is sampled at the same sites as the water samples. At each site sediment is taken with a spade from two pits 50-100 m apart. From each pit one 2.5-3.0 kg sample is collected from the uppermost ten cm and another from the lower half of the sediment. In most cases the thickness of the sediment is 40-60 cm. The upper sample is believed to reflect anthropogenic influence, while the lower one should be pristine (Ottesen et al., 1989).

Overburden: Humus and **till** sampling is being carried out at 20 randomly selected sites within each drainage area. 1.5-2 l of humus (A horizon) and about 2 kg of till from the upper part of the C horizon (ca 80 cm depth) are taken at each site. The samples will later be combined into one grand composite sample of each material for each drainage area.

PROBLEMS AND EXPERIENCES

In projects of this type a variety of problems are encountered. Working across national borders causes a large number of difficulties of practical and administrative character, such as finding suitable maps, getting permission to work in different countries, and problems with transport, mailing and customs.
In Fennoscandinavia these difficulties are quite easy to handle because we can easily cross the borders, we speak the same language, and we have the same type of society. In many parts of the world major practical problems will be met with in a global sampling program.

The expences are high because of long distances between sample sites and high daily allowances. Much time is used for planning and preparatory work and it is difficult to get funding for work in foreign countries.

Large samples and sample containers cause problems; you need large space for storage and a big car for transportation. It is difficult to dry and sieve the samples because of lack of equipment for large samples.

The water sampling is causing particular difficulties because one person cannot do the sampling every month at 49 stations. Even less frequent sampling would cause problems. In our project we approached Government and local authorities and private persons, which now are doing the sampling and freezing the samples without charge. In this way our part is limited to the delivery of clean bottles and the collection of the frozen samples after completion of the sampling.

EXPENDITURE

The project is funded mainly by the Finnish Academy of Science. The approximate time and money demanded for the 49 stations in the area of 1 million km^2 in three countries are:

Labour	person months
Planning and preparatory work	3
Overbank sediment sampling, delivery of bottles to the samplers and collection of the sampled waters	5
Sampling of till and humus	
- 35 urban areas; developed road network	10
- 14 remote areas	6
Laboratory work (washing of bottles, drying, sieving)	14
Data processing, map drawing	5
Reporting	2
	50 months

Expenditure	US$
Researcher, 3.5 years	210 000
Assistant, 1.5 years	35 000
Travelling expences	60 000
Bottles, boxes, bags	5 000
Maps	5 000
Chemical analyses	10 000
Data processing and map drawing	5 000
	US$ 330 000

RESULTS

This far we have got chemical analyses of stream water (one sample from each site) analyzed on ICP, and of the deeper samples of overbank sediment, analyzed on ICP after leach of the fine fraction (-0.062 mm) with hot HCl-HNO_3-H_2O (3:1:2).

The water samples were taken during one month in late spring - early summer. Thus some samples are taken from flooding rivers, some are taken before the flood and most of them after the flood. Therefore the results are not completely comparable.

The electric conductivity is very low in most rivers, 15 - 40 µS/cm, and it gets higher from north to south. Some rivers along the coasts of Finland and Sweden have values over 100, reflecting metal-rich overburden and sulfide-rich clays in these areas. Ca, Mg and Na show good correlation with the conductivity.

Many elements show anomaly patterns clearly related to known geological features. Fe in Fig. 2a shows a typical pattern, being distinctly higher in stream water in the Proterozoic than in the Archean. In the Svecofennian Domain the values are higher in Finland than in Sweden. The sulfide-rich clay and till along the west coast of Finland and northeastern coast of Sweden are reflected as very high Fe-contents. Within the Southwestern Domain, western Sweden has higher Fe-contents than southern and western Norway. This reflects lithological differences. The Caledonides have very low Fe-contents.

The overbank sediments show clear differences between the Archean and the Svecofennian Domains, and even within these major geological units there are variations, which in most cases can be related to known geological features. E.g., the sample from The Granulite Belt in Lapland often differs from the other samples. Fig. 2b shows the patterns of K in the samples from the lower part of the overbank sediments. There is again a distinct difference between the Archean and the Proterozoic, and within the latter the contents are higher in Finland than in Sweden. In the Southwestern Domain three "subprovinces" are distuingished; western Norway has somewhat higher K values than western Sweden, while southern Norway is very poor in K. The Caledonides have relatively high K values.

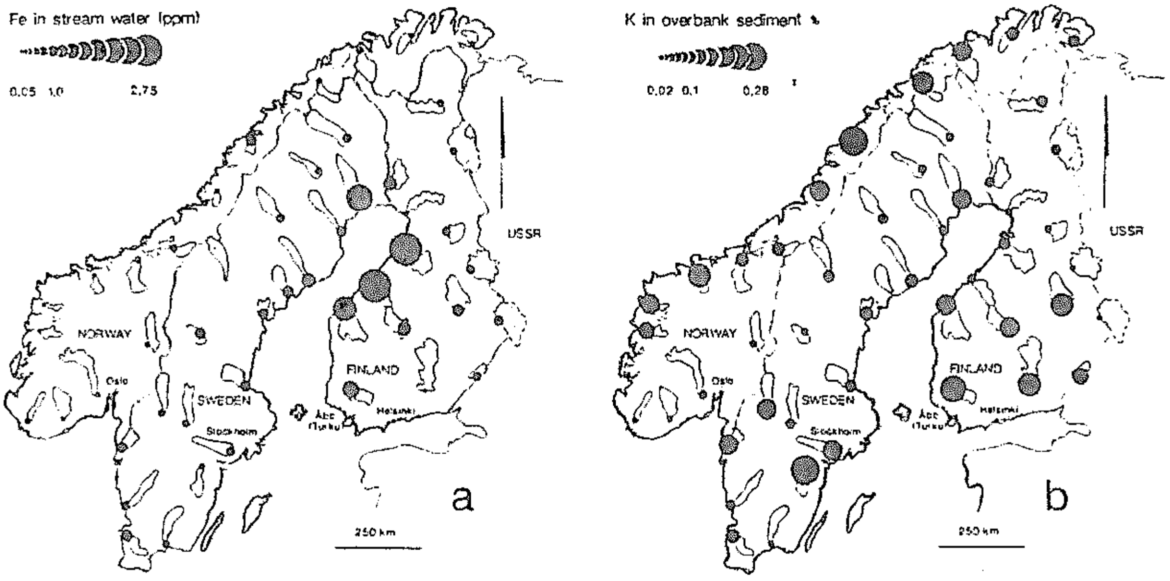

Fig. 2. a. Iron in stream water. b. Potassium in the lower part of the overbank stream sediment (see also the geological map in Fig. 1).

The geochemical differences between the geological Domains also appears in the median values (Fig. 3). Ca and Zn (Fig. 3a) are increasing from the Archean through the Svecofennian and the Southwestern Domains to the Caledonides. Mg is on the same level in the three first Domains, while it reaches a much higher level in the Caledonides. Co, Cu and Ni show the same pattern as Mg. Pb and La (Fig. 3b) show an increasing trend in the three first Domains, but decrease in the Caledonides to the same level as in the Archean Domain.

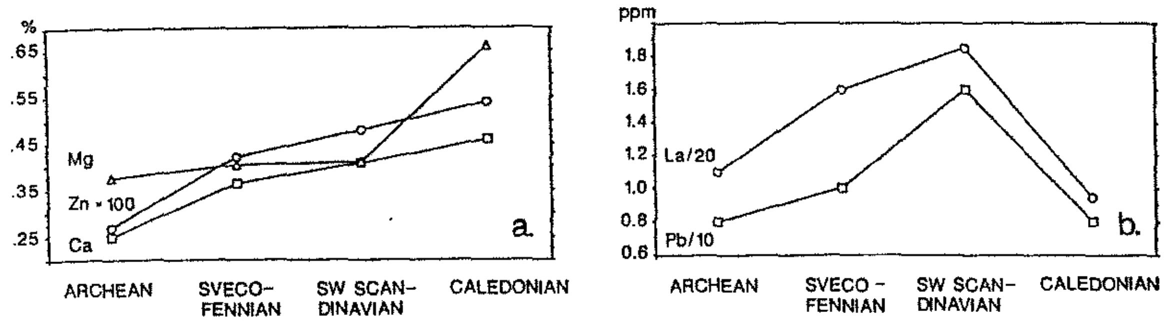

Fig. 3. The medians of Mg, Zn, Ca, La and Pb for the geological Domains in the deeper sample of the overbank sediments. The various factors have been used to bring the lines to the same level in the diagrams.

CONCLUSIONS AND SUGGESTIONS

From these preliminary results we can see, that both stream water and overbank stream sediment show regional anomaly patterns, which are related to geological features. They are thus useful as sampling media in glaciated terrains in the future Global Sampling Program.

Our experience this far shows, that in order to save both time and money, organizations from all involved countries should take part in this kind of a project. They could form a working group for planning and coordination and field trips to standardize methods. In this way the costs for travelling, maps and equipments will be considerably lowered. Much of the work can also be done within the ordinary budgets of the organizations.

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A GRAPHICAL TOOL TO AID INTERPRETATION OF GOSSAN GEOCHEMICAL DATA

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Successful interpretation of gossan geochemical data relies heavily on the recognition of complex multi-element signatures which characterise mineralisation, from the more obvious geochemical expressions of bedrock and the effects of weathering and secondary dispersion. Interpretation becomes more difficult if comparisons are to be made between gossan geochemical data from other deposits.

Although multivariate statistical techniques such as discriminant function analysis (Taylor and Scott, 1982; Andrew, 1984; Smith, *et al.*, 1984) and principal components analysis (Joyce and Clema, 1974) have been successfully applied to gossan characterisation and classification studies, these techniques have serious disadvantages. These include: (i) the requirement for known training geochemical data sets; (ii) the need for a thorough understanding of complex multivariate statistical techniques; (iii) sophisticated computing facilities; and, (iv) results that are expressed in unfamiliar terms to the average exploration geologist (e.g. canonical scores, discriminant scores, factor scores, probability estimates, Mahalanobis D^2 distance, etc.).

One of the more useful ways to present multi-element geochemical data, such that the relationships of a large number of elements can be easily appreciated, are the log-linear multi-element "spider" diagram plots\ commonly used for petrological and mineralogical studies (Thompson, 1982; Gromet, *et al.*, 1984; Nakamura, 1974; Howarth and Turner, 1987; Richards, 1990). In these plots, sample concentrations are normalised to "average" concentrations of some "external" reference material. In igneous petrology, for example, the most popular normalising materials include: (i) chondrites; (ii) 'primitive' or 'primordial' mantle; and (iii) MORB (Rock, 1987a).

This paper proposes the AIG (Average Ironstone Gossan)-normalised plot, where ironstone or suspected gossan geochemical data are normalised to "average" concentrations of ore and pathfinder elements and plotted on a log-linear multi-element "spider" diagram. The element norms have been estimated utilising a large geochemical database (i.e. > 10,000 samples) representing ironstone and gossan material from Australia and South Africa.

Basic statistical parameters (Tables 1 & 2) computed for Ag, As, Au, Ba, Bi, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sb, Sn, W, and Zn indicate the extreme positive skew (asymmetry) and kurtosis (peakedness) which suggest that the arithmetic mean would be inappropriate for estimation of central tendency (Andrews, *et al.* 1972; Howarth, 1984; Rock, 1986). Statistically robust estimates (i.e. estimates less susceptible than the arithmetic mean to the skewness and kurtosis of the distribution and to the presence of outliers) were used to calculate normalising values such as: (i) geometric mean; (ii) median (i.e. 50'th percentile); (iii) trimmed (15%); (iv) Hampel; and, (v) biweight.

The geometric mean and median represent the arithmetic mean of $\log_{10}$-transformed values and the 50'th percentile respectively and are commonly used measures of location in geochemistry. The trimmed mean rejects a percentage (for this study 30%) of the upper and lower tails of the data and computes the arithmetic mean using the remaining data. Hampel and biweight estimates (Rock, 1987b; Dixon, 1988) assign higher weights to observations close to the median than to those far from the median and have been shown to perform very well with highly skewed data sets (Andrews, *et al.*, 1972).

Tables 1 and 2, confirm Rocks (1986) observation *"...that the mean is by far the worst estimator of location for non-normally distributed data"*. The robust estimates (Table 2) are in good agreement (Figs. 1 & 2) and are certainly well within the limits of analytical variability. Final normalising values were estimated using the arithmetic mean of the five robust estimates: Ag (0.3 ppm), As (23 ppm), Au (1.2 ppb), Ba (90 ppm), Bi (2 ppm), Co (11 ppm), Cr (155 ppm), Cu (52 ppm), Mn (202 ppm), Mo (3.6 ppm), Ni (28 ppm), P (518 ppm), Pb (47 ppm), Sb (4.5 ppm), Sn (3.2 ppm), W (6.2 ppm), and Zn (47 ppm).

A number of example spider plots are presented (Figs. 5 to 6) which illustrate the usefulness of this technique for the interpretation of gossan geochemical data.

Table 1 STATISTICAL SUMMARY FOR GOSSAN AND IRONSTONE GEOCHEMICAL DATA (All values in ppm except Au in ppb).

	Descriptive statistics					Percentiles				
Element	No. of samples	Mean	Standard Deviation	Range	C.V. (%)	10	25	50	75	90
Ag	9256	7.7	70	<0.2 - 4500	906	<0.2	0.1	0.2	0.9	5
As	8515	108	471	<1 - 9 100	435	4	12	22	42	160
Au	2994	3.6	22.2	<1 - 827	626	<1	1	1	3	6
Ba	8153	1097	11250	<1 - 500000	1025	10	20	92	368	915
Bi	8404	15.5	218	<1 - 9260	1406	<1	1	2	5	37
Co	10230	32	119	<1 - 7500	366	3	4	10	30	70
Cr	8115	460	1058	1 - 9999	230	10	50	158	365	1105
Cu	10482	1233	11952	<1 - 527000	969	6	13	49	155	865
Mn	9951	3801	19613	<1 - 300000	516	31	70	160	500	3021
Mo	8908	10.2	48	<1 - 2100	475	1	2	3	7	17
Ni	10062	98	465	<1 - 9750	475	5	14	30	60	140
P	3599	1391	2857	<10 - 66350	205	50	210	510	1400	3406
Pb	10358	4778	33972	<1 - 699000	711	10	20	40	88	1086
Sb	6861	40	215	<1 - 5429	535	1	2	4	11	37
Sn	7730	32	282	<1 - 8400	882	1	2	3	6	14
W	6476	13	78	<1 - 5884	618	3	5	5	13	25
Zn	10496	1446	13895	<1 - 470000	961	7	14	37	165	1100

Table 2 MOMENT MEASURES AND ROBUST ESTIMATES OF LOCATION FOR GOSSAN AND IRONSTONE GEOCHEMICAL DATA (All values in ppm except Au in ppb, robust estimates calculated using $\log_{10}$-transformed data).

	Moments				Robust estimates of location[a]				
	Skewness[b]		Kurtosis[c]		Geometric[d]	Median[e]	Trimmed[f]		
Element	1	2	3	4	mean		15%	Hampel[g]	Biweight[h]
Ag	38	1.5	2071	1.5	0.4	0.2	0.3	0.2	0.3
As	12	0.6	163	1.4	24	22	24	23	22
Au	28	1	908	1	1.3	1	1.1	1.2	1.2
Ba	26	-0.1	9	0.4	85	92	92	91	91
Bi	28	2.1	909	7.5	2.2	2	1.9	2	2
Co	33	0.5	1769	-0.1	12	10	11	12	12
Cr	6	-0.5	41	0.2	125	158	162	164	164
Cu	23	0.7	679	0.9	56	49	53	52	51
Mn	8	1	81	1.7	230	160	216	206	200
Mo	23	1	763	1.7	3.9	3	3.8	3.8	3.7
Ni	13	0.2	201	1.4	29	30	28	27	28
P	8	-0.3	117	0.1	516	510	519	522	523
Pb	12	1.7	169	3.5	63	40	49	42	40
Sb	13	1.4	209	2.1	5.3	4	4.6	4.6	4.2
Sn	17	1.9	335	6.1	3.7	3	3.2	3.1	3
W	67	0.8	4984	1.4	6.9	5	6.3	6.2	6.5
Zn	20	0.8	477	0.9	56	37	49	47	47

Notes:

[a] Statistics which are less sensitive than the mean to outliers and departures from normality, but use more of the data than does the simple median (Andrews *et al.* 1972).

[b] Skewness 1 = raw data, 2 = $\log_{10}$-transformed data.Value should be near zero for a normal distribution.

[c] Kurtosis 3 = raw data, 4 = $\log_{10}$-transformed data.Value should be near zero for a normal disribution.

[d] Arithmetic mean $\log_{10}$-transformed data.

[e] 50'th percentile.

[f] The arithmetic mean of the results after 15% of the lower data and 15% of the top data have been removed.

[g/h] Central values receive higher weights than more extreme cases, but fractional weights are assigned to intermediate cases (Dixon, 1988).

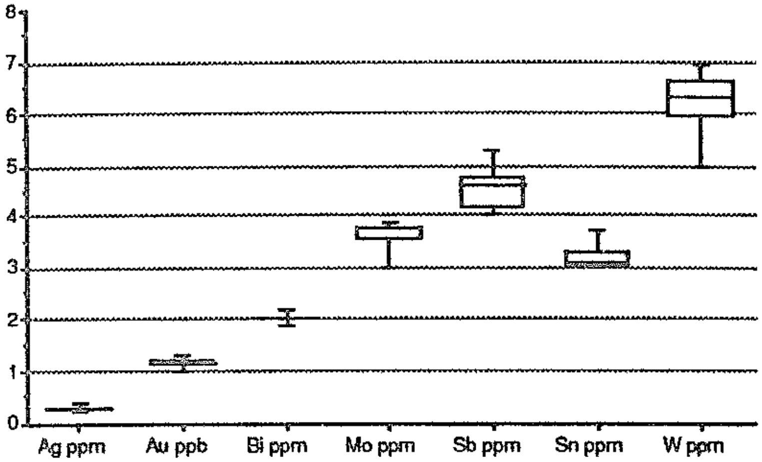

Fig. 1 Box and whisker plots illustrating ranges of values for robust estimates computed for gossan and ironstone geochemical data (Ag, Au, Bi, Mo, Sb, Sn, and W).

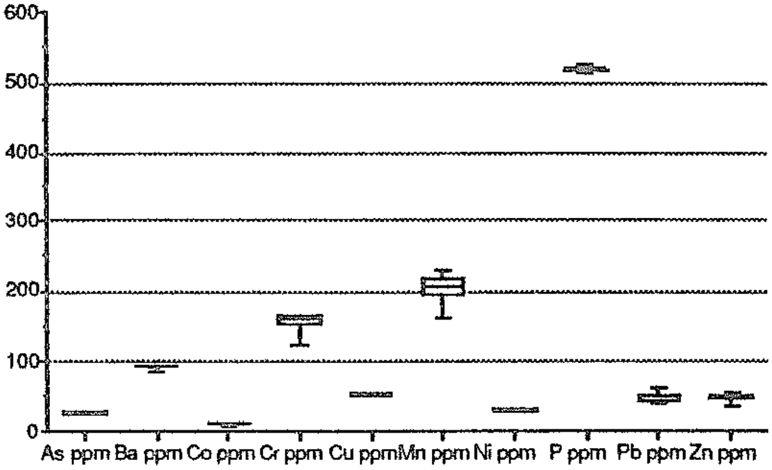

Fig. 2 Box and whisker plots illustrating ranges of values for robust estimates computed for gossan and ironstone geochemical data (As, Ba, Co, Cr, Cu, Mn, Ni, P, Pb, and Zn).

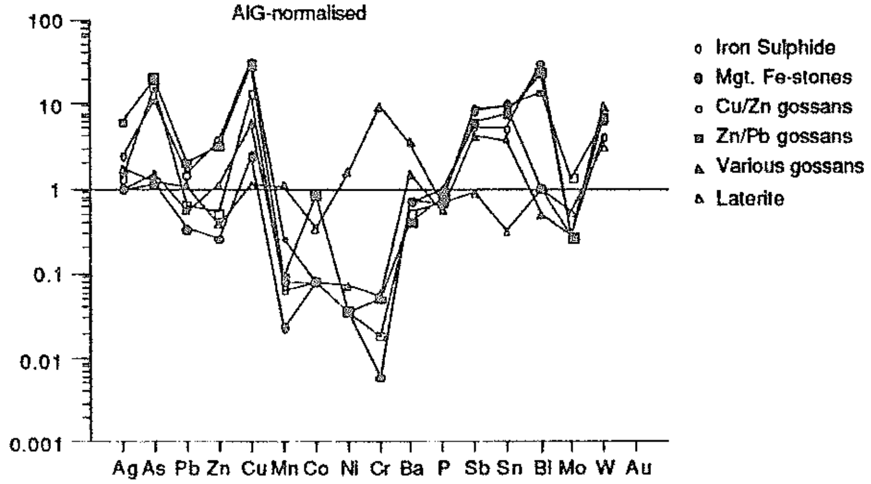

Fig. 3 AIG-normalised plot illustrating characteristic patterns of enrichment and depletion for Ag, As, Pb, Zn, Cu, Mn, Co, Ni, Cr, Ba, P, Sb, Sn, Bi, Mo, and W for various gossan types and barren laterite from the Golden Grove Cu-Zn-Pb deposit, Western Australia (data from Smith, *et al.* 1982).

Notes:

iron sulphide:	*Iron sulphide gossans adjacent to mineralisation*	Cu/Zn gossans:	*Base metal (Cu-Zn) gossans*
		various gossans:	*Miscelaneous gossans*
Mgt. Fe-ironstones:	*Ironstones on massive magnetite*	Zn/Pb gossans:	*Base metal (Zn-Pb) gossans*
Laterite:	*Pisolitic laterite*		

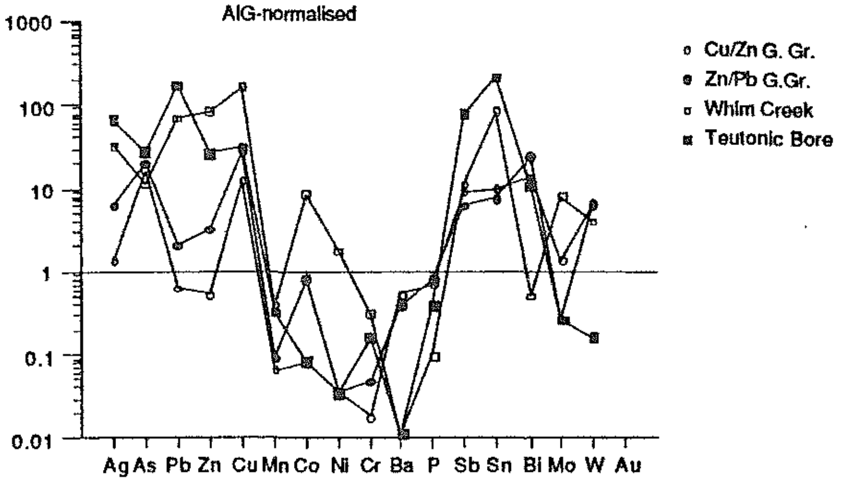

Fig. 4 AIG-normalised plot illustrating characteristic patterns of enrichment and depletion for Ag, As, Pb, Zn, Cu, Mn, Co, Ni, Cr, Ba, P, Sb, Sn, Bi, Mo, and W mean values for a number of volcanogenic massive sulphide gossan types from the Golden Grove Cu-Zn-Pb deposit (Cu/Zn G.Gr., Zn/Pb G. Gr.) and gossans from Whim Creek and Teutonic Bore, Western Australia (data from Smith, *et al.* 1982, note generally similar multi-element patterns for gossans from the three deposits).

Notes:

Cu/Zn G. Gr.:	*Base metal (Cu-Zn) gossans from Golden Grove*	Cu/Zn gossans:	*Base metal (Cu-Zn) gossans*
		Teutonic Bore:	*Teutonic Bore gossans*
Whim Creek:	*Whim Creek gossans*		

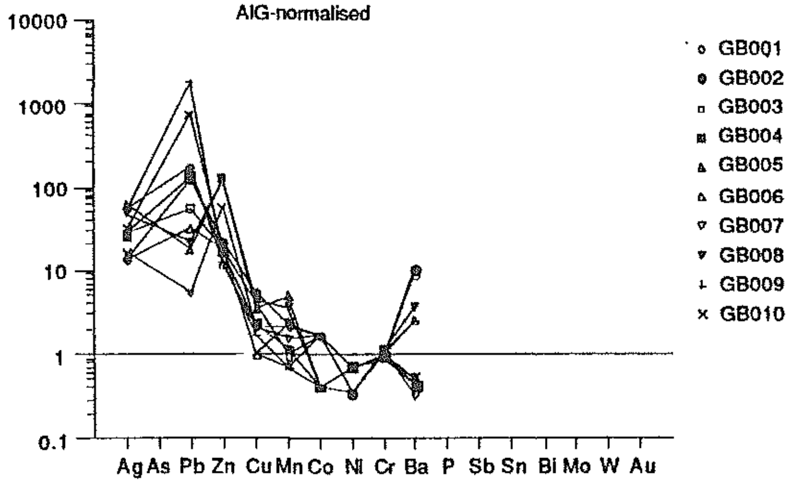

Fig. 5 AIG-normalised plot illustrating characteristic patterns of enrichment and depletion for Ag, As, Pb, Zn, Cu, Mn, Co, Ni, Cr, Ba, P, Sb, Sn, Bi, Mo, and W for mean values for gossans from the Gamsberg Pb/Zn deposit, Southern Africa (data from Andrew, 1984 note highly enriched Pb and Mn).

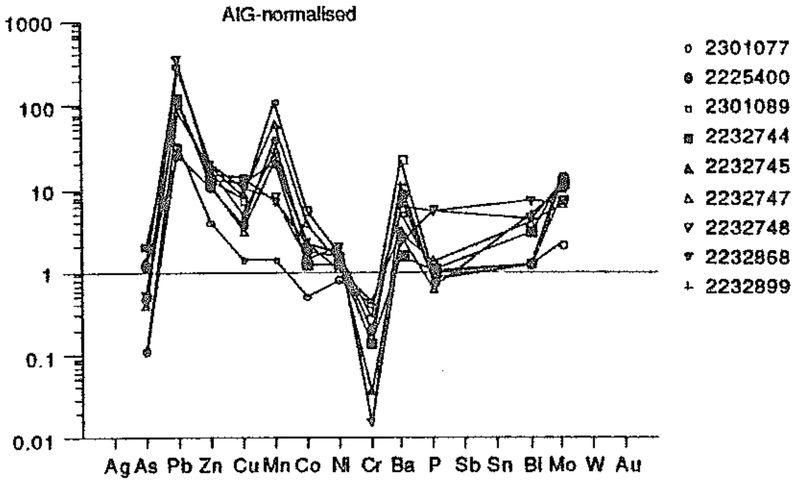

Fig. 6 AIG-normalised plot illustrating characteristic patterns of enrichment and depletion for Ag, As, Pb, Zn, Cu, Mn, Co, Ni, Cr, Ba, P, Sb, Sn, Bi, Mo, and W for gossans from Tethys prospect, Rudall area, Western Australia (CRAE data).

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THE USE OF LAKE SEDIMENT CORES TO MAP ENVIRONMENTAL CHANGE IN ONTARIO, CANADA

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Abstract

Analyses of lake sediment cores are used to describe (1) the pH history of acid Ontario lakes during the past 100 years and (2) how surface lake sediment material is used to map areas where increased levels of As, Pb, Cu, Ni, and Zn (due to anthropogenic fallout) occur. Results from pre- and post-Ambrosia based regional lake sediment geochemical mapping near Wawa, Ontario, illustrate how baseline geochemistry can be successfully mapped in areas of significant anthropogenic metal pollution. Implications of this research in relation to global change and global geochemical mapping are discussed at the end of the paper.

INTRODUCTION

In the 1970's, reconnaissance geochemical mapping based on lake sediments and lake waters was initiated in Ontario for mineral resource appraisal purposes (Fiske 1985). During the 1980's, research at the Ontario Geological Survey (OGS) was aimed at updating the reconnaissance lake sediment geochemical mapping technique to meet current needs. To achieve this, four significant departures from the traditional technique were researched and standardized. These innovations were: (1) an increase of the average sample density from 1 sample/13 km sq. to 1 sample/1.5 km sq. (to produce "Regional Geochemical Maps", see Fortescue and Vida 1990); (2) a change from "grab" to lake sediment core sampling; (3) the determination of as many as 35 elements in each sample (with strict quality control for each element) and (4) the broadening of the survey objective to include an environmental component. This paper is concerned briefly with point (3) and largely with point (4).

ALL ONTARIO QUALITY CONTROL DATA			HERMAN LAKE MAP AREA QUALITY CONTROL DATA			
ELEMENT	CLARKE INDEX-I (ppm)	GDS DATUM	MEDIAN	MINIMUM	MAXIMUM	RANGE
Mg (K)*	27640.0	0.07	0.14	0.13	0.14	0.02
Ti (K)	6320.0	0.11	0.22	0.21	0.24	0.03
Mn (K)*	1060.0	0.12	0.81	0.76	0.85	0.09
Fe (K)*	62200.0	0.12	0.60	0.58	0.63	0.05
Na (K)	22700.0	0.13	0.24	0.22	0.28	0.06
K (K)*	18400.0	0.15	0.33	0.29	0.36	0.07
Sr (K)*	384.0	0.15	0.22	0.21	0.23	0.02
Ni (K)*	99.0	0.16	0.24	0.21	0.27	0.06
Ca (K)	46600.0	0.18	0.17	0.15	0.23	0.07
V (K)	136.0	0.18	0.24	0.22	0.25	0.03
Sc (K)	25.0	0.20	0.24	0.18	0.28	0.09
Co (K)	29.0	0.21	0.14	0.10	0.31	0.21
Cr (K)	122.0	0.22	0.27	0.25	0.30	0.06
Be (K)	2.0	0.25	0.25	0.25	0.50	0.25
Al (K)*	83600.0	0.29	0.32	0.30	0.33	0.03
Lu (K)	0.54	0.37	0.37	0.19	0.74	0.56
Th (K)	8.1	0.37	0.40	0.35	0.43	0.09
Ba (K)*	390.0	0.38	0.51	0.26	0.54	0.28
Cu (K)*	68.0	0.49	1.10	1.04	1.16	0.12
Au (K)*	0.004	0.50	1.00	0.50	2.00	1.50
Pb (K)*	13.0	0.62	4.15	3.85	5.08	1.23
La (K)*	34.6	0.69	0.90	0.72	1.01	0.29
Hf (K)	2.8	0.71	1.07	0.71	1.43	0.71
P (K)*	1120.0	0.72	0.37	0.34	0.47	0.13
U (K)*	2.3	0.74	0.48	0.22	0.65	0.43
Mo (K)	1.2	0.83	0.83	0.83	1.67	0.83
Zn (K)*	76.0	1.00	1.53	1.41	1.76	0.36
Sb (K)*	0.2	1.00	4.50	4.00	5.00	1.00
As (K)*	1.8	1.11	69.44	66.11	95.00	28.89
Ta (K)	1.7	1.18	1.18	1.18	1.18	0.00
W (K)	1.2	1.67	1.67	1.67	1.67	0.00
Br (K)	2.5	8.40	4.40	3.64	4.84	1.20

GDS DATUM: LAKE SEDIMENTS FROM ONTARIO (n=3000)
HERMAN LAKE AREA QUALITY CONTROL DATA (n= 43).

Table 1. Clarke Index-1 values and median values for all elements included in the lake sediment General Datum Signature (GDS). (Elements discussed in this paper are marked with an asterix).

CHEMICAL ANALYSIS TO SUPPORT REGIONAL GEOCHEMICAL MAPPING

The aim of regional geochemical mapping is to discover "geochemical anomalies" and "geochemical provinces" on these maps. The recognition of "geochemical anomalies" is familiar to all exploration geochemists. The positive identification of geochemical provinces always requires high quality geochemical information based on standardized field, laboratory and data processing methodologies.

In order to facilitate the standardized processing of multielement geochemical data sets at the OGS since 1980, a Clarke Index-I transform (Fortescue 1985a) has been applied to all geochemical map data sets. The Clarke Index-I transforms chemical data as recieved from a laboratory, into geochemical data, thereby simplifying standardized plotting of multielement data sets (Table 1). To transform ppm element data into Clarke Index-I (=K) units, each result is divided by a Clarke value assigned to that element.

Using K units, multielement "geochemical signatures" for a sample material (e.g. lake sediment) are obtained by plotting ranked median values for all elements in a data set. Figure 1 includes a lake sediment "datum signature" for 32 elements in 3,000 lake sediment samples collected from central Ontario. The "datum signature" provides comparative information on background levels for elements in lake sediments.

Also on Figure 1, median values for each element obtained from 43 separate analyses of the same lake sediment sample (including error bars) are plotted with the datum signature. It is evident from Figure 1 that (1) the median levels in the standard are similar to those in the datum signature; and (2) the precision of the standard data is, in general, adequate for regional geochemical mapping purposes. For these reasons, Figure 1 provides a convenient overview of the performance of the standardized methodology used to obtain the geochemical

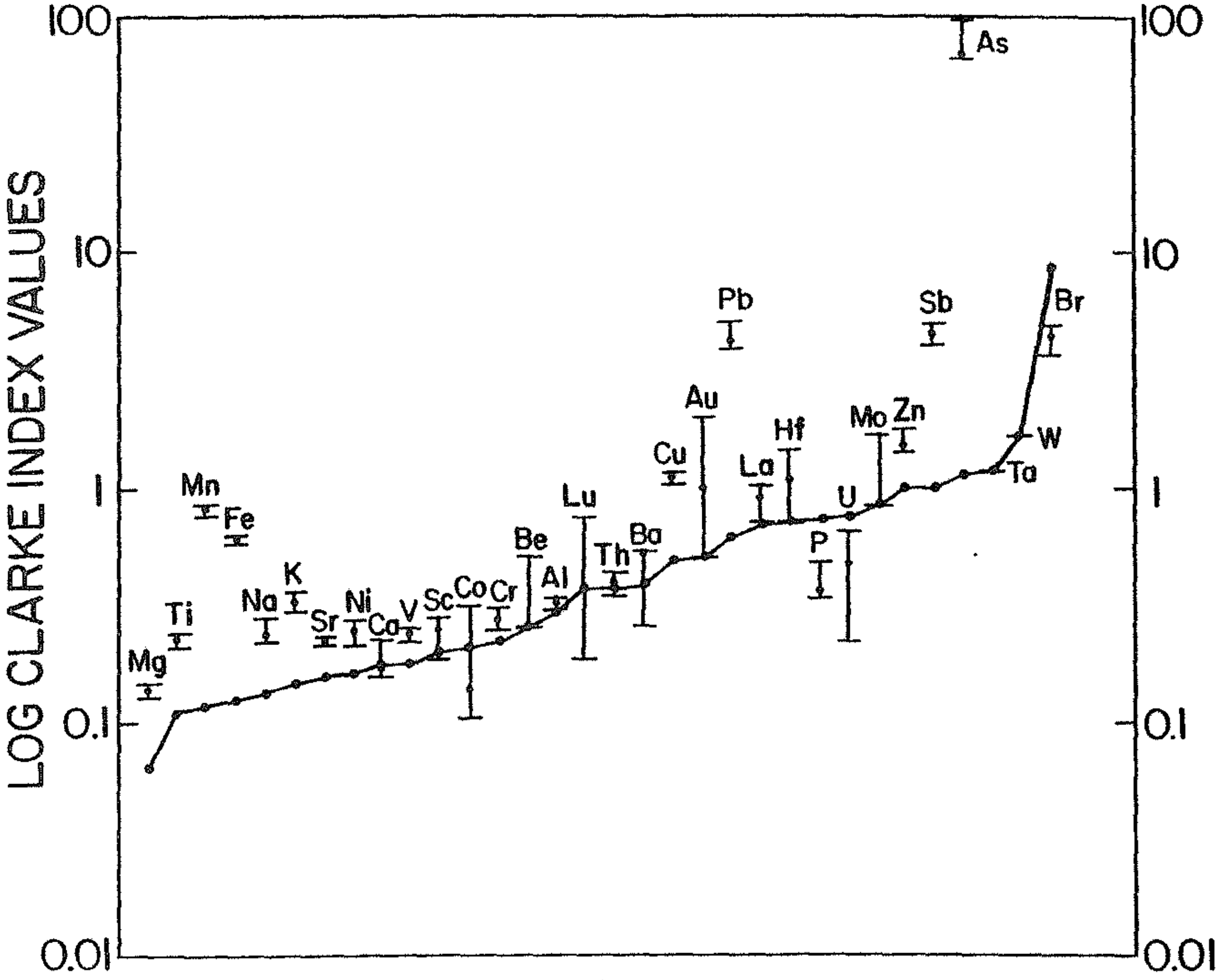


Figure 1 Global Datum Signature (GDS) for median values of 3,000 pre-Ambrosia lake sediments plus medians and error bars for 43 replicates of a reference standard randomized in the sequence of unknown samples from the Herman Lake area near Wawa. (For further information see Table 1).

information included in this paper.

SAMPLING LAKE SEDIMENTS FOR GEOCHEMICAL MAPPING

The Canadian Shield of Ontario includes thousands of lakes and ponds which are suitable for use in geochemical mapping. Initially, because of the large number of samples required for reconnaissance geochemical mapping, the simplest of sediment sampling techniques (i.e. a "grab" sampler) was employed. When mounted on a helicopter float, over 100 samples/day could be collected. The main advantage of using the grab sampler was that it was rugged and simple to operate. The disadvantage was the sample collected was almost always a mixture of surface and subsurface sediment.

Prior to 1980, a more careful approach to lake sediment sampling had been developed by limnologists and palynologists. These scientists were interested in using lake sediment cores as an 'environmental history book' to describe limnological and plant cover changes in catchment areas. In central Ontario, such cores could be used to date events during the 9,000 years since the departure of the ice cover. Sample collection by these methods generally provided a core several metres deep. The disadvantage of this methodology was that it often required an entire day to collect a single core.

In the mid-1980's, research at the OGS demonstrated the feasibility of regional geochemical mapping based on lake sediment <u>cores</u>. During this research, a simple reliable gravity corer was perfected. This made it possible for a crew of two to collect and extrude 75 lake sediment cores per day on a helicopter float (Fortescue 1988). "Short" (i.e 25 - 40 cm long) lake sediment core samples obtained by this method are now used as a basis for OGS regional geochemical mapping.

PRE- AND POST-AMBROSIA LAKE SEDIMENT

Short cores tend to be the same colour throughout. For this reason, colour cannot be used as a guide to core stratigraphy.

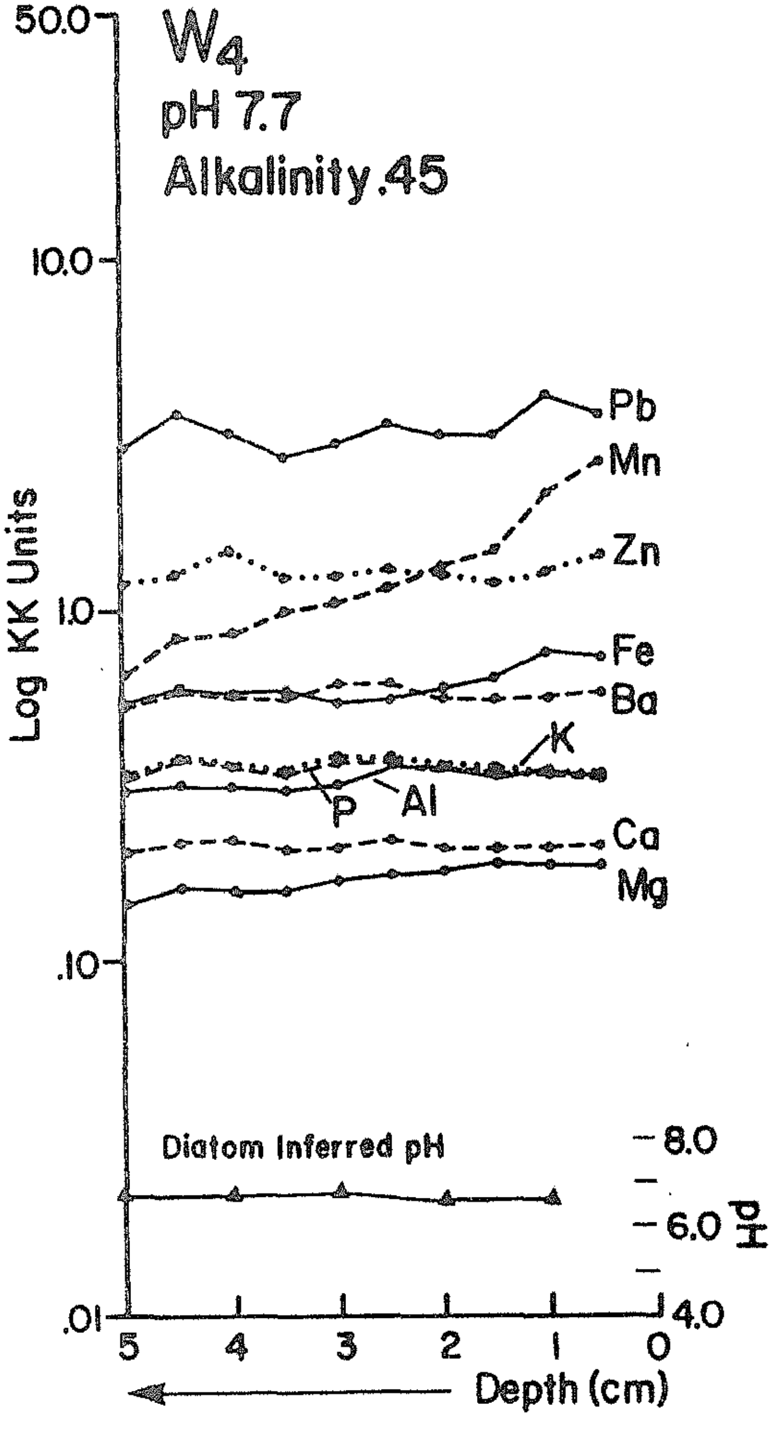


Figure 2 Concentration levels for 10 elements in a lake sediment core (0-5 cm) deep taken from the Wawa area in 1982 (from Fortescue et al 1984).

Fortunately, two subtle indicators of stratigraphy occur in these cores which can be used to date them. One is the detection of a pollen layer - the "Ambrosia" rise - which was laid down in central Ontario lakes between 1830 and 1890 (Dickman and Fortescue 1984). The other is radioactivity associated with fallout during the atmospheric testing of nuclear weapons in the mid-1960's.

In the early 1980's, Professor Mike Dickman, of the Department of Biological Sciences at Brock University, St Catharines, Ontario, and his coworkers showed that the "Ambrosia rise" always occurs at a depth of 14 to 18 cm in Central Ontario mid-lake basin sediments (Fortescue et al 1984).

Using this information, "short" lake sediment cores are now divided into three parts: (1) a "post-Ambrosia" sample (0-14 cm deep in the core) representing the period 1900-present; (2) a "transition zone" sample (15 - 20 cm deep in the core) representing the period from around 1880 to 1900; and (3) a "pre-Ambrosia" sample (> 20cm in the core) laid down prior to 1880.

ENVIRONMENTAL GEOCHEMICAL INFORMATION FROM SHORT CORES

Short cores are collected and used two ways. The first, involves the separation of pre- and post- Ambrosia samples on the helicopter float and their use for the preparation of separate geochemical maps. The second requires the collection and preservation of entire "short" cores for detailed study.

Let us consider a detailed geochemical investigation of the top 5 cm of a "short" core (i.e. totally within the post-Ambrosia material). The experiment was designed to discover if vertical mixing occurred during collection of such a core (Figure 2). The core was extruded to produce samples at 0.5 cm intervals for geochemical analysis. Element values in Figure 2 have been transformed into K units (see Table 1).

Figure 2 shows that vertical distribution patterns in the core for Pb, Zn, Fe, Ba, K, Al, P, Ca and Mg are simple and

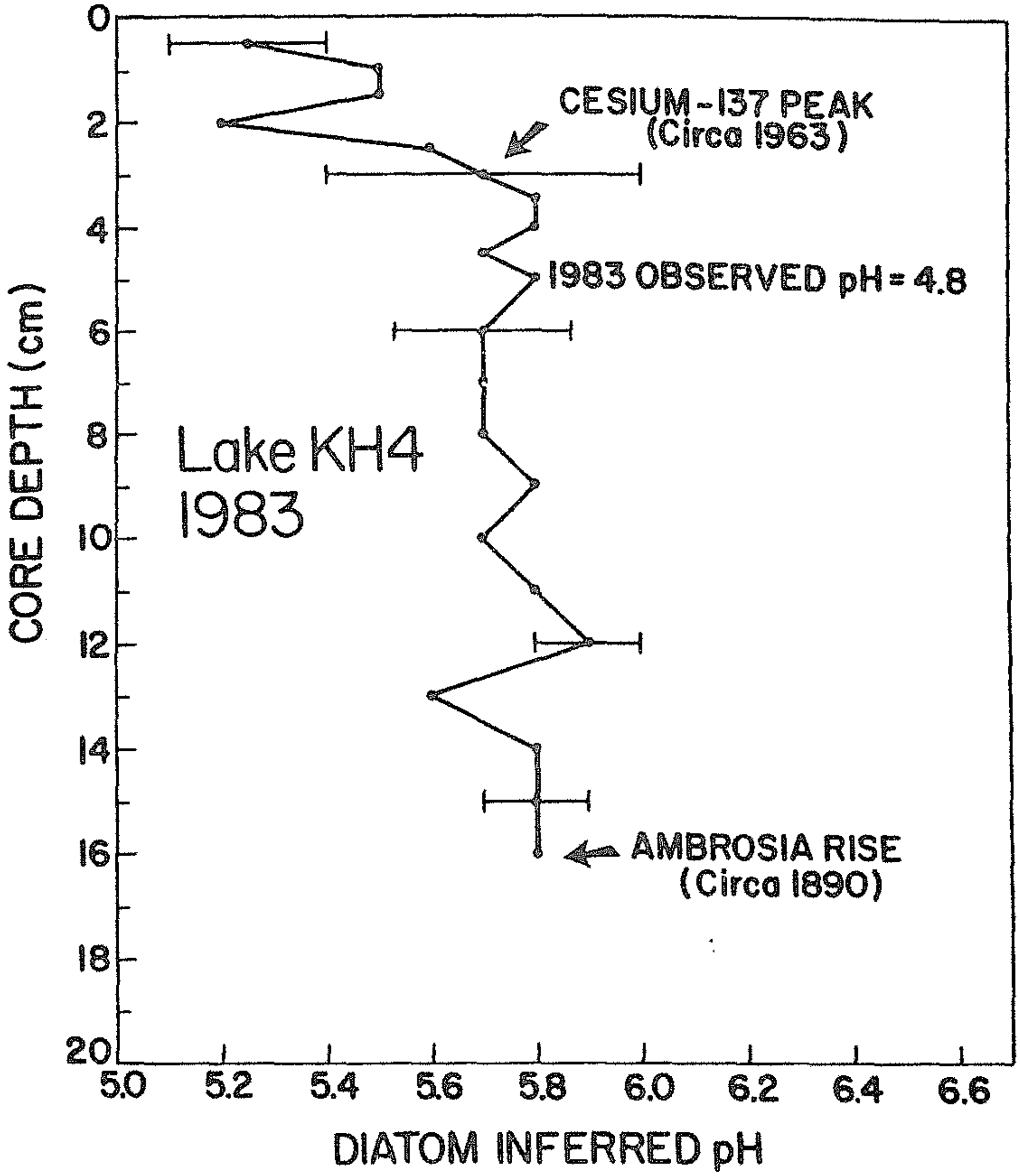


Figure 3 Downcore diatom-inferred pH for an oligotrophic lake (KH4) (from Fortescue 1985).

similar. This indicates uniform sedimentation during several decades. The relatively high level for Pb in post-Ambrosia sediment is due to anthropogenic fallout as described by Dillon and Evans (1982). Manganese has a positive concentration gradient with time. This suggests (1) a new Mn source derived from the lake catchment area and/or (2) a change in the chemical environment of the lake leading to secondary enrichment.

Note, the "diatom inferred pH" curve plotted at the bottom of Figure 2. This curve shows that the lakewater pH was constant during the period of sedimentation under review. In the early summer of 1980, the pH of the lakewater was measured at 7.7 (Figure 1). The sample was collected during a seasonal fluctuation towards alkalinity. This is not uncommon in Central Ontario lakes at this time of year. It was concluded mixing of core material did not occur during the collection of this short core.

The "diatom inferred pH' methodology was developed by Professor Dickman to provide detailed historical records of changes in lakewater pH during sedimentation. Such data are of interest in environmental geochemistry and particularly in acid rain studies.

Figure 3 is a graph of diatom inferred pH measurements obtained northeast of Sudbury in 1983 (Fortescue 1985b). In this case, the pH of lakewater was relatively constant from the Ambrosia rise (= 16 cm) until 1963. After 1962, the lakewater rapidly became more acidic due to the anthropogenic fallout of chemicals derived from the Sudbury smelters. Further examples of the use of diatom inferred pH measurements are described by Dickman et al (1984) and Dickman and Fortescue (1984).

THE USE OF "SHORT CORES" TO DESCRIBE AN ANTHROPOGENIC GEOCHEMICAL GRADIENT

Pre- and post- Ambrosia lake sediments were used by Fortescue and Stahl (1987) to describe effects of anthropogenic

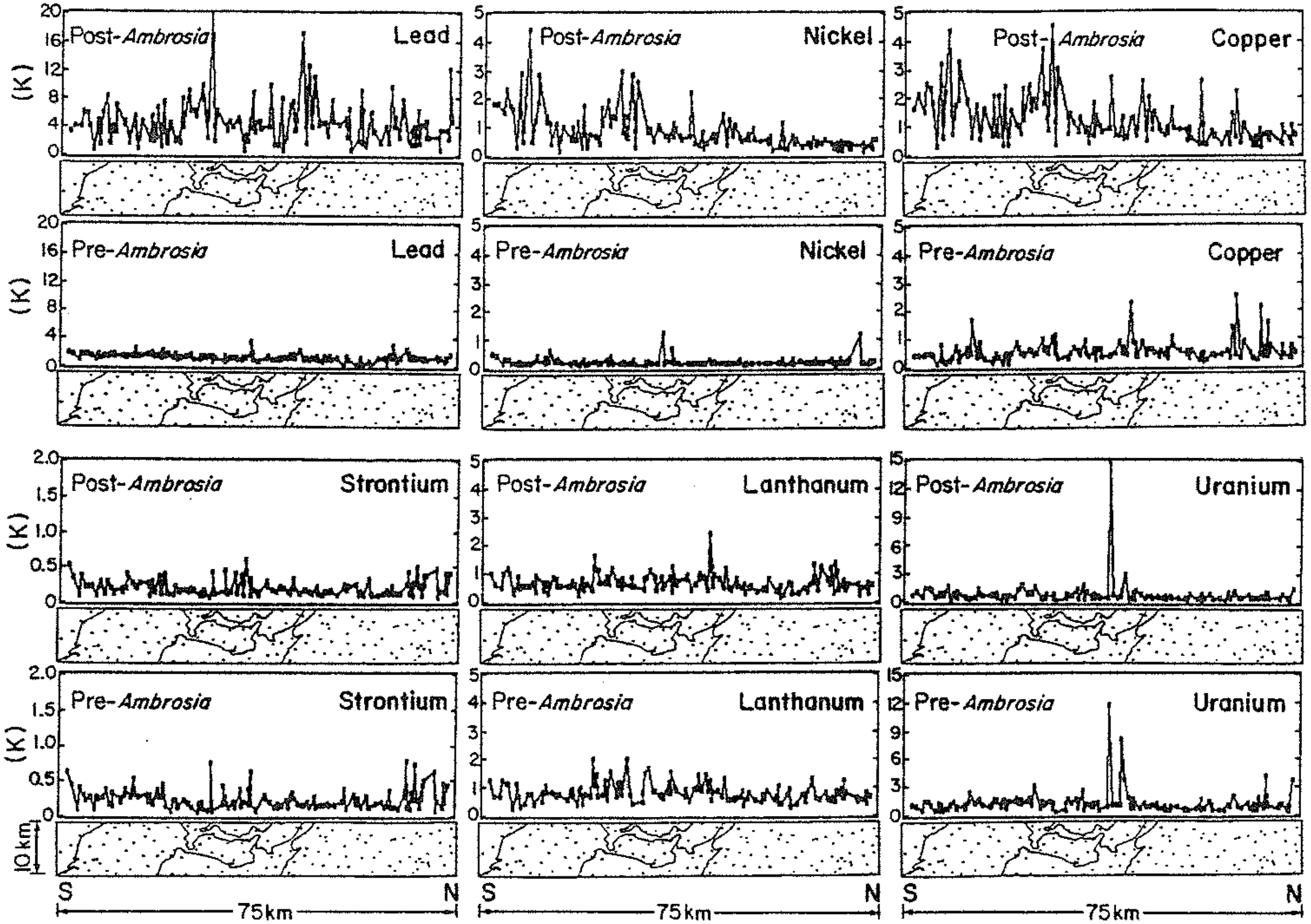


Figure 4 Graphs showing the level of 6 elements in pre- and post-Ambrosia lake sediments collected along a map strip northeast of Sudbury (redrawn from Fortescue and Stahl 1987)

fallout of Ni and Cu from smelters on a regional scale. Figure 4 includes geochemical profiles for six elements (Pb, Ni, Cu, Sr, La and U) in pre- and post-Ambrosia sediments collected from 139 lakes in a 75 x 10 km field site northeast of Sudbury, Ontario. As expected, Pb levels were consistantly higher in the post-Ambrosia samples due to anthropogenic atmospheric fallout. The pre- and post-Ambrosia profiles for Ni and Cu both show a significant regional geochemical gradient away from the smelters (i.e from left to right on Figure 4). The pre- and post- Ambrosia profiles for Sr, La and U were included in Figure 4 as controls. This is because these elements do not occur in anthropogenic fallout.

THE USE OF "SHORT CORES" IN REGIONAL GEOCHEMICAL MAPPING

The Michipocoten greenstone belt, which includes the Herman Lake regional geochemical map area, is located northeast of Lake Superior, near Wawa, Ontario (Figure 5a).

The Herman Lake area is situated downwind from a sintering plant at Wawa which has been in almost continuous operation since the mid-1930s. The deposition of chemicals derived from this plant has caused a large fume kill in forests northeast of Wawa. Part of the fume kill is in the Herman Lake map area.

Figure 5b includes pre- and post-Ambrosia regional geochemical maps for 7 elements (Pb, Zn, Cu, As, Sb, Au and Mn). As expected, the post-Ambrosia Pb map shows uniformly high levels compared with the pre-Ambrosia map for this element. This Pb pattern does not appear to be influenced by atmospheric fallout from the Wawa sinter plant. This is in contrast to the post-Ambrosia patterns for As and Sb which are modified by atmospheric fallout derived from the sintering plant.

It is interesting that Cu patterns were similar in both the pre- and post-Ambrosia, suggesting no significant fallout of this element from the smelter plume. Results for Au are similar to those for Cu (Figure 5b) except that the post-Ambrosia Au map

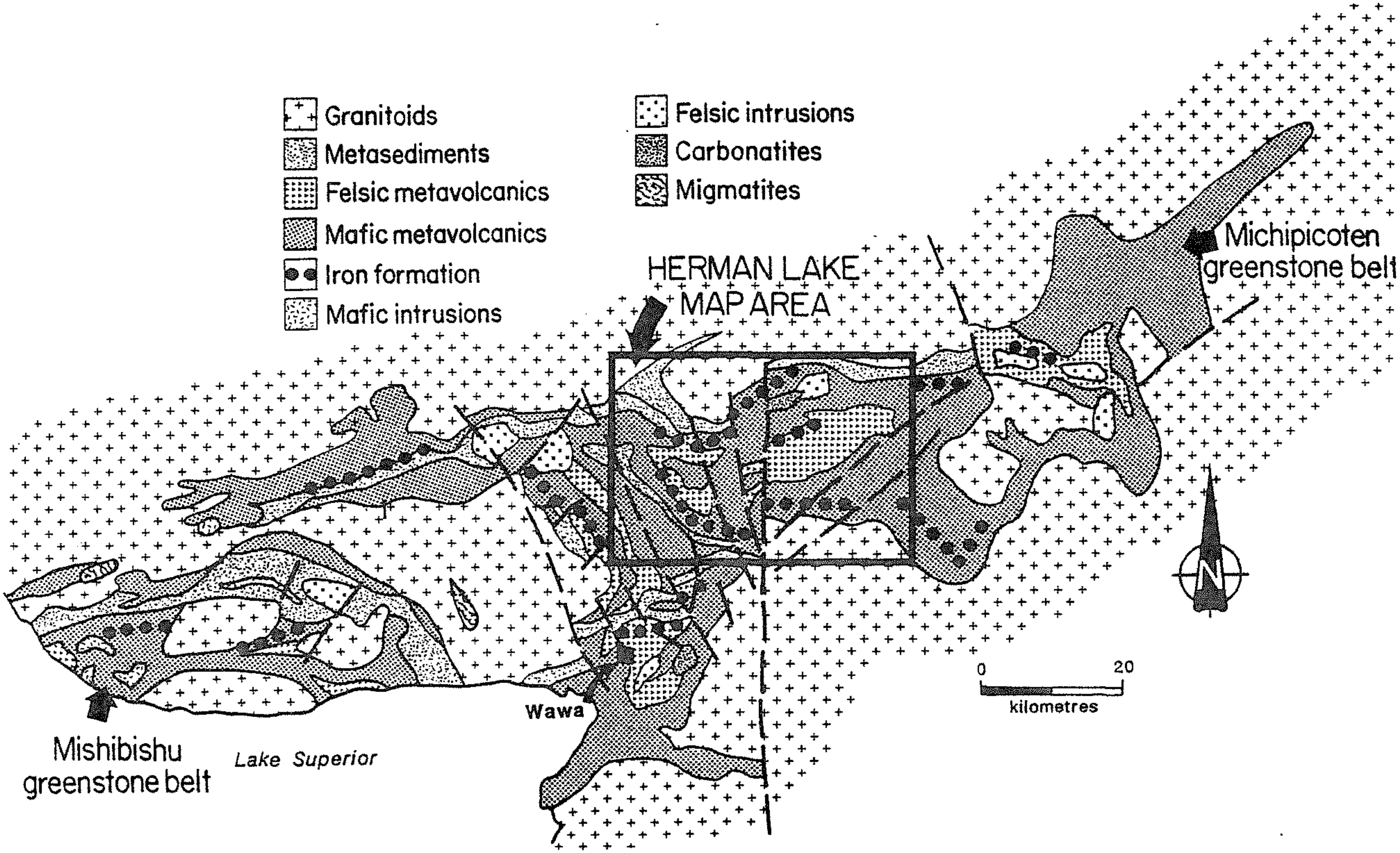


Figure 5a Generalized geology map of the Michipicoten greenstone belt including the Herman Lake geochemical map sheet boundaries (after R.Sage; from Fortescue and Vida 1990).

includes two patterns (A, and B). These are known to be due to contamination from recent exploration and/or previous mining activities. Manganese patterns, like those for Cu and Au, are similar in both maps. The Zn maps were included to show some pre-/post-Ambrosia geochemical patterns may be more difficult to explain. In the case of Zn, the post-Ambrosia map was considered to include high values due to both anthropogenic fallout and exploration activities.

SUMMARY AND DISCUSSION

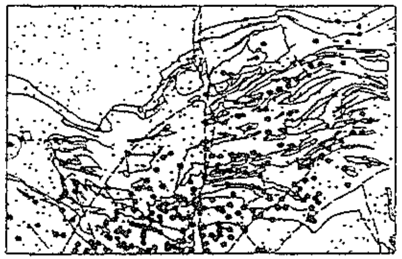
A standardized approach to regional geochemical mapping based on lake sediment cores has been described. This proceedure may produce regional geochemical maps of direct importance for: (1) mineral resource appraisal;(2) mineral exploration; and (3) environmental geochemistry. In addition, the multielement geochemical databases generated during such projects provide information suitable for direct incorporation into Geographical Information Systems (GIS).

Pairs of geochemical sections and maps showing pre- and post-Ambrosia patterns for 5 elements (Pb, Ni, Cu, As and Sb) in areas affected by anthropogenic fallout demonstrate the importance of lake sediments for environmental geochemistry in Ontario.

The research described has focussed on the importance of anthropogenically derived atmospheric fallout in regional geochemical mapping for mineral resource appraisal purposes. Our research has demonstrated that pre- and post-Ambrosia geochemical patterns must be interpreted on an element to element basis. It is concluded that global geochemical mapping must always take into account effects of anthropogenic fallout.

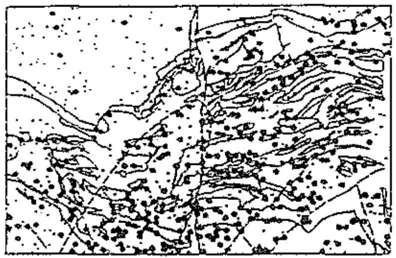
Our experience suggests that, from the viewpoint of environmental geochemistry, all sample sites chosen for global geochemistry should include samples of both pre- and post-anthropogenic material.

Post-*Ambrosia*



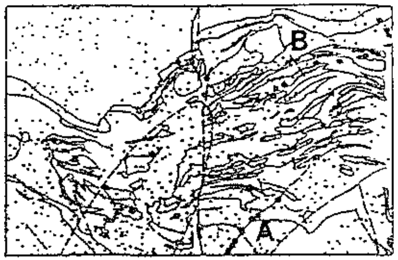
As (K) ≥10.0 (18.0 ppm)

Post-*Ambrosia*



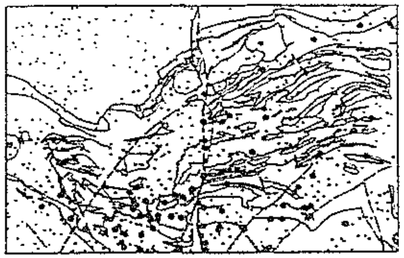
Sb (K) ≥2.5 (0.5 ppm)

Post-*Ambrosia*



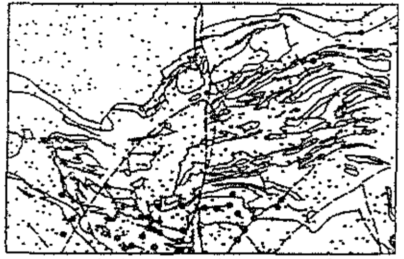
Au (K) ≥3.0 (12.0 ppb)

Post-*Ambrosia*



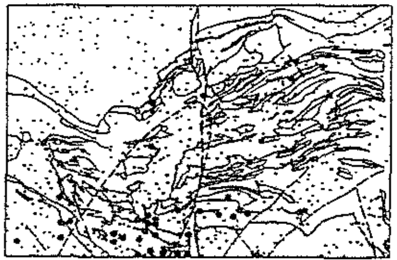
Zn (K) ≥2.0 (152.0 ppm)

Pre-*Ambrosia*



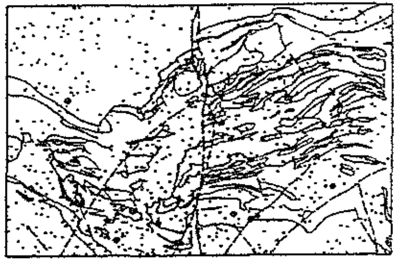
As (K) ≥10.0 (18.0 ppm)

Pre-*Ambrosia*



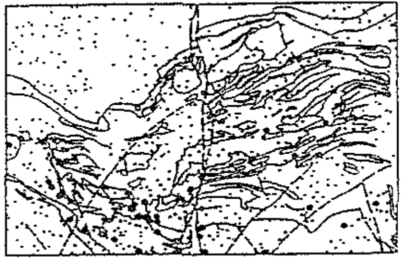
Sb (K) ≥2.5 (0.5 ppm)

Pre-*Ambrosia*



Au (K) ≥3.0 (12.0 ppb)

Pre-*Ambrosia*

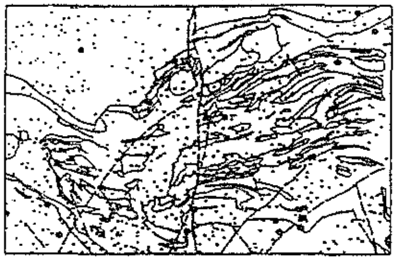


Zn (K) ≥2.0 (152.0 ppm)

Post-*Ambrosia*

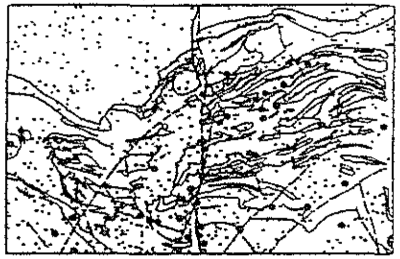
Pb (K) ≥1.5 (19.5 ppm)

Post-*Ambrosia*



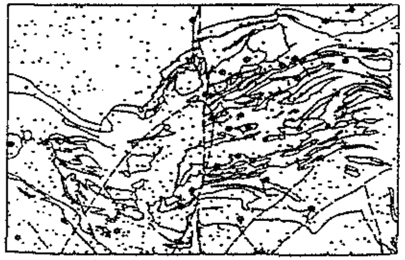
Cu (K) ≥2.0 (136.0 ppm)

Post-*Ambrosia*



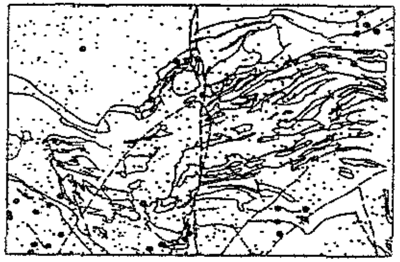
Mn (K) ≥1.0 (1060 ppm)

Pre-*Ambrosia*



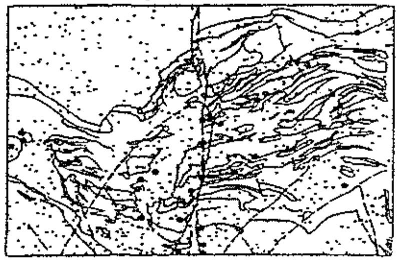
Pb (K) ≥1.5 (19.5 ppm)

Pre-*Ambrosia*



Cu (K) ≥2.0 (136.0 ppm)

Pre-*Ambrosia*



Mn (K) ≥1.0 (1060 ppm)

Figure 5b Single element pre- and post-Ambrosia geochemical maps of the Herman Lake area. (see also Figure 5a). For explanation of the maps see text.)

Similarly, if the geochemistry of landscapes has been changed significantly by global change, this should be detectable on regional "geochemical change" maps. Such maps would be based on lake sediment cores (or other material which can be dated) that are resampled at regular intervals.

CONCLUSIONS

1) By paying close attention to sampling techniques, we have demonstrated that time dependent regional geochemical patterns can be observed in geochemical maps based on lake sediments.

2) Although our geochemical mapping has been on a relatively small scale by global standards, we believe that the results we have obtained may be of importance in the planning of future global geochemical mapping and in relation to global change detection studies.

ACKNOWLEDGMENTS

This paper is published by permission of the director, Ontario Geological Survey. The views expressed in this paper are those of the writers and do not necessarily reflect policy of the Ontario Geological Survey.

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The geochemical map of the Precambrian of the Ukrainian Shield /an approach to regional geochemical research underlain by new techniques/

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The multielement geochemical map of the Ukrainian Shield /US/ has been compiled for the first time.

The new techniques are underlain by a regional information-logical system "Geomet - Ukrainian Shield" :geology, geochemistry, metallogeny of the US/ consisting of a base of geological-geochemical data and mesns of their analysis including elements of the expert system. There has been created a hierarchic system of regional geochemical backgrounds of objects of increasing complexity; lithologic differences of rocks, rock associations - stratigraphic units, rock complexes, geological formation, structural elements of the Shield and, eventually, region as a whole. If necessary, the system can provide data for construction and analysis of the "non genetic" field of compositional matter distribution within the shield and its individual parts. Thus, there were created conditions for characterization of elements of a regional geological structure in terms of the substance distribution and vice versa.

The geological map of the Precambrian of the Ukrainian Shield based upon the above mentioned information can be characterized as follows:

- geochemical zonin was established on the ground of distribution of petrogenic elements /Si, K, Na, Fe, etc./ affecting the environment of geochemical processes in geological formation;
- geochemical background of supra-rock elements of the regional geological structure /formations, structural-formational zones, geoblocks, etc./ were determinated on the basis of average weight of chemical element contents in a lower-order objects - for example in rocks, as to their volumetric ration in a higher-order object;
- both positive and negative geochemical specializations of geological formations are revealed and accordingly mapped;
-the confinement of geochemical anomalies and anomalous fields to elements of geological structure of the region is mapped as peculiar kind of geochemical information;
- the performed analysis of "geochemical contrast range" of various systems of the shield division into structural material complexes makes it possible to choose a well-founded geological basis of the geochemical map.

The Ukrainian Shield is considered to be a complex-differentiated geochemical province. The analysis of material related to regional geochemistry of the Ulrainian Shield shows that there exist certain regularities in arrangement of chemically heterogenous structural -formational complexes and geological formations constituting them what predetermines geochemical zoning of the granite-metamorphic layer of the shield crust which, on the other hand, stipulates metallogenic specialization of regions, blocks, zones.

In this connection the geochemical map of the Ukrainian Shield has been compiled to complete the set of maps of the Precambrian of the Shield of scale 1:1 000 000. It is based on the map of geological formations which reflects not only the geological structure of the region but also the most general geochemical peculiarities in distribution of petrogenic elements /Si, K, Na, Fe and others/ in geological formations, as their behaviour has a paramount importance for the course of geochemical processes.

Rock, as a rule, serves as an object of direct analytical research in geochemical studies. The geochemical characteristic of any complex geological object combines geochemical characteristics of rocks constituting it which account of volume-space relations. When compiling the geochemical map of Ukrainian Shield, geological formation was chosen as an elementary object.

For each geological formation, for each separate geoblock, formulas of geochemical specialization were derived, as represented by a fraction where the numerator is expressed by symbol of elements with Kk 3/characterizing positive geochemical specialization/, and the denominator is expressed by symbols of elements with Kk 3/characterizing negative geochemical specialization/. Analysis of the formulas for geochemical specialization of individual formations allowed to distinguish 17 types of geochemical associations of elements characterizing positive geochemical specialization of geological formations and 6 geochemical associations characterizing their negative geochemical specialization. On the map each of 17 "positive" associations is shown in contours of the formations corresponding to this specialization in sharp colours whereas "negative" associations are shown in colour shades. Simultaneous mapping of positive and negative geochemical specialization makes possible to more edaquately reflect areal geochemical zonation, contrasting gradation of the geochemical multielement field as well as regions of active migration, removal and accumulation of chemical elements, primarily ore elements.

Geographical ranges where areal geochemical anomalies are developed /anomalous geochemical fields/ and local concentrations of ore elements are also singled out an the geochemical map of the Shield. Both mainly issue from superimposed /epigenetic/ processes /hydrothermal activity, metasomatism, contact metamorphism, etc./. Manifestation of these processes, in addition to derivation of local high-contrast concentrations of ore elements, i.e. deposits or metal ore shows, results in formation of anomalous geochemical fields, occupying large areas, with alternating high or low contents of elements in rocks or formations and with developed areal complex geochemical anomalies. Separation of anomalous geochemical fields and local concentration of ore elements, on the geochemical map, allows the geochemical view of the Ukrainian Shield to be reflected more adequately and disturbance sites of primary-constitutional distribution of elements, active redistribution and concentration of ore components to be underlined.

Coming out from the performed work the following stable associations of chemical elements were established: 1/ tin- yttrium -ytterbium - niobium; 2/ zirconium - beryllium; 3/ manganese - iron - vanadium - scandium - /zinc/; 4/ nickel -chromium- cobalt; 5/ barium - strontium.

Geochemical specialization of geological formations in the Ukrainian Shield as a whole is controlled by elements of siderophile and lithophilic groups and, to a smaller extent, by chalcophilic elements. This also stipulated the principal metallogenic profile of the Shield.

The most geochemically specialized formation of the Shield are as followed:

1. Aplogranite Volyn region, subalkaline granite, alkaline and nepheline-syenite Azov region formations are specialized in association of element constituting the first and second groups: tin-yttrium-ytterbium-niobium and zirconium-beryllium, sometimes with molybdenum.
2. Gabbro Korosten complex and bipyroxene gneiss and crystalline-slate Dniester-Bug series formations are specialized in association of element of the third group: manganese-iron-vanadium-scandium, sometimes with phosphorus.
3. Ultramafic formation Belava Tserkov, Bug and Dnieper ares and gabbro-pyroxene Dnieper area are specialized in elements of the fourth group association: nickel-cobalt-chromium.
4. the formation of alkaline ultramafic complexes and carbonatites in the Azov area /Chernigov complex/ has a specific rare metal - rare earth elements specialization.

Futher statistical processing of data to obtain mean contents of chemical elements in geological formations and in separate members of formations arranged in geochronological succession makes possible to evaluate geochemical specialization of the Shield formations of different age.

Archean formations are as a whole primary concentrators and accumulators of siderophilic elements; Cr, Ni and V. This results in prevailing occurrence of ultrabasic and basic magmatic-volcanogenic formations and chemically poorly differentiated greywackes, pyroclastic and clastic rocks associated with them in the Archean /especially in the Upper Archean/.

Formation of the transient Archean-Lower Proterozoic period are geochemically specialized in Fe, Mn, Co, Cr and Cu. This period is characterized by a strong variation in the chemical composition of hydrosphere and atmosphere, by transition from the reducing to oxidation potential of sedimentation and deposition environment. An accumulation of siderophile /mostly

Fe/ and, to lesser extent, chalcophilic elements, occur in the world ocean that are in favour of geochemical specialization of sedimentarv-volcanogenic formations of this period.

Geological formations of the lower part of Lower Proterozoic completing the transient period show no clear specialization.

Starting the upper parts of the Lower Proterozoic and especially the Upper Proterozoic, Precambrian formations of Shield were found to function as concentrators and accumulators of lithophilic elements, particullary rare metals - Zr, Sn, Be and rare earth elements of the yttrium group.

The change of element association, geochemically specializing geological objects, reflect the time /from Archean to Upper Proterozoic/ evolution in the composition of Precambrian formations of the Shield as the crust of continental type was being formed and tectono -magmatic activities occured under platformal conditions. The investigation of such an evolution gives allows to outline the develonment of geochemical epochs which predermine the metallogenic epochs during the formation of the Shield.

Analysis of geochemical map of the Shield gives an evidence for the occurence of certain regularity in the location of chemically heterogenous structural complexes and geological formations which results in lateral and vertical geochemical zoning of the region under study. An investigation based on detailed analysis of geochemical, geological, structural data and metamorhic facies allowed to establish a geochemical zoning to occur within the Shield.

In this connection the Ukrainian Shield as a whole is regarded as a geochemical province - a large geostructural element of the Earth's crust with high degree of geochemical differentiation. Geochemical aresa /blocks/, interblock geochemical zones, geochemical regions and structural-geochemical zones are distinguished within its limits. The degree of geochemical differentiation of areas which is controlled by the degree of inhomogeneity in distribution of chemical elements is responsible for their metal content. The greater part ot the established ore manifestations and deposits is confined to differentiated and especially to highly differentiated geochemical regions /Volyn, Kirovograd and Azov/ and interblock zones /Inguletsk - Krivoy Rog/.

Within these regions on the boundary, geochemical zones with disturbance in the primary element distribution which control the position of particular structural metallogenic zones, ore-bearing structures and ore regions of the Shield were identified.

General geochemical and metallogenic zoning of the Shield and surrounding structures was established as follows: rare earth and rare metal pegmatites, metasomatic mineralization of Zr, Mo, W are characteristic of the Shield's central parts; alkaline metasomatites with Be, Ta, Nb, rare alkali metals, rare metals skarns /W,Sn, Be, REE/, carbonatites /Nb, Y/, fluorite mineralization occur in marginal parts; metasomatic and hydrothermal mineralization of fluorite, base metals, rare metals occur along the Shield's slope; base metals, noble metals, Hg, Sb were found in adjacent troughs.

The common vertical geochemical zoning is expressed in the occurence of Be, Nb, Zr, REE, Sn, W and Mo in the Precambrian of the Shield, i.e. there are the elements of the lower parts of regular zonal distribution of elements in primary geochemical aureoles. At the same time the structures surrounding the Shield were found to contain mostly Pb, Zn, Au, Ag, F, Hg and Sb which corresponds to the central and upper parts of the general geochemical series.

So, the investigation of space/time regularities in the chemical element distribution of the Ukrainian Shield allows to do some prognostication, i.e. to indentify potentially ore-bearing structures and in general to improve the efficieny of prognostic metallogenic studies in search for minerals in various regions.

HIGH-SELECTIVITY ATOMIC ABSORPTION ANALYZERS FOR THE DETERMINATION OF THE MERCURY CONCENTRATION IN GAS, LIQUID AND SOLID SAMPLES.

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At present geochemists and ecologists pay regard to the problem of mercury detection in various media. This attention can be explain by two reasons: mercury is a pathfinder of different kinds of deposits and mercury is a toxic element, whose concentration in air, water and food must be kept under control.

In the Leningrad State University two high-selection atomic absorption analyzers for an express determination of the atomic mercury concentration are elaborated. Using commercial atomizers or barbaters and our instruments one can detect mercury in gas, liquid and soild samples without any preliminary treatment procedure. Both analyzers are based on differentical atomic absorption spectrometry, but they differ in the manner of realization of two-wave scheme. In the first instrument, the source of light is in the constant magnetic field, as a result the resonance mercury line is splitted into several components /it is a direct Zeeman effect/. One of these components takes place in analytical line and another - reference line. By means of polarization modulator the radiation of the Zeeman components penetrates the analyte cell in turn and then it is detected by PMT. In another analyzer the discharge in the spectral lamp with the mixture of two mercury isotopes is excited by the high-frequency generator which is modulated by radiofrequency voltage. Due to spectral-phase effects it is possible to detect the radiation corresponding to each component. In this case the radiation of one isotope component takes place i analytical line and another - reference line. Further treatment of signals is carried out in traditonal algorythm for differencial techniques.

Since the distance in wavelengths between the analytical and reference radiation does not exceed 0.5 sm^{-1}, the influence of unselective molecular absorption and of scattering on particles, on the analytical signal is practically negligible. As an exception a disturbance can occur while connecting with the rotary structure, unforbidden nearby the mercury resonance line of 254 nm /since the rotary structure constant /$\sim 1\ sm^{-1}$/ is approximately equal to the atomic absorption line width/.

The analyzer selectivity has been checked while leaking in the analytical ditch of acetone vapours, ethyl alcohol and petrol as well as of smoke /simulator of areosol disturbance/, the general attenuation of intensity of mercury resonance radiation being controlled.

The disturbance influence, exceeding the noise level, has not been noted. The analyzer calibration has been carried out by way of leaking of measured quantity of mercury in the drawn through analytical cell as well as by means of equivalent concentrations - for this purpose the cells of different thickness with saturated mercury vapours were used.

The detection limits of analyzers were comparable - 10 ngr/m^3 for mercury in the air and 10^{-5} % in samples. The time constant of analyzers is 5 sec., the time of one sampling /when analyzing solid and liquid samples/ is 1-2 min.

In geochemical and ecological practice two types of selective analyzers have been used. The first of them enables to determine mercury directly in the air without sampling stage. In these analyzers an open multipath cell /6 paths/ has been used. A similar type has been used when registrating mercury aureoles in motion /the analyzers were set up on board of a plane, helicopter, car, vessel/. For local determinations as well as for conductiong the absolute measurements and registrating mercury in gas, the type with pumping of analyzed air through the cell has been used. The air has been periodically drawn through the filter absorbing the mercury vapours, thus enabling to eliminate the influence on the results of long-term drifts of analyzers. The pumping rate was 7-10 l/min - at such rates the influence of desorption, deposited on walls of mercury cell, is practically absent.

For determination of mercury in solid and liquid samples the helical oven has been used in which the sample has been installed. The air has been drawn through the oven and analytical cell. The comparison of results, obtained with the help of our analyzers and on the basis of well-known methods /chemical, accumulation on gold sorbent/ has shown their satisfactory coincidence.

On the basis of established selective analyzers and using the pyrolysis /when scanning the pyrolyzator temperature/ the technique of determination of metal-organic compounds of mercury in air and gases has been developed and checked. The detection limit of mercury-organic compounds is 10 ngr/m^3 provided the atomic mercury content is < 500 ngr/m^3; otherwise it is 2% of mercury content.

GEOCHEMICAL PROSPECTING FOR OIL AND GAS FIELDS IN THE NORTH-EAST OF THE USSR

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The north-eastern areas of the USSR measuring about 1.5 000 000 sq km seem to peninsulate the Eurasian continent. In the north they are washed by the Arctic Ocean and by the Pacific Ocean in the south and east (Fig. 1). Within this region the major lithosphere plates as Atlantic, Pacific, North American and Eurasian join together. The origination and development of the Earth's crust, which was peculiar within these plates, and also the different relationship of oceanic and continental lithosphere blocks resulted in an intricate and prolonged geological history of the North-East of the USSR and influenced its geographic position, geomorphologic features and neotectonic movements. In the course of these geological processes in the North-East of the USSR territory about 20 sedimentary basins were formed measuring about several thousands of square kilometers, with sedimentary cover up to ten thousand meters thick and, may be, even more. Many of these basins are promising for oil and gas; commercial fields of hydrocarbons have been already found within Anadyr and Khatyrka basins. All these sedimentary basins occur within a cryolithic zone, which is both continuous and discontinuous, with perennial frozen rocks more than 100 m thick.

While performing gas and geochemical prospecting over the upper portion of the cryolithic zone, that is season thawing layer, the regular (seasonal) over-all drastic changes were considered. A seasonally thawed layer is indeed "transparent" for hydrocarbon gases migrating upward. During this period the microbial activity is intensified in such a layer, and the underground water is constantly renewed; physical and chemical conditions of the summer season in the whole do not favour preservation of epigenetic hydrocarbon gases in seasonally thawed layer.

Fall in temperature and freezing of seasonally thawed layer result in local temporal accumulation of epigenetic gases, which is peculiar, that is the fall in temperature below zero increases the adsorptional capacity of the solid phase, with heat occurring through gas adsorption with solid sorbents being always positive, and also favours the considerable increase in the most solid ice phase. Besides this, the capacity space may transform and closed pores expand. When a seasonally thawed layer is completely frozen, water and gas metabolic processes cease and microbial activity stops. These processes in their aggregate determine accumulation of hydrocarbon gases in seasonally thawed layer during winter period (Table 1).

Syngenetic biochemical anomalies caused by anaerobic methane-producing microorganisms are excluded during winter period since they may occur only under above-zero temperatures. Considering these properties one may elucidate the origination of methane both in soils and in near-surface air. The evidences of the content of hydrocarbon gases in the air when soil is thawed are used obtained in situ. When thawing processes just begin, the presence of methane is maximal in near-surface air due to seasonally thawed layer degassing within the areas of epigenetic anomalies. As the temperature of soil is risen, the methane content of air is higher in the areas where it is produced by modern bacteria (Fig. 2).

Table 1

Average content of hydrocarbon gas
at the bottom of seasonally thawed layer, Anadyr Basin
$(n \cdot 10^{-3}\ cm^3/kg)$

Rocks	Beginning of winter period				Termination of winter period			
	methane (C_1) + ethane (C_2)	propane (C_3)	butane (C_4)	$\frac{C_1+C_2}{C_3+C_4}$	methane (C_1) + ethane (C_2)	propane (C_3)	butane (C_4)	$\frac{C_1+C_2}{C_3+C_4}$
				Verkhne-Echin area				
Peat	89.0	2.50	n/e*	35.6	786.70	8.77	4.16	60.80
Loam	72.31	9.42	0.85	7.04	384.36	17.35	1.47	17.62
Sandy loam	5.07	0.04	n/e*	126.75	223.66	8.48	4.02	17.89
				Verkhne-Telekai area				
Peat	108.58	0.89	n/e*	122.0	832.65	9.08	n/i*	-
Loam	61.30	8.05	0.7	7.00	206.65	49.2	n/i*	-

*n/e - not evident, n/i - not identified

It is noteworthy that the photochemical activity of methane is not considered in the course of interpretation of atmospheric and geochemical evidences for northern and other regions. In fact, methane is not stable. Under the influence of ultra-violet radiation with wavelength of 305 to 320 nm the reactions as follows are near the surface during summer season:

$$NO_2 \overset{\text{light}}{\quad} NO + O$$

$$CH_4 + 4NO \qquad CO_2 + 2H_2O + 2N_2$$

A wide range of methane anomalies in the near-surface air has been revealed dependent upon the intensity of ultra-violet radiation (Fig.3).

The Earth's bowels are known as the only source of atmospheric methane. A so-called microbial filter is present at the atmosphere and lithosphere's interface, and the occurrence of hydrocarbons in the interior of the Earth may be judged by the intensity of vital functions of hydrocarbon oxidizing bacteria, which is a so-called biogeochemical prospecting for oil and gas fields. The microbial filter is of a local character in tundra because of short vegetative season, occurrence of tanning agents in soils and other factors. (Table 2)

Table 2

The content of hydrocarbon oxidizing bacteria in seasonally thawed layer

1. Anadyr basin

Soils	Hydrocarbon oxidizing bacteria (conventional numbers)			
	CH_4	C_3H_8	C_5H_{12}	C_6H_{14}
1. Peat	0	0	40	0
2. Loam	0	0	50	20
3. Loam	0	0	120	0
4. Fine sand	0	0	190	30
5. Humic sandy loam	0	0	0	12
6. Humic sandy loam	90	0	0	0
7. Humic sandy loam	0	0	0	170
8. Loam	80	0	0	0
9. Pebbles	0	16	120	500
10. Loam	0	0	0	90
11. Sandy loam	0	0	50	0
12. Pebbles, rock debris	0	0	40	0

32 samples do not yield hydrocarbon oxidizing bacteria.

Table 2

(continued)

The content of hydrocarbon oxidizing bacteria in seasonally thawed layer

2.Khatyrka basin. Uglovaya area

Soils	Hydrocarbon oxidizing bacteria (conventional numbers)			
	CH_4	C_3H_8	C_5H_{12}	C_6H_{14}
1.Coarse gravel with sand	0	0	150	40
2.Coarse gravel with sandy loam	140	0	0	50
3.Sand with pebbles	0	0	0	100
4.Peat	0	0	200	0
5.Loam of medium plasticity	0	0	200	100
6.Aleurite	0	56	120	200
7.Loam	240	0	70	200
8.Loam with pebbles	0	0	200	90
9.Coarse gravel with sand	40	100	60	0
10.Coarse gravel with sand	0	0	200	0

5 samples do not yield hydrocarbon oxidizing bacteria.

The microbial filter locations are confined to southerly exposed slopes in the areas of non-frosty period less than 90 days. There, the tundra lichen as reindeer moss, cladonia and others still occurring everywhere in tundra serve as the microbial filters. It means that lichen grow due to absorption of carbon dioxide and water from the atmosphere. Besides water and carbon dioxide lichen also absorb hydrocarbons including low-boiling gasolene fraction. Thus, in the vicinity of a motor road in operation the content of hydrocarbons is 0.97-1.4 cm^3/kg, in lichen mats, while moving away from it the content falls to 0.14-0.2 cm^3/kg and makes up 0.37-0.56 cm^3/kg in oil field. At this, lichen also absorb methane homologs up to methylcyclohexane and aromatic matter, that is benzene, toluene, from industrially polluted atmosphere. Lichen contain methane, ethane and propane within oil-producing area and outside it methane is predominant.

Taking into consideration the gasgeochemical properties of seasonally thawed layer and peculiar gas-to-atmosphere metabolic processes we have elaborated some copyrighted techniques permitting solution of the problems, which earlier seemed unsolvable, with common means. This is, for example, to distinguish between the methane anomaly caused by methane-producing bacteria in near-surface air and the anomaly caused by gas flows from the Earth's interior, also to register the industrial pollution, etc. The efficiency of these methods has been proved by the discovery of Verkhne-Telekai oil field in Anadyr basin.

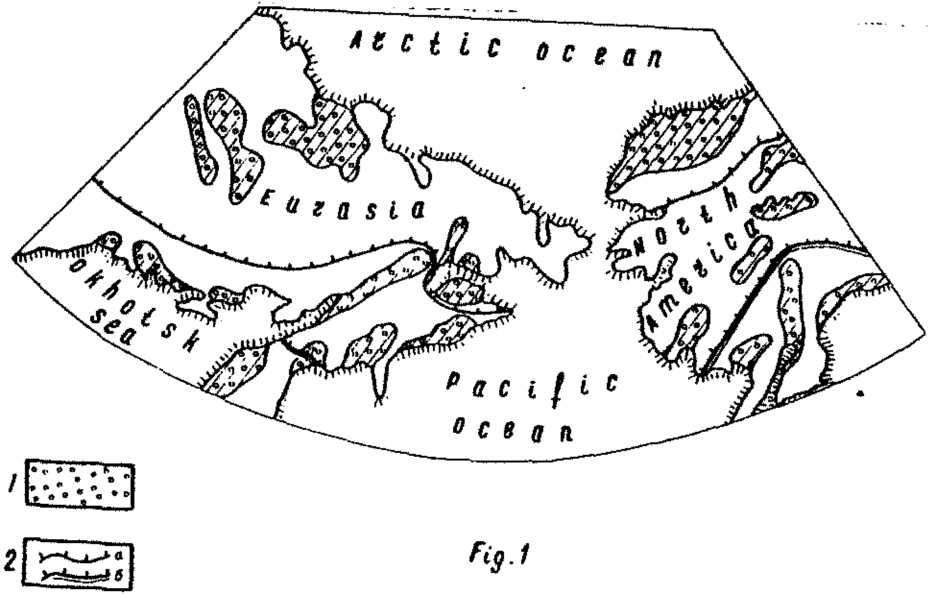

Fig.1

Fig. 1- Zone of junction of Euroasia and North America. 1 - sedimentary basins; 2 - southern boundary of zone of perenial frozen rocks: a - continuous distribution, b - discontinuous distribution.

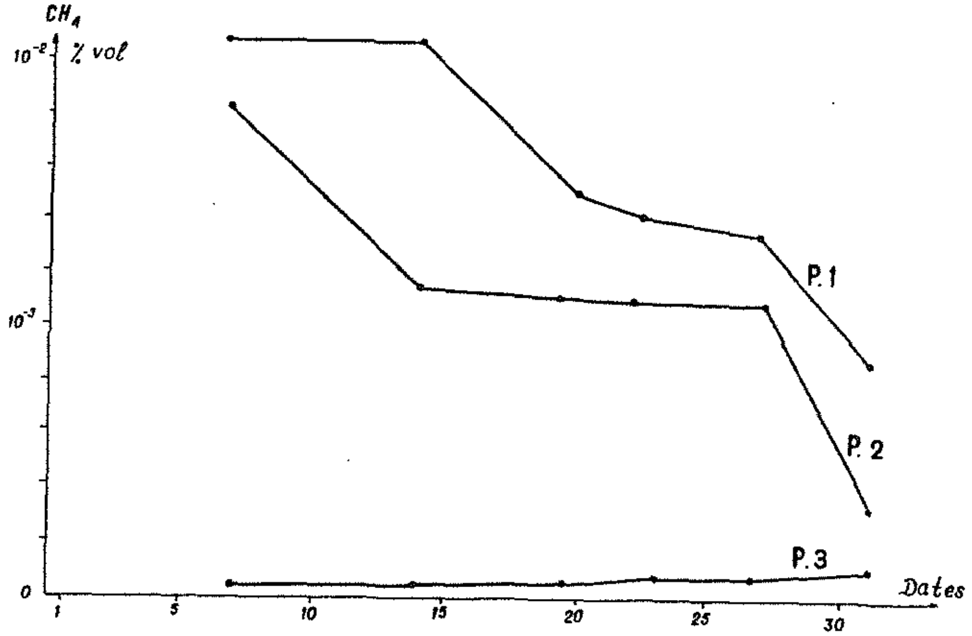

Fig. 2 - Changes in methane content of near-surfaceair in early summer (Anadyr basin at 8 AM local time).

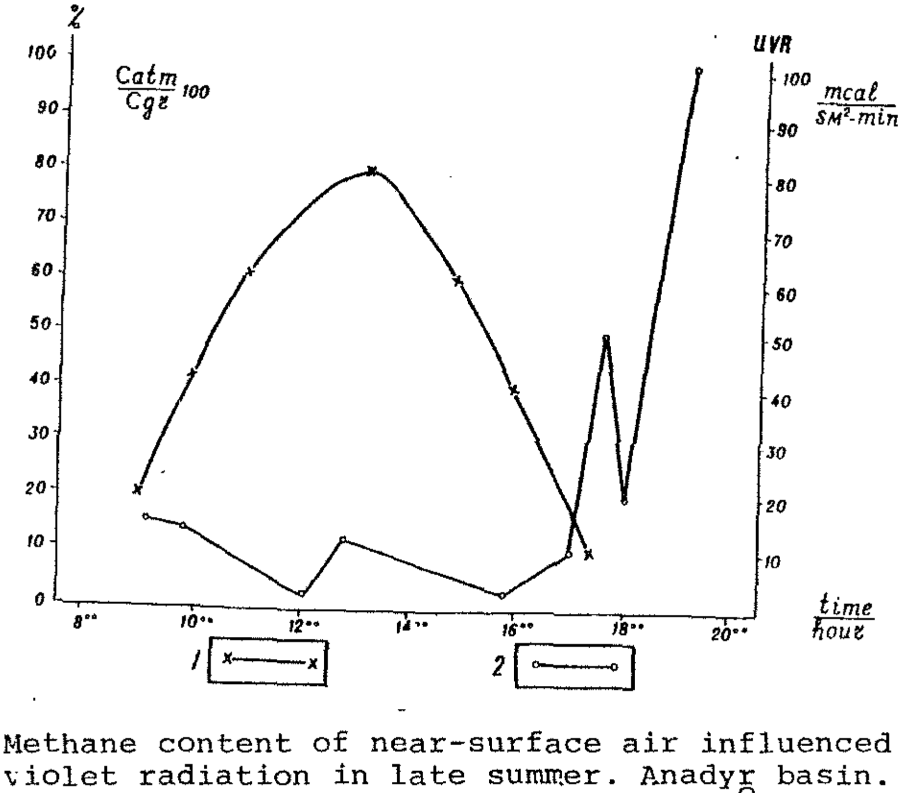

Fig. 3 - Methane content of near-surface air influenced by ultra-violet radiation in late summer. Anadyr basin. Run of ultra-violet radiation intensity at 64° north in early September - 1. The percentage of CH_4 in atmosphere and soil - 2.

The regional base of geochemical anomalies in the Ukraine /an approach to the development and exploitation/.

B.A. Gorlitsky, L.S. Galetsky

Geochemical anomalies preserve particular "most metallogenic" geochemical information. Sometimes anomalies fix certain varieties of geochemically contrasting rock-forming processes, i.e. micro-ore facies of these processes.

Geochemical anomalies more often result from secondary, as from "background-forming", local ore-generation processes. They may be either "autochtonous" - related to redistribution of the primary /"syngenetic"/ matter of country rocks /under autometasomatism or metamorphism/ - or "allochthonous" - associated with the matter supply by ore-bearing fluids circulating in zones of high permeability. Quite common is combination of both types of generation of anomalous concentrations.

The interpretation of anomalies is aimed as a possibly more exact identification of the ore-generating process, and evaluation of its intensity and spatial direction. With this view the "internal" information on anomalies is studied for the composition of the anomalous element association, character of the enclosing rock and signs of secondary alterations, ore and accessory mineralization available. But "external" data are of paramount importance for metallogenic interpretation of the anomalies. They comprise the relation to other anomalies and ore showings of similar or close composition, recognition of the type of rocks they are associated with, spatial /direct or indirect/ geochemical connection with the location of definite formations, stratigraphic divisions, magmatic complexes or zones of disjunctive dislocations, etc.

The "Anomalia" data base comprises evidence from 22 000 anomalies revealed in the Precambrian formations of the Ukrainian Shield in the course of 20 years of geochemical research carried out by Ukrainian geologists.

The regional base of geochemical anomalies is a part of the regional information-logical system /ILS/ "Geomet - Ukrainian Shield" developed by the authors. Techniques of ILS "Geomet" have been used to reveal the whole complex of interdependence between the distribution of geochemical anomalies and elements of the geological structure of the region as a whole and for each tectonic zoning unit separately /geoblocks and interblocks - table 1/. However, the analysis of anomalies of certain elements /or certain associations of anomalous elements/ confined to one or another system of the regional geological structure is of great metallogenic importance, in addition to solution of the problem of the genetic anomaly nature. This implies the following: if geochemical anomalies of certain type /supposedly, related to one and the same ore-forming process/ prove to be confined, for example, to similar geological formations /or to a definite system of tectonic faults/, one can say that processes, the formation of certain type of rocks /or a certain system of tectonic faults/ is associated with, have ore-controlling properties or are genetically related to ore-generating objects in geological space.

Since the information of the "Anomalia" data base is obtained from primary geological data collected before this review was made, the set of positions used for describing the information on anomalies in the data base, is controlled and present by the structure and content of this primary documentation.

The composition of the association of anomalous elements is a relatively reliable characteristic of anomalies. The contrasting nature of anomalies due to particular contents of elements admits rather uncertain interpretation with infrequent and irregular sampling grid available in the region, i.e. the information on a potentially ore-generating object may be given in a form of a little contrasting anomaly, if the sampling site happens to be far from the epicentre of the ore object; the information may be very contrasting, if the central part of the ore object was incidentally sampled. So, at the present stage of geochemical re-

rearch of the region the main estimate of anomaly distribution related to one or another structural material complex /SMC/ or to a part of the territory with specific density of the anomaly /SDA/: the quantity of single element /elements/ anomalies per area or volume unit of a geological body /of its contour on the map/ expressed in absolute or relative units /for example, in per cent of the total anomalies detected in an object/. The specific density estimate of the anomalies characterizes the "anomalous" geochemical specialization of different kinds of SMC on the level of rather large systematic subdivisions when the area /or volume/ of each particular SMC is large enough relative to dimensions of the region. In these cases the SDA estimates do not depend much on inhomogeneity of the stage of the geochemical field investigation. As to the degree of geochemical investigation, "large" SMC /a type of series of supracrustal strata and complexes of magmatic rocks, for example/ may be, supposedly, close, as a whole, to a certain mean level for the region. This level meets the requirements of methods for geochemical studies sheduled for geological survey at the scale 1:50 000 performed for the greater part of the Ukrainian Shield.

Data on anomalies in the "Anomalia" base are as follows:

- name /number/ of the anomaly in the data base,
- source of data /author of the publication, year/,
- authors name of the anomaly,
- point of sampling /borehole, exposure/,
- interval of sampling /from - to/,
- arbitrary coordinates on two levels: coordinates of the plotting board on a 1:50 000 scale and coordinates of the cell sized 1 km^2 on this plotting board,
- name of the rock containing an anomaly,
- stratigraphic position of the anomaly enclosing rocks,
- formational attribution of the anomaly enclosing rocks,
- relation to the subdivision of fault-block tectonics,
- basic rock-forming minerals /4 names as much/,
- accessory and ore minerals /4 names as much/,
- superimposed processes /4 names as much/,
- laboratory sozrce :laboratory, method, year of analysis/,
- analytical data on the content of each anomalous element /g/t/.

In some cases, the described method for estimation of the anomalous geochemical specialization /AGS/ is unacceptable, for example, for assessiment of an anomalous specialization of lineament zones, when AGS is to be traced from "plotting board to plotting board" overcoming differences in the state of their geochemical study. Therefore a method for analyzing the majority series of anomalies /MSA/ has been suggested by the authors to evaluate AGS of certain structural material complexes, the Shield area as a whole and separate fragments of its territory. The method is based on the fact that the total quantity of geochemical anomalies in each plotting board of maps at the scale of 1:50 000 is calculated by means of the shield model. Then an ordered series for frequency of the element occurrence with anomalous concentrations is constructed for each plotting board. Such a series is called a majority one. This procedure makes possible to map and compare the anomalous geochemical specialization of objects differing in degree of the geochemical research state. Diversely studied territories will differ in reliability of the information rather than in its essence. Moreover, the contrasting geochemical specialization can be, most probably, detected.

A system of point-estimation is introduced for the terms of majority series: let the first term have the maximum of points, estimates of other terms in the series become lower depending on their position in the majority series. A set of data on majority series expressed in points can be subjected to statistical processing.

Positionally connected areas and zones, homogenous or close, as to frequent majority series of elements, are identified by the cluster analysis /according to anomalous elements dominating in majority series/.

Three type of problems have been solved. The first type is related to methodic, i.e. problems of sorting anomalies by establishing their reliability, mono and multielement character /the composition of anomalous element associations in multielement anomalies/; positional connection of anomalies close in the geochemical composition relative to each other, and to deposits and ore manifestations of particulat type; the anomaly association with geological signs depriving the anomalies of sense from the metallogenic point of view. For example, it is rather doubtful whether a single monoelement anomaly of nickel in granites is of any practical interest. The second type of problems is associated with revealing and futher geochemical and metallogenic interpretation of indeoendent associations of anomalous elements which represent the most common occurence in the region /or in various regional systems of SMC/. In this connection theny manifest themselves as self-dependent rock-forming processes typical of the region /or of its particular geological systems/. The third type of problems consist of determination of location of the fields and zones of different-type anomalies recognized when solving problems of second type. Each anomaly type suggests an availability of metallogenically valuable geological processes and properties connected with it. Consequently the analysis of the zone and field confinement to certain elements of the regional geological structure allows the genetic nature of potentially ore-forming processes manifested by certain types of geochemical anomalies to be specified, objects and sites of their localization to be identified and classified as to their importance.

The metallogenetic analysis in this respect is reduced to a successive solution of all the three types of problems. The analysis completes in a complex discussion of matallogenically valuable results after determination of relation, in geological space and time, between SMC having a marked "background" geochemical specialization and regions featured by manifestations of the "anomalous" geochemical specialization of a similar group of ore-forming elements.

The problem of the anomaly sorting has been solved in several variants depending on different approaches to sorting criteria and thresholds. The method of sorting is underlain by the anomaly estimation via "reliability points". It means that the anomaly is evaluated by a point for coincidence with each of the following events:

1/ availability of some other anomalies or ore manifestations with a similar content of anomalous elements in the vicinity /for example, in the plotting board on a 1:50 000 scale the anomaly is associated with/,

2/ the anomaly-enclosing magmatic complex or geological formation has a geochemical specialization coinciding with anomalous ones as to association of elements,

3/ the anomaly-enclosing magmatic complex or geological formation has a high SDA value for the elements constitute the anomaly,

4/ the anomaly is of multielement rather than of monoelement character,

5/ the anomaly is associated with superimposed processes,

6/ the anomaly is found to contain ore and accessory minerals.

So, each element is characterized by a set of ore-enclosing rocks, geological formations and magmatic complexes, superimposed processes, ore and accessory minerals. Ore-forming processes may be associated with, suggesting the presence of a particular element. The more points, the more "reliable" is the anomaly. The system of point evaluation may be varied in accordance with specific formulation of problems of metallogenic analysis. This procedure computerized. The variant of separate sorting of each multielement association of anomalous elements in each large geoblock appeared to be the most acceptable.

The matellogenic specialization of structural material complexes implies a high degree confinement of ore-generating element anomalies to the complexes, i.e. high SDA values of these elements.

Analyzing specific density of anomalies in the lithotype sytem for the whole region one can come across high contrast SDA value for such elements in granites /normal and potassium/: Be, Zr, Hf, La, Ce, Y, Yb, Nb; aplite-pegmatite Ta, Nb, Rb, Li, Cs, Be, Th; alcaline rocks

Zr, Ce, La, Be, Sn, Nb, Sr, P; gabbros, amphibolites and ulrabasic rocks: Ce, Ni, Ti, Sc, Ge, Ga, Mo, W; quartzites-sandstones: Au, Ag, Sb, Zn, Co, W /strongly contrasting high SDA values of gold and silver manifestated in this lithotype are in favour of the hypothesis of the occurence of metamorphosed buried placers/; ferruginous quartzites: Fe, Ge; carbonate rocks Mn and, less contrasting, Be, Sn, W, Bi, probably, due to reaction skarns and metasomatic formations and carbonatites associated with this lithotype. Generally, the anomalous specialization of lithotypes coincides with the background specialization and, consequently, is commonly controlled by syngenetic rock-forming processes of differentiation. The mean SDA established for each lithotype is used as a threshold value. Of special metallogenic interest are concrete block-strato-lithotypes of rocks in which SDA exceeds twofold and even more the threshold value for elements with a high geochemical background in respective lithotypes.

The compositional analysis of the anomalous geochemical specialization of large structural-tectonic elements of the shield /geoblocks and interblock zones/ has shown that as a whole the composition of elements with contrasting SDA inherits the geochemical /background/ specialization of blocks where it was markedly contrasting: Volyn, Eastern Priazov :rare-metal specialization/, Pridnieper, Eastern Priazov blocks, Orekhovo-Pavlograd and Central Priazov interblock zones /siderophile and siderophile-lithophilic specialization/. For blocks with neutral or noncontrasting background geochemical specialization, the composition of the association of anomalous elements with high SDA is commonly opposite to their background specialization. So, relatively high SDA is proved for Au, Ag, Mo, Sn, Sc, Ta, Nb in the Belotserkov geoblock, for Zr, Hf, Ti, P in the Podolian block, for Be, Ce, Y, Yb, P, Au, Ag, Bi, Sb in the Kirovgrad geoblock, for Au, Ag, As, Sb, Bi, W in the Golovanevo sutur zone. The anomalous geochemical specialization is in fair accord with relative abundance of anomaly-fixed types of superimposed processes which can be divided into two principal groups: 1/ alkali metasomatism and pneumatolithic-hydrothermal medium -high temperature processes and 2/ medium - low temperature hydrothermal variations /epidotization, chloritization, less frequent - silicification/. On the basis of this information it may be concluded that anomalous specialization and appropriate ore genesis in blocks with different background and anomalous geochemical specialization are associated with a deep seated source and epigenetic superimposed processes. When the both types of geochemical specialization coincide, the significant metallogenic role is attributed to syngenetic exogenous and endogenous processes, metamorphic ore formation wheres superimposed locally manifested processes become important rather than suppressing "participants" of ore genesis.

Table 1

The "anomalous" specialization of rock lithotypes

lithotype	Elements with high specific density of anomalies
granites /normal and potassium/	Be,Zr,Hf,La,Ce,Y,Yb,Th,Nb
pegmatites and aplite.pegmatite granites	Ta,Nb,Rb,Li,Cs,Be,Th
alkaline rocks including metasomatites	Zr,Ce,La,Be,Sn,Nb,Sr,P
gabbros, ultrabasic rocks and amphibolites	Co,Ni,Ti,Sc,Ge,Ga,Mo,W
heterogenous metasomatites, reaction and vein formations	Mo,W,Be,Hf,Au,Ag,As,Bi
gneisses and schists	Au,Ag,As,/Cr?/
quartzites-sandstones	Au,Ag,Sb,Zn,Co,W
ferruginous rocks /quartzites and schists/	Ge, /As?/
carbonaceous rocks	Mn, /Be,Sn,W,Bi/

Note: elements are shown whose SDA exceeds twofold, and even more, the average SDA for the shield as a whole; elements whose SDA is about two are in brackets.

Following this scheme, anomalous geochemical specialization has been investigated in large SMC of geological systems; magmatic complexes and stratigraphic units of the series level /tables 2 and 3/.

Analvsis was also done of the "anomalous" geochemical specialization of SMC at the level of the smallest units of generalization which are accepted in the research - rock-composing certain stratigraphic units within each of large structural-tectonic elements of the region :geoblocks and interblock zones/. Rocognized are block-stratolithotypes of rocks which considerably exceed in SDA mean specific densities of anomalies established in particular lithotvpes for the whole shield.

All other anomalous concentrations, comming out from accepted arguments, are mainly attributed to structural material complexes /SMC/ and preferably to their volume characteristic. For epigeetic processes, determinative are such categories of notions as a ore-controlling structure, confinement to some endo- or exocontact of magmatic rocks, etc., that have neither distinct volume nor contours.

The earlier described method for analysis of majority series of anomalies /MSA/ has been applied to typify and investigate the distribution of geochemical anomalies associated with epigenetic processes and their metallogenic analysis. The authors have compiled a table showing the description of point-evaluated terms of the majority series for 869 cells of the geometrical grid covering the shield territory /the cell size is equal to the plotting board of a 1:50 000 scale/. The table has become an object of factor analysis resulting in revealing associations of elements in geochemical anomalies which most frequently occur together.

Table 2.

The metallogenic specialization of complexes of magmatic and ultrametamorphised Precambrian rocks from the Ukrainian Shield

age	nonstratified complexes of magmatic and ultrametamorphic rocks	elements with high specific density of anomalies
PR_2	Kamennomogilsky	Sn,Mo,W
	Perzhansky	Be,Sn,Mo,W,Pb
PR_1^2	Korostensky	Zr,Hf,La,Y,Yb,Nb
	East Priazov	Mo,Nb,Ce,Y
PR_1^1	Chernigovsky	Mo,La,Ce,Y,Yb,Nb,Li,Sr
	Osnitsky	-
	Priazov	Mo,Nb,Cs,Sr
	Kirivograd-Zitomirsky	Cr /Ta,Rb,Cs,Be/
	Berdichevsky	Th /Hf,Ni,Pb/
	Complex of basic and ultrabasic rocks	Ni,Co,Cu,Sc,Zn,Au,Ag,As,Sb,W,Hf,P
AR_2	Sursko-Tokovsky	/Sc/
	Zvenigorodsky	-
	Gaivoronsky /Nemirovskv/	-
AR_1	Dniepropetrovsky	/Ti/
	Complex of basic and ultrabasic rocks	Ni,Mn,Co,Ti,V,Ge,Sc,Cu,Zn,As,Sb,Mo,Ga,Ba,P

There are all grounds to belive that each of these assocciations was promoted by certain peculiar geological factors /a complex of rock-forming and ore-controlling processes/, controlling common occurence of ore-generating elements incorporated into this assocciation. The most tvpical and common occurrence in the whole territory are the following associations of ore-forming elements:1/ Ce, La, Y; 2/ Ta, Nb, Li, Rb, Cs; 3/ Co, Ni, Cu, sometimes with Cr and V. Other abundant elements in the anomalies /Mo, Pb, Sn, Zr, Ag, Be, W, Bi, Au/ in different geoblocks of the shield enter dissimilar associations of anomalous elements what reflects intraregional pecularities of rock-forming factors controlling them.

In many cases the metallogenic specialization of familiar ore-controlling structures is specified. In other cases grouping and spatial-geological connection of metallogenically promising areas that were regarded earlier as separate areas have become more pronounced. Yet, it is noteworthy to underline that there were revealed new specialized linear structures that were not reflected on existing geological-tectonic and metallogenic maps. They are, for example, sublatitudinal zone, called by the authors the Vinnitsa-Bohuslav zone, metallogenically specialized for association of rare metal elements, or the Southern Kirovograd sublatitudinal zone, specialized in association of Cu, Co and Ni.

The analyzed regularities in distribution of anomalies of ore elements may be useful for compiling new metallogenic maps of the region and for characterization of ore formations of common occurrence in the shield.

Thus, contours of numerous known objects contributing to the metallogenic zoning of the region have been verified and specified by means of ILS "Geomet" and the base of geochemical anomalies forming its part. The new identified and substantiated areas promising for ore-forming elements characteristic of the metallogeny of the Ukrainian Shield are of particular interest because they have been revealed by a formal procedure, which exclude, to a certain extent, subjectivity.

Table 3.

The metallogenic specialization of supracrustal strata of the Ukrainian Shield

age	stratified subdivisions of sedimentary and volcanic.sedimentary rocks	elements with high specific density of geochemical anomalies /SDA/
PR_2	Ovruchskaya series	Hf,W,Zr,La,Ce,Y,Yb,Th
PR_1	Pugachevskava series	Au,Ag
	Klesovskaya series	-
	Teterevskaya series	Mn,V,Sc,Mo,Sn,W,Be,Ga,Y,Nb,Li,Sr,Ba
	Bugskaya series	Au,/As/
	Ingulo-Inguletskaya series	/As,Sb,Ti,Sn,W,Be,Hf/
	Osipenkovskava series	Zn,Pb,Bi,Y,Yb,Nb,Li,Rb,Cs,Sr
	Gulyaipolskaya series	-
	Central-Priazov series	-
AR_2	Dnestrovsko-Bugskaya series	Mn :Ti,Au,Ni,Co/
	Rosinsko-Verkhovtsevskaya series	Ni,Co,Cr,Ti,Ge,Sc,Cu,Zn,Pb,Ag,As,Sb,Bi,Mo,W,Ga,Zr,Y,Yb
	Western-Priazov series	Ge,Cr,Bi,As,Mo,W,La,Sr,Ba,P
AR_1	Akulskaya series	Ni,Co,Cr,Ti,V,Ge,Sc,Au,Bi,Mo,Hf,Y,Ta,Nb,Li,Rb,Cs

Note: shown are the elements of geochemical anomalies with the specific density index of geochemical anomalies exceeding twofold, and even more, the average one for the region /elements with SDA amounting to two are in brackets/.

ORE-GEOCHEMICAL MODELS OF URALIAN PORPHYRY-COPPER DEPOSITS

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Correct interpretation of the structure of geochemical and metasomatic haloes as well as petrological peculiarities of porphyry intrusions is presently a necessary prerequisite for discovery of new porphyry-copper deposits. Solution of the problem set is favoured by a wide-scale character of haloes typical of the object of the above kind.

The Urals is a new porphyry-copper province whose mineralization is related to polycyclic granitoid magmatism of submeridional structura-facial zones of diverse origin. Ore zones /the Salavat and others/ of the main eugeosynclinal structure of the Urals /the Tagil-Magnitogorsk trough/ formed on the oceanic crust are associated with quartz-dioritic porphyry intrusions of the island-arc type S_2, D_2 and O_2 age. Similar S_2-D and D_2 ore zones are fixed in secondary eugeosynclines /volcano-plutonic pelts/ superposed on continental crust of the eastern slope of the Urals. D_3-C_1-C_2 ore zones related to granodiorite-quartz diorite magmatic activity of the precontinental type /the Novonikolayevsk-Tarutinsk one/ are located between the above zones and rigid blocks in graben structures. And, finally, C_2-C_3 zones /the Benkalinsk, the Batalinsk-Zhaltizkolsk/ occur in the most eastern part of the Urals in the marginal region of the median massif associated with early orogenic /epi-eugeosynclinal/ granodiorite-porphyric intrusions. Thus, eastern slope of the Urals is noted for by evolution of productive magmatism and mineralization both in space and time /from S to C_2-C_3/ accompanied by the increasing role of granite-granodioritic phases and potassium incorporated therein.

Many aspects of the ore-geochemical zonality in porphyry-copper deposits are described well enough in the world geological literature. So we focus attention on new fascinating elaborations gained from the exploration of Uralian deposits.

Productive granitoid magmatism and mineralization of the largest ore fields manifest repeatedly within rather short periods /the Novonikolayevsk one/ D_3fm-$C_I t_I$, C_Iv-s. Productive porphyry complexes differ from barren granitoid massives /in case comparable SiO_2 contents/ of other formations by smaller iron concentrations, higher amounts of normative quartz as well as higher total acidity and lower iron contents in dark-coloured minerals.

Large-sized metasomatic haloes /up to 2-15 km along the strike and 0,2 km wide/, which suggest the large-scaled processes of the substance migration are known to provide much information in carrying out geochemical research. To date, there are available new data on the behaviour of carbon dioxide, sulfur and sodium.

For most of the Uralian deposits of the hypabyssal facies, it is found that metasomatic carbonatization is restricted to the hanging walls of haloes - the upper part of the sericitization - chloritization zone /at its boundary with propylites/ or the upper part of the halo. Their thickness reaches first hundreds of metres, being up 700 m at subvolcanic deposits. This permits us to define for them the level of erosion shear and, naturally, forecast position of ore bodies
/Fig. I/ occupying, mostly, the central /and, rarer, peripheral/ part of haloes. It has been established for the first time that sodium removed from the central zone during phyllisitization is dispersed incompletely. At some deposits it settles in the outer part of phyllisite zone with large bodies of quartz albitites /Fig. I/, albitites and carbonate-quartz-albite metasomatites. These apodioritic metasomatites contain 5,5-7,5

wt.% Na_2O /in parent diorites - 3,5-5,0wt.%/ and form due to sodium activity rise in fluid alkalization zones. At two deposits there is fixed increase in sodium activity in zones of acid leaching where paragonite and mixed-layer paragonite-montmorillonite were found at porphyry-copper deposits for the first time. Carbonate-sericite-paragonite-quartz metasomatites occur as isolated areas in carbonate-sericite-quartz metasomatites sometimes alternating with the latter in those few zones whose thickness may reach 100 m and even more.

As it has been known, peripheral parts of porphyry-copper deposits are caracterised by pyrite covers embracing the outher part of phyllisite zone. It is very important for visual esttmation of ore body lokalization. Study of numerous samples received for the Novonikolayevsk deposit permits us to make quantitative appraisal of ore body relations with the pyrite cover.

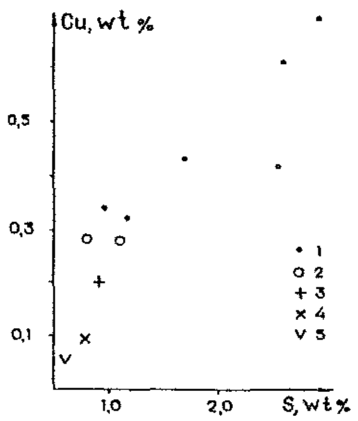

Fig. 1. Position of albitization and carbonatization in hanging wall of a metasomatic halo (Zelenodol deposit).

1 - diorite porphyrites; 2 - tuff sandstones; 3 - tuff aleurolites; 4 - andesite porphyrites; 5 - tuffs; 6 - rock contacts; 7 - contacts of the metasomatite zones; 8 - tectonic zones; 9 - lower contact of the argillization; 10 -contents of the copper.

Fig. 2 shows that in the cover the amount of sulphur (pyrite) is directly related to copper contents in underlying ore bodies.

Data presented here suggst that evolution of the fluid upwards is followed by an increase in its alkalinity and activities of sodium, carbon dioxide and sulphur. A decrease in ferrugunity of minerals to the center of haloes (and as a degree of rock trasformation increases) and S^{34} decrease to the perifery of haloes suggest, most likely, that the oxidizing potential is increasing in the central and outlying parts of haloes, being related to effects of oxidized juvenile and vadose waters, respectively.

Detailed study of carbon dioxide, sodium and sulphur distribution within ore bodies makes our knowledge of the conditions accompanying ore formation more profound and help to forecast ore body position.

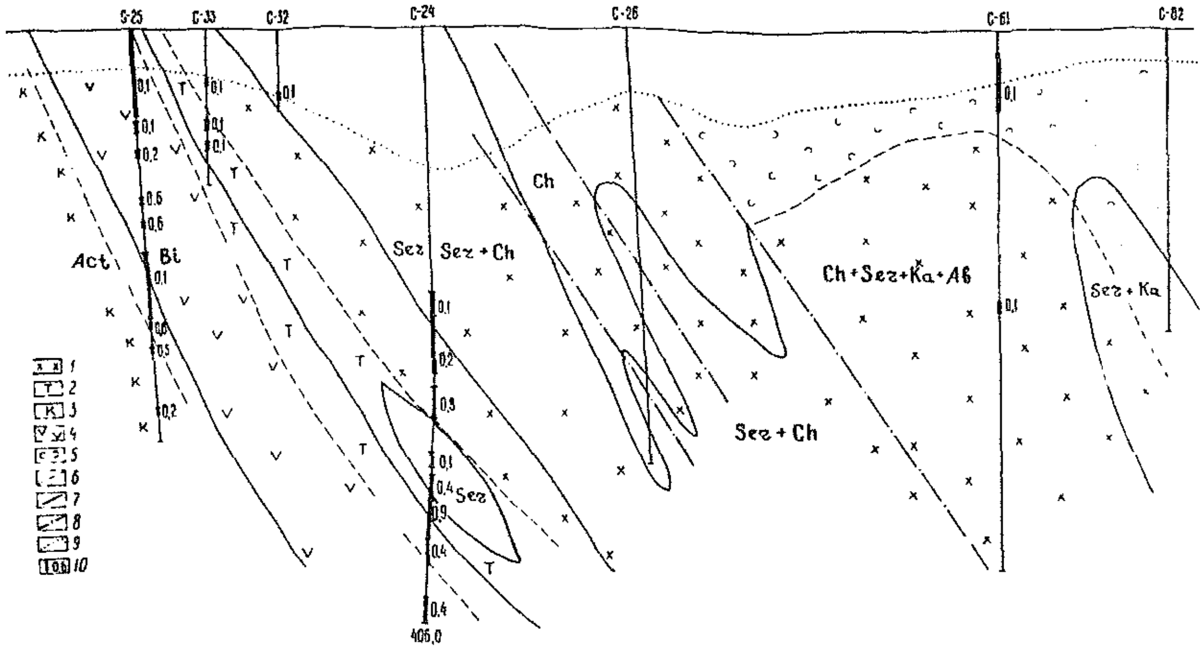

Fig. 2 - Dependence between copper amounts in ore bodies and sulphur contents in the overlying pyrite cover.

RELATIONS BETWEEN THE HYDROCARBON GENETIC FEATURES OF KEROGENS AND THEIR BIOLOGICAL PRECURSOR MATERIAL

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The kerogen is defined by Durand (1980) as the insoluble fraction of sedimentary organic matter of any kind i.e. ancient or recent sediments and in a dispersed or concentrated form. He applies this term to all sedimentary organic matter including e.g. the coals, too. In organic geochemistry it is generally accepted that the sedimentary organic matter is derived from living systems. The insoluble organic matter is the results of consecutive and random repolymerization and polycondensation reactions of a very small fraction of **the** (bio)degradation products of extant biomass.Depending on the nature of the initial organic matter, kerogens can generate various amounts and types of hydrocarbons and NSO compounds by thermal degradation (Tissot-Welte, 1984; Durand, 1980,Tegelaar et al., 1989.) Therefore the type of the kerogen and as a consequence of its hydrocarbon potential depends, first of all, on the biological source of the geopolymer. At the same time the nature of the biological precursor is determined by the paleoenvironment in which the sediments are accumulating. Furthermore, from the same biomass, kerogens of different types can develop as a function of the chemistry of the depositional environment. So the type of the kerogen and its hydrocarbon potential as well as its oil-prone-character vary with the biological, physical and chemical conditions of deposition (Tissot-Welte, 1984).

The algal material is considered to be the best source of the highly oil-prone geopolimer. Owing to its very high resistance to biodegradation and nonoxidative chemical treatments, mainly from the lipid-rich Botryococcus braunii alga,kerogen of excellent oil potential can be formed. In spite of this fact, there are known Botryococcus-derived kerogens of moderate hydrocarbon potential, too. On the other hand, we can find kerogens which,altough derived from continental plants,seem to be significant not only in their gas potential, but in their oil potential, too.

In this work the relationships between the depositional environment and the nature of the precursor material as well as the type and the hydrocarbon generative features of the kerogens were studied on some Hungarian fossil fuels (oil shales and low-rank coals).

The type and thermal maturity as well as the hydrocarbon potential of the kerogens were determined by Rock Eval pyrolysis (Espitalié et al., 1977). Immaturity of the organic matter of the investigated samples offered a possibility to simulate their catagenesis and to measure their liquid hydrocarbon potential by laboratory thermal degradation. The experimental evolution was carried out in a temperature-programmed Hereaus-type furnace under continuous nitrogen flow (Hetényi, 1980, 1987). The products were collected in two traps. The first collector was air-cooled and the second one was cooled by salted ice. The unified oil content of the traps is regarded as liquid hydrocarbon or oil.

a./ Alginites formed in Upper Pannonian maar-type volcanic crater lakes

The alginite and bentonite filled maar-type craters arose 3-5x10^6 years ago by the final basalt volcanism in the Pannonian Basin. The steep walls of the tuff craters are built up from cross-bedded basaltic tuffite (Knutson et al., 1988; Solti and Csirik, 1989). As a consequence of the continuous subsidence during the development of the Upper Pannonian formation the water of the Pliocene Lake System intruded through the lithoclases of the tuff ring into the chilled eruption centre (Jámbor and Solti, 1975). Special depositional environments were formed inside the closed, current-free and non-agitated lakes which were periodically heated by postvolcanic geysers. The depth of the oligohaline water may have been about 50 m (Nagy, 1976; Hajós, 1976). The great amount of the nutrients liberates from basaltic tuff produced favourable conditions for the planktonic life. A very high percentage of died nectonic and planktonic organism was preserved in the anoxic bottom water (Csirik and Solti, 1989). The palynological investigations of the kerogen show a typical Pannonian floral assemblage. The main biological source of the organic matter seems to be the Botryococcus braunii Kütz alga and a small quantity of fungi can also be found (Jámbor and Solti, 1975; Nagy 1976).

In spite of their essentially same biological source material, considerable differences can be observed in the organic geochemical features of the three Hungarian oil shales deposited in maar-type volcanic crater lakes (Fig. 1 and Table 1).

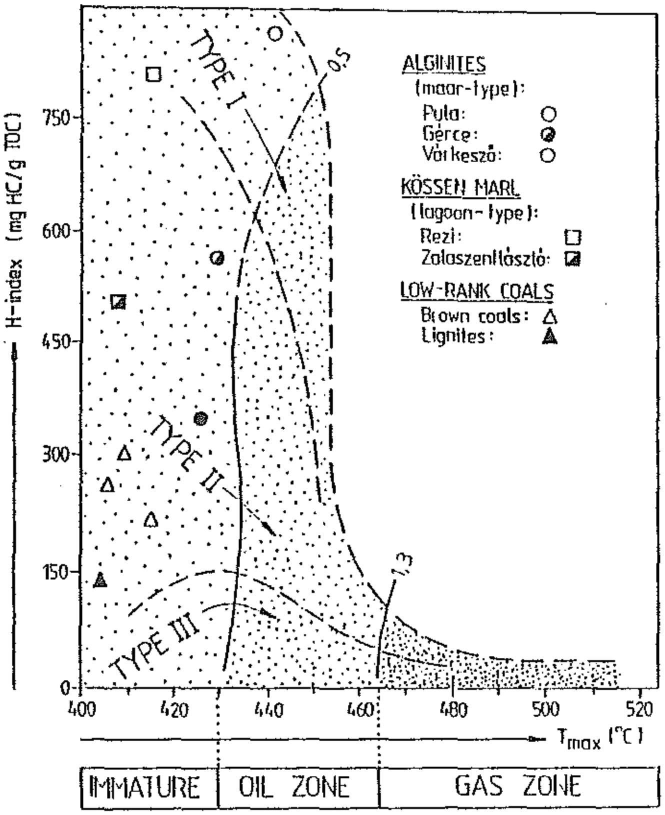

Fig. 1. Classification of organic matters in an hydrogen index-T_{max} diagram.

The absence of the benthic organism in the anoxic bottom water permitted a good preservation of algae and the sporomorph assemblages (Pula). The biologically inactive depositional environment resulted in kerogen of type I with a very high hidrogen index (Fig. 1.). During its laboratory thermal degradation 65 % of the organic carbon could be converted and 700 mgHC/gTOC oil was yielded.

On the basis of the palynological investigations the organic matter of Gérce oil-shale deposited in a biologically active, probably alkaline environment. The kerogen originating mainly from Botryococcus braunii algae reworked by microorganisms proved to be of type II/a (average HI=550 mgHC/gTOC; PC/TOC=45-50 %). Its liquid hydrocarbon potential (440 mg/gTOC) seemed to be a moderate one (Table 1).

Kerogen of type II/b with relatively low hydrogen index (350 mgHC/gTOC), PC/TOC ratio (33 %) and with small liquid hydrocarbon potential filled in the Várkeszö crater lake of special biological activity (Fig. 1. and Table 1.). In addition to the considerably reworked Botryococcus algae sporomorph assemblages were identified in good preservation. Morevoer, the organic matter comprises not only algal material, but in a smaller proportion remnants of land derived higher plants, too. Both the identifiable vegetal debris and the results of the step-by-step oxidation of kerogen (Hetényi, 1983) confirmed the humic contribution to the precursor biomass.

TABLE 1. ORGANIC GEOCHEMICAL FEATURES OF THE KEROGENS AND THEIR BIOLOGICAL PRECURSORS

	TYPE OF KEROGEN	LOCALITY	A GE	DEPOSITIONAL ENVIRONMENT	BIOLOGICAL PRECURSOR	AVERAGE VALUE OF		
						HI mg HC/g TOC	PC/TOC	LIQUID HC-POT. mg/g TOC
OIL SHALES	I. (HI > 750)	PULA	UPPER PANNONIAN	MAAR-TYPE VOLCANIC CRACTER LAKE	BOTRYOCOCCUS BRAUNII ALGAE IN GOOD PRESERVATION	870	65	700 ●
		REZI	UPPER TRIASSIC	SHALLOW MARINE SEQUENCE (LAGOON)		790	70	715 ●
	II./A (HI=500-750)	GÉRCE	UPPER PANNONIAN	MAAR-TYPE VOLCANIC CRATER LAKE	BOTRYOCOCCUS BRANUII REWORKED BY MICROORG.	550	50	440 ●
		ZALASZENT-LÁSZLÓ	UPPER TRIASSIC	SHALLOW MARINE SEQUENCE (LAGOON)	BOTRYOCOCCUS BRANUII EXTENSIVELY REWORKED BY MICROORG.	510	46	290 ●
	II./B (HI=150-500)	VÁRKESZŐ	UPPER PANNONIAN	MAAR-TYPE VOLCANIC CRATER LAKE	A MIXTURE OF REWORKED ALGAL MATERIAL AND HIGHER PLANTS	350	33	290 ●
LOW-RANK COALS		OROSZLÁNY DOROG TATABÁNYA	EOCENE	SEMMITERRISTIC SWAMP	TROPICAL SWAMP VEGETATION	300 260 210	29 20 19	310 ● 190 ● 105 ●
	III. (HI < 150)	BORSOD	MIOCENE	OPEN SWAMP	SUBTROPICAL VEGETATION	135	11	90 ●

b/ Upper Triassic Kössen Marl from southwest part of the Transdanubian Mid-Mountain (Hungary)

The examined Kössen Marl is a pyritic,organic rich, partially laminated shallow-marine sequence which is widespread in the Upper Triassic of the alpine realm. The Alginite Formation of the Kössen Marl was deposited in lagoons in which very favourable conditions developed for accumulating organic rich sediments. The fine laminated structure and high organic matter content of the rocks and the absence of benthic remains indicate that bottom water was anoxic at the time of sediment accumulation (Brukner-Wein and Vető, 1986). The temperature of the shallow, non-agitated water was higher than that of the surrounding open sea. Microscopic examination of the amorphous kerogen revealed that the precursor biomass was composed of Botryococcus braunii algae and associated bacteria in various stages of decomposition.Allochtonous organic matter was not found in significant amount. The small quantity of sporomorph is due to the scattered vegetation near the lagoons. On the other hand, the poor preservation of sporomorph can be attributed to the big quantity of alga colonies covering the water-surface (Góczán, unpublished data).

The examined Upper Triassic Kössen Marl is considered to be a good oil source rock. Nevertheless, the liquid hydrocarbon potential of the samples originating from two neighbouring boreholes (Rezi and Zalaszentlászló) proved to be very different (Table 1.). The difference between the liquid hydrocarbon potential of two samples was higher than it could be expected on the basis of their hydrogen index (Fig. 1.). Altough the sample from the Zalaszentlászló borehole contained kerogen of type II/a its oil potential was equal to that of a kerogen of type II/b (Table 1.). The unfavourable hydrocarbon generative features of this sample may be due to the extensively degraded algal material. A close correlation between the conversion ratio of the organic matter and the oil generated during laboratory thermal degradation was found for all the samples (oil shales and coals, too) except the sample of Zalaszentlászló (Fig.2.). On the contrary, as a consequence of the good preservation of algae the quality of kerogen in the Rezi borehole seemed to be the same in every respect, as that of the type I kerogen filling in Pula volcanic crater lake (Table.1.).

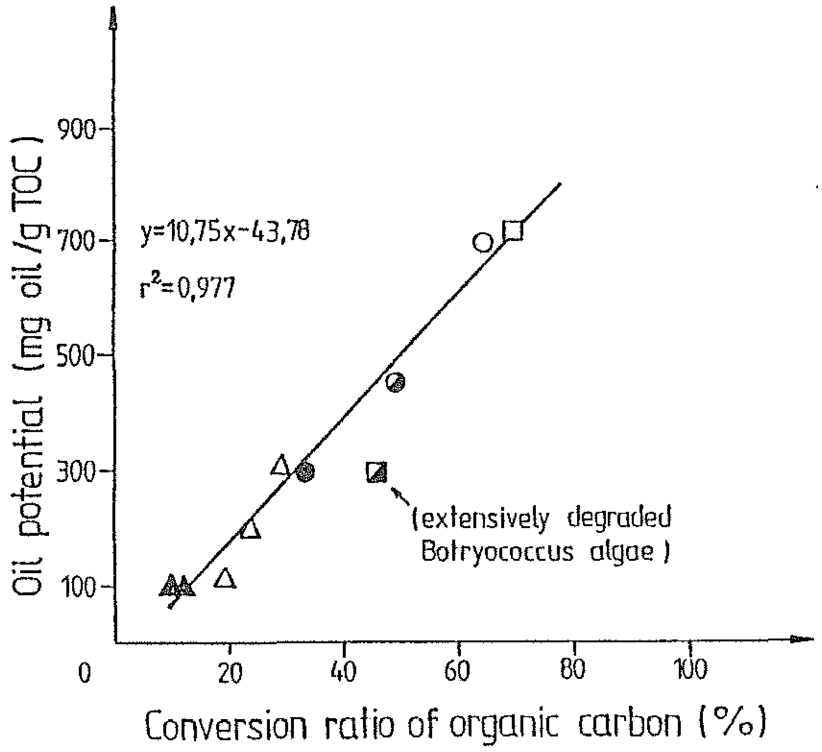

Fig. 2. The change of the oil potential in the function of the conversion ratio of the organic carbon. Legend as in Fig. 1.

c/ Low-rank coals as examples of kerogens derived from terrestrial higher plants

Both the disseminated and the concentrated form of the organic matter derived from terrestrial higher plants were considered to be gas prone kerogen. However, recently this type of organic matter, especially coals, has been regarded not only as source rock for gas but as possible source rock for oil, too (Bertrand, 1984; Bertrand et al. 1986, Durand and Paratte, 1982). Similarly to the algal material, a close correlation can also be supposed between the hydrogen content of the coals and their petroleum(oil and gas)potential. Tipically coals show HI values below about 300 mgHC/gTOC but sometimes it can reach 400-450 mgHC/gTOC (Espitalié et al., 1986; Monthioux et al., 1985; Mukhopadhyay et al. 1989; Peters, 1986). Consequently coals contain kerogen of both type II and III.

The examined Miocene lignites derived from subtropical vegetation and deposited in open swamp contain kerogen of type III. Nevertheless, they generated not only gas, but liquid hydrocarbons, too (90 mg/gTOC). The organic matter of Eocene brown coals originating from tropical vegetation proved to be of type II and their thermal degradation resulted in 100-310 mg/gTOC oil.

The somewhat dissimilar depositional environments and biological precursors are reflected in slightly different hydrocarbon genetic features of the studied brown coals (Fig.2.). On the basic of its liquid hydrocarbon potential, the lipid-rich kerogen of relatively high HI, developed in a periodically inundated Fagaceae semiterrestic swamp (Oroszlány), seems to be very similar to kerogens derived mainly from algal material (Kössen Marl of Zalaszentlászló and Alginite of Várkesző). Whereas, the moderately oxidized organic matter of brown coals formed in a swamp rich in Ericaceae shrub (Tatabánya) is nearly as unfavourable for oil generation as Miocene lignites. The medium hydrogen index and oil potential of the sub-bituminous coals from Dorog can be attributed to the ecological conditions (Hetényi and Sajgó, 1990). The predominant members of the coal-forming plant assemblage were Palms and Myricaceae shrubs. The considerable fungal remnants and the partially destroyed plant microfossills indicate ensymatical activity during the sedimentation.

Key words - kerogen, oil shale, coal, depositional environment, biological precursor, Rock Eval pyrolysis, thermal degradation.

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COLOUR VISUALIZATION OF GEOCHEMICAL DATA

Alexander A. Chebotaryov

Two peculiarities - endlessness of diversity and law-governed character of appearance, differ colour from graphic images, reproduced on maps. These two features of colour, aren't in use in a graphic representation of data in common and in mapping in particular. Always in semantical solution of maps colour using doesn't differ principally from using of marks, symbols and linear images. Only morphological difference of colour from the latter one's is marked out - usually colour plays the role of background on maps. From this point of view the first aspect of the problem consists in reaching the higher level of generalization of primary data on separate elements - obtaining colour image of matter. The second aspect provides as a whole finding ways of using colour variety formation regularities for visual representation of other natural regularities. Here - for visual description of geochemical regularities of chemical elements spatial distribution. The approach, on which the technolology of data processing and visualization is based on, is in the following.

Unique agreed colour index, equivalently satisfied to pure colour, close to spectral one of a definite wave-length, is awarded to every element of the Mendeleev's table. Violet, blue and bright blue colours are appertained to elements with filling of quant orbits of atoms according to "the cupro model". These are metallogenic elements [1,2], which geochemical partner usually is sulphur and its analogues. P,S and halogens - green colours. Rare gases and, as a whole, the atmophiles are exclusions within the scheme described. They haven't awarded colours. Yellow colours - elements with the filling of quant orbits of atoms according to "the rare gas model" of I-IV-th groups. Elements with atoms of transitional type with the filling of inner quant orbits "are coloured" by orange and red. These are petrogenic [1,2] elements, characterized more often by the affinity to O, Si and Al. The difference in building of quant orbits of atoms - the fundamental circumstance, which causes originally all the peculiarities of behaviour of different groups of elements in various geochemical processes [3,4]. In our case it's the principle for the awarding of colour indexes to chemical elements. Colour of visualized matter is the result of proportional mixing [5] of elements colours.

Transformation of data itself consists in an obtaining of proportions of main colours which can be used by a plotter or in a colour monitor. The proportions can be obtained by two ways. 1. Measured contents of every element are normalized relatively to some average contents. According to the aim of concrete task, average contents in the Earth's crust, modal, backgrownd contents, threshold levels, etc. may be used as sort of average values. Obtained numerical characteristics - relative contents (C') are summarized. The sum is taken as 100%. After that a loading (P) of every C' to this sum is calculated. Such contributions are taken as proportions of mixed colours of elements. From the obtained values mixed proportions of 3 main colours are calculated. These 3 colours take part immediately in a colour image as such as it takes place on screen of monitor or on typographical imprint [5]. Database can be the same in it. 2. If measured contents themselves are taken as proportions of colours, obtained colour images will represent, as the matter of fact, matter itself, (exactly, its macrocomposition). It will be mentioned lower about features of such colour images. Thus, two mentioned ways cause two varieties of maps of matter: maps of prevalence and maps of macrocomposition. Other numerical characteristics of elements can be used and colour images can be produced. For example factor loadings. In this case a transformation of them for the obtaining of colours is the same as such as in the 1-st way.

Obtaining of main colours proportions is, as the matter of fact, the key part of the data processing algorhytm but, the same time, the most simple one in it. The author managed to realize the data processing according to the described approach and to obtain coloured maps of matter. The algorhytm was based on of finding of Voronoy regions (neighbourhoods of sampling points). Neibourhoods are painted over according to proportions resulted from described manipulations with chemical compositions on every sampling point. COROLLPRESS - the Hungarian-prodused plotter was used for the painting of maps. Algorhytm had been programmed in FORTRAN. The regularity in correspondence of variety of colours to different elemental composition is observed. Any object colour observed in the real world is known to be characterized by dominating colour of some length of wave and by admixture of achromatic colour. A content of achromatic (black or white) colour determins purity of colour [5,6,7,8,9]. Black colour can be produced by mixing of 3 main colours. In this case proportions reproduction mechanism based on compound additive-subtractive perception of colours is meant. The appearance of achromatic black admixture takes place in our situation inevitably because colours of elements from different parts of Mendeleev's table are mixed. Thus, there is an opportunity to operate by the whole variety of colours. The regularity mentioned can be explained as such as in the next scheme.

1.Close to initial, blue, bright blue, red, orange, green colours (admixture of achromatic and others unsignificant) correspond to concentration fields of metallogenic or petrogenic elements. The sum of C' of one of these groups of elements can exceed several orders C' on another ones.

2. Close to initial yellow colour is typical mostly for macrocomposition maps, because the most part of macrocompositions consist of elements, to which yellow colours were put in correspondence according to the scheme. It means that, macrocomposition maps will be coloured by yellow colous with rare and small (dependently from a scale, however) spots of either green, blue-purple and (even) blue and bright blue or orange, reddish, brown and (even) red, red-purple and purple colours. These spots will show places of concentrations of metallogenic or petrogenic elements correspondingly.

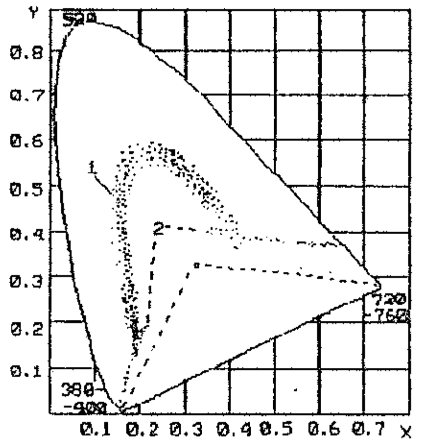
3.Reddish, brown colours - sums of C' or P on petrogenic and lithophile elements unsignificantly differ from each other. Jointly they several times more than sums of C' or P on metallogenic elements. Higher concentrations of metallogenic elements may accompany them. Macrocomposition maps in such representation of their look explain the real situation of existance of dispersion (yellow colour) and concentration fields (another colours on a yellow backgrownd).

4.Gray (black) colour points on almost egual proportions of lithophile, petro- and metallogenic elements. It shows on dispersion fields on distribution maps like macrocomposition maps. In the "ideal" situation of clark contents on all elements of Mendeleev's table gray colour with the brown nuance appears accordingly to colour indexes distribution scheme described.

5.Dark brown and chocolate nuances appear because of removal of dominant tone to extreme red parts of the colourness diagram with the higher proportions of gray. Such colours most probably to be typical for ultrabasic and basic rocks.

6.Purple, red-purple and blue-purple colours appear due to overwhelming majority of summary loadings of petrogenic and metallogenic elements. And correspondingly due to majority in a mixture of red and violet (or blue and bright blue) colours. Such colours will correspond to places of joint concentrations for example, Cu and Ni, Au and Pt, Cu and Mo, Sn and W, etc.

One unexpected conseguence of using of this apporoach seems to be of fair interest for further study of the problem. The thing is that when obtained colour images are presented in dominant wave and black admixture we have an opportunity to put them on the colourness diagram, used in the colour science. In it, colour images of elemental compositions of concentration fields are more resembling to initial colours. And, thus, they occupy outside parts of the diagram. Elemental compositions corresponded to dispersion fields have colour images, which look like achromatic one's and place nearly the central achromatic point of the diagram.



Points of 770 elemental compositions of different rocks are shown on this picture . They had been sampled on even network in the Chulun-Khuriete region in Mongolia by the Institute of Geochemistry in Irkutsk (USSR). 25 elements were analized (Ni, Co, Cr, V, Cu, Pb, As, Bi, Ag, Zn, Sn, Be, Mo, W, B, P, Ba, Sr, K, Na, Li, Rb, Cs). The way of points plotting on the diagram described detailly in [5,7,8]. The points make up two well-shaped trends. The first trend corresponds to elemental compositions, more close to dispersion - compositions of rocks. And the second one - is for concentrations of metallogenic or petrogenic elements.

There no guestions that the colour indexes distribution scheme will have variants.

1.The appertaining of colour codes to atmophiles and may be the reconstruction of the scheme as the whole will be necessary, if this approach will be used for atmocomponent study.

2.Another principle of colour proportions creating might be given if one carry on the study of organic component. This circumstance also will cause some rearrangements within the scheme.

3.For the optimization of visualization characteristics taking the discret numbers instead of waves lengths might be expedient. Such numbers can be taken for example in interval 1-1000. The transforming of compositions into proportions of colours will stay the same. Variants are possible because the study is in the very beginning. But one principle must be immutable: proportions producing must be submitted to common regularities of colour mixing and coloured mixtures perception. Besides, obtained colour images must regularly be visual indexes of natural regularities formed concrete look of one or another chemical composition. This is, perhaps, the main condition to be taken in to account in using and modifications of the approach and the technology of visualization described.

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RECOGNITION OF IMMOBILE/CONSERVED COMPONENTS AND APPLICATION TO HYDROTHERMALLY ALTERED ROCKS

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Hydrothermal alteration has long been recognized both as a guide to ore and as an indicator of the character of solutions associated with ore deposition. However, the confounding classifications and nomenclatures as well as the limited procedures for quantitative evaluation of alteration have presented some obstacles to our understanding and use of alteration as a guide to ore. We know little about the absolute losses or gains of components during an alteration process. Geochemical analytical data commonly provide us the information distorted by the closure effect.

The closure effect can be illustrated as follows: assume that we have an original simple system, S_O, which is composed of three components X, Y and Z.

$$S_O = X_O + Y_O + Z_O = 100 \text{ /gram/} \qquad /1/$$

/upper case letters are used for weights/

During an alteration process each component changes by an amount dX, dY, and dZ respectively. The total change in the system will be:,

$$dS = dX + dY + dZ \qquad /2/$$

In practice, the values of Xo+dX, Yo+dY and Zo+dZ cannot be accessed directly because chemical analytical data conventionally are presented in the following from:

$$s = x + y + z = 100\% \qquad /3/$$

/lower case letters are used for percentages/

The concentration of each component can be further described in the following form:

$$x = 100/X_O+dX/ \; / \; /S_O+dS/ \qquad /4/$$
$$y = 100/Y_O+dY/ \; / \; /S_O+dS/ \qquad /5/$$
$$z = 100/Z_O+dZ/ \; / \; /S_O+dS/ \qquad /6/$$

The above equations indicate that the difference in concentration of a particular component between the unaltered parent and the altered product is affected not only by the absolute change /dX/ of the element itself, but also by the total absolute change in all other components /dS - dX/. This is due to the closure effect. If we cannot remove the closure effect we cannot decipher the real variation of each component, and any explanation about hydrothermal alteration based on the raw data is of doubtful value.

Gresens /1967/ proposed an equation to overcome the problem of distorted data caused by the volume change during metasomatism, as follows:

$$X_n = a/f_V/g_B/g_A/x_B-x_A/ \qquad /7/$$

where

X_n = gain or loss of mass of component;
f_V = volume factor /volume ratio of product, B, to parent, A/;
g_A = specific gravity of parent, A;
b_B = specific gravity of product, B;
x_A = weight percent of component X in parent A;
x_B = weight percent of component X in product B;
a = initial weight of rock A, commonly 100 grams so that X_n will be numerically equivalent to weight percent change of a component oxide, n.

Gresens´ equation has been used sporadically by economic geologists to quantify losses and gains of elements during metasomatic alteration processes /e.g. Babcock, 1973; Grant, 1986; Sketchley and Sinclair, 1987; et./.

Pearce /1968/ divised a ratio variation diagram to remove the closure effect of geochemical data. Pearce element ratios are defined with a conserved constituent in their denominator, that is, conserved in a system undergoing change. The Pearce element ratio, r_i, is:

$$r_i = \frac{x.n_x/m_x}{z.n_z/mZ} \qquad /8/$$

where x and z = wt % of mobile /unconserved/ oxide i and immobile /conserved/ oxide z, respectively;

n_x and n_z .. the number of cations of x and z in the oxide formula, respectively;

m_x and m_z = the molecular weight of oxide i and z, respectively.

Because n_x, n_z, m_x and m_z are constants, the above equation can be simplified to the following form:

$$ri = K_{x,z}.x/z \qquad /9/$$

To date the application of Pearce element ratio diagrams has been limited mainly to the study of geochemical variation in magmatic, especially basaltic, systems. However, the potential of this approach in the study of hydrothermal alteration has been suggested by Pearce /1968/ and Russel et al /1989/.

RELATION BETWEEN GRESENS´ EQUATION AND PEARCE ELEMENT RATIOS

Gresens´ equation and Pearce element ratio diagrams are superficially different, but they are used to solve similar problems. Given that component Z is immobile /conserved in a metasomatic system, i.e. dZ = 0, we have:

$$z = 100Z0/ /S_0 + dX + dY/ \qquad /10/$$

For a Pearce element ratio

$$r_X = K_{X,Z}x/z = K_{X,Z}/X_0 + dX/ /Z_0 \qquad /11/$$

$$dX = /x/z - X_0/Z_0/ \ Z_0$$
$$= Z_0/x/z/ - X_0 \qquad /12/$$

For Gresens´ equation, given X_n = dZ = 0, then

$$f_V /gB/gA/ = Z_0/z \qquad /13/$$

Therefore, Gresens´ equation can be written in the form of dX. Thus,

$$dX/a = /Z_0/z/ x-X_0 \qquad /14/$$

But, a is an arbitrary constant, so let us assume a = 1 and we have

$$dX = /Z_0/z/ x-X_0 \qquad /15/$$

In this form Gresens' equation is simply a particular Pearce element ratio, showing clearly that the designers of these two approaches, although having different starting points, reached the same destination. Even though an independent solution exist for Gresens' equation where the volume factor /f_V/ is known and the specific gravities of samples have been measured, in practice, the volume factor is very difficult to estimate precisely and convincingly in any way except through the use of an immobile component.

In short, Gresens' equation and Pearce element ratio diagrams are based on the same principle, i.e. use of an immobile/conserved element to remove the closure effect of geochemical data and reveal the real, quantitative, chemical variations attending hydrothermal alteration. Before applying these approaches, two conditions must be met. First, a suite of samples for which variations are to be evaluated, must be the alteration products of a common parent rock characterized by chemical homogeneity.
Second, at least one immobile component must be identified with which to decipher the true variation of each mobile component. Once these conditions are satisfied, computations will give meaningful results.

RECOGNITION OF IMMOBILE /CONSERVED COMPONENTS

Conventionally, the first condition, i.e. recognition of the composition of a parent rock, is determined by careful consideration of the field relations and petrology of an area. The hydrothermal products, altered to various degrees from an homogeneous parent, may show gradational contacts between each other. Moreover, the primary textural and structural features commonly remain identifiable in altered derivatives.

To meet the second condition, we generally assume one or more components to be immobile based on their expected geochemical behaviors in hydrothermal systems. For example, TiO_2, Al_2O_3, and ZrO etc. commonly are thought to be immobile because of their relative insolubities in many hydrothermal fluids. The main criterion for recognition of immobile/conserved elements widely used by petrologists, is the theorem that the ratio of two immobile/conserved elements is constant throughout a set of data /e.g. McLean etc al, 1989/. This theorem can be proven as follows: given that both dx and dz are equal to zero, we have:

$$\frac{x}{z} = \frac{100XO/\ /So+dS/}{100ZO/\ /So+dS/} \quad \frac{XO}{ZO} \qquad /16/$$

It is recommended that both the foregoing approaches be used in identifying immobile/conserved components. Otherwise, errors of interpretation are possible as will be discussed in the following sections.

The geochemical behavior of certain components can help us infer which components might be immobile in a hydrothermal alteration system. In practice, if this inference is correct for a certain set of data, the ratio of any two such components must remain constant throughout the data set. For example, in the data set from Erickson, TiO_2, ZrO, and Al_2O_3 might be assumed to be immobile components. However, the values of some ratios might have a high dispersion, perhaps too high for all components to be interpreted as immobile. If we arbitrarily treat them all as immobile components and use them to decipher the absolute change of other mobile components during the alteration process, we might not feel confident with the final outcome. There are several possible explanations for this problem. One is that the data set does not meet the first premise, i.e. some samples are not the alteration derivatives from an homogeneous parent rock; or, as certain component, such as ZrO, might not be distributed homogeneously in the parent rock on the sampling scale used. In other words, the initial ratios of these components in some samples were different from others before alteration process. Another possible interpretation that is often ignored is that at least one component in each ratio became mobile locally during the alteration process.

In summary, it is reasonable to infer some candidates for immobile components on the basis of understanding the behaviors of these components and thegeological process in which they are involved. Nevertheless, we emphasize that it could be risky to assume these components as being immobile without further tests.

Through the foregoing discussion, we see that it is efficient and rational to choose the candidates of immobile components from a data set on the basis of the theorem that the ratios of immobile components remain constant. However, it is well known that there is no perfect constant ratio of immobile components in reality because of errors arising from the analyses of the samples. The ratio values in all cases will show a statistical dispersion. In general, we treat certain paired components as immobile if their ratios have low dispersion. Considering the influence of analytical error, Russel and Nicholls /1988/ and Stanley and Russell /1989/ suggested that one could test for immobile/conserved components with Pearce element ratio diagrams accompanied with the calculation of analytical error propagation. If the dispersion /standard deviation/ of ratio of two immobile/conserved components is less than or equal to the analytical error, the dispersion can be interpreted as resulting entirely from analytical error. In such a case, the two elements involved are candidates for use as immobile/conserved elements. This rule has been used in the study of basaltic systems by Russel et al. /1989/.

CURRENT OPTIMAL PROCEDURE TO RECOGNIZE IMMOBILE COMPONENTS FOR HYDROTHERMAL ALTERATION SYSTEMS

In the recognition of immobile/conserved components in hydrothermal systems the following procedure appears to be the optimal status quo.

/1/ Obtain samples of parent material and various altered derivaties with special consideration of the field relations and petrology of the geological locale.

/2/ High quality chemically analyses are required with awareness of the analytical precision provides for confident interpretation.

/3/ Calculate the ratios of every possible pair of components and the statistics of the ratio values for each pair of components. If a pair of components are candidates for immobility, their ratio will be characterized by a minimum value of coefficient of variation.

/4/ Calculate the propagation of analytical error to the ratio value according to following formula:

$$s_{a/b} = \frac{b.s_a + a.s_b}{b^2} \qquad /17/$$

where $s_{a/b}$ = absolute error of the ratio of a/b;

a = value of the mean of component a;

b = value of the mean of component b;

s_a = absolute error of component a;

s_b = absolute error of component b.

/5/ Compare the $s_{a/b}$ with the standard deviation of the ratio value of components a and b. If the former value is the greater of the two, observed variations could result solely from analytical error. Otherwise, some initial differences in these two components must exist among the samples and reflects geological factors.

However, some frustrating prob ems arise in using the above procedure. Even for the ratios constructed with the most likely candidates /Al or Ti/ none of the dispersions of the ratio S may be less than the corresponding propogated analytical error. Consequently, no component can be recognized as immobile.

DISCUSSION

/1/ The variation of a particular component in different samplesshould be the results of geological variance and/or analytical uncertainty. Theoretically speaking, the immobile component has no geological variance among the samples. In reality, no component is absolutely immobile, but if the geological variance for a component is significantly small, it can be treated as immobile. In some cases the geological variance of a component may be completely overshadowed by analytical uncertainty. Thus, ideally, an immobile component should have smaller relative variability than the analytical variability. On the other hand, a mobile component will have a geological variance that is large relative to analytical uncertainty.

The scale of geological variability can differ for various components. One can imagine that a rare component /e.g. sphene or zircon/ might be irregularly distributed on the scale of a small sample; whereas, abundant or essential components might be uniformly distributed in samples of the same small size. Thus definition of an immobile element depends to some extent on size of samples. With large sample size we increase the liklihood that more elements will be recognized as immobile. Of course, we must guard against samples so large that they smooth out important variability in a hydrothermal system.

In brief, the variation of a component in its absolute amount is composed of geological variance and analytical uncertainty. The magnitude of the geological variance relative to analytical error determines whether or not a component is classed as mobile or immobile.

/2/ Because of the closure effect, we must use a ratio of at least two components to represent their apparent variation. In the process of calculation the ratio, the components in the denominator and numerator contribute to uncertainty of the ratio. If a component in the denominator of the ratio has a very large analytical uncertainty and small magnitude of abundance, i.e. its relative analytical error is very large, the error propagation of analytical uncertainty for this ratio could be great enough to overshadow the geological variance of a mobile component in the numerator.

/3/ Multiple stages of alteration might or might not be exactly superimposed and different components might be immobile during the various stages. Moreover, in alteration systems, commonly gradational in character, it is unrealistic to expect that all components have been mobile everywhere. That is, it is likely that in an alteration system, components can be immobile over only part of the system. Such components we define as locally immobile. Those components that remain immobile throughout an entire system are universally immobile. It is clear that locally immobile components are common in many hydrothermal alteration systems and their confident identification would add substantially to our ability to interpret mass transfer in alteration systems. One simple approach is the use of profiles of ratios of pairs of potential immobile elements. On such profiles it may be possible to recognize more than one spatial domain of ratio values.

/4/ The premise for the general procedure outlined above is that at least two components remain immobile throughout the whole set of data. If only one component is immobile throughout the entire system its immobile character cannot be recognized through the above procedure. Profiles of ratios involving all potential immobile components in the denominator may assist in the recognition of a single immobile component.

The probability of existence of locally immobile component is much greater than that of universally immobile components. The practical significance of identifying such locally imobile components is that two or more may overlap and extend across the entire alteration system; thus, the closure effect can be removed by a multistep process rather than by using a single universally immobile component.

ACKNOWLEDGEMENTS

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THE USE OF A GOLD DEPOSIT GEOCHEMICAL MODEL IN PROGNOSTICATION AND PROSPECTING

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INTRODUCTION

The building-up and subsequent use of geochemical models of ore deposits is of a great applied importance in the practice of prospecting work. In three-dimensional geochemical modelling, a studied target is expressed, to this or that extent, by a multi-indicator space of a geochemical field where every point is characterized by qualitative and quantitative characteristics innate only in this point. After a set of indications, describing adequetely enough an ore deposit has been compiled, the base for prospecting and assessment of geochemical anomalies, revealed within the deposit in question and also within targets of similar geological-geochemical structure, is built up.

Such a work can be examplified by a package of geochemical investigations at a specific primary gold deposit. This package consists of building-up a gold deposit geochemical model, studying the regularities in relationship between its structure and special features in the pattern of geochemical anomalies within gold-ore field, establishing the analogy in geochemical structures of ore targets of different ranks (orebody, ore deposit, ore field) in "ore field" system. The regularities revealed were subsequently used in tackling prognostication and prospecting tasks for the corresponding type of mineralization.

SPECIFIC FEATURES OF GEOCHEMICAL STRUCTURE OF THE PRIMARY GOLD DEPOSIT

The deposit that has been studied belongs to the mediumtemperature hydrothermal metasomatic type of gold-sulphide-quartz formation. It consists of a stockwork of stringer and stringer-impregnated ores of gold-arsenic-bismuth composition and is localized in a zone of the contact between gabbro-diorite and granodiorite intrusions.

The data of geochemical survey at the deposit formed a basis for construction of the geochemical model. The principal consept of the model recognizes within it three haloe areas of different characteristics: central, intermediate and outer. In geological plan, the central area is controlled by a diagonal topographical sink at the contact of gabbro-diorite and granodiorite intrusions and is displaced to the endocontact zone of the friabler granodiorites. This area coincides with the most productive deposit sector characterized by development of gold-rich shoots and en-echelon veins of arsenopyrite and quartz-arsenopyrite composition.

Geochemically, it is bounded by a distribution limit of the conjugated highly contrast haloes of gold, arsenic and bismuth, low-contrast haloes of barium, copper and lead and negative (lower-than-background) haloes of vanadium and cobalt which are isometric and isometric-elongated in vertical section (Table 1)

Table 1 PARAMETERS OF THE PRIMARY HALOES OF CERTAIN INDICATOR-ELEMENTS OF VARIOUS MORPHOLOGICAL TYPES

Halo type	Gold			Arsenic			Bismuth		
	Ca	M	L	Ca	M	L	Ca	M	L
isometric	1.0-6.0	10-200	100-1000	>1	20-200	20-300	0.003-0.015	30-140	0.1-2.0
linear	0.4-2.0	10-50	10-100	0.4-1.0 >1.0	10-50	5-40	0.001-0.004	10-50	0.015-0.1
spotty	0.1-0.3	3-20	0.5-4,0	0.1-0.4	1.0-10	0.3-6.0	0.001-0.003	2-10	0.002-0.035

Symbols accepted: Ca - average anomalous content (in %, Au - in arbitrary unities), M - true thickness of halosection (m), L - linear productivity (m %).

Of all elements characterized by anamalous concentrations, arsenic and bismuth (positive correlation), and vanadium and copper (negative correlation) form stable significant correlations with gold (Table 2).

Table 2 COEFFICIENTS OF RANK CORRELATION OF CHEMICAL ELEMENTS IN THE CENTRAL (A) AND INTERMEDIATE (B) AREAS OF THE GOLD DEPOSIT

A

	Au	As	Bi	Pb	Cu	V	Co
Au	☒	0.71	0.37	-0.01	-0.48	-0.34	-0.01
As		☒	0.83	0.26	0.20	0.14	0.17
Bi			☒	0.36	-0.11	-0.11	0.07
Pb				☒	0.03	0.13	0.19
Cu					☒	0.22	-0.02
V						☒	0.40
Co							☒

B

	Au	As	Bi	Ag	Mo	Pb	Cu	V	Co	Sn
Au	☒	0.66	0.69	0.68	0.14	-0.23	0.44	-0.22	-0.66	0.48
As		☒	0.86	0.63	0.25	0.01	0.30	-0.32	0.06	0.75
Bi			☒	0.75	0.23	0.02	0.45	-0.37	0.13	0.83
Ag				☒	0.18	-0.28	0.77	-0.27	0.08	0.54
Mo					☒	0.22	-0.13	-0.31	0.08	0.10
Pb						☒	-0.29	0.42	0.40	0.10
Cu							☒	0.03	0.14	0.37
V								☒	0.52	-0.05
Co									☒	0.06
Sn										☒

Gold-arsenic-bismuth association is found to be the leading association in this area. The anomality coefficient* of gold varies from 0.8 to 1.0.

The central area is kind of a core, the embryonic part of the deposit, bounded from all sides by the intermediate halo area. The last named is confined to a flexural near EW-trending bend of the contact between the granodiorite and the gabbro-diorite intrusions, and is characterized by a lesser productivity. Within its limits at the areas of favourable geological and structural settings (mostly at the intersections of variously oriented faults) individual ore zones of a paystreak character are developed. Paystreak zones are characterized by a nestlike impregnations with thin fine-grained quartz arsenopyrite stringers.

The intermediate halo area is characterized by development of contrast linear haloes of many elements. In addition to gold, arsenic, and bismuth (Table 1) haloes of silver, molybdenum, tin, tungsten, lead, copper of a maximum contrast are developed here. Vanadium forms both positive and negative haloes morphologically close to the haloes of the linear type. Spatial superposition of vanadium haloes with gold haloes and the development, on the flanks of gold halo, of the last vanadium haloes are noted.

The amount of significant correlations of gold with indicator-elements is increased (Table 2). Apart from commonly found arsenic and bismuth, gold intemately correlates with silver, copper, tin, and preserves significant negative correlation with vanadium.

The density of the packing of the incorporating medium by gold haloes decreases. Anomality coefficient varies from 0.2 to 0.8 and averages 0.5, which is due to the fact that disconnected haloes interspaced by the space of background values are developed peripheral to this area.

Gold-arsenic-silver and gold-arsenic-molibdenum associations are the leading association of the area in question. The former is developed in the upper apical and central parts of the area. In the central part it can be complemented by lead if the incorporating medium consists of granodiorites, or by copper if the halo is developed in gabbro-diorites. The second association features the central and lower horizons of the area. Laterally, the gold-arsenic-silver association occupies the intermediate position between gold-arsenic-bismuth association and gold-arsenic-molybdenum association.

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* - The anomality coefficient is understood as a ratio between the surface area of all anomalies of the locality and the overall surface area of the locality.

Detail study of the intersections of individual ore zones in this area shows that the central part possesses maximum contents of gold, arcenic and bismuth whose haloes have an isometric outline, and is encircled by linear haloes of silver, molybdenum, copper, less frequent lead, tin, tungsten.

The central and intermediate areas make up the productive part of the ore deposit. The outer halo areas developed next to the above two areas, make up a zone of fine and very fine sulphide impregnation of no economic importance. Special features of this area consist of low-contrast haloes of gold and its by-products in the form of separate spots (Table 1, spotty type of haloes) irregular in shape and small in sizes. The anomality coefficient of this area is not in excess of 0.15-0.20. The halo compositions is multicomponental, however, due to the difficulty in formation of a representative sample set, there is no possibility in computing the rank correlation of the indicator-elements. The molybdenum-gold-tungsten association is the leading one in this area.

In addition to symmetrical concentric horizontal zonality expressed by a regular change, from centre to periphery, of qualitative and quantitative characteristics of geochemical field, there is also a distinct asymmetric vertical geochemical zonality developed in the central and intermediate halo areas. It is expressed by vertically differentiated positions of the centres of maximum deposition of chemical elements. Since the elemental composition of these halo areas differs, the rows of vertical geochemical zonality were calculated in each them by the known method (Beus A. A., Grigoriyan S. V., 1975); the rows are as follows (in ascending order):

central area

barium-lead-gold-arsenic-bismuth-copper-cobalt-vanadium

intermediate area

silver-lead-gold-bismuth-arsenic-copper-molibdenum-tungsten

Based on these rows zonality indexes were selected and evaluated in metrics of known orebodies,

$$K_Z^1 = \frac{Ba^2}{Co \cdot Cu} \quad \text{and} \quad K_Z^2 = \frac{Ag \cdot Pb}{Mo^2}$$

The values of these parameters are strictly determined for various parts of geochemical anomalies and can be used in evaluation of their exposed erosion level (Table 3) in the central (K_Z^1) and intermediate (K_Z^2) halo regions, respectively. The K evaluation for geochemical anomalies of the outher halo area produced exclusively the values characteristic of the subore section of the anomalies.

Table 3 LIMITS OF VARIATIONS IN THE VALUES OF CERTAIN MULTIPLICATIVE INDEXES WITHIN THE GOLD DEPOSIT

N	Erosion level of the anomaly	Indexes			
		$\frac{Ba^2}{Cu \cdot Co}$	$\frac{Ag \cdot Pb}{Mo^2}$	$\frac{Au \cdot As \cdot Bi}{V^2 \cdot Co}$	$\frac{As \cdot Bi}{V \cdot Co}$
1	barren	>10000	>5	<10	<10
2	upper ore	10000-1000	5-0.5	10-40	10-100
3	ore	1000-10	0.5-0.1	40-100	>100
4	lower ore	10-0.1	0.1-0.01	40-1.0	100-10
5	subore	<0.1	<0.01	<1.0	<10

The other specific feature of the central and intermediate areas consists of the fact that the intensity of the conjugated positive (gold, arsenic, bismuth) and negative (vanadium, cobalt) haloes are in the direct relation ship with the gold concentration: the highre content of gold, the higher concentrations of arsenic and bismuth and the lower contents of vanadium and cobalt. This formed a basis for calculation of the intensity indexes (Grigoriyan S. V., 1987) workable in both halo areas (Table 3) and characterizing the economic importance of an appraised anomaly, when equally evaluated.

The above-mentioned specific features of geochemical structure of the deposit reliably define the space of the geochemical field and allow to carry out the quantitative appraisal of the geochemical anomalies. The availability of data on elemental composition of the disclosed anomaly, its contrast and morphology, correlation of gold with other elements and the Knowledge of the leading geochemical association and coefficient of anomality open the possibility of determining of the parts of the deposit geochemical field in which a given anomaly (anomaly section) occurs. To get still deeper insight into its characteristics by calculation of zonality index and intensity coefficient, its level of erosion and economic importance are determined.

The above parameters were used for evaluation of geochemical parameters, revealed on the flanks and on the deep horizons of the studied deposit.

GEOCHEMICAL STRUCTURE OF ORE FIELD

Concurrently with the study of the geochemical structure of the deposit, similar investigations were carried out over the area of host ore field.

The composition of primary haloes within the ore field is multicomponental. First of all there is gold, lead, copper, zinc, arsenic, molybdenum, cobalt, vanadium. However the contrast and dimentions of the haloes (except the former two) are extremely small. Analysis of their position on the surface area, the study of their inner structure do not allow to conclusively determine the space and structure of the geochemical field. This problem is simply enough tackled only by construction and interpretation of the multiplicative haloes. The following five multiplicative indexes have been calculated and plotted:

1. Au · As · Bi · Pb · Zn · Cu · Mo · Be · W
2. Co · V · Mn · Ti · Cr · Ni
3. Au · As · Bi
4. Pb · Zn · Cu
5. Mo · Be · W

The first index was calculated with the use the of elements whose haloes or sporadic abnormal samples accompany the primary haloes of gold and spatially entirely or partly coinciding with them. The second index relates to elements whose contents are lower-than-background in the ore localization zones. The last three parameters include elements whose haloes are conjugated localized at the same areas. The haloes of all multiplicative indexes turned out to be contrast, extensive and, as a result, informative enough.

The study of geochemical structure of ore field attests to its considerable similarity to the geochemical model of the deposit. Likewise at the deposit, there are three haloe areas at the ore fielde:

- the central area, including the deposit and characterized by development of conjugated contrast isometric haloes of gold, the first and the third multiplicative indexes, development of weakly contrast spotty haloes of the second, the fourth and the fifth indexes or the lack of them;
- intermediate, including a number of the primary gold occurrences and characterized by development of numerous contrast linear haloes of gold and practically all multiplicative indexes. Geochemical structure of the ore occurrences is similar to the structure of orebodies and ore zones of the deposit's intermediate halo area. Ore occurrences containing all three halo areas are the most productive ones;
- outer, with the second index contrast haloes which are linear or, occasionally isometric in shape, contrast linear haloes of the first, fourth and fifth indexes and weak spotty gold haloes of the third index. No ore occurrence was detected in this area.

The similarity in geochemical structure of ore targets of various rank was used in the process of further prognostic-prospecting work at the ore field area. This work had the following special features:

1. Relocation of prospecting programmes with the reduction of their volumes in the outer area and detail study of central halo area (flanks and deeper horizons of the deposits) and individual anomalies of the intermediate area.

2. First priority study of the geochemical anomalies having a complex zonal-concentric structure.

3. The appraisal of the newly revealed geochemical anomalies through the use of the methods worked out and tested at the deposit.

CONCLUSION

The geochemical identity of a gold deposit, its orebodies and surrounding ore field was established by the study of the structure of geochemical fields. As a result, specific features of the geochemical model of the gold deposit, the central link of the "ore field" system, were applied to evaluation of geochemical anomalies not only on the flanks and deep horizons but also on the territory of ore field. This enabled to reveal a number of promising geochemical anomalies. Subsequent field check proved the efficiency of the methods applied.

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ASPECTS OF SMALL-SCALE REGIONAL GEOCHEMICAL MAPPING

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Abstract

Regional geochemical mapping of whole countries or continents with sampling density as low as one sample per several hundred or even several thousand square kilometres has recently been proposed. Although some geologists have expressed skepticism about the usefulness of this kind of mapping, skills in regional mapping have nevertheless increased dramatically of late, enough to make this kind of mapping both possible and reasonable. We believe that much valuable geological and environmental information can be obtained through small-scale mapping and that such studies should be continued. To allow comparability among the results of separate studies, however, the problems encountered in sampling, analysis, and presentation should be discussed more thoroughly than has been done so far.

Small-scale geochemical mapping was done in Finland at a density of one sample per 300 km^2 and was based on the fine fraction of till (<0.06 mm) as study material. The maps that were produced revealed distinct areal differences, allowing the country to be divided into geochemical domains and several provinces. Tectonic, often hydrothermally altered, zones with characteristic chemical composition, are only some tens of kilometres broad and a denser sampling grid than used here is to be recommended in such zones even in small-scale reconnaissance mapping. In general, a variable sampling grid appropriate to the major geological units is proposed.

Introduction

Finland was mapped with a sampling density of one sample per 300 km^2 for the purposes of *The Geochemical Atlas of Finland, Part 2: Till* (Koljonen, 1991). The whole country altogether 340,000 km^2, was investigated through chemical analysis of the fine fraction (<0.06 mm) of 1047 composite samples of till (Fig. 1.A). The sampling density was selected at the planning stage as an "educated guess". The results have nevertheless proved highly satisfactory from the geological point of view, and, among other things, have provided considerable empirical information regarding the selection of sampling densities for optimal results.

Bedrock, sediments, and soils

The sedimentary cover is relatively thin in Finland; composed mostly of till it is on average only ca. seven metres thick. As is usual in glaciated areas the bedrock and overlying sediments lie in sharp contact: a geological discontinuity prevails between the bedrock, which is everywhere over 1200 million years old, and the young sediments and soils, which are no more than 50,000 years old and in general younger than 15,000 years.

Fig. 1.A. The geochemical map of zinc, where sampling sites are the centres of dots. Sampling density one sample/300 km^2; analytical method ICP–AES after aqua regia leach. The geochemical provinces are indicated by letters (see Table 1). **1.B.** Same as 1.A., but sampling density one sample/4 km^2. The sampling material used was the fine fraction of till (<0.06 mm).

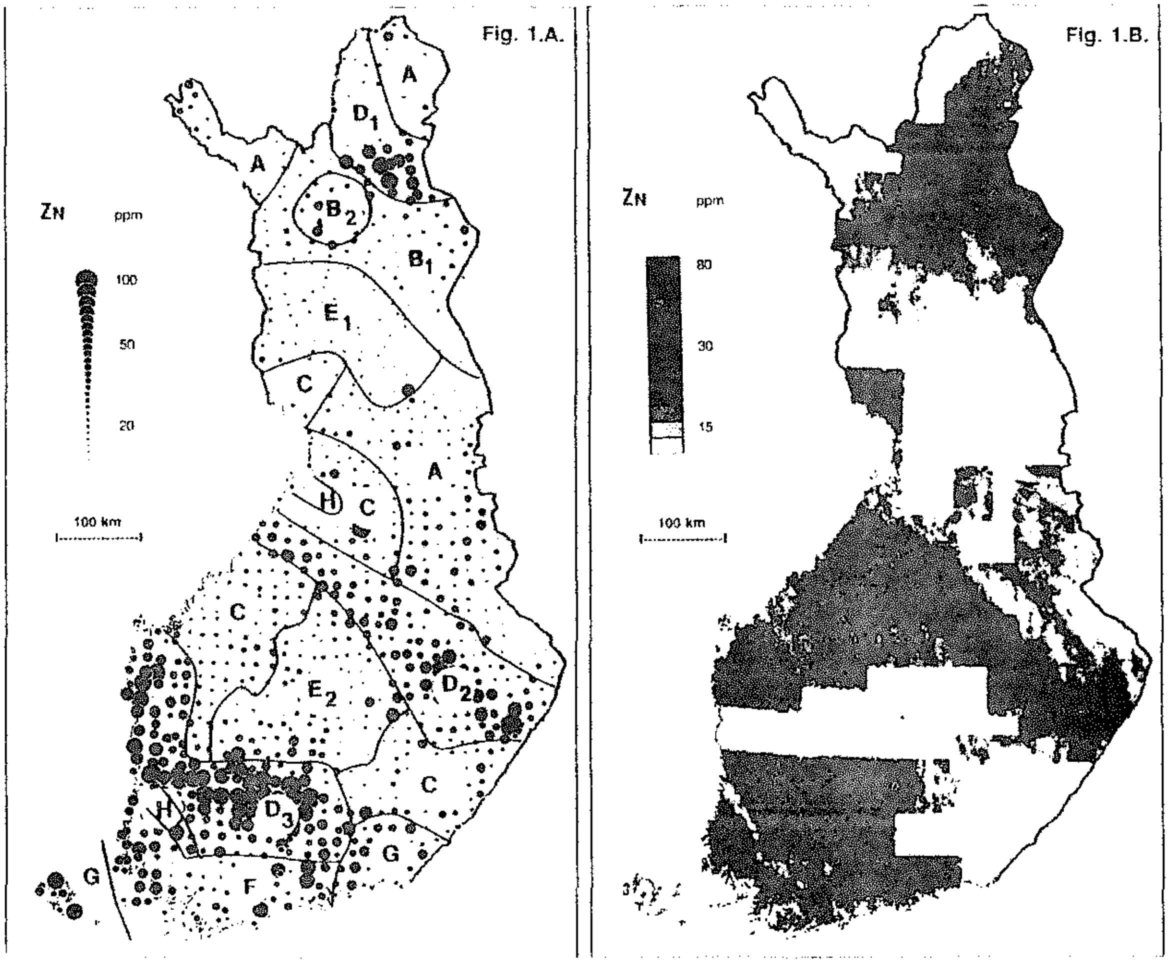

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Fig. 2.A. Geochemical map of elements characteristic of mafic rocks. Sampling density one sample/300 km^2 and analytical method ICP–AES after aqua regia leach. The concentrations of Cr, Fe, Mg, Ni, and Ti have been multiplied together. **2.B.** Same as 2.A., but sampling density one sample/4 km^2. **2.C.** Geochemical map of elements characteristic of granites and pegmatites. Total concentrations determined by ICP–AES (K and Li) and NAA (Ta, Th, U, and Rb) are multiplied together. Sampling density one sample/300 km^2. **2.D.** Geochemical map of barium. Sampling density one sample/4 km^2 and analytical method ICP–AES after aqua regia leach. The sampling material used was the fine fraction of till (<0.06 mm).

Fig. 2.A.

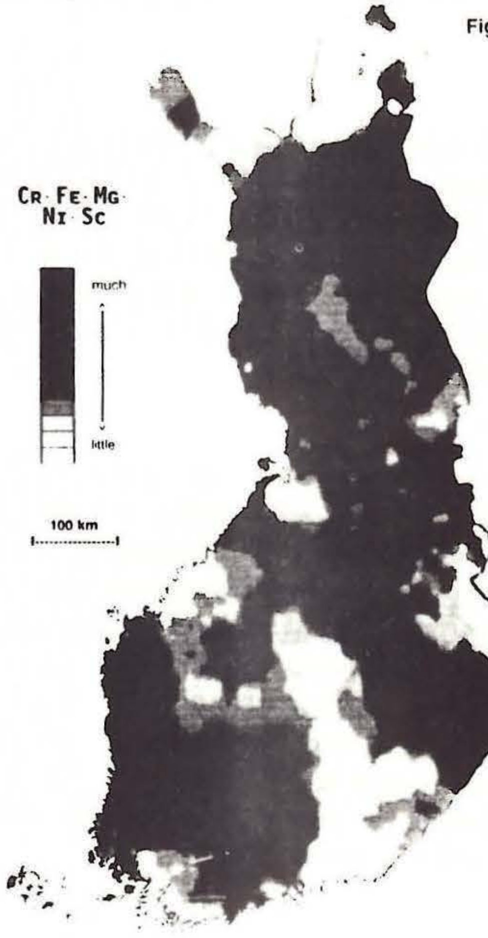


Fig. 2.B.

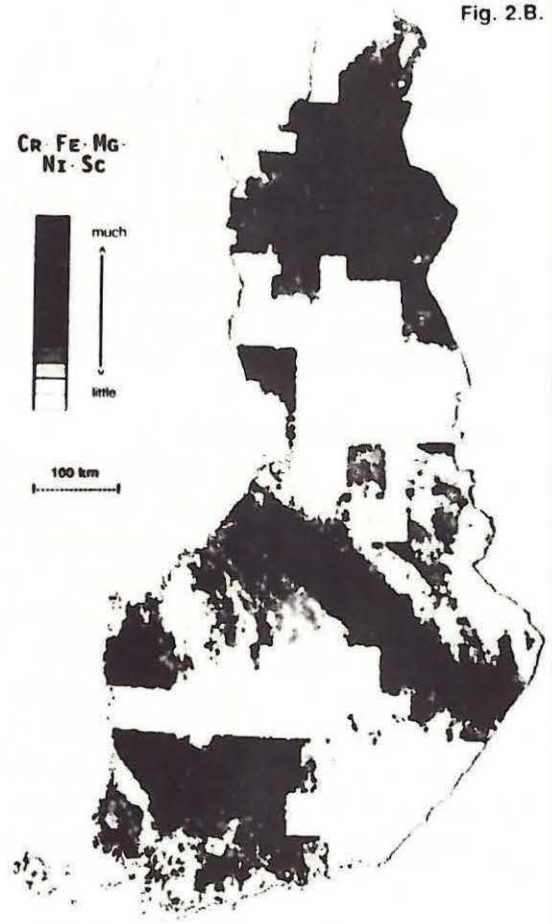


Fig. 2.C.

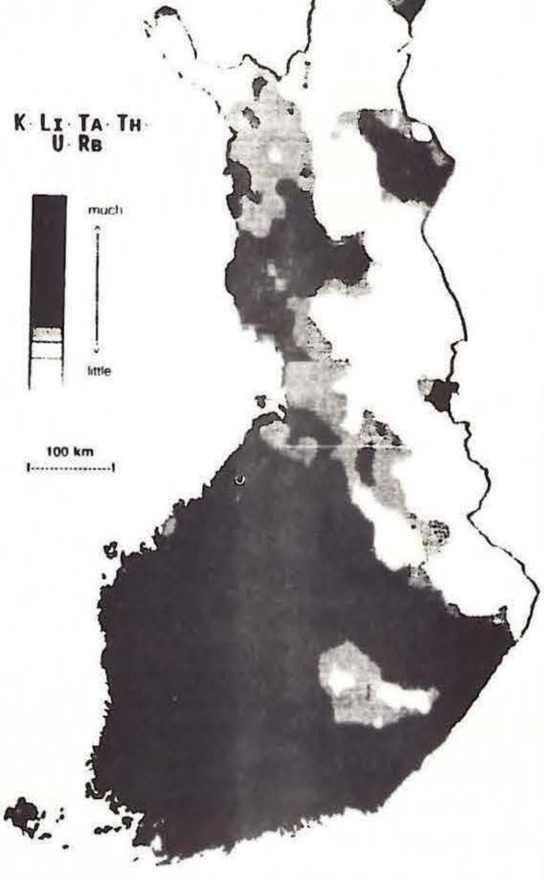
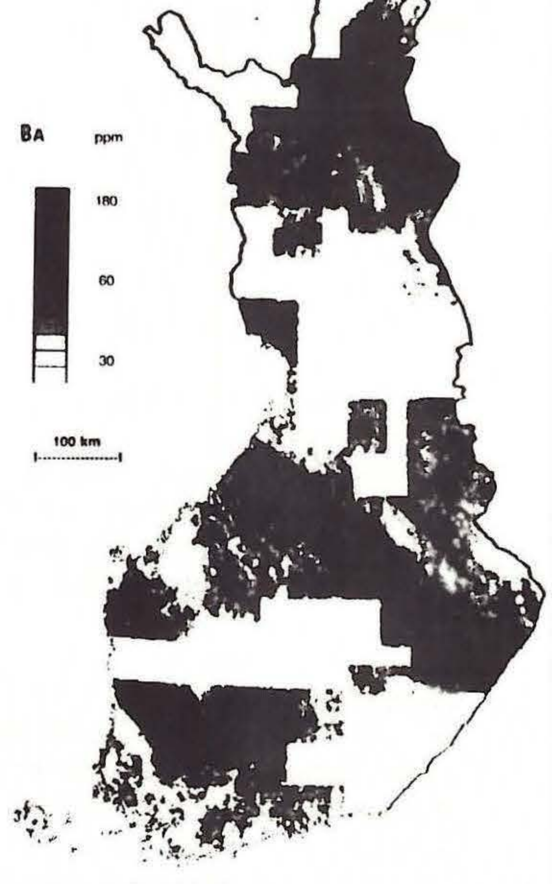


Fig. 2.D.



Till in geochemical studies

Compared with other possible sampling materials, till, which was the sole material used in the study, is an exceptionally good choice for geochemical studies. The fine fraction, in particular, is useful because it is fairly homogenous, widely available, only slightly altered chemically, and similar to bedrock in mineral and chemical composition. The direction of glacial flow at various times is usually known and the distance of transport is generally short, typically no more than a few kilometres and often only some hundreds of metres.

Analytical methods

Most analyses presented in the Atlas study were done by plasma emission spectrometry (ICP–AES) and neutron activation analysis (NAA). Many of the elements were determined after both total and partial dissolution. This two-pronged approach allowed the solubilities of a great many elements to be studied, and the total contents, the aqua regia extractable contents, and even the ratios of these to be presented on maps. The solubility of elements in aqua regia, as in acids in general, provides important information about the form in which elements are present in minerals, how they weather and migrate in sediments, and how readily they are available to plants and animals as nutrients. Studies using also weaker acids than those here, or using the buffered solutions common in soil studies, are recommended in regional studies.

Table 1. The geochemical domains and provinces of Finland.

ARCHAEAN DOMAIN
- Gneisses (A)
- Greenstones and komatiites (B_1 and B_2)

PROTEROZOIC DOMAIN
- Svecokarelian schists and gneisses (C)
- Granitoids of central Lapland (E_1)
- Granitoids of central Finland (E_2)
- High-metamorphic belt of southern Finland (F_1 and F_2)
- Rapakivi granites (G_1 and G_2)
- Sandstones and siltstones (H)

TECTONO-VOLCANIC DOMAINS
- Granulite (D_1)
- Lake Ladoga–Gulf of Bothnia zone (D_2)
- Volcanic–sedimentary zone of southwestern Finland (D_3)

Discussion

The sampling density in regional mapping should be chosen on the basis of large-scale geological features and processes, characterizing areas of perhaps thousands of square kilometres. In our view, the most important variables in this respect are 1) the thickness of the crust (≈10–70 km), which affects the dimensions of magmatic and metamorphic rock suites, 2) the breadth of the surface features associated with the collision and subduction of plates (≈20–100 km or more), 3) the distance between a subduction zone and its island arc (≈300 km), and 4) the breadth of mobile belts and rift zones with their associated volcanism (≈20–100 km).

Many geochemical features appear as zones some hundreds of kilometers long but only tens of kilometers broad (see Koljonen et al. 1989). Thus, to be visible on geochemical maps, at least 2 or 3 samples would need to be taken in a transverse section of the zones. This defines the sampling density to be one sample from an area 100 to 400 km^2 or less. In continental shields, on the other hand, where vast areas are covered with silicic magmatic and sedimentary rocks of relatively homogenous chemical composition, a sampling density of one sample per 400–3,000 km^2 or more should be sufficient. On the ocean floor the density could generally be very low, possibly one sample per 10,000 km^2 or more.

Conclusions

Distinct geochemical units can be recognized in the maps, which are usually coloured in the *Atlas* but are here presented in gray tone (Table 1 and Figs. 1 and 2). The most prominent units, are some hundreds of square kilometres in size exhibiting clearly distinct chemical compositions. Comparison of maps produced with different sampling densities shows a large degree of similarity, with, of course, much more detail in the case of the denser sampling grid. The most prominent difference in composition is between the Archaean basement, representing the chemical composition of the oldest continental crust (Table 1, A and B), and the Proterozoic continental crust representing the composition of the transitional crust formed near the continental margin (Table 1, C, E, F, G, and H). The major units in the two crusts are separated by plate tectonic zones (D_1, D_2, and D_3) enriched with elements characteristic of mafic rocks and hydrothermal solutions. (D_1 is a continental collision zone from the NE, D_2 a subduction zone of oceanic and continental plates implaced from the SW and D_3 an island arc.) Of the various rock types, greenstones and komatiites (B_1 and B_2) can most clearly be discerned in northern and eastern Finland and the post orogenic rapakivi granites (G_1 and G_2) in southern Finland. Mafic rocks in general, especially volcanogenic mafic rocks, show better than granitoid rocks. The chemical differences in the rock suites of Archaean gneisses, synorogenic granitoids, and sand and siltstones can be discerned only poorly and a dense sampling grid is needed to study these properly.

The discovery of geochemical features through small-scale mapping cannot be expected to be as easy everywhere as in Finland; the task will be more difficult, for example, in tropical areas where lateritic soils prevail and sediments are thoroughly weathered and millions of years old.

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GEOCHEMICAL ZONALITY OF THE MOLODYOZHNY COPPER DEPOZIT /SOUTH URALS/.

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The deposit is located in the north-eastern part of the Middle Devonian volcanic belt /the Magnitogorsk zone of South Urals/. The ore bodies are laid in the south-eastern slope of the paleovolcano. There are singled out four units in the section of the deposit: the lower one composed of amigdaloidal tholeiitic basalts and their tuffs; the second or ore-bearing unit represented by natrium dacitic porphyrites and their tuffs; the third one consisting of limestones and their breccias and the upper unit including tuffites, andesitic porphyrites. Major ore resources of the deposit are concentrated in two lens-shaped accumulations of the eastern dip. The ore body morphology is complicated by discontinuity dislocations.

The highest metal content is found inside the ore bodies. There are three groups of elements with more strong correlation bonds: copper-selenium-bismuth-cobalt, zinc-lead-arsenic, uranium-thorium /table/. Chemical elements of the first group are suggested to preserve their position beginning with the hydrothermal-sedimentary ore formation stage. Those of the second group were redistributed at the hydrothermal-metasomatic stage being brought from inner zones. Uranium and thorium were, probably, introduced at the third stage of ore formation, that is at the hydrothermal-metasomatic one. Maxima in zinc, gold, silver, arsenic, antimony, cobalt, selenium, bismuth, lead are spatially related to the zone of north-western dislocations feathering the mineralizing channel.

In vertical sections the general circumore geochemical halo of complex composition is traced in the lying wall of the deposit while in the hanging wall it is rather vague. At flanks deep boreholes cut the geochemical halo. Combination of steeply dipping haloes spreading to the depth along mineralizing channels and those outpinching laterally defines the generally mushroom shape of geochemical halo.

Table. PAIRED CORRELATION RATIOS.

	U	Th	Co	Zn	Cu	Pb	As	Te	Se	Bi
U	1.00	0.52	-0.38	-0.29	-0.04	-0.34	-0.08	-0.09	0.12	0.18
Th	0.52	1.00	-0.31	-0.02	-0.19	0.02	0.03	0.33	-0.26	-0.25
Co	-0.38	-0.31	1.00	0.15	0.48	-0.10	0.11	-0.31	0.36	0.24
Zn	-0.29	-0.02	0.15	1.00	0.06	0.61	0.04	-0.12	-0.32	-0.19
Cu	-0.04	-0.19	0.48	0.06	1.00	-0.05	0.34	-0.25	0.62	0.84
Pb	-0,34	0.02	-0,10	0.61	-0.05	1.00	0.36	0.01	-0.32	-0.31
As	-0.08	0.03	0.11	0.04	0.34	0.36	1.00	0.25	0.15	0.18
Te	-0.09	0.33	-0.31	-0.12	-0.25	0.01	0.25	1.00	-0.15	-0.18
Se	0.12	-0,26	0.36	-0.32	0.62	-0.32	0.15	0.15	1.00	0.73
Bi	0.18	-0.25	0.24	-0.19	0.84	-0.31	0.18	-0.18	0.73	1.00

UTILIZATION OF PHYTOGEOCHEMICALLY DETECTED METASTABLE STATES OF ELEMENTS FOR PRACTICAL PURPOSES

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Excessive concentrations of chemical elements induced by a natural or technogenetic source are accompanied by dispersion haloes in all geochemical spheres /1/. Based on this phenomenon are various techniques of geochemical prospection for mineral deposits and environmental monitoring.

The essential feature of dispersion process making possible its multiple use for practical purposes is the transformation of states /forms of occurrence/ descriptive of the dispersing elements due to various media they are found in pertaining to different parts of lithosphere, hydrosphere, atmosphere or biosphere.

The main trend revealed by the dispersing elements is the increasing probability of a more stable state for a longer period of time. This state may be characteristic of a particular type of medium or object /2/. Thus the element´s state is informative both on the type of source and the medium of migration which is highly valuable for solving various applied problems. This fact is particularly important over the initial period of the dispersion halo formation when the metastable state is prominent against the minimum background. The metastable state reflects accurately basic signs and specific features of the elements-source indicators while the complex of elements in this initial state proves to be its most contrasting "image". In the course of time the element´s state stabilizes and it transforms in accordance with the characteristics of matrix medium.

For analyses aimed at recognizing dispersion haloes in different media, the elements occurring in a metastable state and, consequently, loosely connected with the medium substrate may be separated with the use of extragents of varied composition and concentration. They are extracted from samples of friable deposits, plants and zoo-organisms with water, acid and alkali extracts and organic solvents. This technique is applicable both in prospecting for mineral deposits and environment control.

This technical approach in geochemical investigations may be favourably described as simple, easy to perform, reliable and rather rapid. As for example, graded as highly efficient is the technique of indicating dispersion haloes of metals with the help of short-time water and hydrochloric acid extracts from plants and analyses of the obtained solutions /3/. It is essential that the technique is meant for extracting dissolved compounds of elements. The comparison of data yielded by analyses of extracts from live /green/ and dead /naturally dry/ leaves suggests unambiguously that about 80% of metal content come from transpiration solution and the remaining part is likely to result from mechanical sedimentation in the atmosphere. The technique proves to be rather sensitive in detecting ore bodiges expanding into the oxidation zone /Table 1/.

Table 1. Ore mineralization effect on metal content of water extracts from oak leaves

A. Polymetallic ore body

Distance from the ore body, m		0	800	1200
Content of heavy metals, mcg/l	Dead leaves	7	0.1	0.1
	Live leaves	90-180	0.1	0.1

B. Copper ore body

Distance from the ore body, m	0	50	250	500	1000	1500
Content of heavy metals, mcg/l	16	18	15	12	5	5

As can be judged from Table 1, anomalies of heavy metals in water extracts obtained and analysed right away in the field contrast by up to 2-3 orders.

The paper gives ground to the possibility of applyind this technique when prospecting for oil and gas bearing structures. Samples of water and hydrochloric acid extracts from birch leaves were taken along the profile located across the strike of one of West Siberian structures. The water extracts were analysed for K, Na, Sr, Ca and Mg, while the hydrochloric acid ones for Zn, Pb, Cu and Cd /with polarography/. The yielded data show that anomalous are K, Na, Zn and Cd with Na and Zn increasing within the oil-gas bearing structure and K and Cd decreasing against the background values /Table 2/. Two couples of geochemically related elements were pointed up notable for their contrary-to-the-usual behavior in the migration of the elements´ mobile part through plants throughout the oil-gas bearing area.

The technique is rather efficient in environmetal control. This may be examplified by the results of studying the technogenic effect of an operative motor road through analysing water and hydrochloric acid extracts from the surface of spruce needles, birch leaves and grass given in Table 3.

Table 2. Distribution of Na/K and Zn/Cd ratios in the area of oil-gas bearing structures

Elements	Distance from the structure center, km							
	Within the structure				Out of the structure			
	3.6	1.2	3.6	4.8	6.0	8.4	12.0	13.2
Na/K	3.57	0.55	0.65	20.1	0.23	0.23	0.25	0.20
Zn/Cd	163	421	305	445	125	225	139	126

Table 3. Motor road effect on metal content /mcg/l/ in acid extracts from the surface of spruce needles

Metals	Distance from the motor road, m					Control sample
	20	120	270	420	520	
Zn	734	56	70	160	86	1.5
Pb	376	35	47	47	9	3.4
Cu	13	39	33	21	36	18.2
Cd	3.8	0.4	1.0	0.4	0.2	0.1

The cited data are another proof of one of V.I. Vernadsky´s fundamental theses stating co-realiton and interdependence of geochemical processes occurring in the Earth´s crust.

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REGIONAL GEOCHEMICAL MAPPING OF GRANITOIDS (MONGOL-OKHOTSK ZONE)

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INTRODUCTION

Searching for the primary environment is principal objective of the applied geochemistry, provides the key to solve many problems of prospecting, metallogeny, environment geochemistry. The geochemical mapping from bedrocks is one of the main approaches to solve these problems. Two principal approaches are available: (a) routine or "formal" approach based on a more or less regular grid sampling and compiling of single-element, multi-element and geochemical associations maps; (b) representation of the geochemical essence in the geological objects to be mapped. In the last case these are the geologo-geochemical maps which need geochemical classification of geological objects. The analysis of geological mapping procedure and rock classifications indicates that this approach is developed from the approach created earlier and its further step to a new informational level of rock composition study.

This approach was tested in compiling the map of granitoid geochemical types of the Mongol-Okhotsk zone (scale 1:1500000).

GEOLOGY

The Mongol-Ohkotsk zone (MOZ) is the area of Post-Paleozoic orogenesis, rifting structures, intense intrusive and volcanic activity and various mineralization (Fig.1). As a wide (up to 1000 km) belt it penetrates into the Asian continent along the Mongol-Okhotsk lineament for 2000-3000 km from the eastern continental margin (Fersman, 1926; Mesozoiskaya..., 1975; Kuzmin, 1985; Koval, 1987a etc.). Over 150000 sq. km (5-10%) of the MOZ area is occupied by the Mesozoic granitoids. Two main stages are distinguished in the tectonic-magmatic activity of the MOZ: the Early Mesozoic ($T-J_{1-2}$) and the Late Mesozoic (J_3-K_1). The zonal magmatic areas are formed at both stages.

The central zones of the areas are occupied by large granodioritic plutons and smaller granitic and leucogranitic intrusions, surrounded by the zone of granitoid and andesite-basaltic magmatism with heightened alakalinity.

The Mesozoic structures and magmatism overlapped a heterogenic fold-block basement, which varies in age from the Early Precambrian to the Hercynian.

Various mineralizations are represented as classic deposits of Sn-W and Mo-W formations; Mo and Mo-Cu porphyry deposits; rare-metal (Ta, Nb, Li, etc.), base-metal, rare-metal -base-metal, gold, fluorite and other mineralizations (Rudonosnost..., 1988).

Because of peculiar and complex features of the intracontinental MOZ structures were differently tectonically and geodynamically interpreted (Geologia...,1973; Mesozoiskaya..., 1975; Zorin et al., 1982; Kovalenko et al., 1984; Filippova et al., 1984; etc.). The author is prone to consider the model combining the mantle diapirism and intraplate collision, as mostly preferable (Koval, 1987a).

CLASSIFICATION

The geochemical rock classification approach is assumed as a basis for classification of granitoids (Mesozoiskaya..., 1975; Tauson, 1977, 1984; Koval, 1987b). A geochemical type involves natural rock populations mainly of the same class (plutonic or volcanic) with similar genetic provenance. They are classified according to the following features: (a) member of the same rock group, the same alkalinity rank and series type; (b) similarity of the chemical, trace-element and mineral composition and its evolution; (c) ability to produce individual massifs and volcanic structures; (d) geochemical similarity of the associated metasomatites and mineralization (Koval, 1987b).

The obtained set-up of geochemical granitoid types and their relations to petrological parameters according to (Klassifikatsiya..., 1981) are shown in Table 1. The non-classified granitoids of alkali basic-syenite series are also present in the region.

In accordance with the above presented definition, the basic classification parameters are the following: SiO_2 (rock groups and families); (Na_2O + K_2O) and mineralogical criteria (alkalinity rank); K/Na (magmatic series); contents of fully mobile trace-elements (Rb, Ba, partly Sr) and F; distribution of accessory trace elements(REE, Nb, Zr, Ta, Hf) as defined by the substratum composition and system alkalinity; the patterns of geochemical evolution of intrusions and associated ore mineralization. Some appropriate diagrams are shown at Fig.2-5.

Average contents of major and trace elements for geochemical granitoid types of the MOZ are listed in Table 2.

The further type subdivision can be carried out in the facies and subfacies of virtual volatiles (F, B, S, et al.) and trace (e.g. Li) elements and also melting and crystallization conditions of magmas (subsolvus and hypersolvus granites, porphyraceous palingenetic granitoids with or without ovoid inclusions). The geochemical data for some important facies (e.g. RLF) are given in Table 2. A distinction of facies and subfacies of geochemical rock types gives the opportunity for appropriate detailed elaboration of classification for different scale works.

The accepted set-up of geochemical types (Table 1) includes 4 groups of types: palingenetic granitoids, granitoids of syenite-alaskite intrusions, rare-metal granitoids and granitoids of homodromic basic-granitoid associations. They belong to granitoids proper (first 3 groups) and basic-granitoid series of normal, subalkaline and alkline ranks. Granitoid series proper are as a rule represented with a large intrusion of palingenetic or syenite-alaskite types and late preferably small massifs of rare-metal granites of the corresponding types which in some cases form the following pairs: PGN and MG-RGP, PGS-RGS, SAA-RAS, SAA-RGA. Granitoids of basic-granitoid group includes the types of tholeiitic, trachyandesitic, latitic and nonclassified alkaline series.

Formation of great bulk of palingenetic granitoids is accompanied by the supply of majority of incompatible elements of the mantle. This tendency increases in low basic syenite-alaskite and rare-metal types, except for alkali-earth elements: Ca, Mg, Sr, Ba and Eu, their concentrations decreasing. Nb, Zr, Hf and REE contents correlate roughly with the change of alkalinity rank. The maximal fractionation of trace elements (except for W, Sr, Mn) is typical of rare-metal agpaitic granites.

A set of the associated ore formations is common to each geochemical type (Table 3). As distinct from the approach of B. Chappel and A.White, this one also takes into account the variations of alkalinity and the models (ways) of granite formation and correspondingly provides a more detailed classification (Table 4).

SPATIAL-TEMPORAL DISTRIBUTION OF GRANITOIDS AND MINERALIZATION

The granitoid magmatism scale of the MOZ is comparable to magmatic activity of the continental margin regions of the Andian type and the continent-continent collision. However, it differes from the last two in a great variety of geochemical types of magmatic rocks, which involve the types common to the active continental margins of the Andian type, collisional and rifting settings. On the whole, the heightened alkalinity of the granitoids and a wide distribution of subalkaline magmatic rocks are typical of the MOZ. The total area of granitoids ($\sim$160000 sq.km) shares between the palingenetic, syenite-alaskite, rare-metal and basic-granitoid groups as 80:7:10:3, correspondingly (Fig.6). The Late Mesozoic granitoids occupy one half as much as the Early Mesozoic ones. The rocks with heightened alkalinity are less distributed among the Late Mesozoic granitoids. While the granitoids of the latitic and alkaline basic-granitoid with carbonatites series are not discovered among the Early Mesozoic ones. The rare-metal agpaitic granites are not evident in the Late Mesozoic.

The analysis of the spatial distribution of different geochemical granitoid types indicates the main specific features of the Mesozoic magmatism zonation of the MOZ (Mesozoiskaya...,1975; Koval, 1982, 1987a):

(i) symmetric-asymmetric "half-concentric" zonation pattern of the areas, with the center occupied by the zone of normal alkalinity magmatism (palingenetic granitoid types of normal alkalinity and plumasitic rare-metal granites) surrounded in the north-west and south by the magmatism zone of heightened alkalinity (geochemical granitoid types of subalkaline and alkaline ranks).

(ii) mosaic-block structure, which correlates with tectonic blocks of the continental lithosphere of different orders: alkalinity zones, alkalinity subzones, the blocks of magmatic associations which articulate with each other along the fault zones of the corresponding ranks (main boundary faults or suture, regional faults, zones of tectonic steps).

(iii) the whole correlation of alkalinity increase of magmatism and the maturity degree (the preceding granitization) of the host continental blocks, which roughly corresponds to the basement age.

(iv) conformity to the main Mesozoic structures, basins and rift zones.

(v) more complicated differentiated structure of the Late Mesozoic magmatism area.

(vi) zonation of depth facies, correlated with the Mesoizoic structures of the region.

The correlation of endogenic mineralization with geochemical granitoid types and the zonation distribution of the latter permits to use for the metallogenic analysis of the regions the maps of magmatic rock geochemical types. The analysis involves the total metallogenic assessmont of the region; the classification of ore belts, zones, districts; ore productivity assesement of magmatic associations and massifs; forecast of new ore-bearing massifs and types of commercial mineralization.

CONCLUSIONS

The use of geochemical classification of the MOZ granitoids indicates that the geochemical mapping of the primary seetings (bedrocks) may be performed with application of the geochemical classification of geological objects and its demonstration on the geological maps. In general, this approach needs the geochemical classification (typification) of all rock groups to be done. It is more appropriate for compiling global and regional maps. In case of more detailed works the further subdivision of geochemical rock types, particularly to various facies is useful. In practice the maps of geochemical rock types may be used in tectonic and metallogenic analysis as well as the basis for mineralization forecast maps.

The geochemical field patterns (e.g. anomalies, multielement associations) obtained in routine mapping of the primary and secondary environments may be also shown on such maps.

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TABLE 1

Correlation of geochemical igneous rock types of intracontinental mobile zones and some principal petrological categories

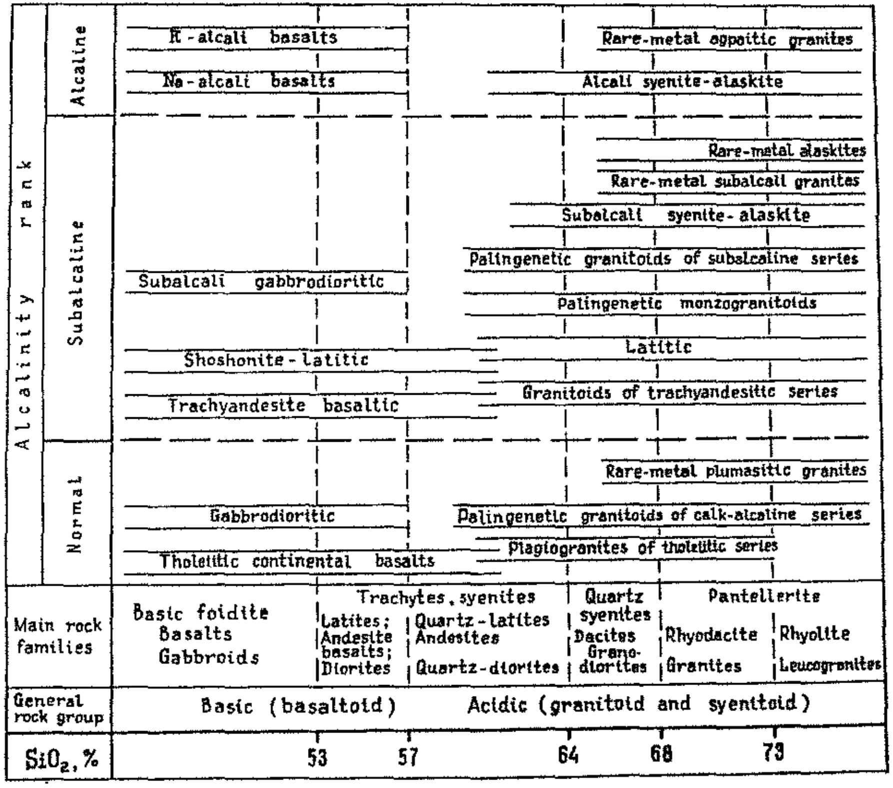

TABLE 3

Ore-bearing potential of geochemical granitoid types (Mongol-Okhotsk zone)

Geochemical types of granitoids	Ore mineralization
Plagiogranites of tholeitic series (TG)	?
Palingenetic granitoids of normal alcalinity (PGN)	Sn-W*; scheelite-skarn*; Au*.
Rare-metal plumasitic granites (RGP)	Sn-W; Mo-W; Ta,Nb,Li; Sn,Pb,Zn
Palingenetic monzogranitoids (MG)	Mo; Au.
Palingenetic granitoids of subalcaline series (PGS)	Sn*.
Rare-metal subalcali granites (RGS)	Mo-W (Be); Ta-Be.
Subalcali syenite-alaskite (SAS)	Sn-Pb-Zn(Cu,W,Au,Ag); Be-F.
Rare-metal alaskite (RAS)	?
Granitoids of trachyandesitic series (TAG)	Mo; Mo-Cu(Au); Au (Pb,Zn).
Latitic (LG)	Cu-Mo(Ag, Re, Pb, Zn); Au-Pb-Zn; Pb-Zn, Ag-Pb-Zn.
Alcali syenite-alaskite (SAA)	Be-F (?).
Rare-metal agpaitic granites (RGA)	Zr-Nb*; REE*.

* Small deposites and disslminated mineralization.

Table 2

Chemical compositions (mass%) and trace element content (ppm) of geochemical granitoid types (Mongol-Okhotsk zone)

Types	PGN	RGP	RLF	MG	PGS	PGS*	SAS	RAS	SAA	RGA*	TG	TAG*	LG*
SiO_2	68,04	73,32	74,69	69,96	67,59	73,95	70,37	75,49	69,42	74,6I	6I,76	69.00	62,74
TiO_2	0,43	0,25	0,I3	0,40	0,54	0,20	0,37	0,I7	0,48	0,22	I,27	0,44	0,6I
Al_2O_3	I5,24	I3,50	I2,97	I4,52	I5,2I	I3,I9	I4,60	I2,I2	I4,50	II,60	I5,63	I4,94	I5,42
Fe_2O_3	3,78	2,29	I,72	2,9I	3,94	2,06	2,76	2,22	3,I9	3,65	6,38	3,45	4,79
MnO	0,04	0,03	0,05	0,05	0,08	0,04	0,05	0,05	0,II	0,04	0,I2	0,07	0,07
MgO	I,45	0,40	0,I8	I,0I	I,II	0,36	0,38	0,I5	0,40	0,07	2,49	0,96	2,68
CaO	2,78	I,00	0,92	I,9I	2,36	0,65	0,78	0,4I	0,65	0,37	4,07	I,70	3,47
Na_2O	3,98	3,75	3,86	3,92	4,54	4,28	4,64	3,64	5,27	4,33	3,79	4,5I	4,23
K_2O	3,62	4,73	4,24	4,49	3,88	4,77	5,I4	4,8I	5,23	4,46	I,86	3,45	4,I9
P_2O_5	0,09	0,06	0,02	0,I2	0,I3	0,05	0,I0	0,05	0,07	0,02	0,22	0,I3	0,25
K_A	0,68	0,83	0,84	0,78	0,76	0,93	0,90	0,92	0,98	I,03	0,53	0,75	0,74
Li	39	8I	I82	29	22	44	I5	I9	36	84	I3	I5	30
Rb	III	290	56I	I60	99	2I4	I6I	I75	I97	320	40	I08	I24
Sr	329	I32	I05	305	420	I95	I08	47	62	43	340	343	797
Ba	959	39I	39	75I	I004	450	4I4	95	297	I39	640	829	II67
Zr	I90	2I6	I5I	202	36I	I2I	309	598	574	3565	–	346	277
Hf	4,3	5,8	8,3	4,5	8,I	3,7	7,0	I4	II	26	–	6,5	7,0
Nb	7,7	22	44	6,7	9,2	I8	I2	32	22	I38	–	II	I5
Ta	0,6	2,5	9,6	0,8	0,6	I,7	0,9	2,3	I,2	7,6	–	0,79	I,0
Sn	4,5	9,9	27	2,8	3,0	4,7	4,2	5,I	5,I	37	2,6	4,5	3,2
W	I,5	3,4	8,0	I,8	≤I,2	≤2,2	I,6	2,3	I,6	I,8	–	I,2	I,6
Mo	I,4	2,3	I,4	2,0	≤I,7	≤2,0	I,9	2,I	I,5	I,4	–	≤3,6	2,2
Pb	26	33	43	25	20	20	25	27	35	69	I5	24	30
Zn	55	50	63	35	50	46	46	63	39	24I	I07	64	59
Cu	I2	9,6	5,8	I8	I5	n.d.	I6	I0	I4	7,6	30	26	–
Ni	I6	7,I	6,7	20	I2	n.d.	8,7	I2	5,4	I0	30	I7	I6
Co	9,6	5,0	2,I	7,7	8,0	n.d.	3,3	3,I	2,7	<I,0	2I	8,9	3,6
Cr	36	I6	I0	34	22	n.d.	2I	I2	II	I5	55	27	38
V	45	20	5,5	36	44	n.d.	II	6,5	I3	I0	I00	37	28
B	I6	23	I9	I9	25	n.d.	22	I7	22	99	57	60	49
Be	2,5	6,2	I6	2,6	2,I	4,I	3,5	4,4	5,8	I5	I,3	2,5	3,2
F	0,05	0,I37	0,50	0,072	0,06	0,056	0,07I	0,087	0,I0	0,360	0,060	0,047	0,08I
Ba/Rb	8,6	I,3	0,07	4,7	I0	2,I	2,6	0,54	I,5	0,4	I6	7,7	9,4
La	30	46	I3	36	26	n.d.	33	66	54	59	n.d.	29	48,4
Ce	52	84	29	58	42	n.d	63	II0	84	I28	n.d	56	7I,I
Pr	(6,2)	(9,I)	(2,I)	(4,4)	(5,2)	n.d.	(6,3)	(II)	(I2)	(I3)	n.d	(6,4)	(7,9)
Nd	24	38	I4	22	22	n.d.	24	48	42	69	n.d	27	28,8
Sm	4,7	7,9	4,5	4,4	3,6	n.d.	4,0	8,5	9,3	I5	n.d	5,0	6,2
Eu	0,98	0,66	<0,II	0,82	0,72	n.d.	0,47	0,20	0,40	0,45	n.d.	0,9I	I,2
Gd	5,5	9,3	5,7	3,4	3,0	n.d.	4,6	9,2	I2	I9	n.d.	4,0	5,I
Tb	(I,2)	(3,6)	(I,7)	(0,2)	(I,6)	n.d.	n.d.	n.d.	(5,I)	(4,2)	n.d	(I,5)	n.d.
Dy	5,2	8,I	7,9	I,8	2,3	n.d.	2,9	7,8	I4	I8	n.d.	3,3	3,5
Ho	(0,92)	(I,8)	(I,4)	(0,34)	(0,74)	n.d.	(0,69)	(I,I)	(2,4)	(4,0)	n.d.	(0,79)	(0,74)
Er	(2,7)	(5,I)	(5,0)	(I,4)	(2,2)	n.d.	(I,8)	(2,7)	(6,5)	(I0)	n.d.	(2,6)	(2,4)
Yb	2,3	4,9	5,4	0,84	I,6	n.d.	I,9	2,7	7,3	7,7	n.d.	2,0	2,0
Lu	(0,29)	(0,69)	(0,86)	(0,25)	(0,24)	n.d	(0,30)	(0,3)	(I,0)	(I,6)	n.d.	(0,25)	(0,3I)
Y	20	36	34	II	I4	n.d.	I6	3I	5I	54	n.d.	I7	I8
ΣREE	I36	2I9	9I	I34	III	n.d.	I43	267	250	349	n.d.	I39	I78

Table 2 (continued)

Types	PGN	RGP	RLF	MG	PGS	RGS*	SAS	RAS	SAA	RGA*	TG	TAG*	LG*
N_m	II94	694	35	470	350	40	395	63	379	I9	4	247	73
N_t	I62I	94I	6I	I002	329	86	273	II2	258	I6	5	208	73
N_e	I5I	77	25	I8	52	n.d.	49	I	I9	7	n.d.	84	≫7

Notes: Letter type codes: PGN-palingenetic granitoids of normal alkalinity, RGP - rare-metal plumasitic granites, RLF - the same, leucogranites of Li-F facies (plus albite granites for REE), MG - palingenetic monzogranitoids, PGS - palingenetic granitoids of subalkaline series, RGS - rare-metal subalkali granites, SAS - subalkali syenite-alaskite, RAS - rare-metal alaskites, SAA - alkali syenite-alaskite, RGA -rare-metal agpaitic granites, TG - plagiogranites of tholeiitic series, TAG - granitoids of trachyandesitic series, LG -latitic. The area of rock distribution (besides * remark) was taken into account in average calculation. * -average data. Fe_2O_3 - total. K_A - agpaitic index. N_m, N_t, N_e - sample numbers, used for content estimation of major, trace and RE elements, accordingly. Analytical methods: chemical, AAA, OES, RFA, OES with preliminary chemical enrichment (Nb, Ta, Zr, Hf, REE, W). The data of Mezozoiskya...(1975), Kozlov (1984), Tauson et al.,(1984), Kuzmin (1985) were used also.

TABLE 4

Correlation of some geochemical classification of granitoids

Geochemical types*, this paper	Chappel, White (1974), Collins et al. (1982), Whalen et al. (1987) etc	Tischendorf u.a. (1985)	Xu Kegin et al. (1987)	Examples
TG	M (mantle)	J_{MT} (mantle, alpinotype)	IV. Mantle-Derived Series: 9. Mantle differentiation type	Troodos; Westsajen; Bentog and Xigin.
AG TAG LG		J_{OK} (oceanic crust, andinotype)	II. Syntexis Series: 6. Deep fault-controlled syntexis type	Tannuola, Sajen; South China.
PGN₁	J («orthocrustal»)		5. Continental magin syntexis type	S-E China; Peru; Sierra Nevada.
PGN₁			I. Continental Crust Transformation Series: 4. Unmatured-crust remelting type	Jiangnan; Sudan: Arabia.
PGN₁ RGP		J_{KK} (mainly ortho-continental crust, hercynotype)		Lachlen; Erzgebirge; South Mountain.
PGN₂ RGP RLF	S («paracrustal»)	S_I (mainly paracontinental crust, hercynotype)	3. Continental plate collision type 2. Crustal remelting type	South China; Manaslu. Nepal; Lachlen; Erzgebirge: Cornubian Bth.
PGN₂ PGS		S_s (mainly paracontinental crust, hercynotype preorogenic)	1. Migmatite and migmatitic granite type	Loch Coire; Lausitz.
SAS SAA RAS RGA	A («depleted» crust)	I_{MA} (mantal, riftotype)	III. Alcaline Series: 7. Continental rift type 8. Tensional continental-plate magin type	Oslo-region; Yangtze-Valley. Change-Nanao; Jinshajiang-Tibet.

Notes.* Letter type codes are the same as in Table 2.
PGN_1 – mainly granodiorite – granate facies with ovoid inclusions;
PGN_2 and PGS_2 – mainly gneissose – granite plutons.

FIGURE CAPTIONS

Fig.1. Location of the Mongol-Okhotsk zone. The lineament and the main faults are given with solid lines. The largest granitoid plutons are shown with black spots.

Fig.2. Diagram of agpaitic index (Ka) - Ba/Rb for granitoids of different geochemical types. Geochemical granitoid types (for abbreviations see notes to Table 2): 1 - TG (MOR -middle oceanic ridge, VA - volcanic arc); 2 - AG (granitoids of andesitic series (Tauson, 1977; 1984)) 3 - TAG; 4 - LG; 5 - PGN$_1$; 6 - PGN$_2$; 7 - PGS; 8 - MG; 9 - SAS; 10 - SAA; 11 - RGP; 12- RLF; 13 - the same, ongonite; 14 - RGS; 15 - RAS; 16 - the same, Li-F facies; 17 - RGA; 18 - the same, Li-F facies; 19 - BGS-granitoid of basic-syenite series. The bigger signs correspond to MOZ, smaller ones show the literature data (Collins et al., 1982; Jackson et al., 1984; Kuzmin, 1985; Neary et al., 1976; O'Halloran, 1985; Pearce et al., 1984; Stone, Exlly, 1985; Vidal et al., 1982, Whalen et al., 1987; etc.).

Fig.3. Diagram Li-Ba/Rb for granitoids of different geochemical types. Signs are the same, as on Fig.2.

Fig.4. Diagram Zr-Ba/Rb for granitoids of different geochemical types. Signs are the same, as on Fig.2.

Fig.5. Diagram Zr-Y for granitoids of different geochemical types. Signs are the same, as on Fig.2.

Fig.6. Distribution of geochemical granitoid types for Early (MZ$_1$) and Late (MZ$_2$) Mesozoic magmatic areas of the MOZ. The type abbreviations are given in notes to Table 2.

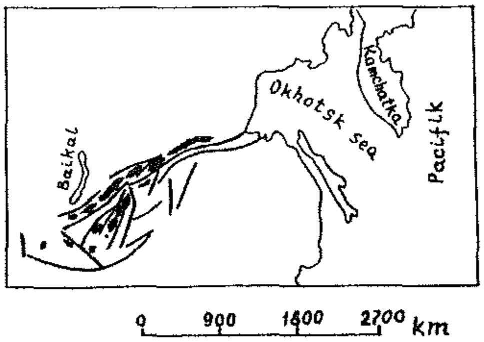

Figure 1.

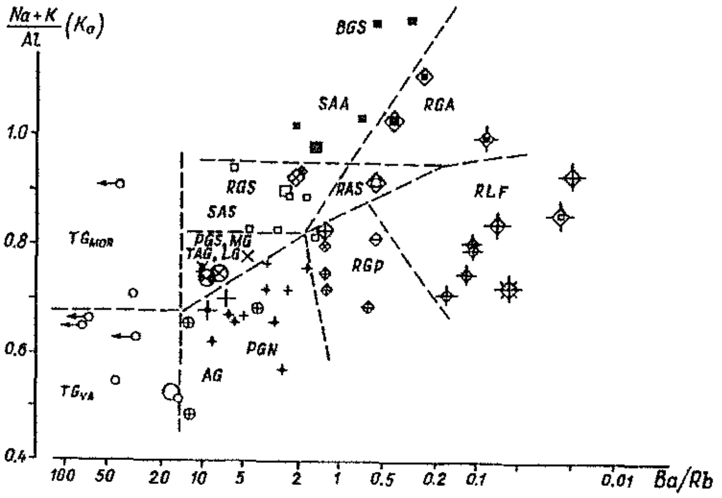

Figure 2.

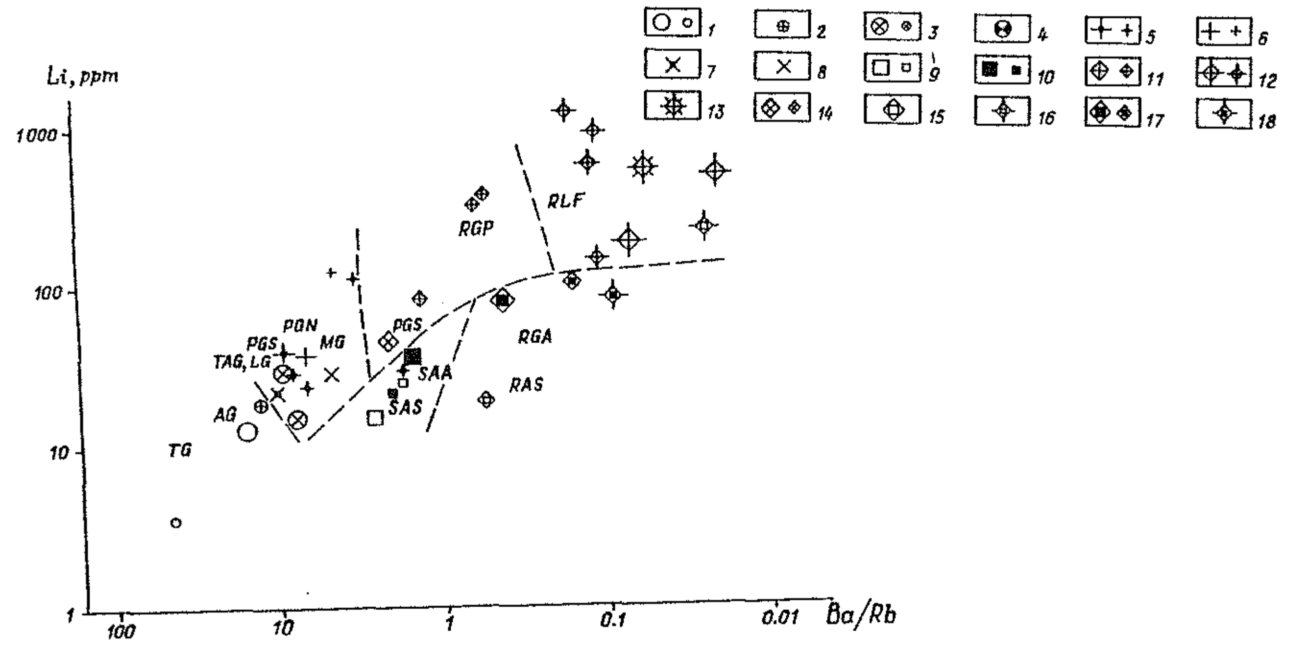

Figure 3.

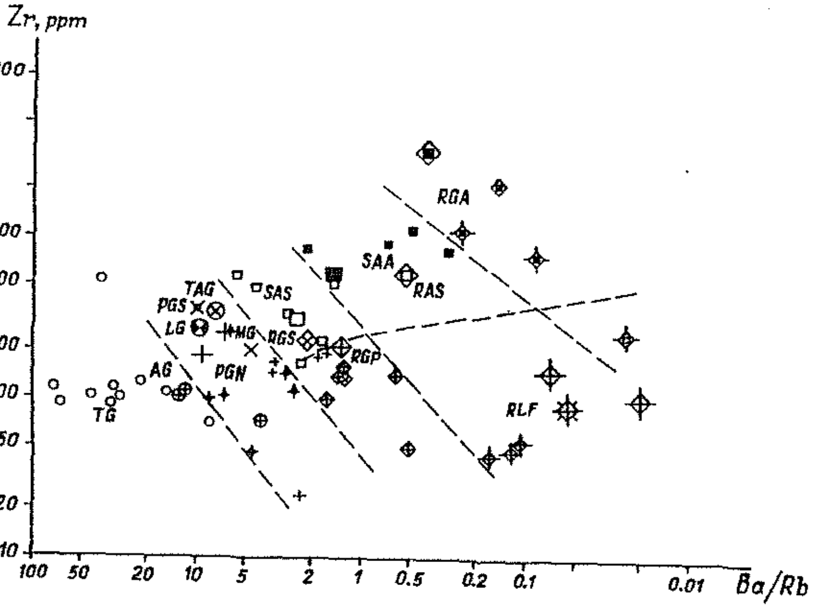

Figure 4.

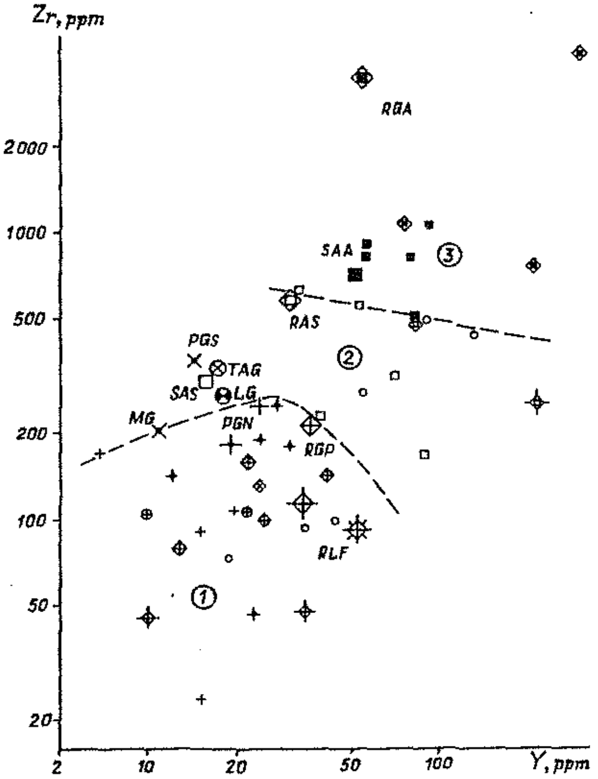

Figure 5.

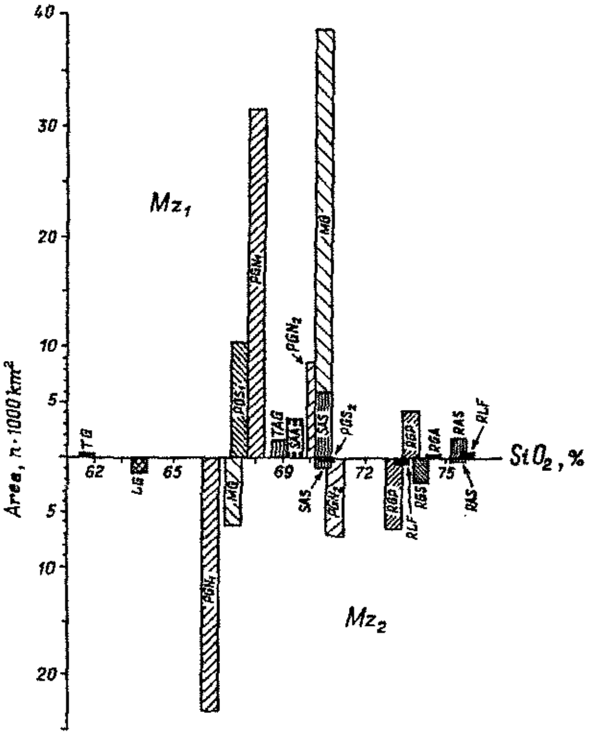

Figure 6.

MAIN MODELS OF THE BIOGEOCHEMICAL EXPLORATION FOR MINERAL DEPOSITS

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For the present time the numerous actual data on the depth of revealing and other characteristics of biogeochemical prospecting for mineral deposits are accumulated. Analysis of these data show their contradictions. The thicknesses of the loose allochtonous covers which do not obstacle of the biogeochemical haloes forming, for example, are varying from I to 200 m. Biogeochemical haloes of gold, tin, tungtsten and berillium are observed not above all mineral types of these ores. One of the most important cause of these seeming contradictions is the presence of indicator elements various forms in the rootinhabited zone of soils and rocks. The dependence of biogeochemical haloes intensity from the mineral forms of the corresponding indicator elements is the object of the long special investigations. This problem is elucidated in some our publications (Kovalevskii, I968, I975, I984 - in Russian; Kovalevskii, I974, I979a, b, I987 - in English). In this report will be discussed data on the main causes of various depth of biogeochemical exploration stipulated by the presence of indicator elements in the rootinhabited zone in solid, liquid and gaseous phases.

Analysis of the actual data on the depth of revealing of mineral deposits by biogeochemical exploration shows that it depends not only from the depth of the investigated plants root system but includes several components. The main component is the extent of upward migration of indicator elements. For various liquid - water phases these extents are measured by tens and hundreds meters and for gaseous phases may reach hundreds and even I000-4000 m.

The forming of biogeochemical haloes is influenced also by various intensity of the plant accumulation of chemical elements which are presented in the rootinhabited zone in solid, water and gaseous phases. As it is seen from the data of table I the average intensities of chemical elements accumulation from solid, water and gaseous phases are related between themselves as I:3000:300 000. Two very significant and simultaneously acting factors: the extent of upward migration across loose covers and various intensity of accumulation by the plants of chemical elements presented in solid, water and gaseous phases made it possible to choose three main models of prospecting by indicator elements in plants: litho-, hydro- and atmobiogeochemical explorations (Kovalevskii, I984, I985, I986, I988a - in Russian; Kovalevsky, I987). As it is clear from the names of these models the main sources of the corresponding ore biogeochemical haloes for these models are litho-, hydro-, and atmogeochemical haloes of ore bodies and deposits (fig. I). In real conditions the main sources of the biogeochemical haloes may be complex.

The most frequently is observed the influence of solid and water forms of indicator elements in rootinhabited zone, i.e. a model of complex lithohydrobiogeochemical prospecting. In this model the main sources of the observed biogeochemical haloes and anomalies may be the sorbed forms of the solid phase which are formed by sorption of indicator elements in the ways of their upward migration in water phase. These secondary lithogeochemical haloes and anomalies may be named hydrolithogeochemical ones. According to approximate calculations in the free water phase of the watersaturated loose deposits is presented 0,0003-0,03% (close to 0,001% in the average) of the summary quantity of the majority of metals. With the accounting of the average value of plant-water coefficient - FWC=3000 in the average only I/30 part of their observed quantity is accumulated by plants from the free water phase (Kovalevskii, I975, P.94 - in Russian).

For the elements - gaseous migrants is observed the most frequently the model of the complex lithoatmobiogeochemical exploration. It is stipulated by the sorption of the main mass of these gaseous migrants by the absorbing complex of soils and rocks. For many gases and gaseous compounds in sorbed forms are presented more 99,9% of their summary qu-

Table I. ELEMENTAL ACCUMULATION COEFFICIENTS FOR NON-BARRIER SPECIES AND PARTS OF PLANTS

Accumulation coefficient	Value of coefficient		Elements
	Range	Mean	
Plant-soil coefficient (PSC)	<0,00I-0,2	0,I	Au, Fe, Hg, B, Al, Si, Sn, Pb, W, Fe
	0,I-0,5	0,3	Be, Ce, Th, Fe
	0,5-2,0	I,0	The most of elements
	2,0-5,0	3,0	Cu, Ag, Mg, Tl, Mo
	5-30	I0	K, Ca, Sr, Ba, Zn, Cd, B
	30-300	I00	Zn, Cd, B, N, P
Plant-water coefficient, for roots (PWC_r)	$I0^2$-$I0^5$	$3xI0^3$	The most of elements
Plant-gas coefficient, for aerial parts (PWC_a)	$I0^4$-$I0^7$	$3xI0^5$	$C(CO_2)$, $N(NH_3$, N_2O, NO), $S(SO_2)$, Hg, Se, $F(F_2$,HF), Cl, Br, I
Plant-gas coefficient, for roots (PGC_r)	$I0^5$-$I0^6$	$3xI0^5$	$N(NH_3)$, ect.

antity. In free state in porous space of loose covers are presented 0,00I-0,I% of the corresponding elements or compounds - gaseous migrants accumulated by plants. By the calculations these free gaseous forms bring significantly low part ($<$ I0%) than sorbed formsof the corresponding gaseous compound which are available for the intensive accumulation by the roots of plants.

Also these approximate data must be specified they show that the sorbed forms of water and gaseous migrants which are fastened and stabilized by the absorbtion complex of the loose covers may be the main sources of their quantity observed in plants. At the same time these calculations show that in the ways of the water and gaseous migrants always takes place the forming of the more stable than in water and gaseous phases secondary lithohydrogeochemical and lithoatmogeochemical haloes and anomalies. They render great influence on the biogeochemical haloes and anomalies forming stipulated by them and demand special investigations in proceeding of complex geochemical investigations of drilling cores cuts with biogeochemical anomalies in the squares covered by thick allochtonous covers.

The practical advisability of choosing three main models of biogeochemical explorations and their combinations is stipulated in the first by their various depth of revealing mineral deposits (see fig. I): 2-20 to 70 m for lithobiogeochemical, 20-200 to I000 m for hydrobiogeochemical and from tens to I000-2000 meters for atmobiogeochemical exploration (Kovalevskii, I984, I985 - in Russian). In connection with various main indicator elements, various sources of their ore biogeochemical haloes and also by various depth of the mineral deposits revealing which is determined in the main by the extent of upward migration of chemical elements in corresponding phase, methods of proceeding and expecially of interpretation and detalization of the revealed biogeochemical anomalies of these types by combined geological, geochemical and geophysical investigations are characterized by the significant peculiarity.

In conditions when plant roots reach ore bodies and their primary and residual eluvial haloes lithobiogeochemical haloes of some ore elements (Mo, Au, Ag, Be, Pb) in the non-barrier plant species and parts may be interpreted quantitatively. By corresponding quanti-

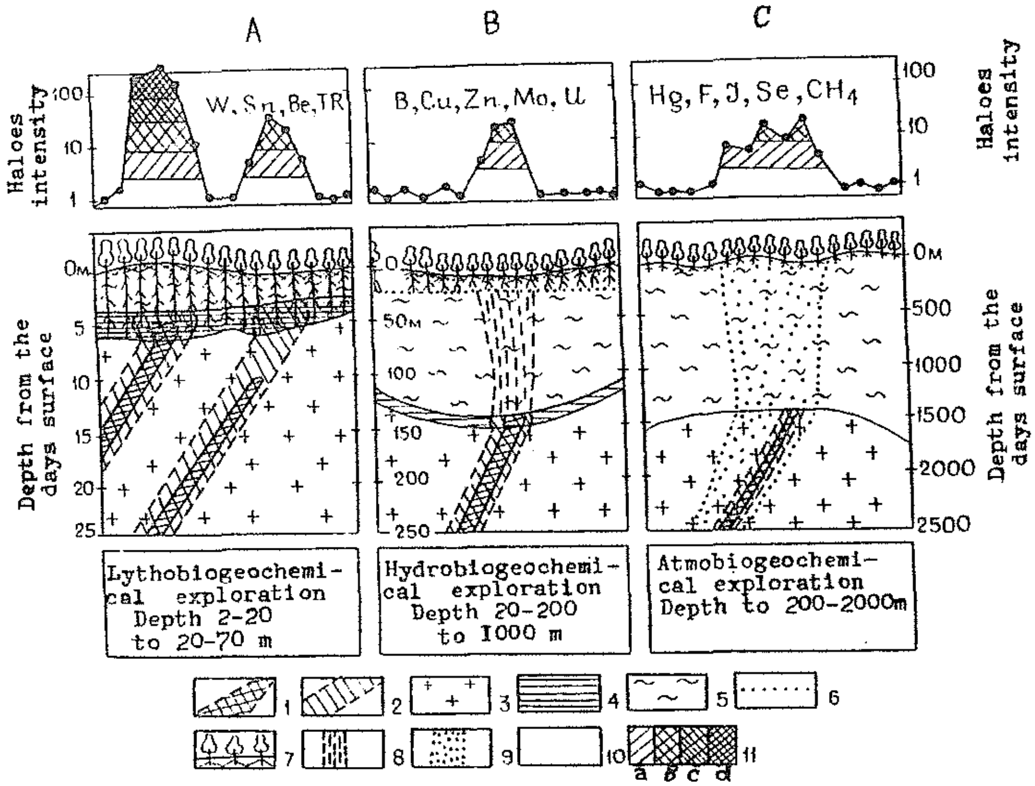

Fig. I. Main models of the biogeochemical exploration: A - lithobiogeochemical, B - hydrobiogeochemical, C - atmobiogeochemical.

I - the ore bodies; 2 - their primary haloes; 3 - the native rocks; 4 - the eluvium; 5 - the allochtonous covers; 6 - the water-bearing horizon; 7 - the plants; 8 - the ore hydrogeochemical haloes; 9 - the ore atmobiogeochemical haloes; IO - the background contents of the indicator elements on profiles; II - their anomal concentrations of various intensities: a - weak (3-IO backgrounds), b - middle (IO-30 backgrounds), c - intensive (30-IOO backgrounds), d - very intensive (> IOO backgrounds).

ty-informative bioobjects the probable contents of ore elements may be determined in native rocks and ores (Kovalevskii, I982, I984, I988 a, b - in Russian; Kovalevskii, I979 a, b, I987 - in English). At the same time it was established that in conditions investigated the quantitative interpretation of easily leachable ore elements is impossible. The examples of such leachable ore elements are zinc and copper. The principal possibilities of quantitative interpretation of the results of the lithobiogeochemical exploration in practice of exploration and prospecting works demand the revealing and investigation the conditions when close quantitative connection between haloes in the nonbarrier bioobjects and in the ore bodies takes place. On the actual data the quantitative interpretation of lithobiogeochemical data is possible when the thickness of the screening loose covers is not exceed 2-20 m. It is evident that the list of the ore elements for which is possible the quantitative interpretation of their lithobiogeochemical haloes would be increased significantly in the near future. The methods of such quantitative interpretation demand the elaboration for concrete geological and landscape conditions. Spheres of the practical application of these methods demand the special investigations.

The practice of such methods elaboration for the lithobiogeochemical haloes shows that it is necessary to determine and to use the next quantitative parameters: I) the length of the channel probes which the most exactly correspond to studied plant species and parts; 2) the values of plant-ore coefficients (POC) for main ore elements in open outcrops of the ore bodies various mineral types; 3) corrective coefficients for the weakening of biogeochemical haloes by slope and allochtonous covers. It is advisable to conduct the quantitative interpretation of lithobiogeochemical haloes in 2-3 stages by the methods of the first, the second and the third approximations. The aims of this quantitative interpretation are the most exact contouring of the rather shallow buried ore bodies and the evaluation of the prognostic resources of the useful components at the level of their erosion cut with the very cautious extrapolation of these data at a depth.

As it is seen from the table 2, the least value of the standard muliplier POC ($\varepsilon^{\pm I}$)

Table 2. THE CHARACTERISTICS OF THE MOLYBDENUM PLANT-ORE COEFFICIENTS (POC) FOR CHANNEL PROBES OF VARIOUS LENGTH

The length of the channel probes, m	Bioobjects nonbarrier to molybdenum								
	the lower parts of Rhododendron dahurica stems			the shoots of the herbal Leguminosae			the suberised cones of Pinus silvestris		
	n	POC$\pm\sigma$	$\varepsilon^{\pm I}$	n	POC$\pm\sigma$	$\varepsilon^{\pm I}$	n	POC$\pm\sigma$	$\varepsilon^{\pm I}$
2	I2	2,4$\pm$0,I4	I,63	I8	I,52$\pm$0,I0	I,74	34	0,84$\pm$0,05	I,56
4	I2	2,0$\pm$0,I6	I,7I	I8	I,6I$\pm$0,I2	I,83	34	0,8I$\pm$0,06	I,50
6	I2	I,9$\pm$0,I9	I,84	I8	I,50$\pm$0,I5	I,92	34	0,78$\pm$0,08	I,64
I0	I2	2,I$\pm$0,26	2,04	I6	I,44$\pm$0,I9	2,I8	28	0,72$\pm$0,II	I,74
The average		2,I$\pm$0,09			I,52$\pm$0,08			0,79$\pm$0,04	
RCBO		2,7$\pm$0,I			I,9$\pm$0,I			I,0 (standard)	

takes place for the lower parts of Rhododendron dahurica stems and for the shoots of the herbal Leguminosae (Vicia unijuga, Lathyrus humilis, Astragalus membranaceus) for the 2 m channel probes; and for pine (Pinus silvestris) suberized cones — for the 4 m channel probes. By the interpolation of the data for pine cones the minimal value of ε will take place for the 3 m channel probes. By the extrapolation of the data for the first two bioobjects the minimal value of ε would take place for the channel probes with the length than lesser 2 m. From the table 2 it is also seen that the POC values - the main quantitative parameter for the interpretation of the lithobiogeochemical anomalies are not similar for various nonbarrier bioobjects. It is necessary to have not lesser than I0-30 comparisons of biogeochemical and channel probes for the determination of POC with the relative error ±5-I0%.

The correction coefficients on the weakening of the biogeochemical haloes are determined by the data of the empirical dependences of the biogeochemical haloes relative intensity from the thickness of the screening loose covers. The examples of these dependences are illustrated in fig. 2. In this figure it is seen that the full weakening of the molybdenum biogeochemical haloes takes place in various plant species and parts and in various thickness of the screening eolian cover. In fig. 2 it is also seen that by the contents of molybdenum in various bioobject sampled simultaneously is possible the determination of the screening cover thickness, i.e. the conduction of the biogeochemical coring (carotage).

Fig. 3 illustrates visible by an eye a good correlation between contents of molybdenum in the shoots of leguminous plants and in the channel probes from the trenches. This correlation is characterized by the following quantitative parameters: POC=I,52$\pm$ 0,08, the value of the linear correlation coefficient - r=0,89 and the value of the standard multiplier ε =I,74$^{\pm I}$ when using the semi-quantitative emission spectral analyse with the standard multiplier ε =I,4$^{\pm I}$.

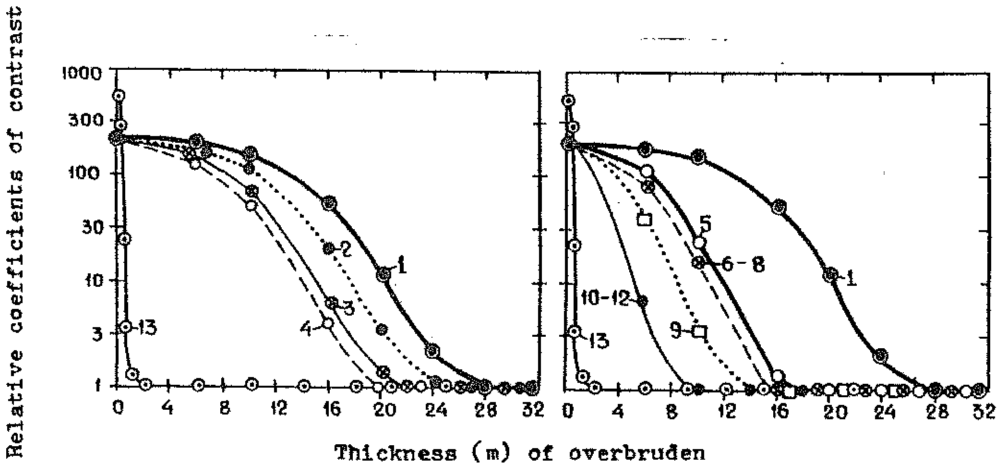

Fig. 2. The dependence of the relative intensity (the relation of the anomal concentrationt to the background) biogeochemical and soil-geochemical haloes from the thickness of the ecraning aeolium cover above the ore bodies of the molybdenum deposits with ~0,I% of molybdenum.

I-4 - parts of the Rhododendron dahurica: I - the lower parts of the stems; 2 - the upper parts of the stems; 3 - the sprouts, 4 - the leaves with sprouts; 5 - the suberized cones of pine (Pinus silvestris) from the forest litter; 6-II - the shoots of the herbaceous plants: 6 - Vicia unijuga; 7 - Vicia sepium; 8 - Vicia cracca; 9 - Astragalus membranaceus; I0 - Artemisia Gmelini; II - Artemisia vulgaris; I2 - the bast of Betula platyphylla; I3 - soil horizon B/C on the depth 0,25-0,35 m.

In fig.3b it is shown that the correlation between contents of molybdenum in plants and in channel probes increases if the content of molybdenum in channel probes is compared with not observed but with the anomal contents of molybdenum in the same leguminous plants- $C_a=C_o-C_b$, where C_a, C_o, C_b are - the anomal, the observed and the background contents of molybdenum in plants. This improvement of the correlation in the system: "the plants - the rocks" may be explained by the fact that in the conditions of the not deeply beryed ore bodies C_a characterizes the accumulation of the studied chemical elements mostly from the lower parts of the rootinhabited zone. At the same time C_b characterizes the accumulation of molybdenum from the upper parts of the rootinhabited zone where the main quantity of sucking roots is situated both in the background and above the ore bodies. That is why we recommend the wide using of the anomal contents - C_a of the main indicator elements in the interpretation of biogeochemical anomalies. This interpretation method has the special significance for the low contrast biogeochemical anomalies as for the high contrast anomalies with contrast coefficient - $CC \geqslant 20$ the values of C_b may be neglected.

The above discussed methods of the lithobiogeochemical haloes and anomalies quantitative interpretation are described in the second edition of the author's monograph "Biogeochemical Exploration for Mineral Deposits" (Kovalevskii, I984 - in Russian; I987 - in English) and in the paper (Kovalevskii, I988b - in Russian).

The quantitative interpretation of hydrobiogeochemical data for the elements - intensive water migrants is advisable in rare cases and only in the conditions when it is possible for the corresponding hydrobiogeochemical haloes (Kolotov et al., I983). The elaboration of semi-quantitative interpretation methods for hydrobiogeochemical haloes and anomalies of high intensity may have a great practical significance and the investigations in this direction are very perspective.

The quantitative interpretation of the atmobiogeochemical anomalies should be considered impossible. It is stipulated by the fact that by the contemporary theoretical notions is impossible the quantitative interpretation of the atmogeochemical haloes of even the direct indicators of corresponding deposits: mercury, sulphur, selenium, radon, methane and

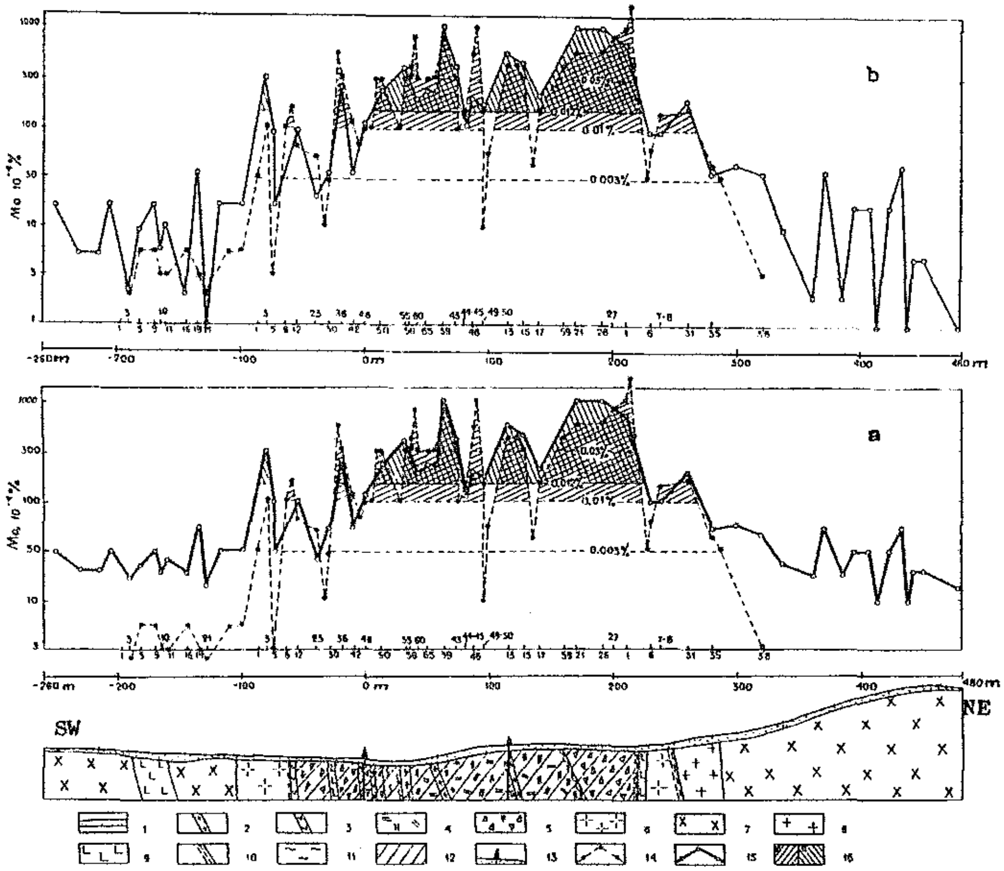

Fig. 3. The comparison of the observed (a) and the truly-anomalous (b) molybdenum contents in the ash of the leguminous plants with the results of the channel sampling in the watershaded part of the molybdenum deposit.

I - quarternary undissected deposits: aeolian sands and sandy loam, deluvial-eluvial formations.

Subvolcanic Sogotinsky Complex (P_2); 2 - dikes of microgranites and syenites; 3 - dikes of syenite-porphyries, orthophyres and syenite-aplites; 4 - mineralized extrusive polymictic breccia on a cement of trachyliparitic porphyres; 5 - mineralized monomictic explosive breccia and brecciated differences of country rock.

Bichursky Complex (PZ_3): 6 - granites and granosyenites, medium graned, leucocratic porphyzaceous; 7 - syenites and quartz-syenites, coarse-graned and inequigranular; 8 - biotitic granites, medium graned.

Dzidinsky Complex (PZ_I): 9 - xenoliths of diorites, syenite-diorites and microdiorites.

Ruptures: IO - zones of crush and brecciation; II - zones of shist formation and milonitization; I2- ore stockwork; I3 - the drill-holes; I4-I5 - molybdenum contents: I4 - in channel probes of the rocks from trenches, I5 - in plant ash of the shoots of herbaceous leguminous plants: Vicia unijuga, Vicia sepium, Vicia cracca; I6 - ore anomalies of molybdenum: a - in the rocks, b - in the plants.

other elements and compounds - gaseous migrants. The possibilities of the semiquantitative interpretation of the atmobiogeochemical anomalies are limited. They demand the special investigations. In the last years the practical significance have the mercurybiogeochemical exploration for ore, nonmetal, oil and gas deposits (Kovalevskii, I983, I984, I985, I989; Lukashev, Gurevich-Dobrovol'skaya, I986; Radchenko, I982 - in Russian; Kovalevskii, I986, I987; Warren et al., I983, I984 - in English). The atmobiogeochemical exploration for oil and gas deposits by the methane and other hydrocarbons in plants should be considered very perspective (Stadnik, I984 - in Russian).

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BIOGEOCHEMICAL PROSPECTING FOR SILVER ORE VEINED BODIES AND DEPOSITS

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The bioobjects nonbarrier to high concentrations of silver in the rootinhabited zone were revealed in the first stage of the investigations (Kovalevskii, Kovalevskaya, 1989). They are: the wood of old including rotten stumps of Pinus silvestris and Larix dahurica with relative contents in these biological objects (RCBO) taken as a standard equal to I,0 and suberized cones of pine from the forest litter (RCBO=0,I, correction xI0).

Detailed biogeochemical survey on the crossed profiles with the intervals between the plant samples I-3 m was done in the square I,2 km^2 with the two early known silver ore occurrences. For the securing of such little intervals between samples they were taken with the deviations from the profiles up to I0-30 m, i.e. in the stripes 20-60 m width. I2450 biogeochemical samples of plants and 2260 lithogeochemical samples of soils, rocks and ores were investigated.

The very intricate biogeochemical field of silver in the nonbarrier bioobjects was revealed. The maximal concentrations of silver in the pine stump wood ash were unique - up to I000-3000 ppm in the background 0,7 ppm. After standartization with the help of plant-rock (PRC) and plant-ore (POC) coefficients this high anomal field became significantly more simple and interpetable. The supposedly ore biogeochemical anomalies (SOBA) were taken with minimal content 70 ppm in the stump wood of pine and larix and 7 in pine cones proceeded from 50 ppm of silver in ores and POC=I,4 for this content in ore. The supposedly nearore biogeochemical anomalies (SNOBA) were taken with 36 ppm of silver in the stump wood and 3,6 ppm in the suberized pine cones which correspond to 20 ppm in rocks, PRC=I,8. In the investigated biogeochemical field were revealed I09 very local SOBA and more I50 local SNOBA of silver mostly of unknown early north-north-east direction. They are divided into 9 geochemical types. The most investigated are three types of silver SOBA: leaden (Pb:Ag=3-30 up to I00), lowleaden (Pb:Ag=0,4-2,5, close to I,0 in the average), nonleaden (Pb:Ag=0,03-0,35, close to 0,I in the average with adsence of statistically trustworthy anomalies of lead).

In the north zone of the 42 SOBA thickening 330 m width these three geochemical types form the approximately simmetrical zoning. Leaden SOBA of silver are situated in the center, lowleaden SOBA of silver conture them from east and west and nonleaden SOBA of silver are situated in the periphery. The quantity of nonleaden SOBA and SNOBA of silver in the west part of the examined cut is 7 and in the east part amount to one. In opening by ditches of various types SOBA of silver were revealed respectively low quartz galena silver, quartz-galena silver and quartz-low sulphur gold-silver mineralization. In the third type of mineralization was discovered the visible native gold with size up to 0,2 mm. SOBA with concentrations of silver 70-3000 ppm are very local and have the width I-8 m. In opening by ditches under them practically without displacing 2-6 thin silver ore bodies or silver-bearing zones with content of silver more than I0 ppm in the background ~0,I ppm were revealed. These bodies and zones are divided by intervals with higher content of silver 0,I-0,8 ppm. By the preliminary data biogeochemical samples of pine correspond to the channel probes of rocks and ores close to 2 m length.

In the east zone of thickening 240 m width all 35 revealed SOBA of silver are situated approximately parallel to 6 buldozer ditches 3-6 m depth with I00-200 m between them. One of these SOBA is confirmed by ore samples with concentration of silver up to 2000 ppm. These ditches were diged out for opening of soil-geochemical anomalies of silver and lead. The example of this zone of thickening SOBA revealing shows that with the help of the detailed biogeochemical prospecting in scales I:500-I:5000 revealing of not only separate veined silver ore bodies but also zones of their thickening with tens of thin veins and veined zones between rare ditches and drilling cores is possible.

The most of the revealed SOBA are not accompanied by soil anomalies (SA). On the revealed SA silver contents are usually in tens and hundreds, sometimes in thousands times lower than on SOBA (see fig.I). This is because of the very significant weakening SA in

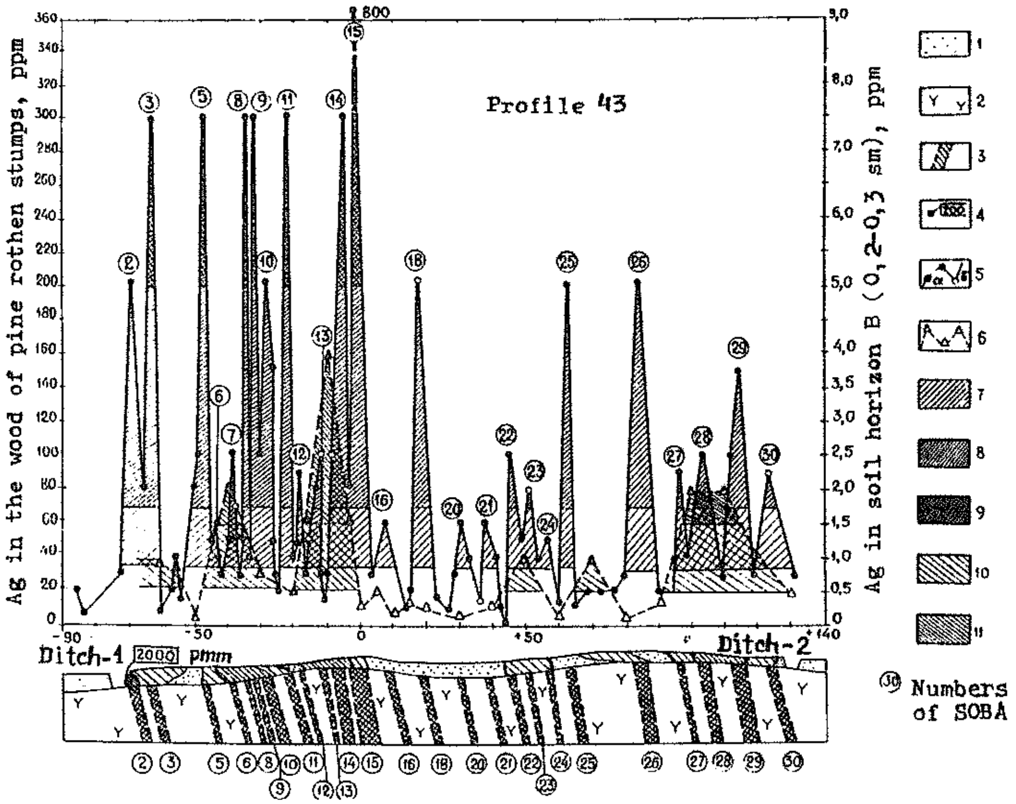

Fig. I. The distribution of silver along profile 43 (the southern taiga landscape, the pine forests).

I - loose sandy cover; 2 - quartz syenites; 3 - the supposedly ore biogeochemical anomalies (SOPA) with concentrations of silver 70-800 ppm in the plants ash (the numerals in the circles - their numbers), 4 - the content of silver (in ppm) in an eluvio-deluvium of the ditch number I; 5-6 - the distribution diagram of silver: 5 - in the plant ash: a - in the rotten stumps of pine (Pinus silvestris), b - in the cones of pine, 6 - in the horizon B, 0,2-0,3 m depth; 7-9 - supposedly nearore (36-70 ppm), ore (70-200 ppm) (the numerals in the circles - their numbers) and rich ore (200-800 ppm) biogeochemical anomalies of silver; IO-II - minimal (0,5-I,5 ppm) and middle intensive (I,6-4 ppm) soil-geochemical anomalies of silver.

the passage from ore bodies to soils. In connection with this SA in the difference from SOBA in investigated conditions cannot be interpreted quantitatively with evaluation of silver geological prognostic resourses.

The investigated part of silver biogeochemical field may be depleted by the model of the original wave field. In one of their cuts three zones of SOBA thickening are interchanged and contoured by the zones of their absence. This wave structure is seen more distinctly in analyzing of biogeochemical anomalies of the haloforming elements complex (Ag, Au,Pt, Pb, Cu, Zn, Hg, Cd, Na, Fe, Mn). This model of biogeochemical field reminds the wave field of thickening and weeking (thinning) out of tectonic zones written by V.V.Bogatzkii (I986).

Data testify that in investigated conditions revealing, contouring and mapping of veined silver ore bodies and evaluation of geologic prognostic resources may be done with the help of nonbarrier bioobjects. This method may be named the Nonbarrier Biogeochemical Prospecting (NBP) of day surface of known and proposed silver ore deposits, silver-bearing ore fields and revealed litho-, hydro- and biogeochemical anomalies of silver and their indicators. The concrete NBP methods must be elaborated for various landscape, geological and metallogenic conditions. When various geochemical types of SOBA are presented as it takes place in the investigated square the preliminary mineralogical and technological mapping of silver ore deposits and silver-bearing zones may be done. The correlation between silver and their companions and also the values of PRC of silver and their companions in the biogeochemical samples may be used for this purpose.

Our experience of NBP for silver ore bodies and deposits may suggest the next peculiarities.

I. The revealing of separate silver ore veined bodies up to 2 m thick is possible only when the sufficient little step of sampling (I-2 m) of nonbarrier and practically nonbarrier bioobjects is used. These bioobjects must be revealed for concrete conditions of exploration.

2. For the garanteeing of such little step the method of striped sampling must be used when sampling of the choosen bioobjects takes place in the stripes 20-60 m width i.e. in the distance up to I0-30 m in both sides of profiles.

3. For the drawing up of the detailed biogeochemical maps it is necessary to provide the exact binding of biogeochemical samples to the profiles fastened in the investigated squares by pegs. This is a special problem which demands the conformable expenditures. The permissible errors of such binding may be ±0,I-0,2 m as the biogeochemical samples of woody plants correspond to the channel probes of rocks and ores close to 2 m length.

4. It is necessary to use the crossed system of profiles for the determination of the corret directions of SOBA and SNOBA. When using the parallel net of the profiles as it is usually the rough mistakes may be possible. Such mistakes took place at the beginning of our works in the investigated silver-bearing field. In the most complicated parts of the biogeochemical fields it is expedient to provide the continuous biogeochemical sampling by the net 2x2 - 5x5 m in order to exclude the possible mistakes. The complexing of such biogeochemical sampling with micromagnetic, microelectric, microbiolocation and other surveys by the net 5x5 - I0xI0 m is expedient.

5. For the revealing, contouring and mapping of the leaden SOBA of silver it is expedient to use the high productive roentgen-biogeochemical surveys by determinations of lead in the trunk cork of living trees or their stumps with the minimal possible step between points of investigations on profiles and measuring in the beginning all plant species situated in the supposed and then in the revealed directions of anomalies expansion. After lead which is the most reliable indicator for silver by the RBS it is advisable to determine Zn, Cu, Na, Fe, Mn, which have relatively high background contents determined with the help of contemporary roentgen-radiometric analysers (RRA). Till the construction of the RRA with the sensitivity sufficient for the revealing SNOBA of silver immediately in the points of investigations the contemporary RRA may by used for the determinations of silver in the ash of the stump wood and the wood of living plants as after ashing their concentrations is increased in I00-500 times. It is advisable to organize the system of the week cirle: Sunday - sampling, Monday - ashing in the field conditions, Wednesday - measuring of the ashed samples with the help of RRA, Saturday - detalization of the revealing anomalies, Friday - opening the SOBA of silver by ditches and their measuring by the help of RRA. The first two main stages of this system are usual in our persistent field works. The using of the high productive RRA determinations of the indicator elements per hundreds - up to I000 points of investigations for a day has the great perspectives in the exploration and prospecting for silver and other deposits.

6. It is necessary to use only nonbarrier bioobjects for the quantitative evaluation of the prognostic geological resources of silver in the SOBA. Practically nonbarrier bioobjects with the limit of silver accumulation exceed the background 30-300, I00 times in the average are unfit for this purpose. Such nonbarrier bioobjects in the investigated silver-bearing field are only three: the Pinus silvestris wood of the old, rotten stumps and the suberized cones and the Larix dahurica wood of the old, rotten stumps.

7. For the revealing of the most informative nonbarrier and practically nonbarrier, weakly barrier bioobjects of any plant specie it is expedient to examine the concentrational dependences in the system: the most informative known bioobject of the studied plant specie - the not studyed early parts of the same specie sampled simultaneously. The results of such system investigation for pine (Pinus silvestris) are demonstrated in fig. 2.

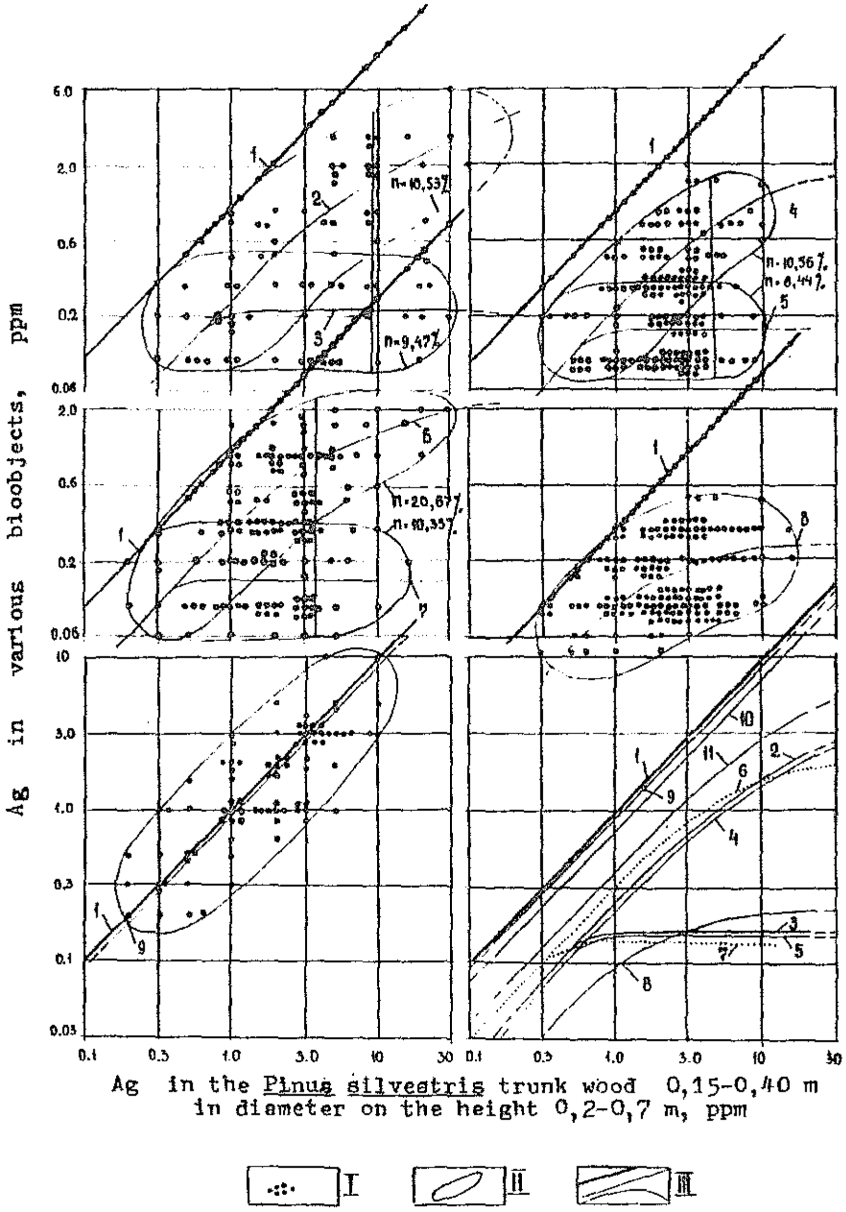

Fig. 2. Fields of points and lines best fit for the concentration dependence of Ag in the system: the known nonbarrier bioobject - the investigated bioobjects in the high anomaly square in the landscape of the southern taiga.

I-II - numbers of bioobjects: I - lower parts of the living pine (Pinus silvestris) trunk wood an the height 0,2-0,7 m; 2 and 4 - the close-to-backgroundbarrier cork of stumps and living pines 0,I5-0,4 m in diameter; 3 and 5 - backgroundbarrier cork of stumps and living pines 0,I5-0,4 m in diameter; 6-7 - close-to-backgroundbarrier and backgroundbarrier suberized pine cones; 8 - the cork with bast of trunk pine 0,I5-0,4 m in diameter; 9 - the wood of trunks 0,I5-0,4 m in diameter at the height 0,7-I,2 m; I0-II - the wood of thin trunks 0,04-0,09 m in diameter at the height 0,2-I,0 m and 3-6 m.

I - factual points; II - the field points contours; III - the lines of the best fit.

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THE PRINCIPLES OF GEOCHEMICAL MAPPING OF GRANITOIDS WITH FORECASTING AIMS

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The geochemical mapping in geology is the base of the contemporary methods of forecasting ore deposits as well as ecological analysis of the Earth surface.

The forecast geochemical mapping of granitoids should be based on existing genetic relationships between granitoids and complex rare-metal mineralization represented by the ores of tin, tungsten, molybdenum and typical rare-metallic ore - of lithium, beryllium, tantalum, niobium, etc. The indicators of rare-metal mineralization connected with granites are so-called granitophyle elements. The main of them are F, B, Li, Rb, Be, Sn, W, Mo (to lesser extent Pb, Ta, Nb, U, Th, Y, Yb), which largerly concentrated in ore-bearing granites.

On the whole, the degree of concentration of granitophyle elements in granites is correlated with intensity of rare-metal mineralization, connected with these granites /Kozlov, 1985/.

The nessesary condition for realization of the potential ore-bearing capacity of rare-metal granite intrusions is their magmatic differentiation. It intensifies the degree of concentration of granitophyle elements in final melts and as a result, in products of their crystallization, i.e. leucogranites of the late intrusive phases, the bodies of which associated directly with the most productive rare-metal mineralization. Simultaneously, such leucogranites have lowered concentrations of Sr and Ba, while low concentrations of these non-granitophyle elements are indicative of ore-bearing granites, too.

From said above it is obvious, why the geochemical mapping of granitoids should necessarily reflect the level of concentration of granitophyle elements as well as Sr and Ba.

But in contemporary practice this condition is normally not taken into account. In most cases, in granitoids the concentrations of rare earth elements, siderophyle or chalcophyle elements are analysed. However, relative to the rare-metal ore capacity of granites only rare earth elements may be of secondary significance, but siderophyle elements (Ti, V, Cr, Co, Ni) and mean chalcophyle elements have nothing to do with this.

Considering the above facts, the methods of assessment of granitophyle elements concentration in granites and their comparative ore-bearing capacity have been developed. These methods may be used for geologo-geochemical mapping of granitoids. They are based on the concentrations of granitophyle elements in investigated granites normalized to clarke concentrations of these elements in granites as is common for prospecting geochemistry. Using these normalized data, the geochemical features of each granite variety may be represented as Element formulas and Index of concentration (INC) which characterize the anomaly of each granite variety in number of clarkes of each granitophyle element and their sum (Table 1).

It is shown, that if INC is calculated for the constant group of the granitophyle elements (F,B,Li,Rb,Be,Sn,W,Mo,Pb) - the dispersed rare-metal mineralization takes place in connection with such intrusive bodies. INC in these granites range from 4 to 6 clarkes; such granites were named subrare-metal.

Table 1. The estimation of element formulas and INC

Elements	%			ppm									
	Na	K	F	Li	Rb	Be	Sr	Ba	B	Sn	W	Zn	Pb
Clarke concentration of granites	2.8	3.3	0.08	40	170	3	300	800	15	3	1.5	50	20
Plumasitic rare-metal leucogranites of Transbaikalia	2.6	3.7	0.15	100	290	6.5	170	450	31	9.3	2.8	47	31
Calculation of clarke of concentration (CC) for rare-metal leucogranites of Transbaikalia	0.9	1.1	1.9	2.5	1.7	2.2	0.6	0.6	2	3.1	1.9	1	1.5
Element formula of rare-metal leucogranites of Transbaikalia	$\frac{\text{Sn } 3.1\text{-Li } 2.5\text{-Be } 2.2\text{-B } 2\text{-F } 1.9\text{-W } 1.9\text{-Rb } 1.7\text{-Pb } 1.5}{\text{Sr } 0.6\text{-Ba } 0.6}$												
Calculation formula of INC	$INC = CC_1+CC_2+CC_3+ \ldots +CC_n - n$, where n is a number of granitophyle elements												
Calculation of INC for rare-metal leucogranites of Transbaikalia	$INC = 3.1+2.5+2.2+2+1.9+1.9+1.7+1.5-8 = +8.8$ clarks of granitophyle elements, which number $n = 8$												

The numerous rare-metal ore occurrences, rarely deposits, are connected with the bodies of the rare-metal granites with INC 8-12 clarkes and most numerous rare-metal ore occurrences and productive deposits are related to the bodies of the ultrarare-metal granites with INC 20-50 clarkes.

Thus, in application to the problem of geochemical mapping the element formulas and INC may be used for legend. This allows to make the united polyelement map instead of numerous monoelement maps which are usually used in the prospecting geochemistry. The boundaries between the geochemical fields of the granitoids are represented by geological boundaries between the phase-facial varieties of the granitoids. Therefore, the geological maps of granitoid massifs of corresponding scale, which show the fields of the phase-facial varieties of granites are the necessary preliminary basis for the geochemical mapping.

Owing to homogeneity of the granitoids, as well as any magmatic rocks, the representative geochemical characteristics may be obtained from 10-20 samples. So, there is no need to apply the principle of the equal number of the geochemical samples from equal square. Practically, for large-scale mapping the representative geochemical sampling of granitoid massifs may be carried out by taking 5-10 samples from each varieties of the granites shown on the geological map. It means that for small massifs there must be frequent sampling while for large massifs - the scarce sampling. As a result, the considerable decrease of sampling and analytical work is achieved and the difficulties connected with quantitative analyses of the samples are compensated by the limitation of their number.

The above said may be illustrated by some examples.

Figure 1 illustrates small-scale geologo-geochemical scheme (nearly 1:500 000) of Daurian zone of Central Transbaikal, where the granites are dominant. From geological data it follows that the mostly dominant are Paleozoic - Low Triassic granitoids ~~and granites~~ of the batholith massifs are intruded by Mesozoic leucogranite complexes which were all considered as ore-bearing. The geochemical results show considerable simplification of this geological scheme and its metallogenic interpretation. The geochemical heterogeneity of the Mesozoic leucogranites is revealed unambiguously. In extensive north range of leucogranitic massifs (No 1, 2, 9, 10, 11, 12, 13) the rare-metal granites compose only their western part (No 1-2), which corresponds to the position of the Asakan-Shumilovsky ore region with tin-tungsten mineralization. The rest massifs (No 10, 11, 12, 13) are composed of nonrare-metal leucogranites and are practically barren. From the numerous leucogranitic massifs of the south-eastern part of the Daurian zone only four, (No 3,4,5,6) are composed of typical rare-metal granites and are accompanied by rare-metal mineralization. Greater part of other massifs are not rare-metal and are barren. But they contain some bodies (No 7) composed of subrare-metal leucogranites accompanied by dispersed quartz-cassiterite-scheelite mineralization.

Figure 2 provides the results by V.K.Khrustalev on geochemical separation of the Paleozoic leucogranite massifs of the South Vitim plateau (West Transbaikal region) which are petrochemically identical. The scheme (nearly 1:200 000 scale) show that the massifs are subdivided into rare-metallic and nonrare-metallic groups, the first group spatially associated with tin mineralization.

The most representative are the results of the geochemical mapping of granitoids of the Iultin ore region of Central Chukotka (North-East of the USSR) given in Fig. 3. The granite massifs are geologically divided into ancient granodiorite-granite complex (of numerous big massifs) and late ore-bearing (tin-tungsten) granite-leucogranite complex represented by one massif and several local domes (stocks). Geochemically, the first complex is represented only by subrare-metal granitoids, including the late leucogranitic bodies, while the second - by rare-metal and ultrarare-metal granites and leucogranites. Only non-commercial mineralization is related to widespread subrare-metal and rare-metal granites and leucogranites. The commercial mineralization is closely associated with isolated stocks composed of ultrarare-metal leucogranites. Based on their geochemical peculiarities and geological setting these stocks were distinguished in the final intrusive phase of the second complex. The geochemical scheme (Fig. 3) of 1:100 000 scale demonstrates low capacity of widespread mineralization associated with all massifs and bodies of subrare-metal and rare-metal granites and indicates the importance of mapping of bodies of ultra-rare-metal granites, which in their apical zone incorporate commercial tin-tungsten mineralization.

The geochemical scheme (Fig. 4) illustrates the results of large-scale (1:50 000) geochemical mapping of the Sakhanay granite system of Central Transbaikal. In the process of magmatic differentiation of the intrusive system there are formed the phase-facial varieties of granites which differ in their rare-metallicity degree. The ultrarare-metal, which make up the apical part of the Zun-Undur satellite dome, are accompanied by mostly intensive (nearly commercial) tin-tungsten mineralization. Figure 4 illustrates the possibility of detailed geological mapping of granite massifs (Figure 4a) via geochemical mapping (Figure 4b) and simultaneously the increase of accuracy in mineralization forecast. It is evident, that numerous occurrences of mineralization which are spatially connected with subrare-metal and rare-metal granites of the main Sakhanay massif of the intrusive system are of no commercial value.

The geochemical polyelement maps of granitoid massifs, the examples of which were considered before may be used as applications to the geological maps, although ideally this must be a united geologo-geochemical map. But the complexity consists in working out the united geologo-geochemical legend.

At last, the methods suggested, may reveal the geochemical infrastructure of the granitoid fields (massifs) which may enhance the details in mapping which in fact should be geologo-geochemical. Practically, on the basis of such mapping the granite massifs may be divided into a numerous group of barren ones and poor group of ore-bearing ones. The latter may be further divided according to their potential ore-bearing degree. The geochemical mapping of separate granite massifs provides the next degree of the mapping details by revealing the geologo-geochemical infrastructure of the massifs and ultrarare-metal bodies of their late differentiates, with which the most productive rare-metallic mineralization is likely associated.

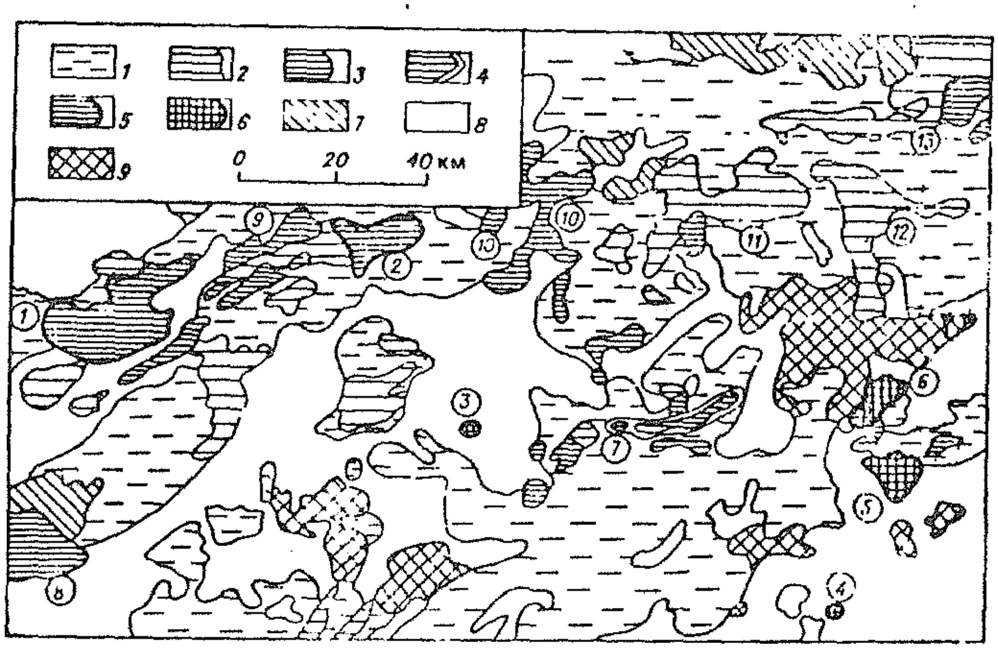

Fig. 1. The geological-geochemical scheme of the granitoid magmatism of Daurian zone of Central Transbaikalia. 1 - granodiorites and granites of late paleozoic-early mesozoic batholith massifs; 2—3 - postbatholithic intrusions of granites (2) and leucogranites (3); 4 - subrare-metal leucogranites; 5 - rare-metal leucogranite intrusions of North-west part of Daurian zone; 6 - rare-metal leucogranite intrusions of South-East part of Daurian zone; 7 - early paleozoic granitoids; 8 - sandstone-schists of paleozoic and mesozoic rocks; 9 - mesozoic dacites.

The circules are given the numbers of massifs.

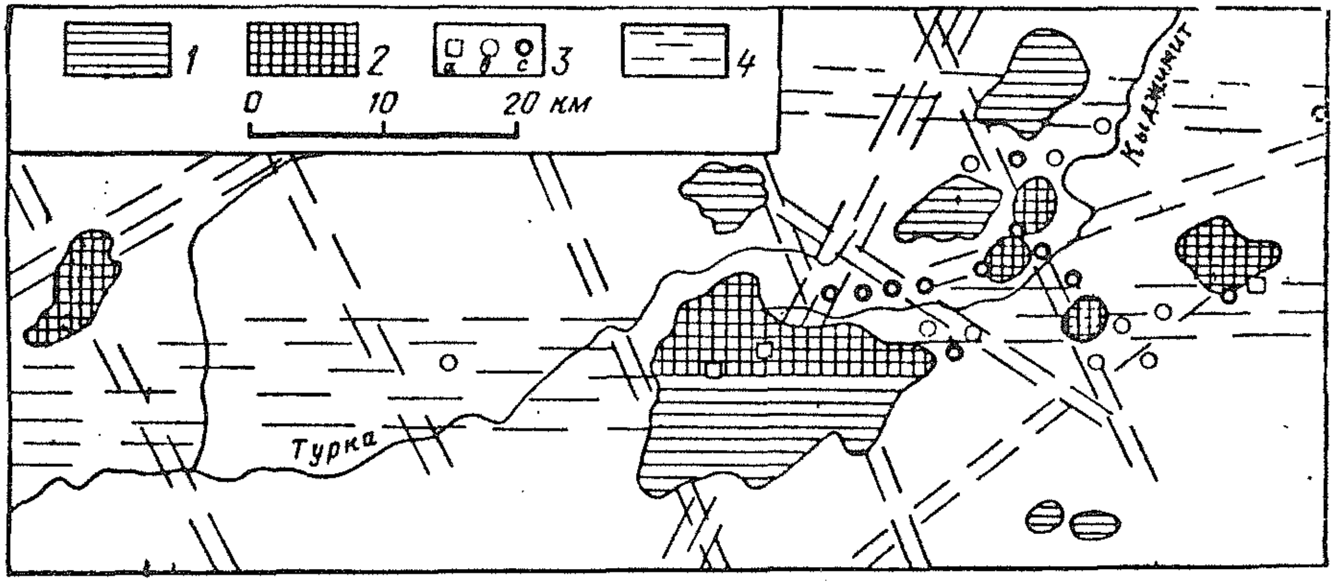

Fig.2. The geological-geochemical scheme of upper paleozoic leucogranite massifs of South Vitim plate, West Transbaikalia (by V.K.Khrustalev).
1 - nonrare-metal leucogranites; 2 - rare-metal leucogranites; 3 - the mineralization: a - tin-bearing pegmatites, b - quartz-cassiteritic, c - cassiterite-tourmaline-sulphidic, d - fault zone.

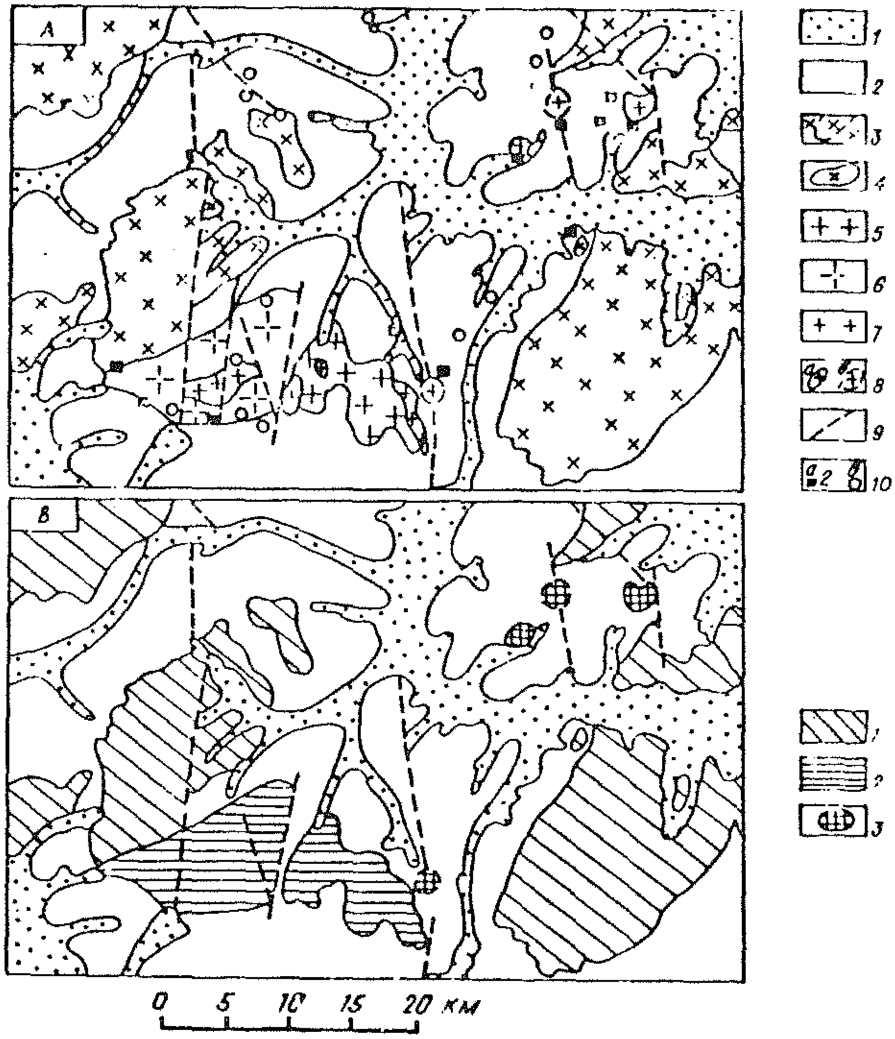

Figure 3 - Geological (A) and geochemical (B) schemes of the granitoid magmatism of Iultin ore region of Central Chukotka (North-East of USSR).
A-geological scheme: 1-Terciary sediments of river valley; 2-rock-wall sandstone-schists Triassic rocks; 3-4 early intrusive complex: 3-granodiorites, diorites and granites of the main intrusive phase, 4-granites of the late phase; 5-8-lateintrusive complex: 5-6 coarse grained granites of the main intrusive phase: 5-porphyry granite, 6-leucogranite, 7-leucogranite of the late intrusive phase, 8-leucogranites of the final intrusive phase (a-erroded, b-hidden). 9-faults, 10-quartz-cassiterite-wolframite deposits (a) and mineralizations (b).

B-Geochemical scheme, the level of rare-metall content of granites: 1-low, 2-normal, 3-high.

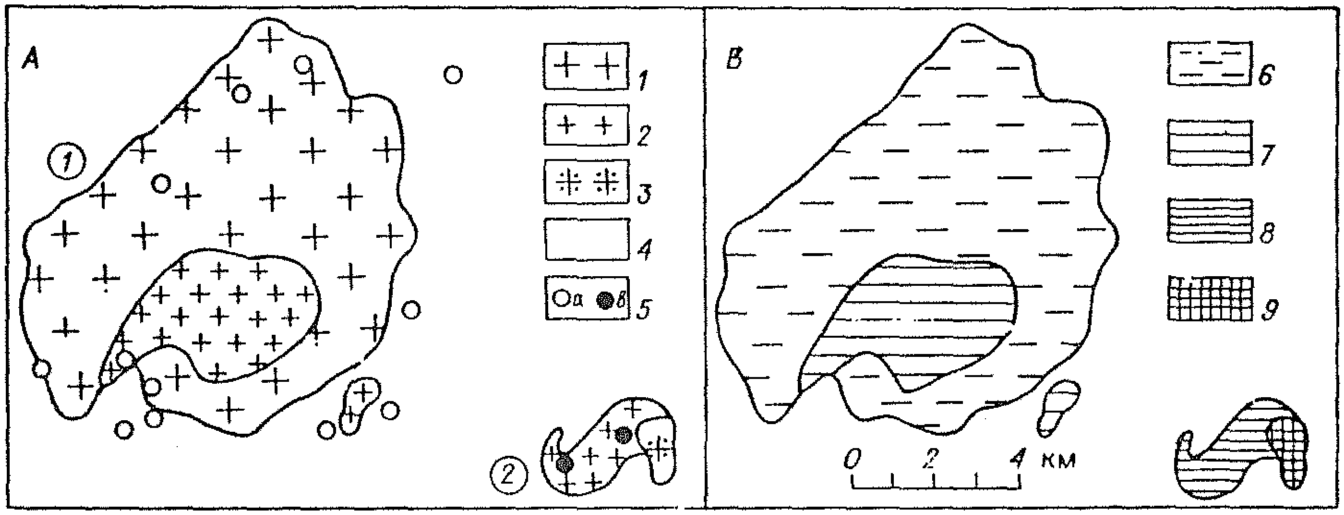

Figure 4.The geological (A) and geochemical (B) schemes of theSakhanay intrusive system of Central Transbaikalia. 1-biotite andmuscovite coarsegrained granite,2-two-micaceous mediumgrained leucogranites, 3-muscovite mediumgrained leucogranites, 4-rock-wall sandstone-schists Triassic rocks, 5-quartz-cassiterite-wolframite mineralization (a) and small deposits (b), 6-9-the level of rare-metall content in granites: 6-high, 7-9 very high (7-more than 20 clarks, 8-more than 30 clarks, 9-more than 50 clarks).

Improvements of Semi-Variograms for Geochemical Prospecting

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Most geochemical measurements show spatial dependencies between the sampling points i.e. neighbouring samples are in most cases more similar than samples far away from each other.
The variability as function of the distance between the sampling points can be completely erratic, inconsistent or more or less continuous. Variograms provide information about the regional dependencies of variables, e.g. elemental concentrations, in the space of investigation. They are the most important geostatistical tools to describe regionalized variables (De Wijs, 1951/53; Matheron,1971; Krige 1978).

In mining geostatistics ore reserve estimation by kriging is based on the information provided by the variograms. The variograms are defined as the expectation values of variance between samples at location **x** and location **(x+h)** (Journel & Huigbregts,1978)

(1) $$2\gamma(h) = E\{[Z(x+h)-Z(x)]^2\} \longrightarrow \text{theoretical}$$

which is identical to the local variogram

(2) $$2\gamma_{(v)}(h) = \frac{1}{V}\int_V [z(x+h)-z(x)]^2\,dx \longrightarrow \text{local}$$

To determine the experimental semi-variance **GAMMA** the half of the mean of the squared differences of all sample-pairs with same distance is calculated and plotted as a function of their distance.

(3) $$2\gamma^*(h) = \frac{1}{n(h)}\sum_{i=1}^{n(h)} [z(x_i+h) - z(x_i)]^2 \longrightarrow \text{experimental}$$

The data used for the calculation of the variogram have to fulfil the so called intrinsic hypothesis i.e for a vector **h** the expectation value of the differences between the values Z_t and Z_{t+h} has to be zero and their variance is finite.

Different theoretical models and combinations of models can then be fitted to the experimental curve in order to decompose different components of a phenomenon. Important functions which are fitted to experimental variograms are the linear, the potential, the logarithmical, and if gamma tends to be constant at greater distances the spherical, the exponential and the Gaussian model (Journel & Huigbregts,1978; Akin & Siemes,1988).
Most often used is the spherical model and combined spherical models. Such combined variograms are characterised by several breaks in the slope of the variance (**Fig.1**) (e.g. Taylor& Burrough,1986).
The characteristical data of a variogram are the range **a**, the nugget-effect C_0 and the sill value C_1.
If the variance increases again at higher distances a drift component is assumed (Fig.2).

Within ore deposits the intrinsic hypothesis can be often assumed.

In geochemical prospecting abrupt geological boundaries are often crossing the area of interest. Differences in the elemental concentrations of several magnitudes can occur if e.g. a mineralised vein is crossing an area of regional background. For testing this situation we have calculated variograms for a simulated sampling-grid 10000x2700m with a sampling distance of 100m in both directions. The area was assumed to have a constant background with a scatter of 30% and no trends. Three examples were calculated, where a vein striking parallel to the small side of the area, crosses the centre of the grid. The veins cover 20%,50% and 80% of the grid respectively.

The concentrations of the veins are five times the background-values.

The experimental variograms for the 3 situations are given in **Fig.3a.**

For the first 2 veins the variance increases with distance until the extension of the veins is reached.

Between this point and half of the maximum distance minus half of the veinsize the variance increases less pronounced but remarkable. At greater distances the variance decreases until a small constant value (nugget- effect of the background) is reached.

For the vein covering 80% of the area the first break in the graph occurs at 10% of the distance. Then the variance increases with increasing slope until 80% of the maximum distance.

Comparing these patterns with the theoretical ones clear differences are obvious. In most practical cases the variograms are used only for one third to the half of the maximum distance.

A second example tests the effect of different vein-positions on the shape of the variograms. Each vein covers 20% of the sampling grid. The veins are located 10%,20% and 40% from the border of the grid.

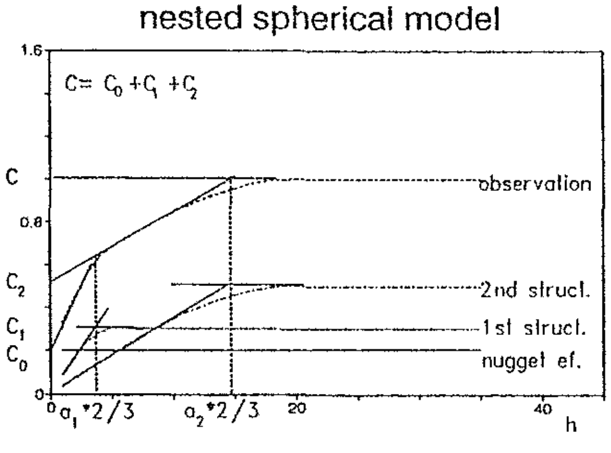


Fig.1: Nested spherical variograms

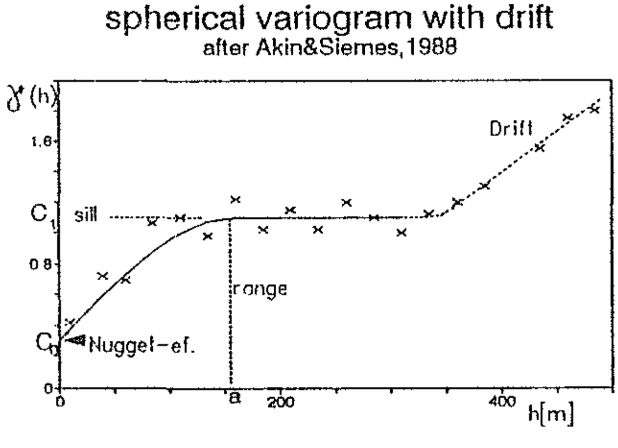
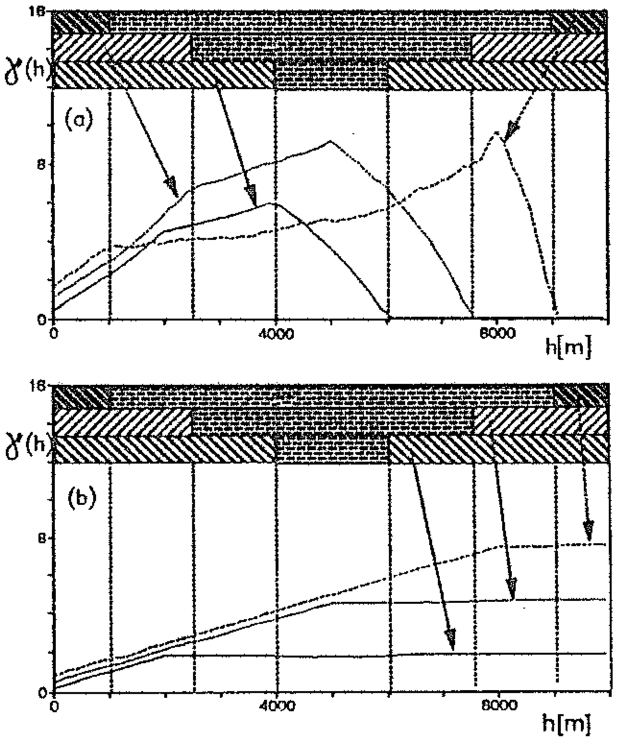


Fig.2: Experimental variogram with drift (after Akin & Siemes, 1988)



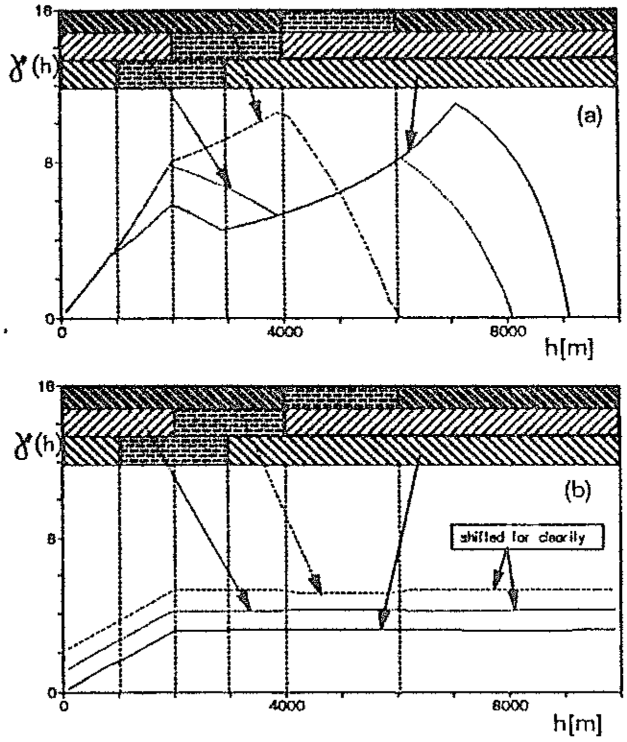
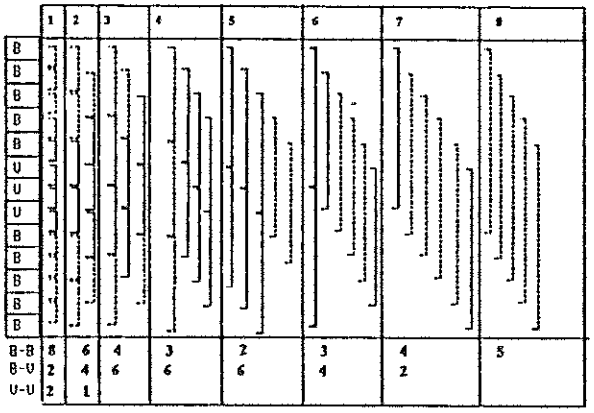


Fig.3: simulated variograms for 3 vein sizes of 2000, 5000 and 8000 m in a sampling grid of 10000m length. - a) convential form. b) extraplolating form.

Fig.4: simulated variograms for 3 vein positions of 1000, 2000 and 4000 m from the border. Veinsize = 2000 m a) convential form. b) extraplolating form.



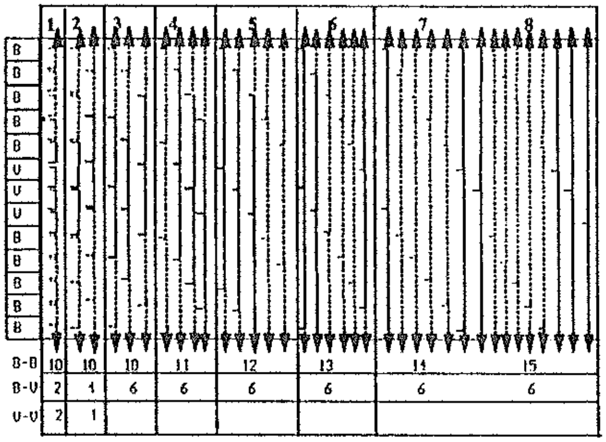


Fig.5: combination-scheme for different sample-type and distances h with number of connections - convetional form.

Fig.5: combination-scheme for different sample-type and distances h with number of connections - extrapolating form.

Using the classical calculation the resulting diagrams are quite different.

The centred vein shows the known pattern from the 20% vein in **Fig.4a**. For the vein starting 20% away from the border, the variance increases until h is equal to the veinsize. After a break the variance decreases until h is equal to 40% . A second break leads to a further increase of the variance. In natural systems this pattern would be interpreted as a hole-effect.

The most complicated diagram is shown by the vein closest to the border. The pattern is similar to the one of the second vein, but an additional break occurs in the first slope, which is normally an indication for a nested structure. The differences of these three patterns are due to linear translation i.e. in practice the shape depends on the selection of the sampling grid. Because the investigation area is always of finite size and sampling distance can not be zero, the number of pairs for the calculation of experimental variograms is not balanced across the area. All Sampling points with a **distance <= h** from one of the borders is only paired once whereas all samples inside the area are paired twice **(Fig.5)**. If a vein crosses a background area three different variances will be obtained for pairs **(x,x+h)**: a small one inside the background area, a slightly higher one for connections inside the vein and the highest for connections **background-vein**. With increasing distance the number of connections **vein-vein**, producing the intermediate variances, decrease and remains at zero when **h** exceeds the vein-size. The number of connections **background- vein**, producing the biggest variances, increase until all points inside the vein are connected with background points. The number of connections **background - background**, producing the smallest variances, decrease until **h** is greater **($x_{max}-x_{vein}$)/2** i.e. the number of **b-b** and **b-v** variances is not balanced, therefore the variance increases. For greater distances the number of connections **background - background** increases again and the number of connections **vein-background** decrease. This explains exactly the shape of the simulated variograms. If the background outside the investigation area can be assumed to be continuous , the background can be extrapolated using expectation-values of concentration and variance **(Fig.6)**. The samples with a **distance <=h** from the border are paired with expectation values outside the area and the number of pairs are adjusted to equality with using the expected variance of the background outside the area. According to this the formula to calculate the experimental variogram modifies as follows:

$$2\gamma_E^{*}(h)=\frac{1}{2n}\Big\{\sum_{i=1}^{n(h)}[z(x_i+h)-z(x_i)]^2+\sum_{i=1}^{n-n(h)}\{[z(x_i)-E(z(x_i-h))]^2+[E(z(x_{n-i+1}+h))-z(x_{n-i+1})]^2$$

$$+E[\gamma(x_{i+1}-h,x_i-h)]+E[\gamma(x_{n-i}+h,x_{n-i+1}+h)]\}+\sum_{i=1}^{n(h)/2}\{E[\gamma(x_{n+i},x_{n+i}+h)]+E[\gamma(x_{1-i},x_{1-i}-h)]\}\Big\} \qquad (4)$$

In the simplest case i.e constant background, the expectation values can be calculated from the average of the samples near the border and their variance.

Fig 3b. shows the results obtained from the modified formula for the situation of the three different veins-sizes described before. From the nugget-effect the variance increases with the distance **h** until **h** is equal to the extension of the respective vein. For greater values of **h** the variance remains constant.

The extrapolated variogram of the different vein positions produces in all three cases the same simple pattern **(Fig.4b)**: The variance increases until the distance **h** is equal to the thickness of the vein and then remains constant. Linear translation has no effect on the shape of the variogram.

Variograms of rhythmical units show in general the same patterns for the conventional calculation and the extrapolated one. In this case care has to be taken for the kind of extrapolation. Using simple averaging models the amplitude tends to decrease with increasing distances. In most cases the rhythmical sections will only cover a part of the investigation area.

The method of balancing experimental variograms using expectation values for the points outside the investigation area can clearly improve the robustness of the variogram. In most cases the resulting variograms can be more easily interpreted and adapted than conventional ones. When a drift is present in the area of investigation or rhythmical units occur close to the border these effect have to be taken into account in the calculation of the expectation values.

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The structural geochemical model of formation the Mardjan Pb-Zn deposit (Armenian SSR).

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The polyfactor modelling of ore emplacement processes in concrete objects is one of the important trends in studying the ore deposits. It is used for having the complete idea about the processes of formation of the endogenic mineralization, and gives the opportunity for concrete appraising the flanges and the deep levels of the studied units.

The present research discusses the structural geochemical model of formation of the endogenic mineralization of the Mardjan deposit within the Pamback-Zangezur structural metallogenic zone, which is located on the territory of the Armenian SSR.

1. Middle Eocene volcanites and volcanoclasts of the Upper Eocene and Oligocene, which broke via dikes of diorite-porphyries and quartz-porphyries and with the late subvolcanic bodies of andesite-basalts contents took part in the geological structure of the deposit.

During the history of the deposit formation three tectonic stages were established. The first stage confirms the time of Preorogen (P_2 - P_3), the time of formation of the Dastachert anticline. The second is the Early Orogen (P_3 - N_1^3), which is characterized by a stir-up of igneous activity and Pb-Zn mineralization formation. The third stage corresponds to the Late Orogen (N_1^3 - Q). During that time the intrusion of subvolcanic bodies of basaltoid contents and the development of realgar-auripigmental mineralization took place.

2. The Pb-Zn mineralization, which is represented by quartz-sulfide veins of N-W and bymeridian strike and have the echelon-like arrangement formed within the second tectonic stage in productive phase of pulsation character of compress strain of paleotectonic stress. The kind of this character conditioned six tectonic subphases during which the mineralile association settled near in time: 1 - quartz-pyrite; 2 - quartz-pyrite-sphalerite; 3 - quartz -sphalerite-galenite; 4 - sulphosalts; 5 - antimonite-barite; 6 - quartz-carbonate.

3. Geochemical anomalies of Pb, Cu, Zn and others elements which correspond to quartz -sulfide mineralization of the deposit were formed within the tectonic phase in the situation caused by N-W compressive strain. The last one permitted to use widely the methods of structural analysis of ore fields and deposits in restoring the condition of paleotectonic stresses in period of ore emplacement assessing the perspectives of geochemical anomalies of mineralization process.

THE APPLICATION OF REGIONAL GEOCHEMICAL MAPS IN ENVIRONMENTAL STUDIES

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INTRODUCTION

The geochemical cycle of natural and anthropogenic elements and compounds in soils and waters is part of the hydrological cycle. Consequently, the geochemical mapping of soils, and of shallow groundwaters, which are ultimately discharged into surface waters, gives a general view of the flux of mobile and non-mobile components in the geochemical cycle. The nationwide mapping of glacial till, the most common forest soil, of groundwater, stream sediments and stream water suggests and establishes natural geochemical controls and background concentrations and, in many cases, the proportion of anthropogenic increments in the flux of elements and compounds. The following presents some informative examples of the environmental interpretation of geochemical mapping results.

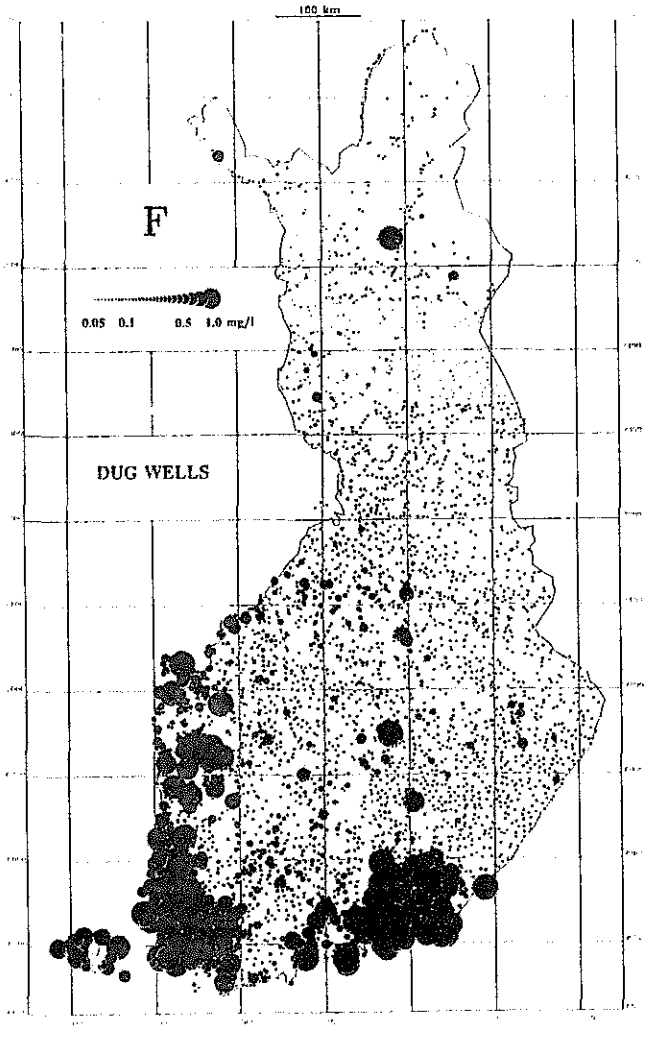


Fig. 1. Areal distribution of F concentrations in dug well waters.

EXAMPLES OF ENVIRONMENTAL INTERPRETATION

The regional distribution of F concentrations in well waters in Finland is controlled by the rapakivi granite areas, which exhibit 5-20 times higher concentrations than the rest of the country (Fig. 1). In the rapakivi areas, adequate F intake through drinking water, the main pathway of the element to man, reduces the incidence of dental caries, and excess amounts of fluorides (more than 3 mg/l) are rare. In most parts of the country F intake is too low.

Occurrences of uranium in till (Fig. 2A) and groundwater (Fig. 2B) are strictly controlled by bedrock composition, i.e. uraniferous granites and migmatites rich in granite veins in southern Finland. The areal distribution patterns of U concentrations in soils and water correlate with each other fairly well. In places, the U-anomalous areas exhibit high radon concentrations in groundwater in drilled bedrock wells. Radon gas released from water and Rn influx from soil and bedrock, in particular, may result in elevated Rn concentrations in house air, especially in dwellings founded on pervious sand and gravel deposits (D). In till soils (C) and bare bedrock (B), Rn fluxes into houses may be moderate, and in clay soils (A) there are no health risks (Fig. 3).

Nitrate pollution is one of the most troublesome threats to the purity of groundwater near the ground surface in pervious aquifer materials. The most polluted private wells occur in eastern and southeastern Finland, where old, deficiently protected wells are quite common (Fig. 4A). The regional distribution of the NO_3/Cl ratio is roughly similar to that of nitrates (Fig. 4B). Because human wastes and animal dung are rich in chlorides, the high NO_3/Cl ratio suggests that a large proportion of the pollution is due to mineral N fertilizers rather than to natural ones. The high Cl concentrations derived from relict marine salts in the groundwater of extensive western coastal areas conspicuously reduce the NO_3/Cl ratio, regardless of the proportion of nitrates and chlorides coming from natural and mineral fertilizers. The main N sources are agriculture and animal husbandry (Fig. 5), and include dung heaps and leaking feed and urine storages (A), mineral and animal fertilizers and tilling of cultivated fields (B), stores of fertilizers, oil, etc. (C), and various wastes from living quarters and houses (D).

Acidification is an alarming phenomenon currently affecting podsol soils and shallow, low-mineralized groundwaters in Finland. Symptoms of the process are a reduction in the pH level and an increasing amount of dissolved load, e.g. SO_4 concentrations. The SO_4 concentrations in spring waters are higher,

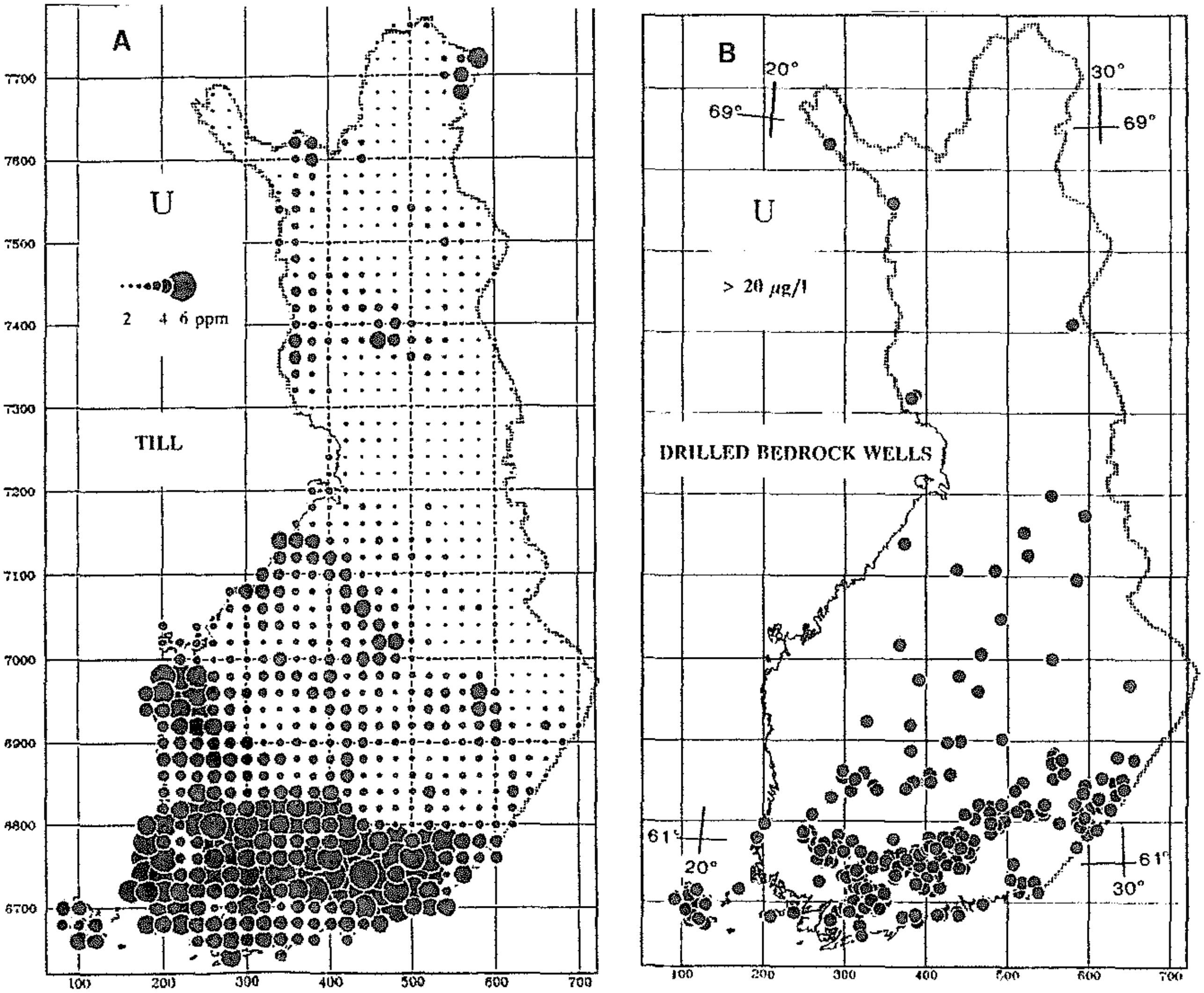


Fig. 2. Regional distribution of U concentrations in the fine fraction (<0.064 mm) of till analysed by NAA method (A) and >20 µg/l concentrations in groundwater from wells drilled into bedrock (B).

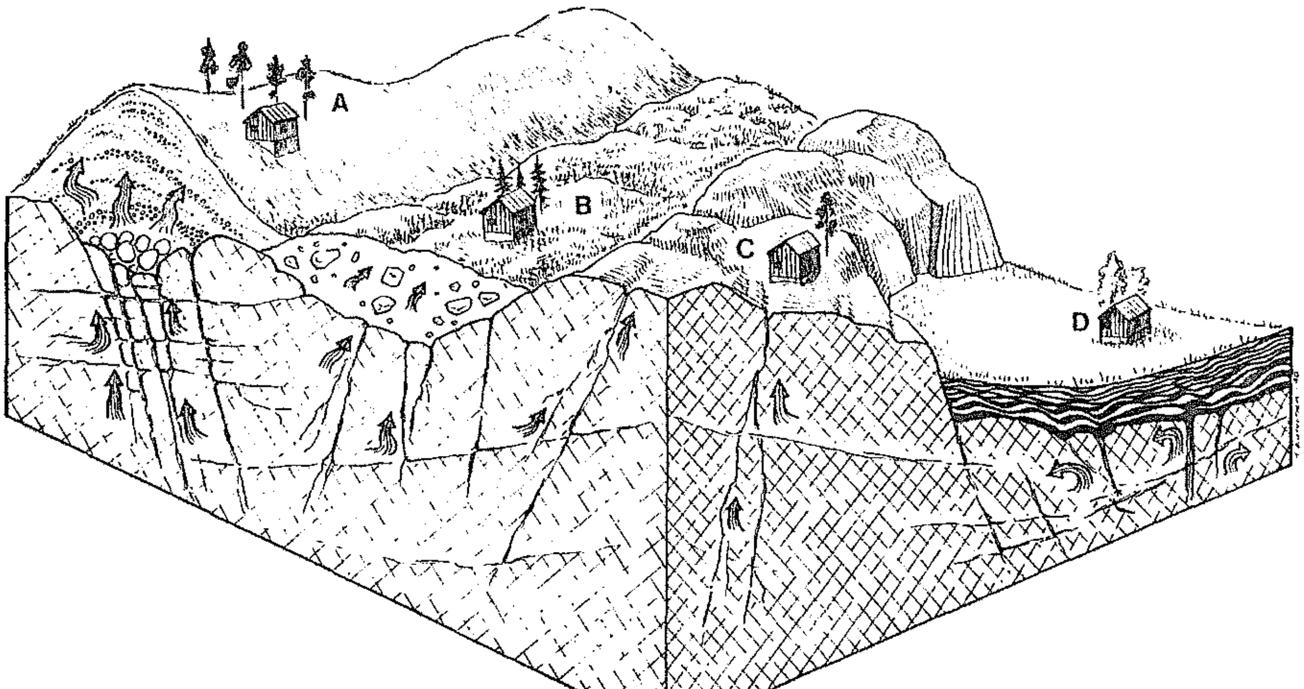


Fig. 3. Radon emanations into dwellings founded on different geological formations. A. Pervious glaciofluvial formations; B. Till; C. Bedrock outcrops; D. Clay deposits. Drawn by H. Kutvonen.

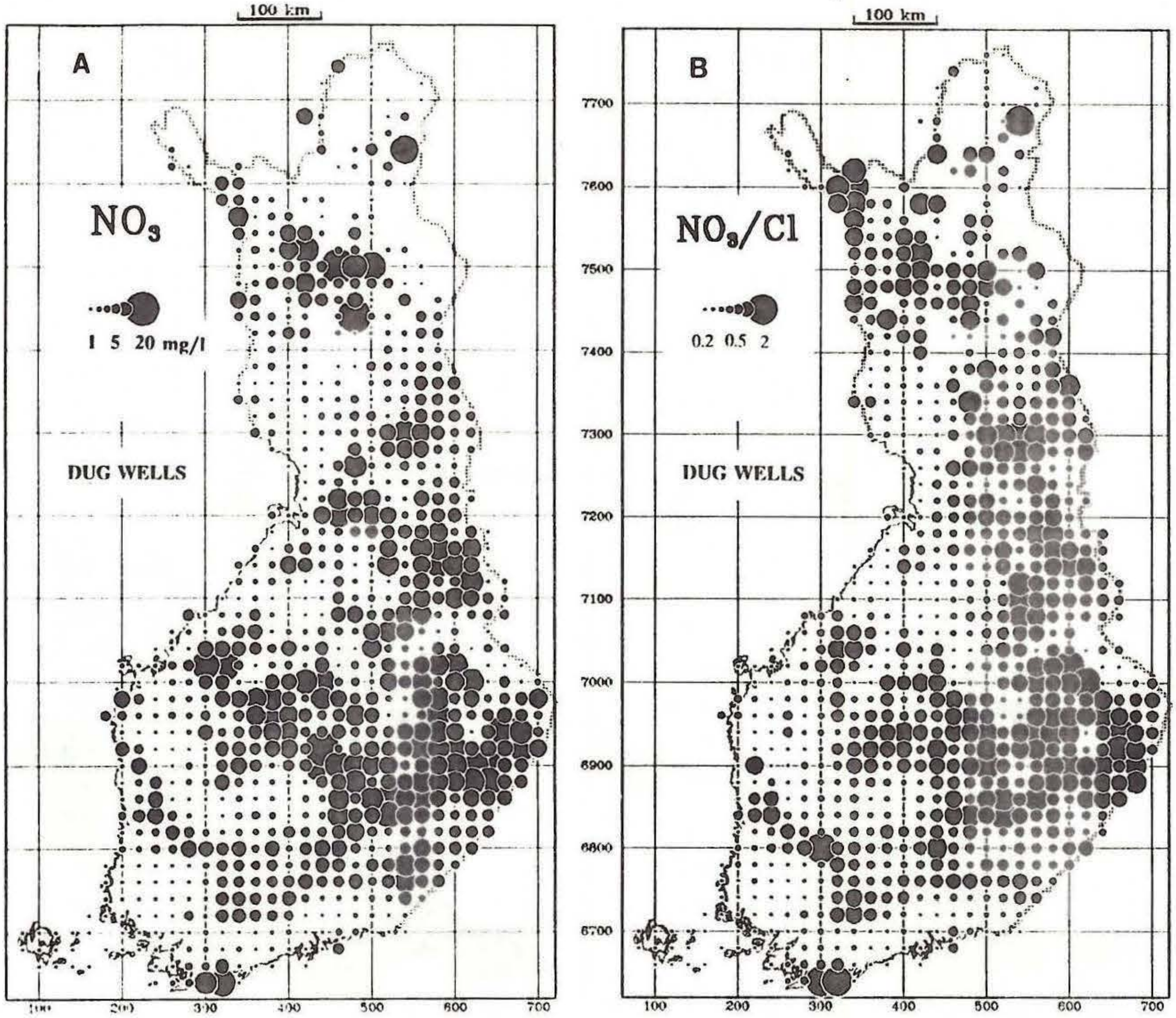
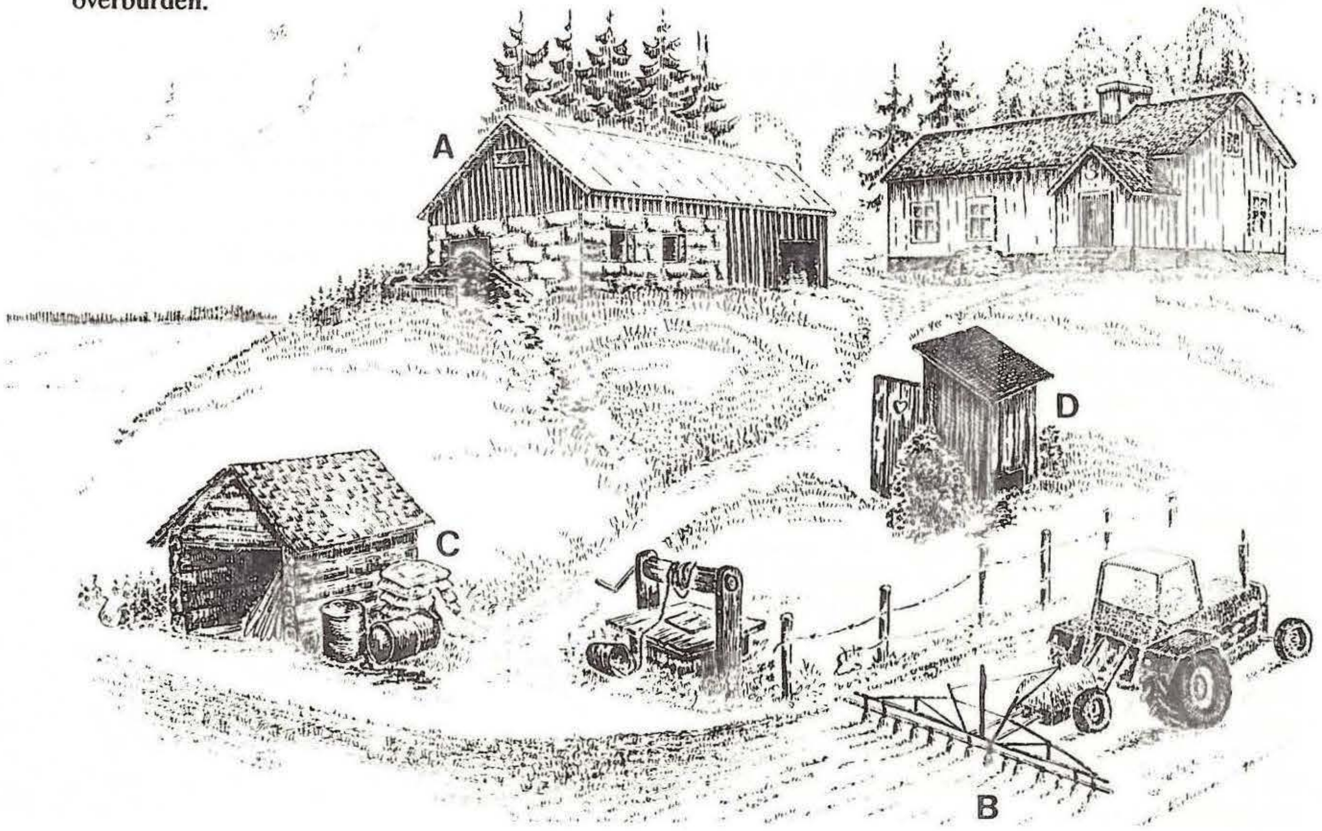


Fig. 4. Regional distribution of NO_3 concentrations (A) and NO_3/Cl ratio (B) in water from wells dug into overburden.



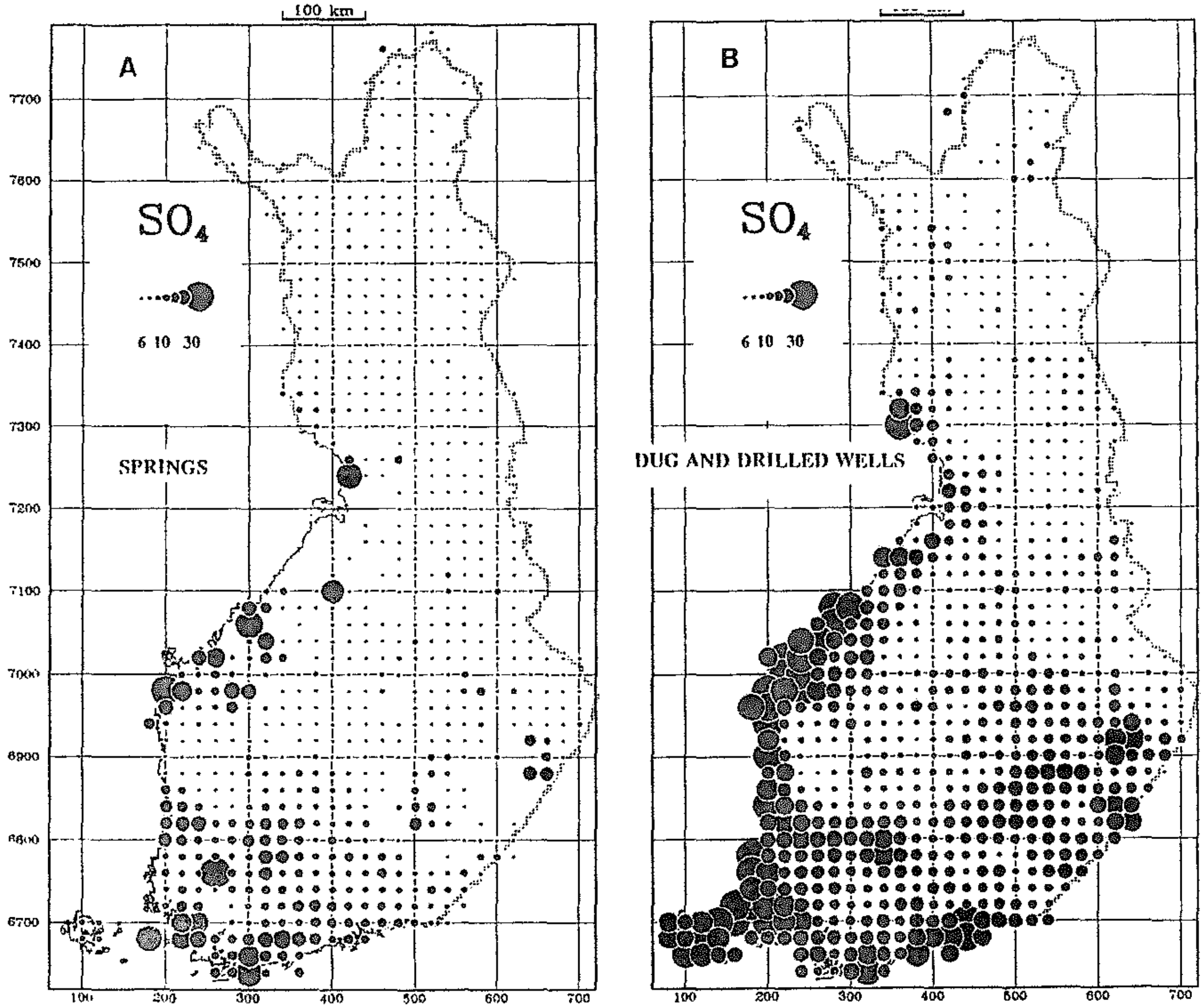


Fig. 6. Regional distribution of SO$_4$ in spring water (A) and in water from wells dug into overburden and drilled into bedrock (B).

on average, in the south of the country than in the north, reflecting higher acid acid fallout (Fig. 6A). The regional SO$_4$ distribution in well waters suggests, however, that acidification of deeper groundwater is also due to many other factors such as weathering of primary sulphide minerals in soils and bedrock and of secondary sulphide precipitates in marine sediments, particularly in a broad coastal belt, and pollution from agricultural and industrial wastes (Fig. 6B, cf. NO$_3$ map). Environmental acidification may mobilize metals such as As and Cd into groundwaters and surface waters in the anomalous areas of the heavy elements concerned.

Potassium is an important plant nutrient which in biological pathways follows cesium, a chemically similar trace element. Although Cs occurs in concentrations several orders of magnitudes lower than K, its regional distribution is largely similar to that of K (Fig. 7A and 7B). This may have an important bearing on fallout of the physiologically harmful radioactive nuclide, ^{137}Cs. The effect of radioactive Cs on humans through different pathway-systems of vegetation-animal-man may well be less marked in areas of anomalously high K-Cs concentrations in soils.

SYNOPSIS

All environmental changes in soils, groundwaters and surface waters are geochemical processes often accompanied and facilitated by biological and bacteriological phenomena. Hence, the geochemical mapping of different geological media is a prerequisite for regional environmental investigations.

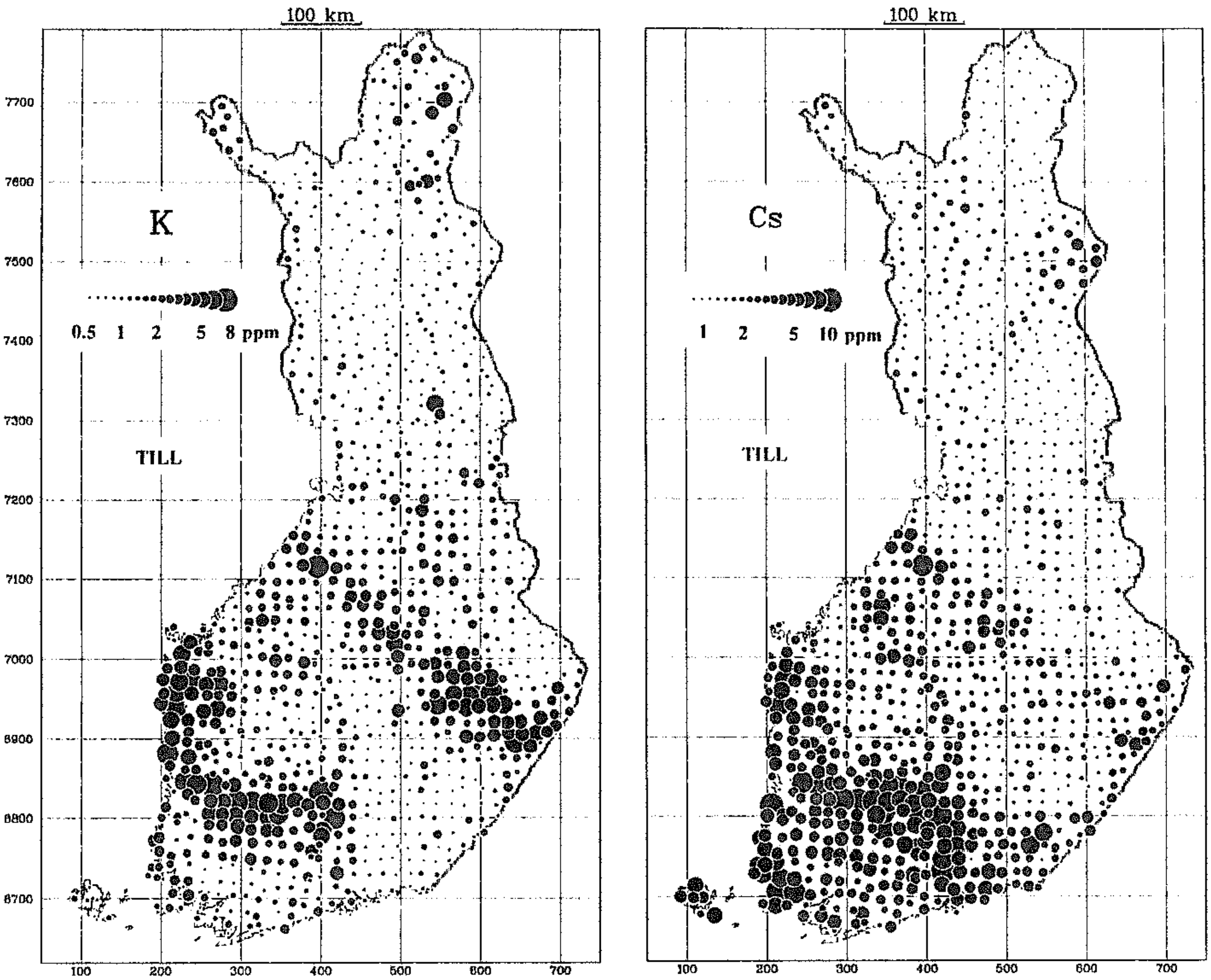


Fig. 7. Regional distribution of partial K concentrations in the fine fraction of till (<0,064 mm) analysed from aqua regia leach by the ICP method (A) and total Cs concentrations analysed by the NAA method (B).

ON HYDROGEOCHEMISTRY IN ORE EXPLORATION IN FINLAND

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Chemical analyses of groundwater and/or surface water have only exceptionally been used as an aid to geochemical exploration in this country. The first experiment was carried out in 1950's by Marmo (1958), who collected some 300 samples from wells dug into the Tampere schist belt, southern Finland, which is composed largely of phyllites, black schists, agglomerates and some scarns, the phyllites being rich in graphite, pyrrhotite and pyrite in places. Some measurements exhibited exceptionally low pH values, below pH 4 in sulphide mineral-rich environments correlating neatly with magnetic anomalies. Although Zn, Cu and Ni analyses at that time, being based on dithitzione methods, were very unsatisfactory, the anomalous concentrations were found in the locations with the highest sulphide mineral-potential.

In spite of this the promising start, the hydrogeochemical exploration method was not used for a long time, until the Nordkalott Project, carried out jointly by the Geological Surveys of Finland, Norway and Sweden in the early 1980's and covering the whole of northern Fennoscandia (above 66° latitude), collected and analyzed till, stream sediments and heavy mineral samples, together with about 6400 stream water samples (Bolviken et al 1986, Bolviken et al 1990). Although the hydrometeorological conditions fluctuated, the electrical conductance and main cation concentrations (Ca, Mg, Sr) in the stream water appeared to be strongly controlled by the bedrock composition, i.e. the proportional distribution of mafic, ultramafic and sporadic carbonate components in relation to more resistant felsic rocks in the catchment areas. The major ore elements generally used as pathfinders, such as Zn, Cu, Ni, Cr, Co and As, nevertheless occur in very low concentrations in natural water, and samples are extremely vulnerable to contamination. In spite of this some of the scattered anomalous Zn concentrations have been linked with known Zn mineralizations, although the sources of the most of them are unknown (Fig. 1).

In a detailed survey of the Sattanen area in central

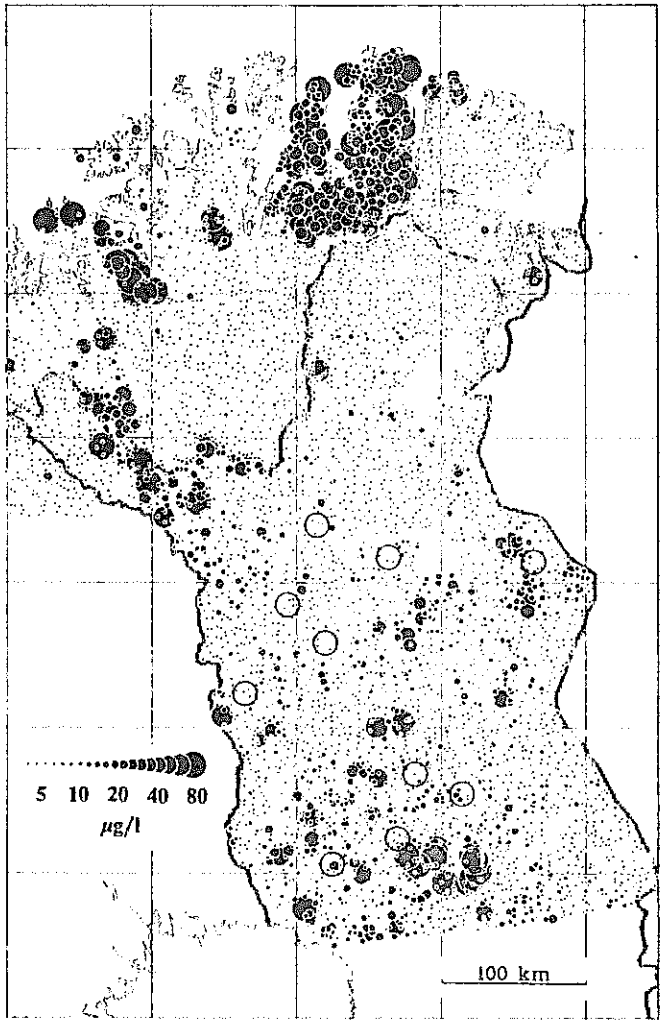

Fig. 1. Areal distribution of Zn concentrations in stream water as determined in the Nordkalott Project (Bolviken et al. 1990). The known mineralizations containing Zn are marked by circles.

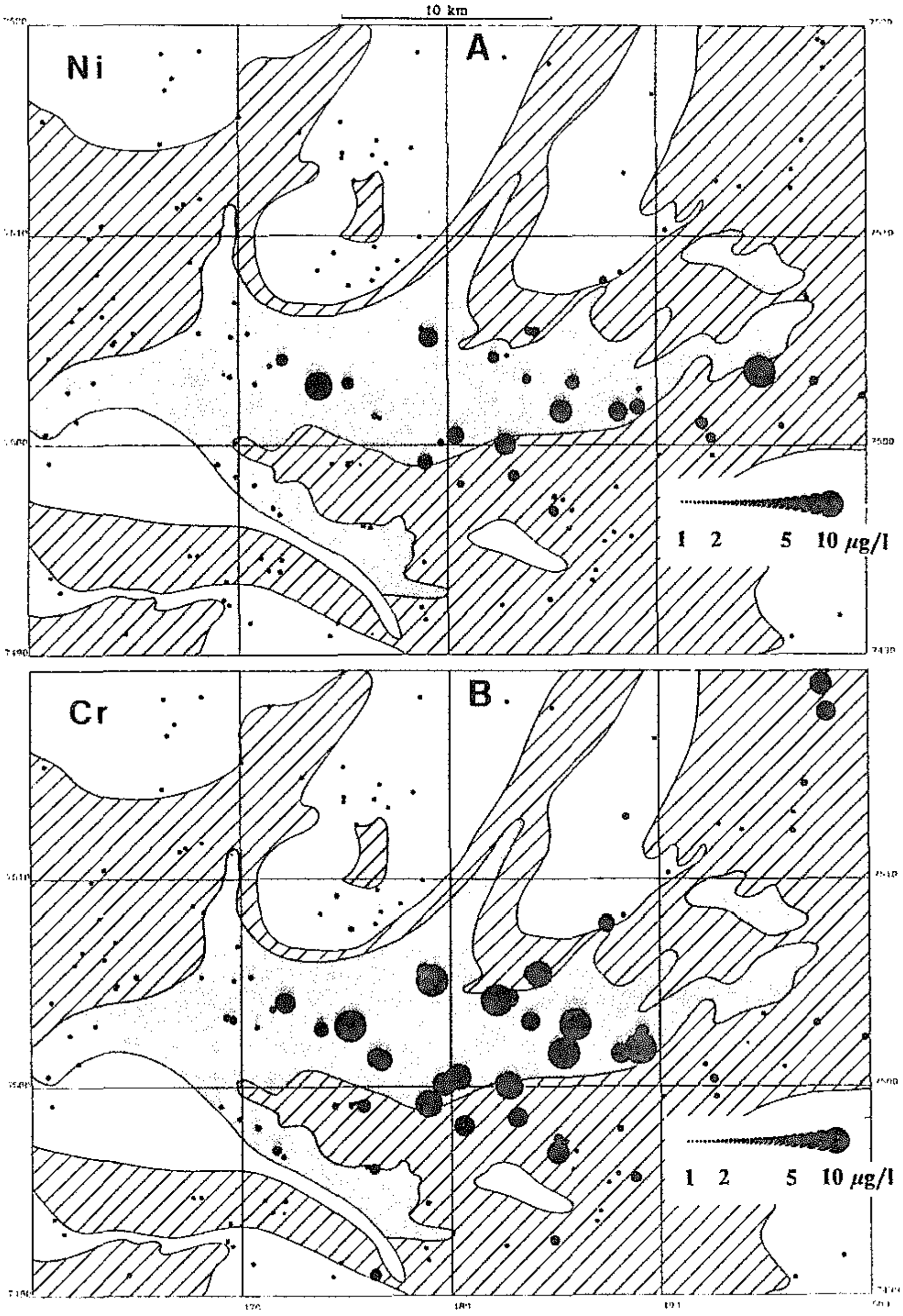

Fig. 2. Areal distribution of Ni (A) and Cr concentrations (B) in stream and spring water in the Sattanen map sheet area. The main features of the Precambrian bedrock are also marked (Tyrväinen 1980): shaded areas, ultramafic rocks (komatiites); ruled areas, mafic volcanic rocks and tuffites.

Finnish Lapland, water samples were collected from streams and springs. The area is situated in the greenstone belt which stretches across Finnish Lapland in the northernmost part of the Baltic Shield. The bedrock is largely composed of Proterozoic sedimentary and volcanic mafic and ultramafic rock associations such as amphibolites, gabbros and komatiites and an Archaean basement. These rocks are characteristically rich in Ni and Cr, as is also seen in their elevated concentrations in spring and stream water (Fig 2). The granite areas and the old Archaean basement composed of granite gneisses are reflected in very low concentrations of dissolved elements, including heavy metals.

As a result of a nationwide hydrogeochemical mapping of groundwater which started in 1978, more than 10 000 samples are currently on file. These were collected from springs and wells dug into the overburden and drilled into the bedrock and analyzed for certain heavy metals such as Zn, Cu, Ni, Pb, Cd and U (Lahermo et al. 1990). Contamination due to water utilization (pumps, pipes, containers, etc.), the sampling procedure, preparation of the samples and the analytical work is omnipresent, particularly where well samples are involved. Contamination is difficult to distinguish from elevated values caused by natural heavy metal sources such as the chemical disintegration of sulphide minerals.

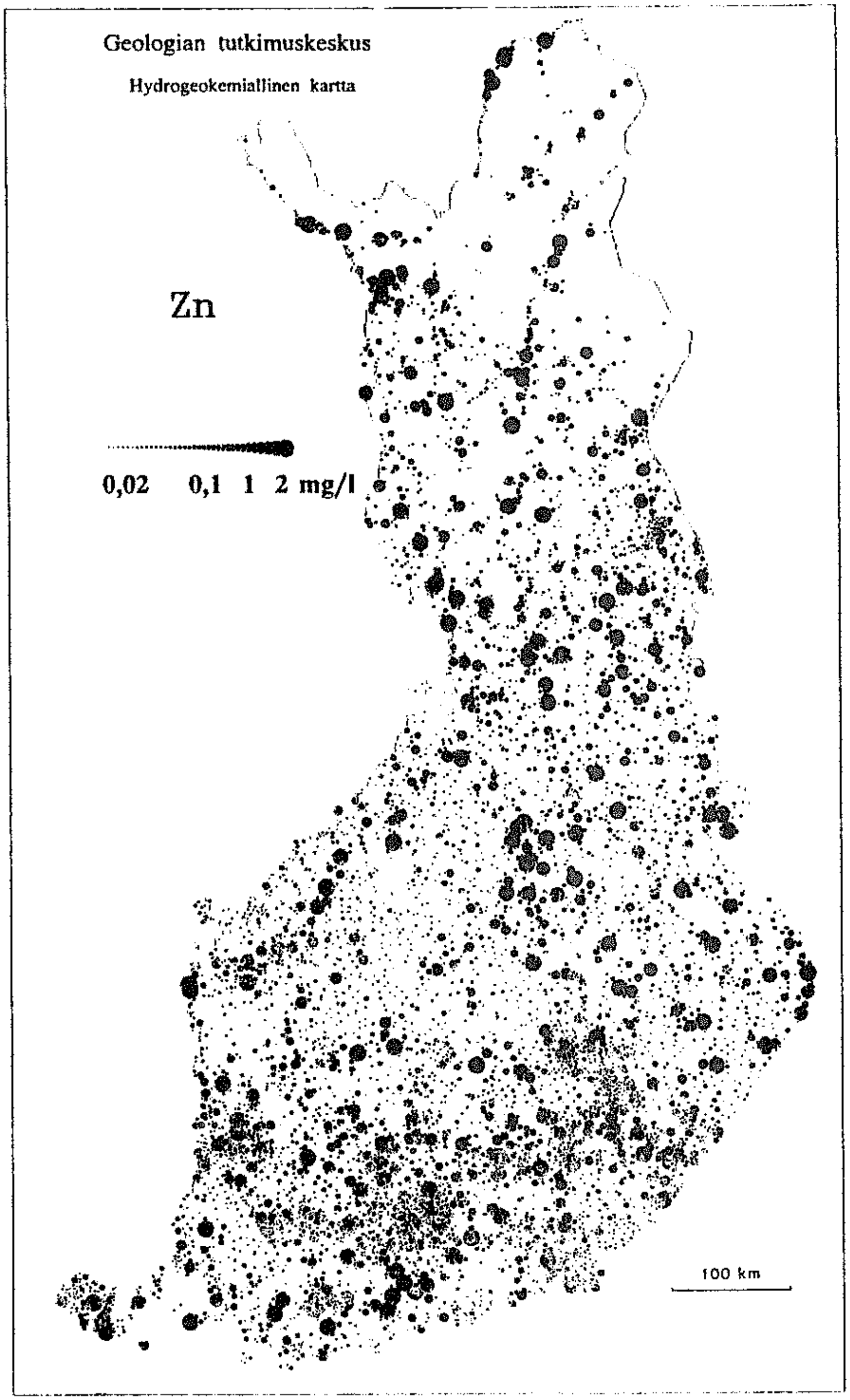

Fig. 3. Areal distribution of Zn concentrations in well water.

The hydrogeochemical maps of Zn, Cu and Ni show anomalous concentrations sporadically all over the country, mostly without any clear connections with known mineralizations. The most feasible hydrogeochemical heavy metal provinces can be detected for nickel (Fig. 3), the largest regional anomaly for which is in the eastern corner of Finland, in the border zone of the old basement gneiss and the Karelian schist belt composed of mica schists and mica gneisses. Although some of the anomalous concentrations may have been derived from contamination, many are superimposed on Ni-anomalous areas found in lake sediments (cf. Tenhola 1987) and glacial till (unpublished material of the GSF). Particularly the Outokumpu sulphide mineral-potential area gives some Ni-signatures in the groundwater. The large hydrogeochemical Ni province around the town of Vaasa on the west coast is derived from primary sulphides in the bedrock and soil and from sulphide-rich clay and silt deposits confining the groundwater. To the south there is another anomalous area coinciding with the Pori-Vammala-Tampere sulphide mineral potential belt.

In a case study of Kikonvaara, Suomussalmi, eastern Finland, groundwater samples from springs and domestic wells were collected for reconnaissance purposes (Fig. 4). Only F was analyzed, because it is a good hydrogeochemical indicator for many ore types, e.g. Sn,

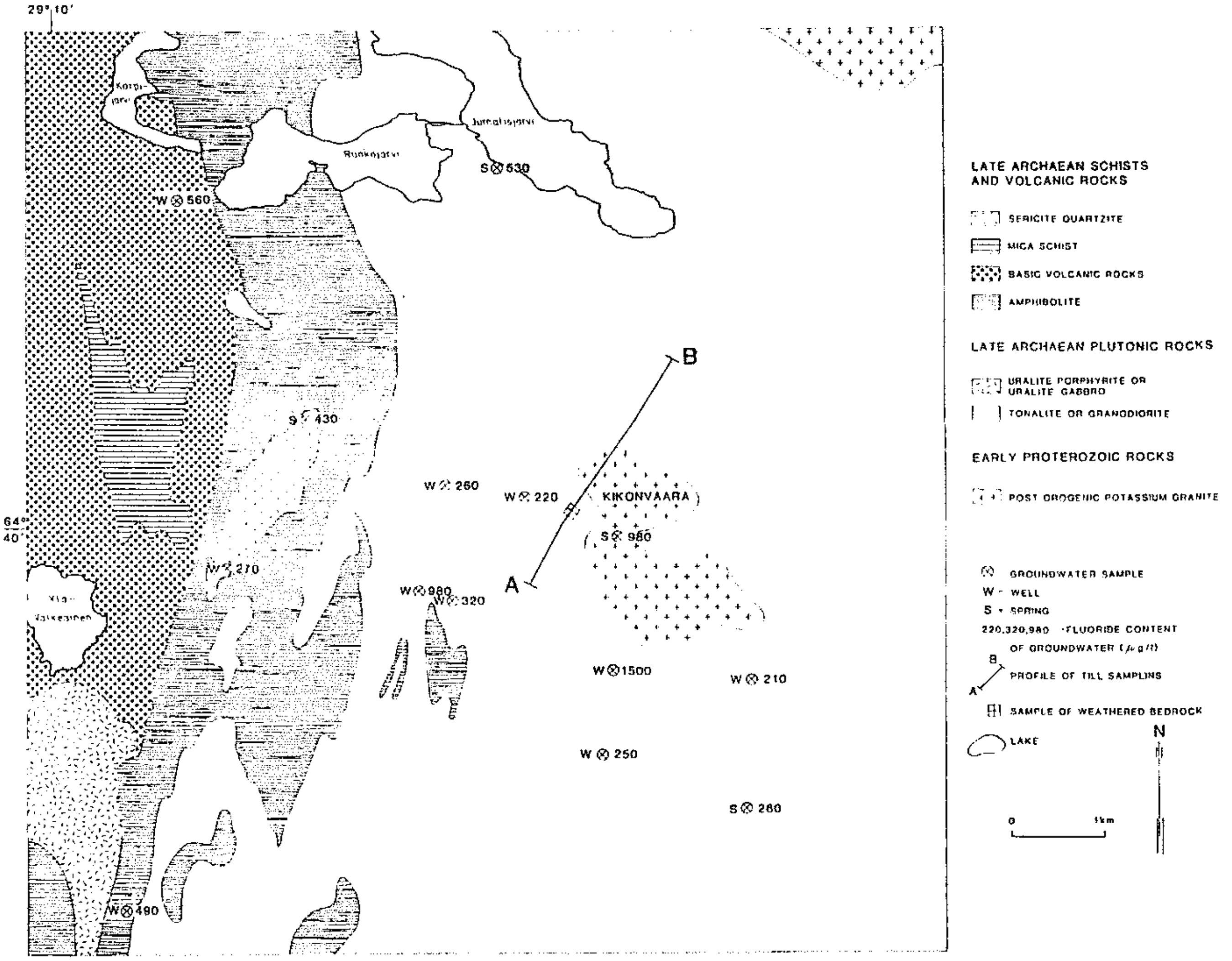

Fig. 4. Geological map of the Kikonvaara area, eastern Finland. Fluoride concentrations in groundwater and the profile A-B used for till sampling are also presented.

W-Be- Li, Mo, massive sulphide and gold ores (Lalonde 1976, Miller 1979, Lavery 1985). For more detailed investigation, till samples were taken along one profile (A-B) with 100 m point spacing with a percussion drill. The fine fraction of the till (< 0.06 mm) was analyzed for total Zn, Cu, Ni, Mo, Sn, Li and F. The area belongs to a large basement gneiss complex in eastern Finland, the age of which is 2.7 Ga. The youngest part of the bedrock consists of post-orogenic potassium granites. The bedrock is covered by glacial till, and in places by glaciofluvial sand and gravel deposits. The depth of the groundwater table is in general 2-3 metres.

The fluoride content of the groundwater is higher than the normal background values in the region (cf. Lalonde 1976, 1983, Lahermo et al. 1990), and is highest of all in the Kikonvaara potassium granite area and its immediate surroundings. The frequency distribution of the main statistical parameters for Zn, Cu, Ni, Mo, Li and F in the till are positively skewed, except for that of Ni. All six elements have higher concentrations over the Kikonvaara granite and its contact zones (Fig. 5). The peak values for Sn, Li and F are especially significant as to ore prospecting. The serrate form of the element profile is due at least partly to the sample spacing of 100 m, which is generally too long for geochemical follow-up prospecting. A denser spacing would have given a more uniform geochemical landscape.

Table 1 presents the chemical analysis of a weathered bedrock sample from the till profile. This alkali and aluminum-rich granite contained fluorite minerals, as shown by the high F content, and Sn, Li and Rb are also anomalously high. The location of this sample shows that the Kikonvaara granite is more extensive in area than was determined by outcrop mapping. Earlier petrological studies of this area have revealed that these granites, which have been called descriptively postorogenic potassium granites, can contain high Mo in places (Luukkonen 1988). On the basis of the geochemical data, we suggest that the Kikonvaara granite should be referred to as an early Proterozoic rapakivi granite. Thus the granite and its contact zones are critical for Sn, Li, Be and F ores. Granites of the same age group (2.4 Ga) occur in many places in the Finnish bedrock and can be considered to constitute a new metallogenic province.

In order to decipher the sulphide ore potential of the Proterozoic Kiiminki schist area in northern Finland, a total of 105 groundwater samples were collected from springs, domestic wells and a few drill holes and analyzed for Zn, Cu, Pb and SO_4 (Fig. 6). Zinc varies in the widest range, showing some high peak values (cf. Miller 1979), while Cu and Pb are mainly low, approaching the detection limits. The highest Zn values occur in areas where also some Zn-rich ore boulders and heavy mineral anomalies are known. The zinc

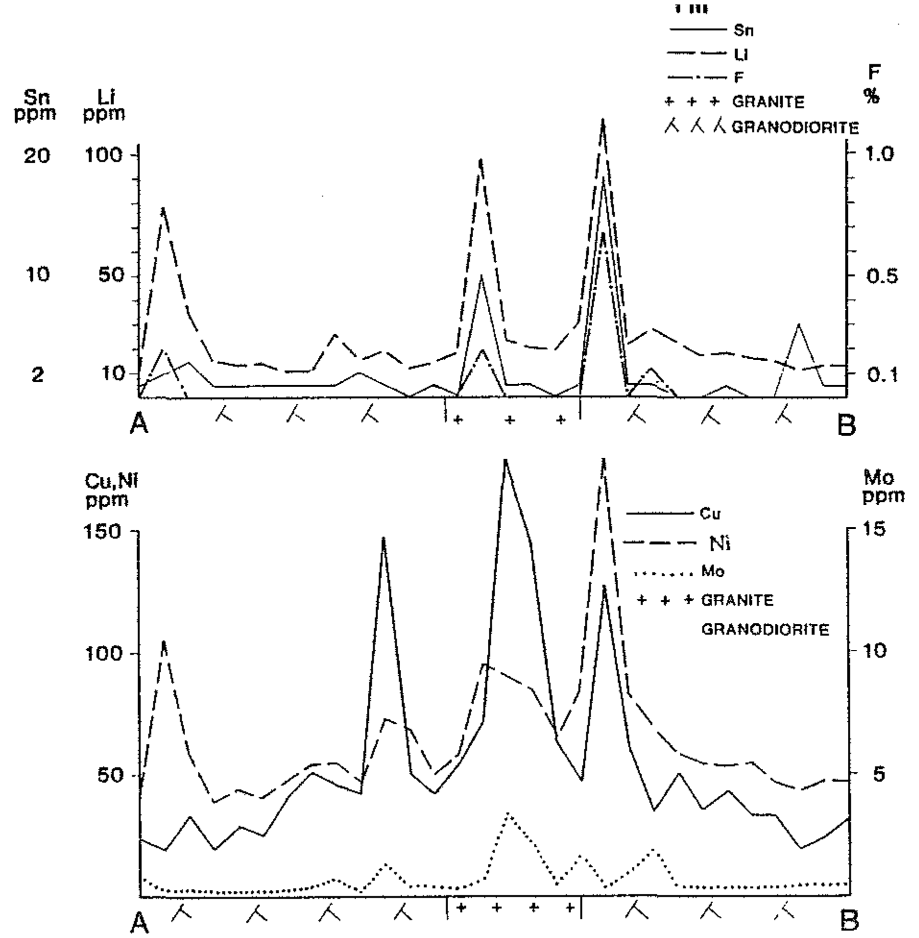

Fig. 5. Concentrations of Sn, Li, F (a) and Cu, Ni and Mo (b) in till analyzed from total dissolution by the AAS method in the Kikonvaara till profile (cf. Fig. 4).

content of the groundwater clearly reveals those places in the volcanic-sedimentary sequence which call for more detailed ore prospecting. In some wells, however, there may be Zn contamination derived from galvanized well buckets, pipes or pumps (cf. Rose et al. 1983, Lahermo and Juntunen 1990). Any technogenic contamination must carefully be screened out when evaluating the significance of the analytical data.

Sulphate concentrations are quite high in places and show the oxidation of possible Zn-Cu-Pb mineralizations and iron sulphides (pyrrhotite and pyrite) associated with the black schist horizons of the area (cf. Hogg and Webber 1976). Another source of sulphates consists of the sulphide-bearing clays and silts which were deposited in places during the postglacial Litorina stage of the Baltic Sea, when the area was subaquatic. Oxidation of the surficial parts of these clays and silts has liberated sulphate ions into the groundwater (cf. Hyyppä 1984, Lahermo 1990).

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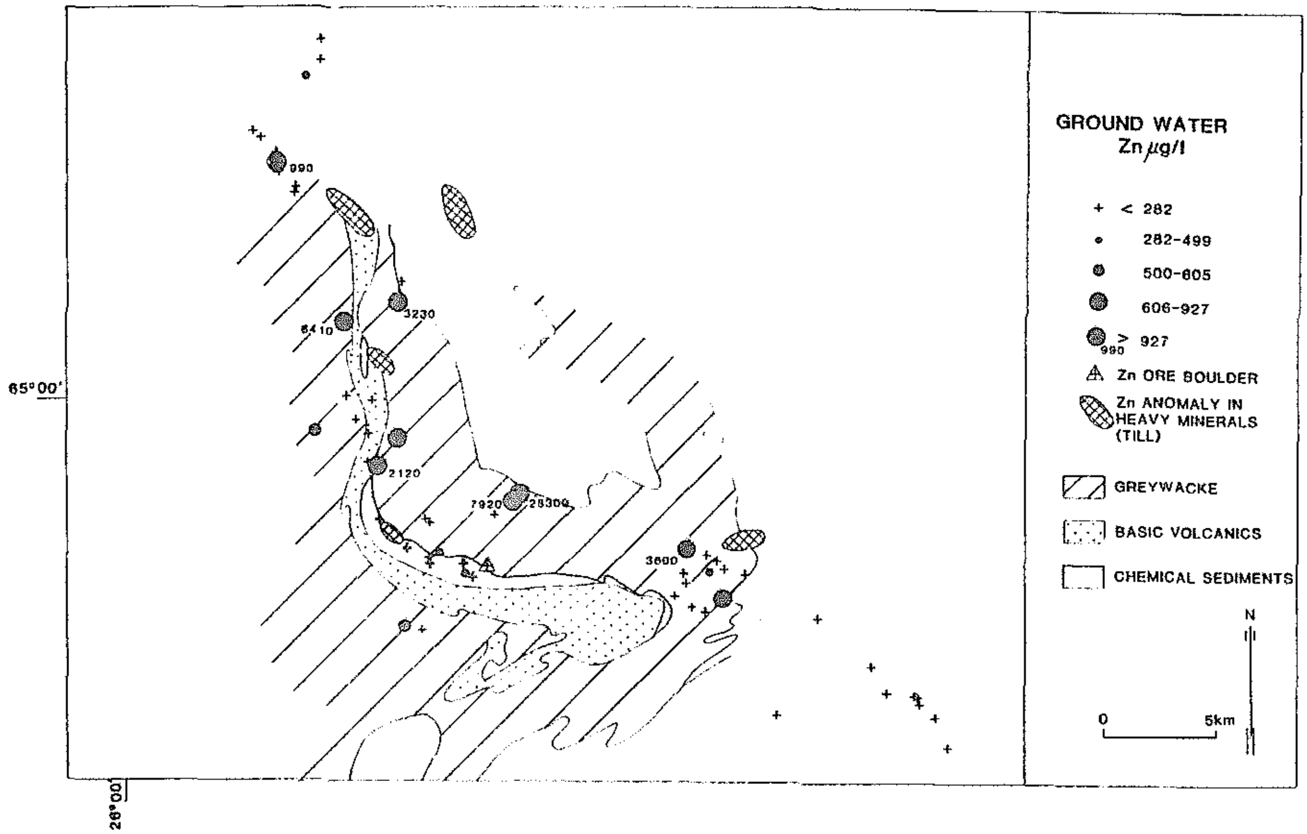

Fig. 6. Geological map of the Kiiminki area, western Finland. Zinc concentrations in the groundwater and the site of Zn-rich erratic boulder and Zn-anomalies in the heavy mineral fraction of the till are also marked.

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GEOCHEMISTRY OF TECHNOGENESIS

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The published abstract of our paper includes some theoretical and applied questions of geochemistry of technogenesis. In the present, the author would discuss several case histories of the environment pollution by heavy metals, radionuclides, nitrates, pesticides, etc.

Complex studies of the environmental conditions of some industrial towns of the Republic are carried out for several years in the laboratory of geochemistry of hypergenesis (Lukashev, Okun', 1984, 1988, 1990). Due to an extensive economic development, Minsk became a city with a very high concentration of industrial units, traffic, and a high density of settlement zones. During the post-war years, the population of the city has increased 6 times, and the industrial output has increased more than 100 times within the same period. The most advanced branches of industry (mechanical and instrument engineering, radio electronics, power industry, etc.) have received the largest development, and had a negative effect upon the environment and health of people. Ecological problems have become recently aggravated in the city.

To characterize urban environmental conditions, we have estimated contents of heavy metals and their distribution in soils of the city. The examination of the soil cover is of the utmost importance when studying technogenic transformations of the city environment. The soil accumulates technogenic pollutants during the whole period of the city existence, and so defines the general geochemical situation over the area.

Metals from the surface soil cover are mostly dangerous for man, as it is a source of about 50-60% of dust in the near-earth atmospheric layer .

Samples have been taken from the upper 10 cm layer (sampling density is 1 km^2). Contents of 40 elements have been determined by emission spectroscopy. Basing on the data obtained, a series of mono- and polyelemental maps showing the distribution of metals in the city soils has been compiled.

Four zones with a highly polluted soil cover have been distinguished within the city territory (see Figure):

Zone I. This anomaly includes lead, zinc and copper, first two being the dominant elements. This zone covers the oldest region of the city - its central part. The principal source of soil pollution in this region is an intensive traffic during many years.

Zone II. Tungsten is a characteristic element of this zone. Its concentration is 100 times the background level in some sites. Besides tungsten, there are high concentrations of zinc, lead and copper.

Zone III. This zone covers the greater part of the industrial part of the city. Major pollutant elements are mercury and zinc; accessory ones - lead, copper, manganese, chromium, nickel.

The formation of the zones II and III are due to a high concentration of industrial units (mechanical engineering, metal working, etc.).

Zone IV. This anomaly includes lead and zinc, locally - high concentrations of silver, copper, chromium and vanadium. The polluted zone is the region of airport and adjacent territories.

We have estimated technogenic pollution of the soil cover in Minsk according to the scale of ecological danger based on calculations of summary indices of soil pollution by metals (Sayet, Smirnova, Revich, et. al., 1982, 1986).

According to the proposed gradation, soils of Minsk are very dissimilar in metal contents, which range from the background to the extremely dangerous level. The concentration of heavy metals can be considered permissible only within 18,7% of the city area, moderately-dangerous - 41,7%, dangerous - 33,7%, and extremely dangerous - within 5,9% of the territory.

Industry and traffic of the city affect suburban areas to dozens of kilometres. Sometimes, this is such a strong influence that it is impossible to develop agriculture there. We have studied the metal differentiation in the suberban area of Minsk using lichens. Metals are transported to dozens of kilometres from the city and fall out according to aerozol particle size. The following succession is formed: Fe Cr (Mn, Cd, Ba, Cu) (Ni, Zn, Al) (Sn, Mo) (Ag, V) Hg Pb. Our data agree well with the above series from the studies of Harrison and Rahn (1979). The particle size they studied ranged from 4 to 0,3 m. Migration and differentiation of metals in alluvial processes have been studied too. Ex. gr., for 40 years Ag migrated to 200 km in the River Svisloch, which runs across Minsk. Methods of investigations (extracts, sorbents, etc.) and modes of metal occurence were characterized more in detail in the other publications.

The Chernobyl accident which took place on the 26th of April, 1986 and resulted in radionuclide pollution of vast territories of the Byelorussian SSR, has rised several geochemical problems: 1) investigation of distribution and behaviour of radionuclides in natural and technogenic landscapes (which are examined according to the results of four-year studies); 2) modes of occurence of radioactive elements in the environment; 3) preliminary estimation of radionuclide migration in the future. The state of art of geochemical studies carried out within the BSSR territory, as well as landscape investigations within 1953-1987 made under the guidance of academician K.I.Lukashev are very important for solving the above questions. According to the results of these investigations, lithogeochemical and hydrogeochemical zoning of the BSSR was made, the radioactive background of the Republic in the sixties was studied, as well as distribution peculiarities of clay minerals, carbonates, Fe-Mn oxides, organic matter, pH - Eh, contents of many chemical elements in the overburden of Byelorussia. All these factors are of great importance for understanding the behaviour of radionuclides.

Radionuclide fallout on the BSSR territory in the first days after the accident was firstly dependent on the air and rain mass movements. In cities, these fallouts were found to be confined to regions with intensive technogenic dust emissions, as well as to river valleys, where degasation of deep-seated zones through faults occured side by side with evaporation. Radionuclide wash out from upland territories can be related to secondary processes. During four years, radioactive emission near the earth surface decreased due to decay of short-lived isotopes, and penetration of radionuclides deeper into the soil. At the same time, their major part occurs at a depth of 1-5 cm. Bogs, peat-bog soils, watered sands with fluctuating level of groundwaters, variable pH -Eh conditions and a high biological activity are factors contributing to radionuclide migration in Byelorussian landscapes. A part of radionuclides is gradually removed from eluvial landscapes and accumulated in subaqual landscapes (lakes, oxbow-lakes, water-storage basins, etc.).

The Chernobyl debris are represented by the following substances: "hot particles", pseudocolloids, aerosols, gaseous compounds. The study of modes of radionuclide occurence in grounds by different methods (extracts, sorbents, etc.) made it possible to estimate the migration capacity of some radionuslides Cs, Sr, Ce, Ru, etc., to distinguish two zones around the reactor - the nearest and remote ones - differing in the ratio of "hot particles" and condensate fallouts, which causes a different migration capacity of radionuclides.

A very important part is assigned to biological processes and organic matter, which cause the destruction of "hot particles", formation of organometallic complexes and water migration of nuclides.

The redistribution of radionuclides in landscapes in the future (within 300 and more years) involves processes of weathering, erosion and sedimentation which will strongly depend on climatic conditions. Side by side with a gradual decay of Cs and Sr, an appreciable accumulation of Am-241, which is very mobile in landscapes should be expected due to decaying Pu-241.

A considerable development of scientific and applied explorations should be also expected in the future and would help in solving problems of radioactive pollution of landscapes.

Many ecological problems are related to agriculture: ex. gr., the disturbance of soils, contamination of the environment and foods by nitrates, pesticides, etc. The author has studied the negative impact of the latters when investigating the relation existed between oncological diseases and geochemical peculiarities of Byelorussian landscapes. These investigations involved, in particular, geochemical analysis of some personal rural plots with sick men and the control ones (K.I.Lukashev, et al., 1989). The composition of soils, drinking waters, as well as some foods (milk, eggs, potatoes) was studied within these plots. 75 parameters were investigated and mathematically treated. 23 statistically significant features were revealed as a result. Their analysis shows as follows:

Areas with cancer suffering persons show higher contents of nitrates in milk and water. There are many references to the connection between oncological diseases and nitrates. Our data agree with them. Pesticides are also more abundant within areas with cancer suffering persons: higher contents of DDT, DDD, HCCH were determined in eggs, of DDT and HCCH - in potatoes. Though in the case of pesticides, the sample was not very representative, several differences are mathematically significant. These factors (fertilizers, pesticides) are obviously due to anthropogenic activities and should be better monitored.

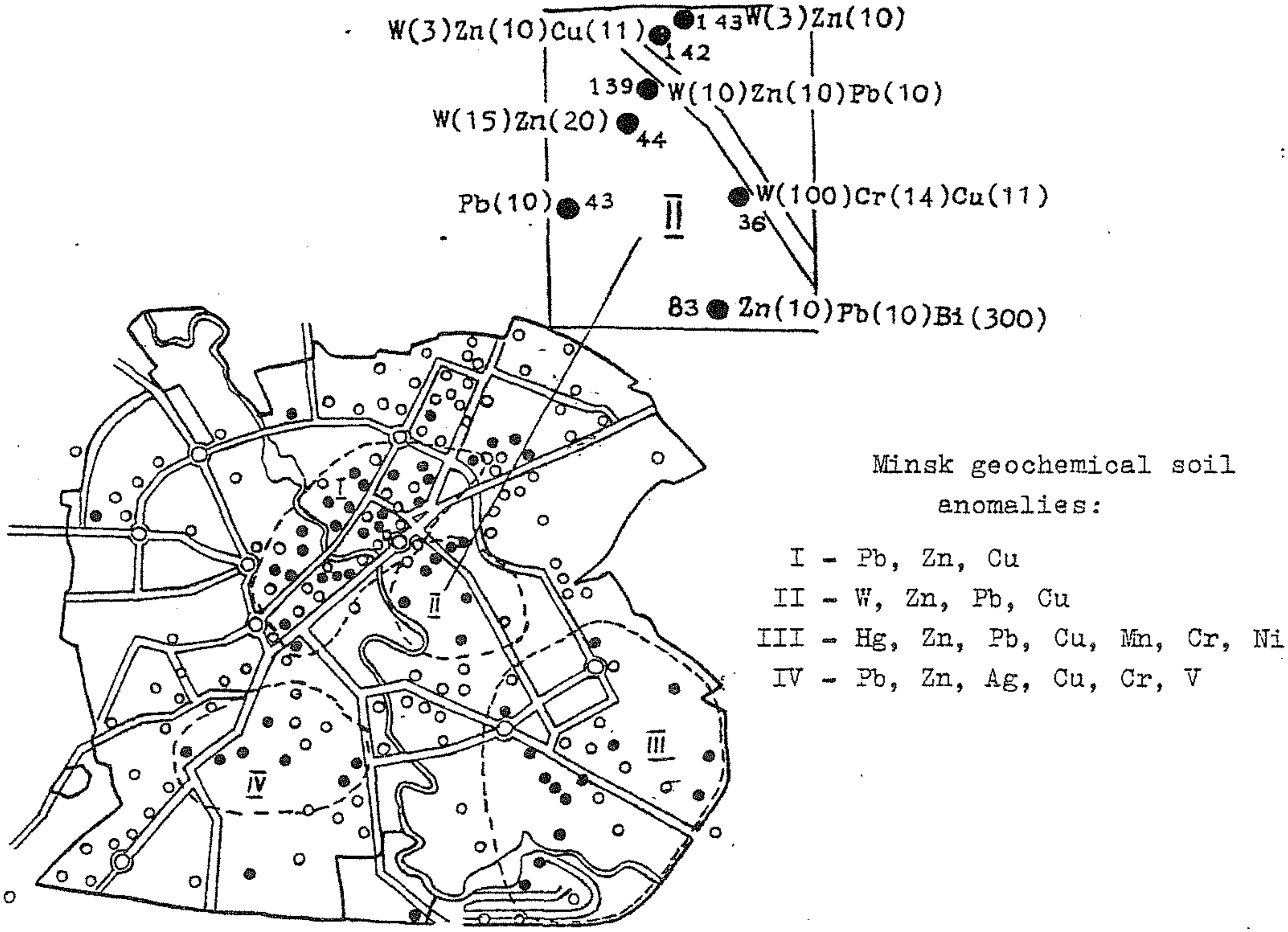
Several differences are related to drinking waters indicating that it is a very important factor of the man health and highly influences the origin of carcinogenic diseases.

The average value of mineralization, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Mn, Cu, NO_3^- are higher in areas with cancer suffering persons. Mn, Pb, Ni, Cu were determined to be the factors of oncological risk. Ti, Zr, Y and Ag were added to the above group. In this stage, it became obvious that the more thorough analysis of the metal modes of occurence is needed, in particular, with the help of sequential extracts. For example, in the northern regions of the BSSR about 45% of Pb occur in mobile form, whereas in southern regions - 90%. It should be noted that the problem of the connection between some chemical elements and the cancer risk is often very complicated, as in many cases these are not direct stimulants of diseases, but accompany the other more real causes. Increased contents of zircon in control plots can be related not to its biological activity, which is poorly studied, but rather to the more dusty character of soils (zircon is accumulated in dust fraction), their better water-physical properties favouring washing, retention and destruction of different organic compounds in soils, i.e. to the quality of soils.

Metals V and Ti, which are in the list of elements associated with oncological risk,are probably connected with some forms of dissolved organic matter.

The author thinks that a cause of oncological diseases is rather a complex of synergistic phenomena than one of the factors taken separately.

For example, most scientists consider that radioactivity can synergistically stimulate oncological diseases together with the other factors, ex. gr. with nitrate pollution. Synergy of landscape-geochemical factors is a new vast area of investigations. The value of our studies carried out for the present is the possibility to reveal several factors which should be firstly taken into account.



Minsk geochemical soil anomalies:

I – Pb, Zn, Cu
II – W, Zn, Pb, Cu
III – Hg, Zn, Pb, Cu, Mn, Cr, Ni
IV – Pb, Zn, Ag, Cu, Cr, V

Methodology of geochemical prospecting applied for Pb-Zn ore in carbonate medium at Djebel Bou Arif; BATNA /ALGERIA/.

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Abstract:

This paper deals with the methology and the results of two geochemical methods /lithogeochemistry and pedogeochemistry/ applied in carbonate environment. Based on statistical analyses of the obtained data, the geochemical anomalies and associations were determined.

The controls of the prospected mineralization were found to be mainly lithological and structural. Consequently, the applied methods can be successsfully used for the prospection of such deposit in similar semi-arid zones.

INTRODUCTION

The first purpose of this work is to try to establish the methodology of geochemical prospecting for searching polymetallic /Pb-Zn/ deposits in carbonate medium.

The second purpose is to study the distribution of elements in rocks and soils.

About 450 soil and rock samples were collected following a mesh of 100 x 20m, in an area of about 1 km2. Chemical analyses were carried out by Plasma Spectrometry for the dermination of the elements: As, Ba, Co, Cu, Fe, La, Mn, Mo, Pb, Sb, Sr, Ti, V, and Zn. The chemical analyses data of rocks and soils were separately worked out /lithogeochemistry and pedogeochemistry/.

LITHOGEOCHEMISTRY

The main objectives of the present work are:

- determination of the distribution character of chemical elements;
- determination of different geochemical associations;
- delineation of geochemical anomalies.

From the correlation of simple geochemical profiles with bedrocks, it is observed that the high grades of As, Cu, Pb. Sb and Zn are particularly related to dolomitic and/or siliceous limestones. It is also noted that the relative abundance of Fe and Mn are related to dolomites. The E-W fault system is often associated with high Pb and Zn contents.
The average trace element contents in limestones of Bou Arif are as follow:

As	Ba	Co	Cu	Fe	La	Mn	Mo	Pb	Sb	Sr	Ti	V	Y	Zn
36	600	19	5	2.2	31	850	13	46	45	220	01	20	19	64

/all in p.p.m except for Fe and Ti which are expressed in %/

STATISTICAL ANALYSIS OF DATA

1. Univariate analysis

Considering the graphic /histograms/ and the mathematical /test of Ahrens/ analyses, it is found that distribution of most elements is lognormal. It was previously indicated by Till, 1974 /In Dejongh, 1985/ that the role of the lognormal distribution predominates in the statistical distribution of trace elements.
The analyses undertaken in this study are based on the works of Lepeltier, 1969 and Sinclair, 1976, and 1986. The probability of the pricipal elements generally reveal polymodal distribution /fig. 2/. The population of high values characterizes the dolomitic limestones. However, the population of the low values corresponds to sandstones as to limestones with intercalations of marls and sandstones away from mineralized zones.

The local geochemical background /b/ for some of the analysed elements i given in the following table:

Elements	As	Ba	Cu	Fe	Mn	Pb	Sb	Sr	Zn
b/p.p.m/	59	399	4	56	553	106	39	63	369

The threshold concentration /t/, was determined using the following formula:

$$\log t = \bar{x} \pm 2s$$

where , $\bar{x}$: denotes the arithmetic mean of logarithms of concentration of the element.

s : denotes the standard deviation of logarithms.

A multi-elements geochemical map of Pb, Zn, Cu, As, and Sb is given in fig. 3.
Analysis of this map revealed that:

- the two lead-zinc and copper mineralization types are shether superposed or separated in space,
- the anomalous As contents follow the two mineralizations,
- the mineralization control is both tectonic and lithologic

2. Bivariate analysis /Correlation matrix/

The significance level of the correlation coeficient is calculated using the following formula /Dixon and Massey, 1957/

$$r_o = \sqrt{T^2 / T^2 + /n - 2/}$$

where T, is the Student value and n is the number of samples.

The significance level in this case is r_o = 125 at a probability level of 99%, with T = 2.33. The following is the high correlation coefficient obtained from the correlation matrix.

a. Cu-Sb /.791/, Cu-As /.757/ and As-Sb /.827/
b. Pb-Zn /.741/, Pb-Cd /.793/ and Zn-Cd /.704/
c. Fe-Mn /.726/.

The first principal association /Cu, As and Sb/ corresponds to the copper mineralization, represented by the grey copper ore.

The second association /Pb, Zn and Cd/ corresponds to the lead-zinc mineralization which is fundamentally represented by galena and sphalerite. The third association /Fe and Mn/ represents the relatively high contents of these element in the ferrodolmites.

Plots represented by dispersion diagrams, clearly reflect the good positive correlations revealed from the correlation matrix.

3. Multivariate analysis /Factorial Analysis/

Data processing by factorial analysis has been used in addition to the other statistical analyses. Its application aims to check the previously obtained correlations and search for new possible ones.

Principal component analysis of the lithologic data has been used in the processing of the "mode R" /concerning the element contents/, /A.M. Karpoff, 1973/. The obtained results with orthogonal rotation of the factorial matrix /Varimax Method/ are given in fig. 4. The factorial analysis has confirmed also the geochemical associations previously obtained

PEDOGEOCHEMISTRY

In certain regions the pedeology surface penalize the direct prospection where large areas are still unexplored /Wilhem and al., 1983/. By the geochemical prospecting of soils, the goals to achieve are the following:

- the study of the behaviour of elements such as Pb, Zn and Cu in soils with carbonate substratum;
- verification of the previously obtained geochemical anomalies;
- determination of the different geochemical associations.

From the simple geochemical profiles and the ratios of the average contents of elements in soils and in bedrocks, an enrichment of some elements such as AS, Cu, Fe, Pb, Sb, V and Zn in soils is observed. This is probably the result of high retention of such element by iron and manganese oxides. It should be noted that the measured pH of soils varies from 7.8 to 8.8 indicating a slightly alkaline medium.

STATISTICAL ANALYSIS OF DATA

a. Univariate analysis

The histograms, probability curves and mathematical processing confirm that the distribution of the principal elements /Pb, Zn and Cu/ approximates the log-normal law with a polymodal character. From Fig. 5 representing the geochemical map of the elements: As, Cu, Pb, Sb and Zn in soils, it is clear that:

- the Pb-Zn mineralization which is often separated from the copper one is also related as well to certain fissures and to the dolomite facies;
- the copper mineralization /Cu, As and Sb/ appears clearly in soil covering the siliceous facies;
- the soil geochemical map reveals as well the lithostructural control and the two principal mineralizations /Pb-Zn and Cu-As-Sb/.

b. Mutivariate analysis

b.1. Simple correlation

The calculated coefficients of correlation clearly reflect the following geochemical associations : Fe, Mn; Ni, V, Co; Pb, Zn, Cd and Cu, Sb, As, Ba. The positive high correlations are given with their corresponding correlation coefficients: Fe-Mn /.859/, Co-Ni /.833/, Zn-Cd /.926/, Zn-Pb /.911/, Pb-As /.855/ and Cu-Sb /.802/. These correlations are also verified using dispersion diagrams.

b.2. Factorial analysis

The results obtained using this method are tabulated below:

Soils /73.1 % explained variance/

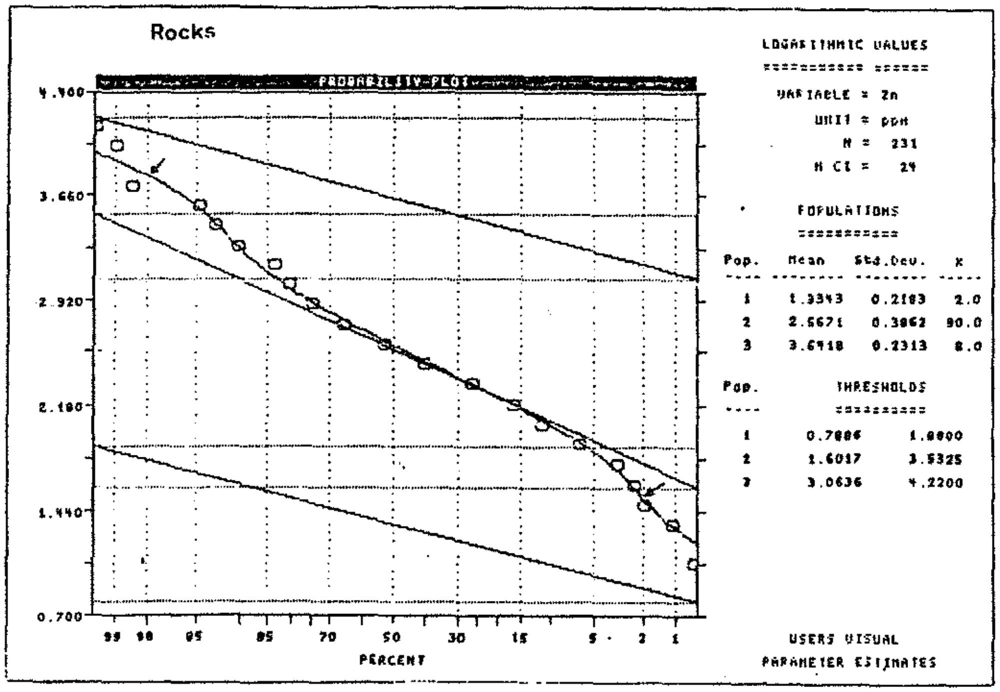
F_1 :Co, Ni, Y, V, Ti /31.4%/
F_2 : Cu, As, Sb, Ba /19.3%/
F_3 :Zn, Pb, Cd /12,2%/
F_4 : Fe, Mn /10,2%/

F_1: accessory mineralization resulting from the process of coprecipitation related to Fe and MN oxides.

F_2: copper mineralization /grey copper and supergene minerals/.

F_3: lead-zinc mineralization /galena and sphalerite and their alteration products: cerussite smithsonite, hemimorphite../

F_4: oxides /or hydroxides/ of iron and manganese.



```
LOGARITHMIC VALUES
=========== ======
VARIABLE = Zn
    UNIT = ppm
       N =  231
    N CL =   29

      POPULATIONS
      ===========
Pop.   Mean    Std.Dev.    %
----  -------  --------  -----
 1    1.3343    0.2183    2.0
 2    2.5671    0.3862   90.0
 3    3.6918    0.2313    8.0

Pop.       THRESHOLDS
----       ==========
 1      0.7886      1.8000
 2      1.6017      3.5325
 3      3.0636      4.2200

     USERS VISUAL
  PARAMETER ESTIMATES
```

Fig.2. Cumulative Frequency Distribution

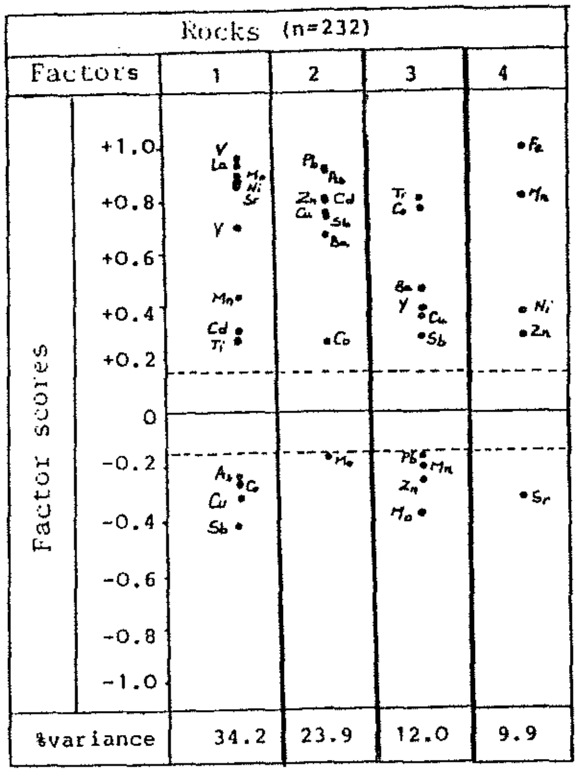
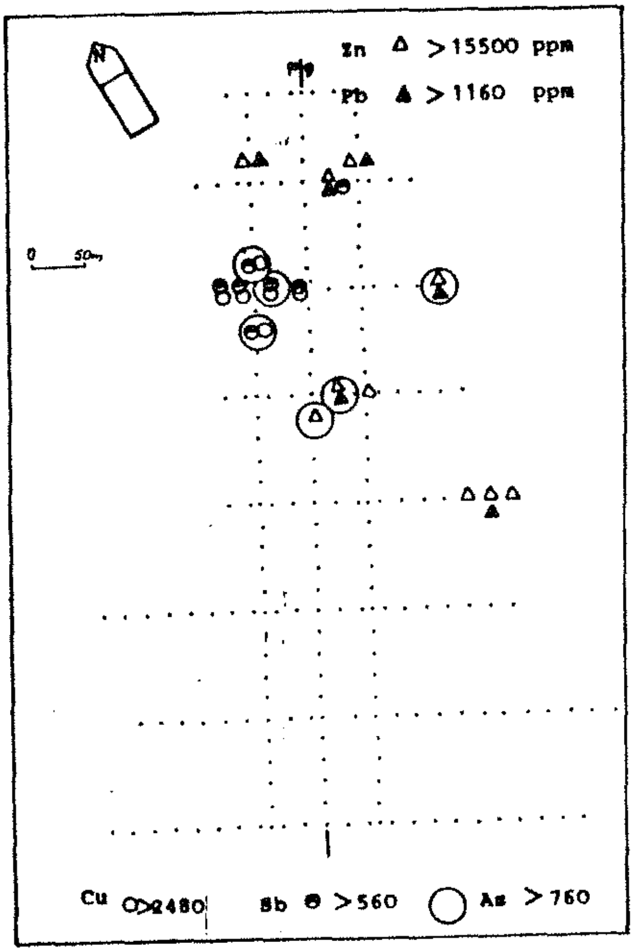


Fig.4. Graphic representation for results of factorial analysis.



Cu, Sb, As in ppm

FiG.5. Multi-elements geochemical map of As, Cu, Pb, Sb and Zn (in soils)

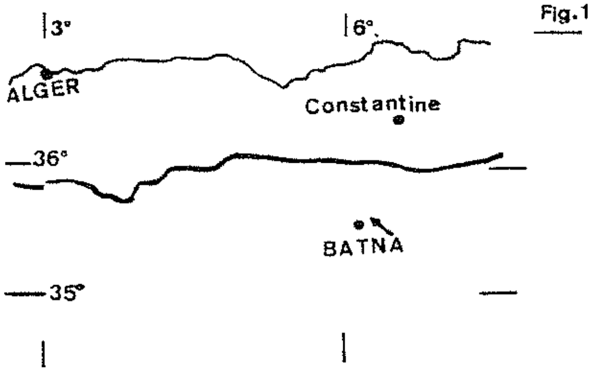
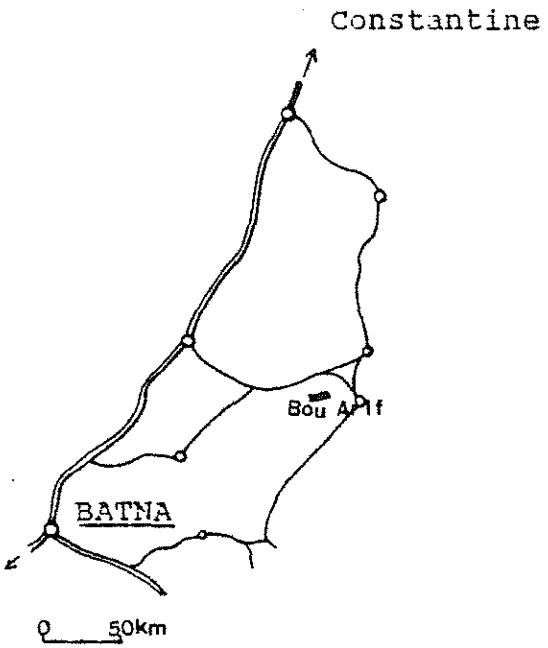


Fig.1. a- Location map.



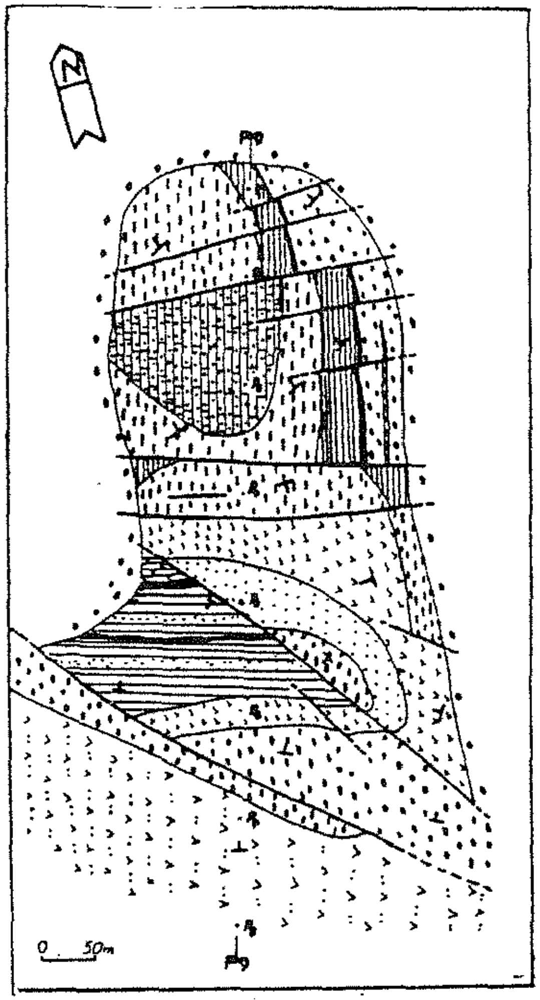


Fig.1. b- Geological map of the area.

1 ▦ 2 ▤ 3 ▤ 4 ▨ 5 ▬ 6 ▤ 7 ▨ 8 ▨

9 ⬚ / Fractures

1. Siliceous Lst _ 2. Lst with brown dots. _3. Lst with Lamellibranch. _4. Orbitolined Lst. _5. Marl. _6. Intercalation of Lst and bedded Sst _7. Yellowish brown dolomite. _8. Arenaceous dolomite. _9. Sst.

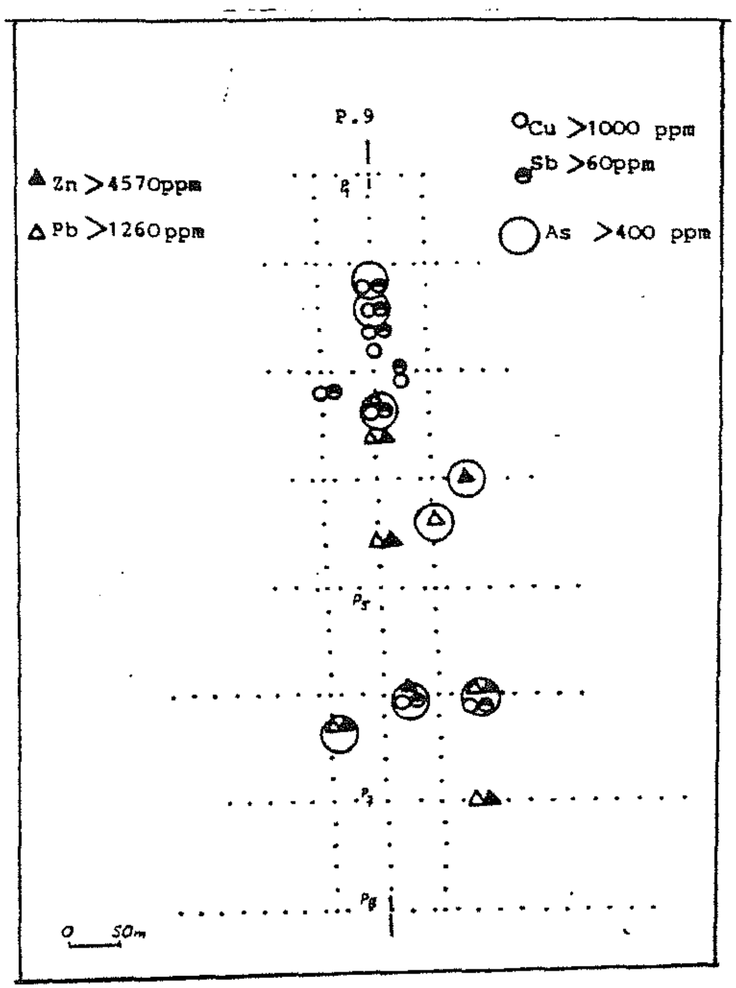


Fig.3. Multi-elements geochemical map of Pb, Zn, Cu, As and Sb (in rocks).

CONCLUSION

The statistical distributions of elements arè found to be lognormal with a bimodal or polymodal character.

Lithogeochemical and pedogeochemical maps showed clear anomalies that correspond to indices of mineralization.

The obtained geochemical associations caracterize the two principal types of Zn, Pb and Cu, As, Sb. mineralizations.

Geological and geochemical maps revealed the lithostructural control.

The technics of this prospection can be satisfactorily used for searching for such ore deposits in similar semi-arid zones.

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THE ROLE OF PATENT SYSTEM IN SOLVING ECOLOGICAL PROBLEMS CONNECTED WITH GEOCHEMICAL RESEARCHES

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Nowadays ecological problems has reached their crucial point on global scale. To solve these problems the efforts of all nations and non-traditional approaches are needed. One of them may be a purposeful ecological reorganization (ecologization) of patent law as well as the reorganization of international and national patent systems.

Scientific-technical progress and industrial society exert negative influence upon ecological systems responsible in the end for life on the planet. At the same time it is this progress that determines the positive development of human society and has the irreversible character. Hence the mission of international community and individual states is to ensure such a control of scientific-technical progress that would secure the highest harmonization of science technology or, at least, minimize technological impact on the environment.

Among different types of human activities inventive creativeness is the first and immediate source of scientific-technical progress and scientific discoveries and inventions are the decisive factors of this progress. Moreover, inventions are the product of not only man's imagination but of a state legal activities. It is the state that determines which technical decisions may be acknowledged as inventions. Only devices, substances, technologies, plants, cultures satisfying the criteria of patent ability which are introduced by a corresponding national legislation are considered inventions. Such criteria in the majority of countries are the world novelty of technical decisions, its evidence to specialists in a given field and industrial utility (usefulness). National and international patent departments examining international, national and foreign claims on the ground of the analyses of these criteria give out (or do not give out) protecting documents - patents. Patents, having state standing, guarantee their owners (inventors or, in many cases - firms) exclusive position on the market and, as a matter of fact, commercial future. It is inventions and patents that reflect technical ideas and tendencies of scientific-technical progress dominating at a given period of time, determine priority directions and most progressive world-wide acknowledged technical decisions, serve as a coordinating factor of world researches and developments. Inventions are somewhat like standards of scientific-technical progress.

But it turns out that many of these standards determining technical development of the world economy have destructive effect upon the environment. For example, inventions in the field of geochemical processes under the influence of ore mineralization oxidation bring about chemical and sanitary pollution of subterranean and surface waters , deterioration of biological qualities of general landscape on adjacent territories, infection of agricultural products.

Indeed, most of inventions affect the environment this way or other. But at present time there are no standards in the international law and national patent laws which eliminate the recognition of ecologically harmful (dangerous) technical decisions as inventions. In practice that means that there is no analysis on the "ecological purity" criterion when analyzing claims for inventions for their patent ability at the state patent examination. As a result the state provides legal protection to technical inventions which are conflicting with the demands of ecological protection of society. Henceforth to exclude ecological consequencies which may arise in applying such inventions their finishing, modification and sometimes complete refusal of their utilization are needed.

These days there are no direct indications to the necessity of non-recognition as inventions of those technical decisions which contradict the requirements of ecology in the USSR legislation regulating inventor's legislative relations as well as in the USSR draft Law "On Inventor's Activity In the USSR." Legislative regulation of questions concerning the protection of environment in the USSR has found its reflection only in state standards of quality of environment, special nature protection legislation (Foundations of the USSR Legislation On Public Health, the USSR Law "On the Protection of Atmospheric Air" and the USSR Law "On Protection and Utilization of Animal World") and State Ecology Program being under consideration.

In industrially advanced countries the absence of legislative regulation of ecological problems within the framework of patent legislation is partially compensated by the practice of state examination of the projects realized by state and private firms (countries-members of EEC, the USA). Such practice has found its application in the USSR, too. Besides, industrial development of various industries took the path of introducing low-waste and no-waste technologies (utilization of wastes and incidentally extracted rocks, recultivation and secondary utilization of metals, utilization and liquidation of chemical wastes, etc.), introducing the systems of closed water circulation and refineries of high efficiency etc. But the modernization of technologies or the reduction of level of their negative impact on environment need additional capital investments.

This situation brings forward the creation of legal conditions for ecological preventive measures in the development of engineering and technology. The introduction of ecological imperatives accepted on the basis of elaborated international or national ecological criteria into the content of patent legislative standards could become the most effective instrument. National patent laws should contain definite standards according to which technical decisions causing harm to the environment can not be considered inventions. These standards may have a more differential character with the possibility of recognition of technical decisions as inventions being dependent upon the meeting of requirements of this or that standard of environment's quality (maximum permissible rates of concentration, overflow disposals, radiation, sanitary and veterinary standards of protection etc.).

Therefore it is of vital interest to have the assistance from the World Organization of Intellectual Property (WOIP) in the elaboration and conclusion of an international agreement on ecologization of patent legislatures and also on their harmonization in this direction. Time has come to supplement the International Classification of Inventions (ICI) with the new headings, including the technical and technological objects, on supervision, estimation and inspection of environmental conditions.

The innovations in the field of patent law ecologization require certain time expenses. But these days it is possible to effectively use the patent system to increase ecological safety of the new technology which is assisted by the ability of the firms to apprehend ecological inventions. A new concept that the creation and utilization of ecologically pure technologies can bring profits.

The following trends of this activity can be pointed out:

- forecasting of the objects of modern technique and technologies on the basis of patent-information researches of technique's world level and trends of its development (search, selection and analysis of the sources of patent information) with the object of optimal formation of scientific-technical policy, the formulation of scientific-research tasks, the selection of the technique's objects meeting the ecological requirements for the introduction and licensing.

- the wider utilization of regulating functions of state patent examination with the object of the reduction of ecologically dengerous inventions: introduction into practice of national patent departments broad interpretation of standards concerning such criteria of the patent ability as "usefulness", "positive effect", as well as the conceptions "benefit for society", "inventions contradicting public interests" etc. Taking into account the requirements of ecological safety for the environment; the establishment in patent departments with this aim subdivisions on ecological examination;

- propagation of ecologically pure inventions, the formation of international and national banks of data about such inventions; the establishment of information edition on ecological inventions; early delivery of such information about them to the potential users;

- - adoption of state programs on the development and utilization of ecological inventions; the foundation of international and national awards for individual authors and firms; state financing of researches having special purposes; preferential duties etc.

This purposeful management of inventor's activity and the utilization of its results should become an integral part of complex decision of ecological problems,

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The use of electron paramagnetic resonance spectroscopy and trace element content of veinquartz in mineral exploration.

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Abstract

The intensity at ambient temperature of the first derivative EPR signal of veinquartz at g 2.0025 enhances the likelyhood that the quartz contains gold. The Ge, Na and K content of the mineral may be used as alternative indicators of mineralisation.

Introduction

Recently laboratory based electron paramagnetic resonance spectroscopy has been used to assess the economic potential of auriferous quartz reefs at Beaconsfield, Tasmania (van Moort and Russell, 1987), at Waihi, New Zealand (van Moort and Brathwaite, 1988) and Fosterville, Victoria (Nand, 1989). The outcome of these three studies was that gold bearing quartz is more paramagnetic than non-gold bearing quartz, as discussed further below for the Chamberlain prospect at Roseberry, Tasmania. In addition it was found microscopically that gold bearing portions of quartz veins are very fine grained.

Determination of trace elements in veinquartz was used as a complementary prospecting method (van Moort et al., 1990). The relations between mineralisation, paramagnetism and trace element content of quartz at Fosterville are presented in some detail in this paper.

The theoretical background of electron paramagnetic resonance spectroscopy (EPR) will be discussed prior to its application to geochemical prospecting.

Theory of EPR spectroscopy

Paramagnetism is caused by the alignment of elementary atomic dipoles in a magnetic field and occurs when <u>unpaired</u> electrons are resent in the atomic orbitals. It is much weaker than the well known ferromagnetism in which interactions between adjacent atoms couples their magnetic moments in rigid parallelism. Perfect quartz, neglecting surfaces, does of course not contain unpaired electrons and thus shows no paramagnetism. Actual quartz, natural or cultured, contains numerous atoms out of place and interstitial impurities, of which some as Fe are inherently paramagnetic. The paramagnetic defects in quartz are well documented (Weil, 1984).

Paramagnetic properties of minerals are routinely used by geologists in magnetic separation techniques like isodynamic separators. Electron paramagnetic resonance spectroscopy, first used by Zavoiski in 1945, provides a far more sensitive and specific technique to study details of paramagnetic properties of minerals, even if only available in microcrystalline or powdered form.

EPR instrumentation basically consists of a cavity in which a standing electro-magnetic wave is created by the supply of microwave energy from an external constant frequency generator called klystron. The cavity is located in a strong homogeneous magnetic field between the centre of two large electromagnets, allowing change of flux density. A small sample is placed in the middle of the cavity. At the given and constant frequency of the standing microwave paramagnetic resonance (alternating parallel and antiparallel alignment of the dipoles of the unpaired electrons) may occur at specific flux densities of the swept magnetic field. The resonance is measured as the first derivative of the absorption of the applied microwave energy. The measurements take little time but are difficult to quantify. EPR instrumentation, in the form of ESR spectrometers, is expensive and machines are not readily available.

Practical EPR spectroscopy

Although superior results are obtained on oriented single crystals at temperatures at or below that of liquid nitrogen EPR spectroscopy at room temperature of microcrystaline material or powders is found to be sufficient for basic geochemical prospecting. Of the gangue minerals quartz was chosen because of its abundance, constant composition and well documented properties.

All quartz was carefully selected on purity, hand ground in an agate mortar and treated overnight with hot nitric acdid in order to remove impurities. Routine X-band EPR powder spectroscopy was carried out at room temperature on the JEOL JES FE 3X analogue ESR spectrometer of the Central Science Laboratory of the University of Tasmania.

Usually three sweeps are made over respectively 500 mT (millitesla), 200 mT and 10 mT. The first two sweeps provide a survey and the ± 5 mT sweep is used for detailed measurement. The position of the first derivative cross-overs are expressed in g values, indicating the position of the calculated effective spectroscopic splitting factor.

Van Moort and Russell (1987) expressed the intensity of the paramagnetism as the heights of the main first derivative peaks at g 2.0025. This measure gives an experimental value and has no theoretical merit, as it measures the <u>rate of change</u> of the absorpton of the microwave energy rather than the absorption itself. The observed data, moreover, can only be compared with those of samples run on similar instruments under similar conditions.

Use of internal standard, double integration of the first derivative EPR signal and shape analysis (providing more precise information on the nature of the signal) are beyond the scope of this article. This paper consequently presents the data in a qualitative way only.

Sampling Program

The sampling program consisted of selecting quartz from core, with known assay values, from drillholes at the localities mentioned above. In addition hundreds of blanks and some poorly mineralised quartz samples were obtained through personal collection or supply by prospectors.

Geology of the vein systems

The Tertiary epithermal Martha Hill deposits at Waihi, New Zealand, was the man producer of the Hauraki godfield with a past production of 1100 t of gold-silver bullion from 11 Mt ore and, at present, a 10 Mt reserve at 2.6 g/t Au. Several stages of vein filling have been recognised.

The Devonian mesothermal Tasmania reef at Beaconsfield, Tasmania, is zoned and consists of auriferous quartz at the margins and ankerite in the centre. It is essentially a single 400 m long body, varying in width from 2 cm to 6 m. The reef produced 27 t Au from 1 Mt ore.

The Devonian mesothermal brecciated shearzone at Fosterville, near Bendigo, Victoria, contains little quartz. The Au is contained in arsenopyrite and pyrite in sandstones, siltstones and shales adjacent to the shearzone. Eight t Au was produced from 36 Mt ore from the alteration zone.

The Devonian mesothermal Rosebery shear, Tasmania, contains at the Chamberlain prospect a some metres wide quartz,-tourmaline reef with minor galena, pyrite and less than 1 ppm Au.

EPR results

Qualitative results published by van Moort and Brathwaite (1988) indicate how EPR spectroscopy can be used to characterise multiple types of quartz veins and how the peakheight of the signal at g 2.0025 can be used as a measure of mineralisation.

Plotting of the EPR peakheight of quartz spot samples against the Au assay values over the corresponding 1 m length of core at both Beaconsfield and Fosterville indicates that when the quartz is not paramagnetic there is no Au and that when there is Au the quartz is paramagnetic. The Au-EPR relation for Fosterville is shown in fig. 1. In both areas paramagnetic quartz unfortunately still may not indicate the presence of Au. All blank samples (samples without Au), taken outside the immediate areas of mineralisation, did exhibit weak paramagnetism only.

The results for a drill hole through the Rosebery shear at the Chamberlain prospect (fig. 2) indicate how accurately the mineralised zones of the reef can be picked up. The grades of the reef are too low to be of economical importance.

Trace elements in quartz

Because of the sometimes inconclusive results of the EPR method in search for gold mineralisation, Nand (1989) for Fosterville and van Moort et al. (1990) for Beaconsfield applied trace element content of quartz by proton induced x-ray emission (PIXE) and atomic absorption spectroscopy(AAS). The preliminary results were that K and Ge in quartz are the elements typically related to Au mineralisation, either in or outside the quartz. The K is associated with the occurrence of submicroscopic sericite inclusions in the extremely fine grained crosscutting quartz veinlets mentioned in the introduction. The Ge is a lattice substitution in the quartz.

Fig. 3 shows the relations at Fosterville between the presence of Ge in the quartzveins and the Au in the hostrock outside the quartzveins. The relation appears to be discontinuous. Fig. 4 shows the continuous correlation between the intensity of the EPR and the Ge content of the quartz. Not shown are the later determined Na-Au relation (also discontinuous), and the very good continuous positive correlation between Na and EPR.

Discussion

The positive correlations between the intensities of the electron paramagnetic resonance of the quartz, its Ge, K and Na content and the Au content of the quartz or the adjacent hostrock are thougt to be rather coincidental than causal. The coincidence appears to be the rapid deposition of quartz and ore in a fracture zone.

The solubility of quartz is strongly temperature dependent and its precipitation will be caused by drop in temperature in ascending hydrothermal fluids (Siever, 1962; Mackrides et al. 1980). GeO is at higher temperatures much more soluble in water than SiO (Morey, 1957; Kennedy, 1950). Consequently it is an element enriched in late magmatic and hydrothermal fluids. This leads to enrichment

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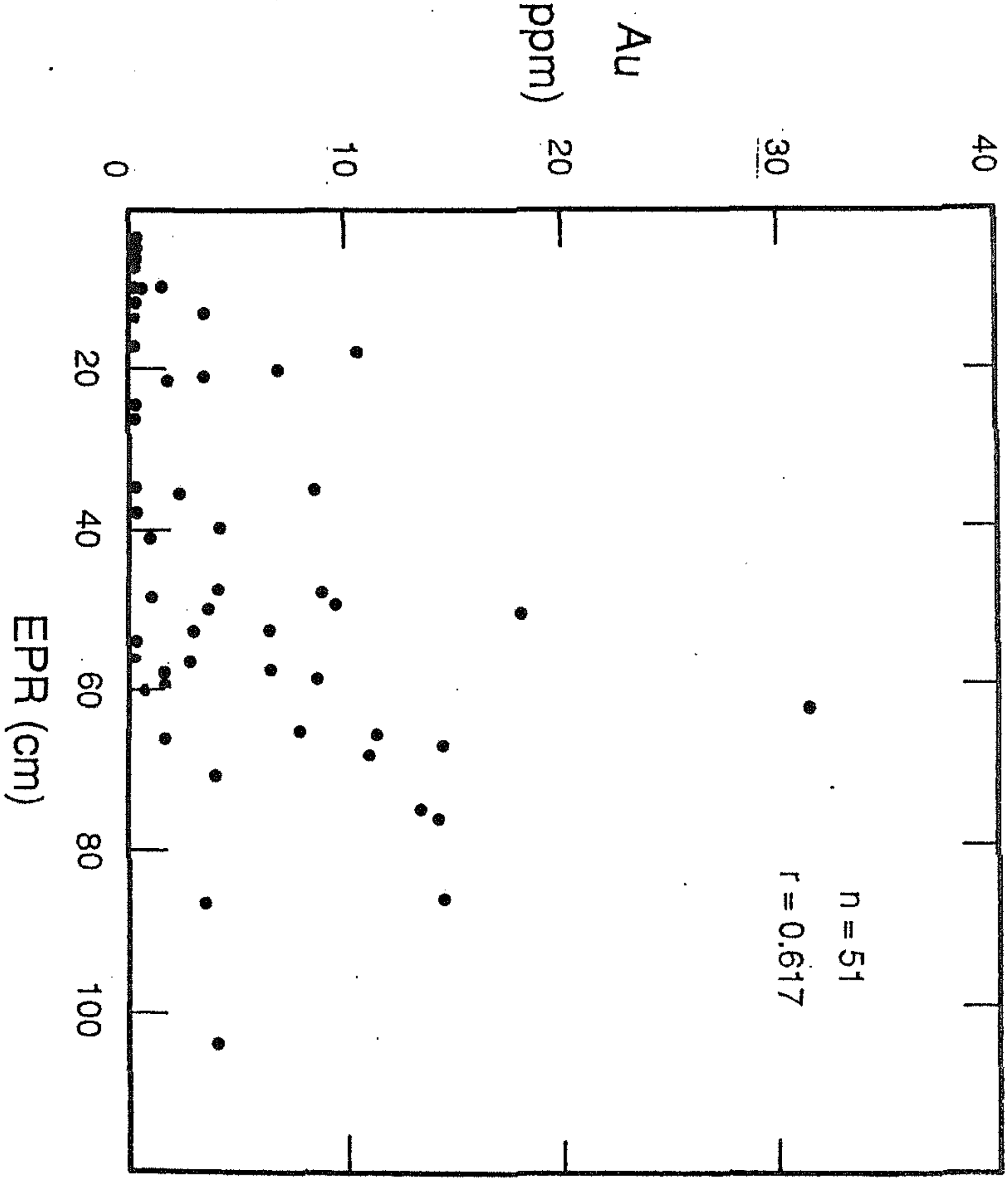

Figure 1: Scatterplot of the paramagnetism of Fosterville vein quartz (measured as the height of the first derivative EPR peak at g 2.0025) against the Au content of the host rock in which the small quartzveins are located. The EPR scale (in cm) is a relative scale. Spearman ranking correlation coefficient of 0.62.

of Ge in quartz, sinters and sulphides, as was established by Blankenberg an Schrön (1982). Au is presumably precipitated through destabilisation of gold complexes in rapidly rising fluids (Seward, 1973).

The paramagnetism of quartz is neither caused by the presence of Au (as can be deduceced from the Fosterville case) nor can it be caused by the presence of Ge, a non paramagnetic element. The strong EPR signal at g 2.0025 has been attributed to the presence of the AlO centre by Imai and Shimakowa (1985). This is unlikely to be the case, as this centre is not visible at room temperature.

The sericite inclusions, common in gold bearing quartz explain the high K content. The presence of Na in Au bearing quartz has to be further investigated.

Exceedingly fine grained quartzveins occur in cracks in earlier quartz, whenever Au is found. Consequently the presence of broken bonds due to imperfect crystallisation may not be excluded as a factor contributing to the paramagnetism of the quartz.

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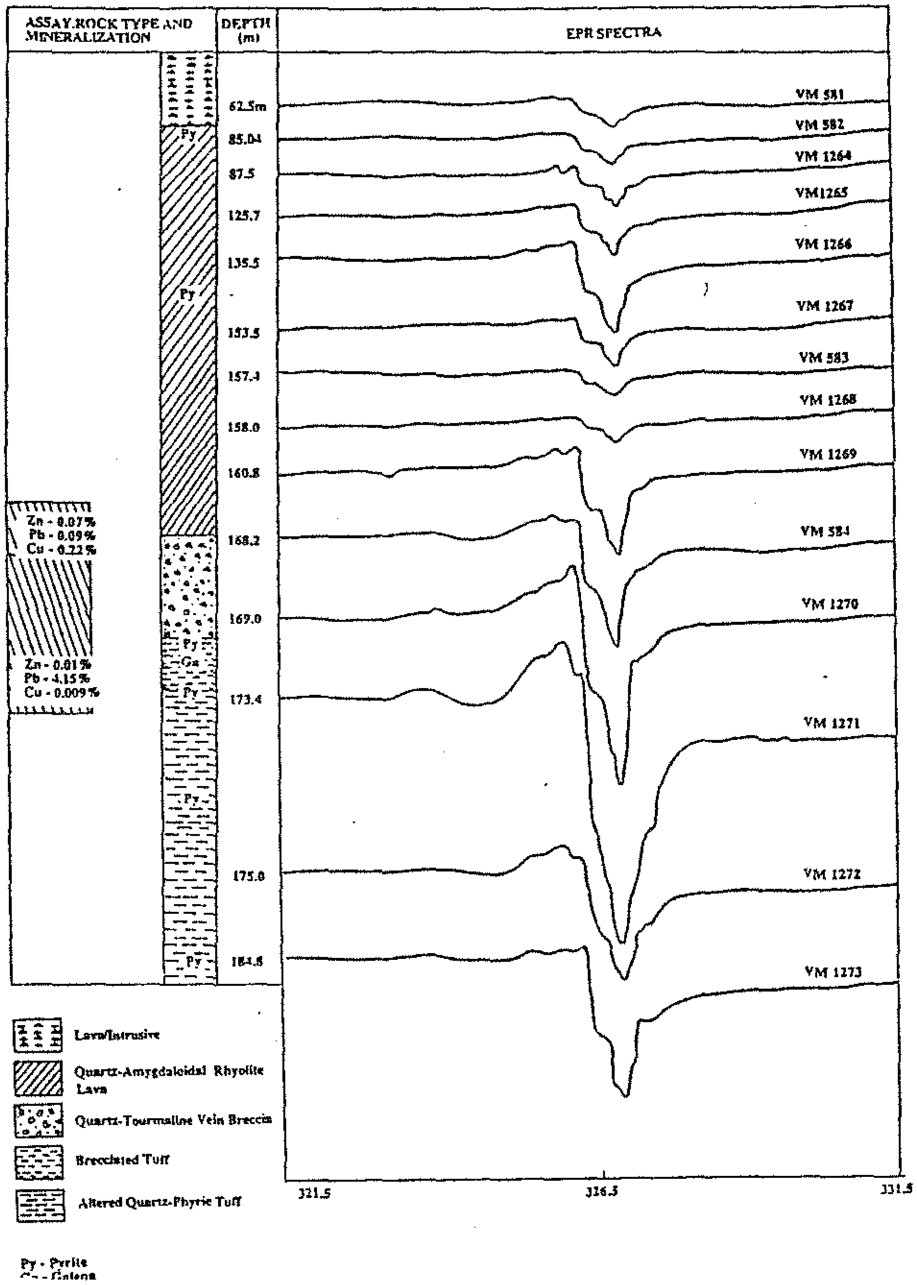

Figure 2: Geology and EPR spectra of quartz from DDH CP 281, Chamberlain prospect, Rosebery. First derivative spectra at magnetic flux density sweeps over 326.5 ± 5.0 mT. The intensity of the central signal at g 2.0025 is much larger in the intersection of the weakly mineralised quartz-tourmaline vein (containing at best 1 ppm Au).

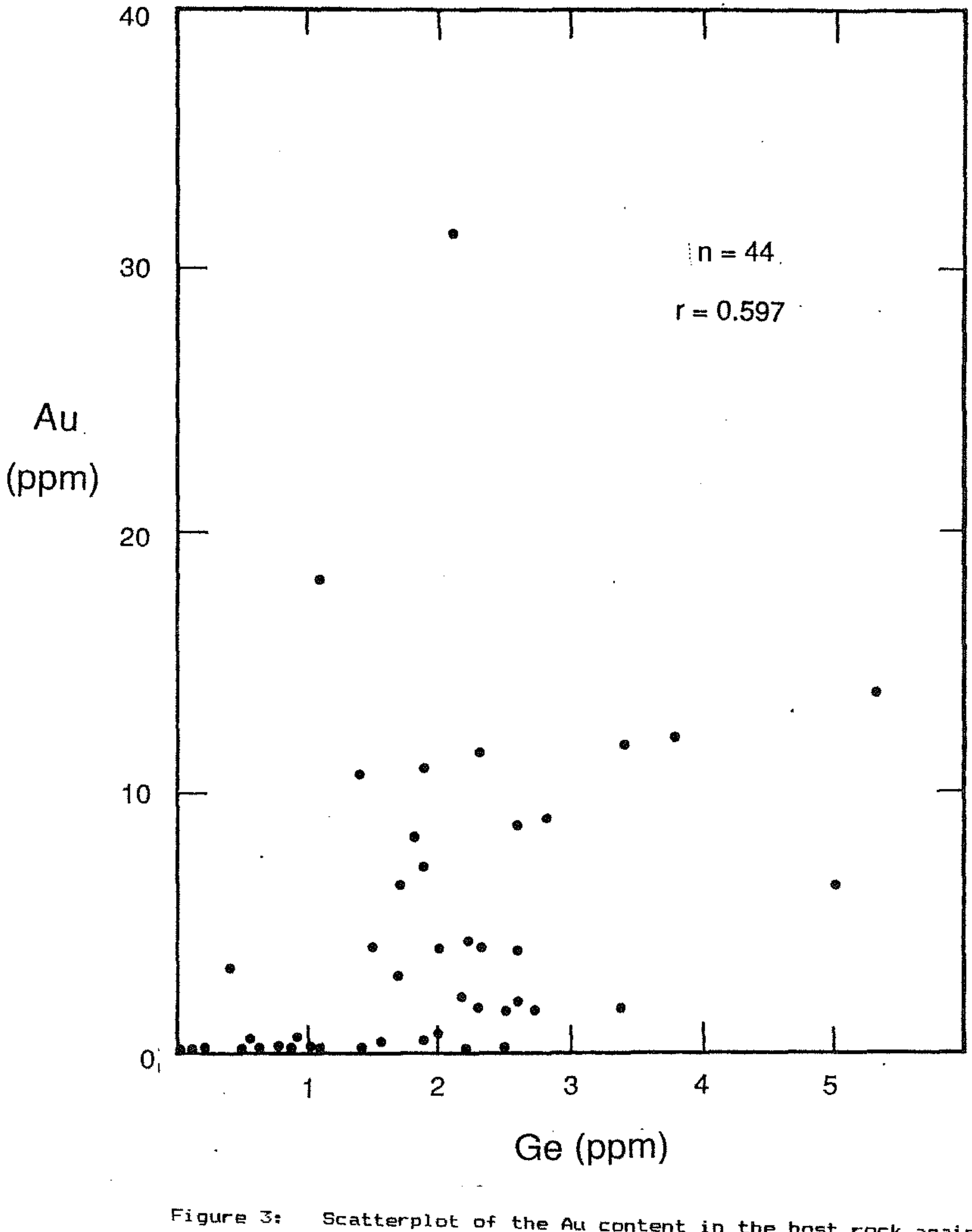

Figure 3: Scatterplot of the Au content in the host rock against the Ge content of the veinquartz at Fosterville. Spearman ranking correlation coefficient of 0.60.

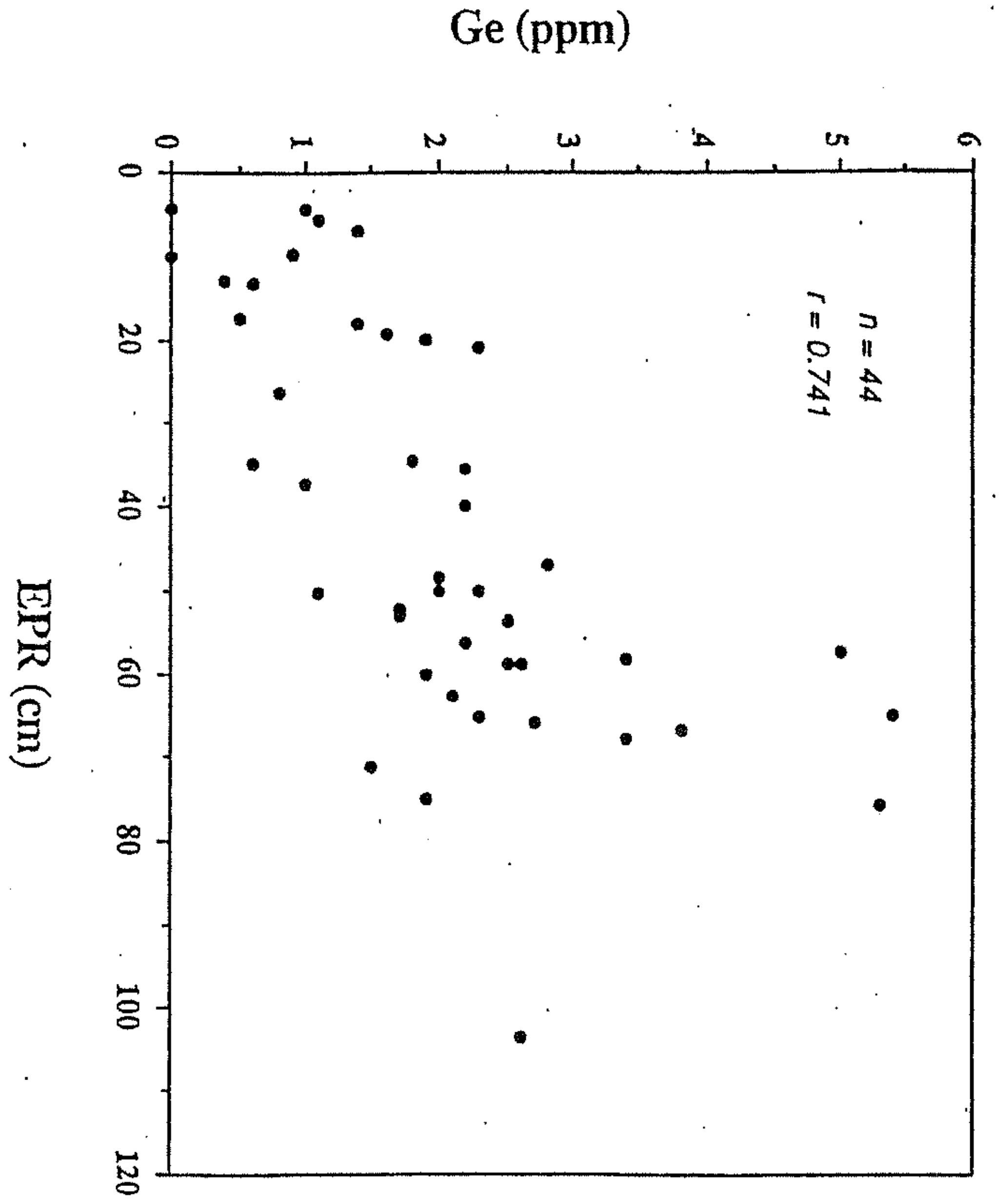

Figure 4: Scatterplot of the Ge content and intensity of paramagnetism of veinquartz at Fosterville. Spearman ranking correlation coefficient of 0.74.

THE CLAY FRACTION OF OVERBANK SEDIMENTS AS A GEOCHEMICAL SAMPLE MEDIUM FOR THE ARID ZONE (CONJOINED WITH PANNED CONCENTRATES)

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ABSTRACT

The clay-size fraction separation technique described here was developed as a result of reviewing the applications of classical -80 mesh stream sediment programs which were unsuccessful in the Australian Arid Zone.

The attempt to develop an homogeneous sample medium was not 100% successful, but the present mixed-medium clay-size fraction of the overbank stream sediments appears to give a much more satisfactory result than any other sample type generally in use in stream sediment sampling for "grass roots" exploration in this environment.

The rationale behind this sampling, the sampling procedure, sample preparation and analytical techniques used are discussed.

The overbank sites sampled were found to contain more heavy minerals than the standard trap sites, negating the need to collect separate samples for panned concentrates.

INTRODUCTION

The results of -80 mesh stream sediment sampling programs in the Australian Arid Zone have been known to be unsatisfactory for some time. Particularly worrying was the lack of correlation between assay results for samples collected at the same site by different samplers and by the same sampler at the same site at different times (An example for two adjacent sample sites sampled on three occasions may be seen in the Appendix).

Experimentation using various techniques to derive a "clay" fraction in the hope of increasing the homogeniety of the sample medium over the past ten years led to the present system. The unpredicted heavy mineral content of overbank silts has allowed the integration of an "ion adsorbtion" sample medium and a "resistate heavy mineral" sample medium (c.f. Sutely et al., 1990) without the cost of collecting separate samples.

A sampling program undertaken in the well exposed Eastern Arunta Province and also in the poorly outcropping northwestern Arunta has allowed the accumulation of a database of more than 2,300 samples with a sampling density of one sample per one to two 1 minute squares (about 3.5 km^2 at this latitude).

RATIONALE

Catchment representation

In the arid and semi-arid zones where vegetation cover is not complete, clay-sized material (-2µm) is suspended by rain-drop impact and moved mechanically from all over any individual catchment to the drainage line. A portion of this material is deposited in the overbank sediments of the floodplain. A sample which represents a number of flood events thus contains clay-sized material which closely represents the *average chemistry of the soil clays in that catchment.*

No other fraction of the stream sediment is derived from the whole catchment nor is its chemistry as representative of the average dispersion chemistry for the whole catchment, as is the clay-size material.

Origin of the clay-size fraction

It had been speculated that much of the clay-size fraction of the overbank sediment might be of aeolian origin as had been demonstrated for the clays in active soil flows on quartzite hills in South Australia (Murrell, 1977). Mabbutt (pers. comm.) however demonstrated that similar soil flows north of Broken Hill NSW were dominated by clays derived from the underlying Mesozoic sediments. The variations in iron content of the clay-size fraction on the Arunta Complex suggests the aeolian influence on the clay fraction to be inconsequential.

In addition, substantial anomalies show up in the clay-size fraction of the overbank sediments many kilometres downstream from old mine workings (at Waukaringa in South Australia and at Home of Bullion 250 km north of this survey area) suggesting that substantial imprints are made on the overbank sediment chemistry in as little as fifty years.

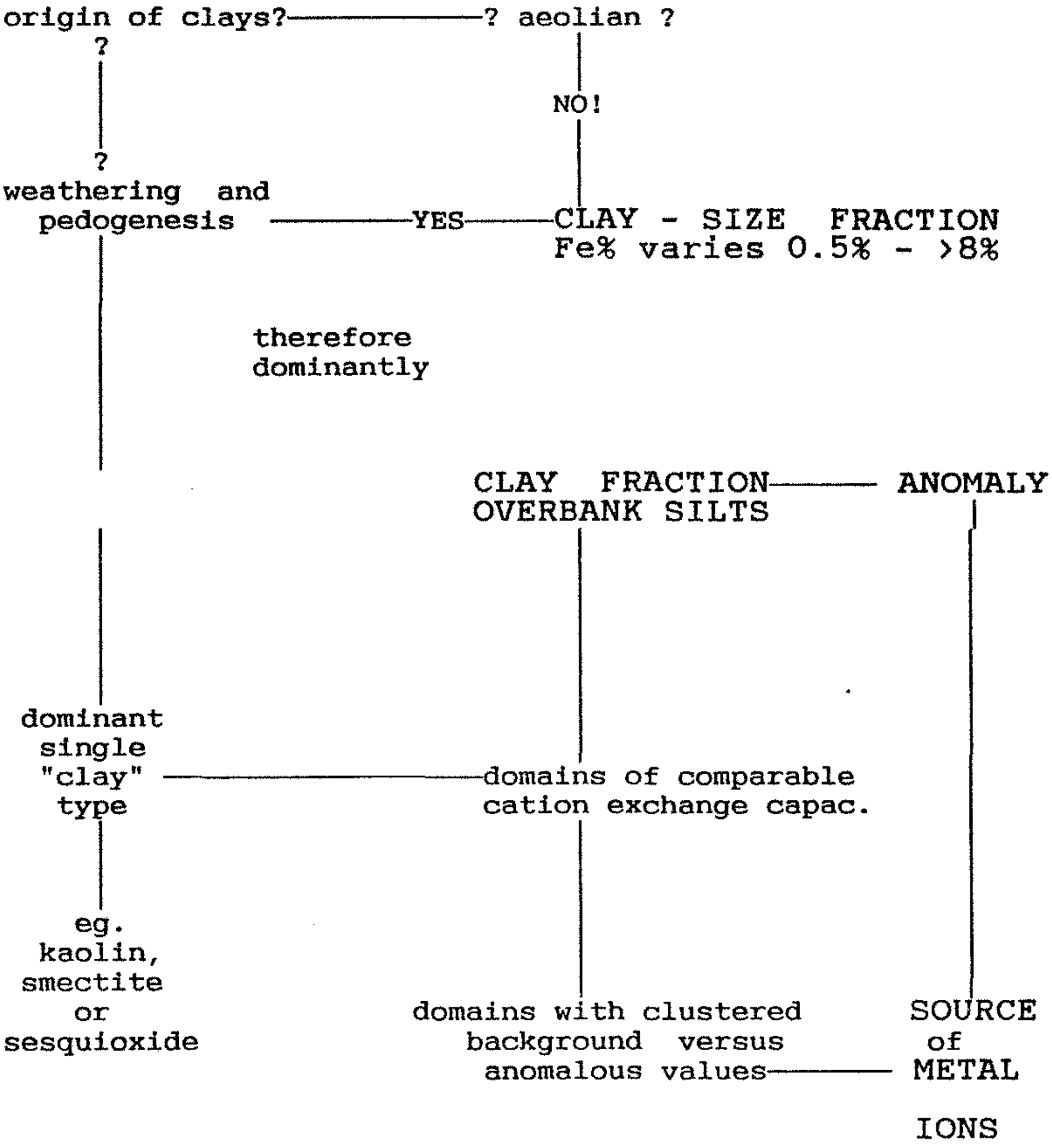
Cation exchange capacity

Clay particles and clay-sized particles of hydrated iron, aluminium and manganese oxides have cation-exchange capacities usually far in excess of the availability of metals in weathering waters (Proposition 2). This is easily demonstrated by comparing analyses of natural clay with those for the same clay which has been treated with a solution containing cations of the target metal(s) and subsequently leached with distilled water.

Dilution of sample

Silicon oxide as quartz does not have appreciable cation exchange capacity so the quartz sand and silt in stream sediment samples acts as an inert dilutent (Proposition 3; see also Bugrov, 1973).

THE ORIGIN OF CLAY-SIZE FRACTION IS PEDOGENESIS



origin of clays? — ? aeolian ?

NO!

weathering and pedogenesis — YES — CLAY - SIZE FRACTION
Fe% varies 0.5% - >8%

therefore dominantly

CLAY FRACTION OVERBANK SILTS — ANOMALY

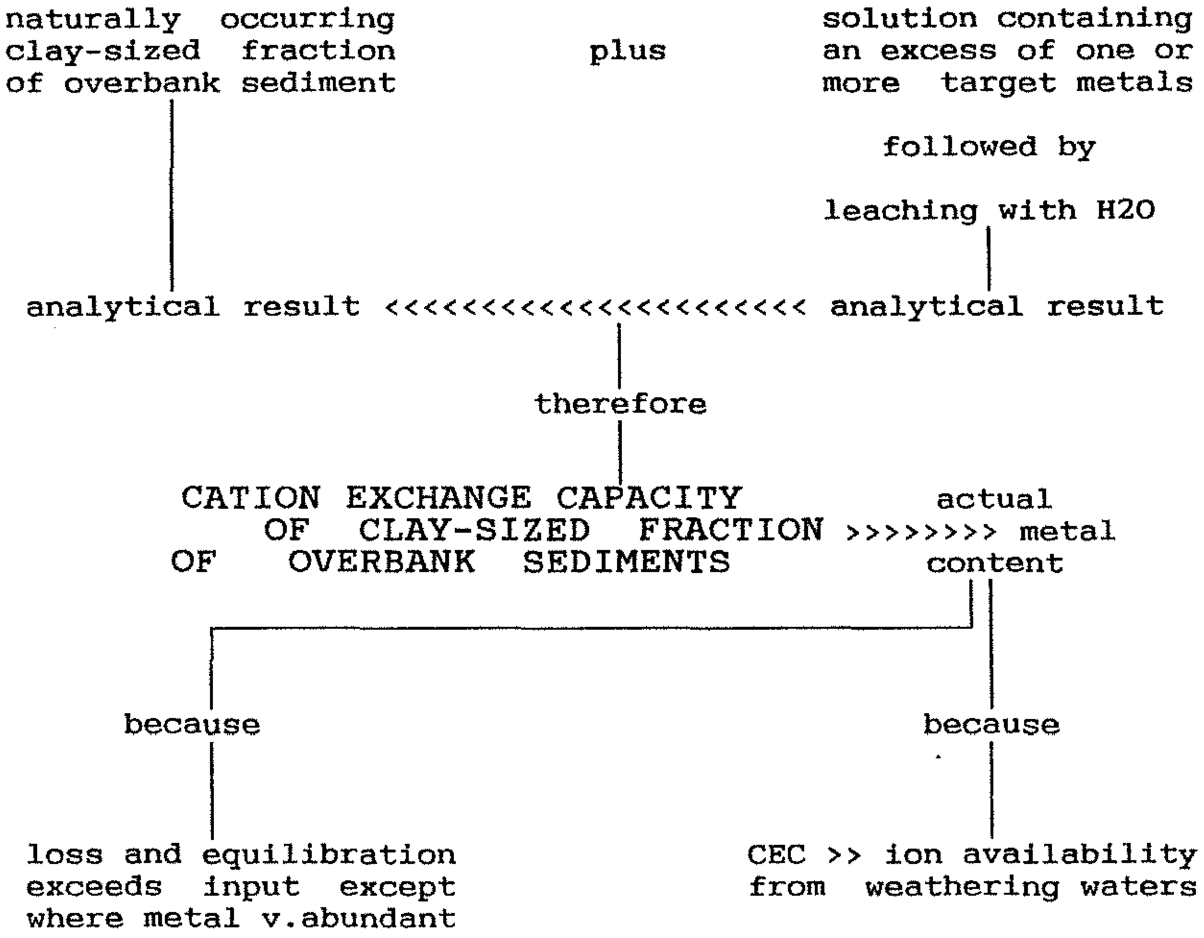
dominant single "clay" type — domains of comparable cation exchange capac.

eg. kaolin, smectite or sesquioxide

domains with clustered background versus anomalous values — SOURCE of METAL IONS

Proposition 1. *The origin of the clay-size fraction of the overbank sediments is dominantly pedogenic clays in Central Australia. Bioturbation by ants and termites probably explain the observed results.*

CATION EXCHANGE CAPACITY OF CLAY-SIZE FRACTION IS UNDER - UTILIZED



naturally occurring
clay-sized fraction
of overbank sediment

plus

solution containing
an excess of one or
more target metals

followed by

leaching with H2O

analytical result <<<<<<<<<<<<<<<<<<<<<< analytical result

therefore

CATION EXCHANGE CAPACITY
OF CLAY-SIZED FRACTION
OF OVERBANK SEDIMENTS >>>>>>>> actual metal content

because

loss and equilibration
exceeds input except
where metal v.abundant

because

CEC >> ion availability
from weathering waters

METAL ANOMALIES COMMONLY ACCOMPANY INCREASES OF Fe%
THEREFORE, CEC PROBABLY ALSO INCREASES IN ANOMALIES

Proposition 2. *That the cation exchange capacity of the overbank clays is always sufficiently undersaturated as to never be a limiting factor in adsorbing available target metal ions. The presence of a significant area where a metal is anomalous in the clay-fraction of the soils will thus be reflected as elevated values in the clay-fraction of the overbank silts.*

In a single set of 100 -80 mesh samples from one stream sediment survey of the Arunta Block, the clay-sized fraction varied in abundance between 0.5% and 99.5%. In a test set of samples collected from the Edwards Creek catchment in the Arunta Block (Figure 1) the dilution is amply illustrated by the difference in the mean of the background populations for the two sample types (Figure 2, a - f). All stream sediments in Central Australia show (by sieve analysis) a component of aeolian quartz grains in the -180µm +100µm fraction similar in appearance, size distribution, roundness and texture to the dune sands of the Simpson Desert to the southeast.

SILICA DILUTES -180µm

CATION EXCHANGE CAPACITY OF QUARTZ SAND AND SILT IS MINIMAL

Within one set of 100 -180µm sseds the claysize component varied from 0.5% - 99.5%

variation from dilution with quartz far exceeds variation of adsorbed M+

In Cent.Aust. stream seds, the 100µm to 180µm fraction are dominated by aeolian quartz

Proposition 3. *The variable dilution of clay-size material (of modest CEC) with quartz (of minimal CEC) far exceeds variability due to adsorbed metal ion content in most -180µm sample results.*

Modification of overbank clay chemistry

The chemistry of the floodplain sediments can be modified by post-depositional leaching (in the case of effluent stream valleys) or enhanced by cations from groundwater outflow where the watertable periodically rises to saturate the floodplain. The presence of several populations can generally be detected from the data set and samples placed in subsets or separate domains according to catchment type. Catchments of similar size in a si gle geomorphic unit (eg. hills vs pediplains) commonly fall within a single domain.

Panned concentrates

Abundant heavy minerals were observed to be consistently present in overbank silts (from small catchments) early in the development of the clay separation technique. It is assumed that when the clays are wet, they stabilize the overbank material which acts as a riffle collecting heavy minerals from the traction load as it is swept across the floodplain during flooding. Percentages of heavy minerals are commonly higher than from materials collected from "trap sites" in the active channel, though the particle size is generally smaller.

The resistate minerals such as zircon, wolframite, tantalite, monazite, the niobium minerals and beryl have no chemical dispersions (except, as in the case of the REE's, where associated minerals release metals which adsorb onto clays). The surprise addition to this list is apatite, the abundance of which in the pan concentrates is not reflected in the phosphorous content of the clay fraction.

SAMPLING

Selection of sample site

Sample sites are selected using stereoscopic viewing of aerial photographs. The sample site is marked on a transparent overlay and the outline of the catchment which it represents is also delineated for later digitising. Sample sites are chosen which represent unique catchments in the order of magnitude between 0.5 km^2 and 5.0 km^2 where invisible gold is sought but may be larger if base metals only are sought.

The sample

A calico sample bag 200mm X 300mm is filled from any overbank site where it appears that silts and clays from a number of flood events have been deposited. In confined channels where little if any overbank is present, samples are collected from behind obstructions such as vegetation, from the tops of islands in the channel and as a last resort, clay curls from drying pool sites (single event samples).

SAMPLE PREPARATION

Equipment

The entire clay separation process is carried out using commercial polyethelyne or polypropylene wash basins of about 12 litres capacity, a mild steel gold pan and a 200mm nylon kitchen sieve with about a 1mm aperture. "Sample bowls" are drilled with a 2mm hole in the rim to take a tie for a "permatag" and a second hole the same diameter drilled directly below about 10mm above the level of the bottom of the basin. This drain hole is covered by a piece of "tessa" packing tape stuck on the outside of the basin until the clay has settled. One basin has been modified ("the separating basin") by the addition of a standard pvc plumbing fitting, a straight pipe about 50mm long and 35mm internal diameter, threaded on the outside with an hexagonal nut flange on one end. This pipe is fitted through an appropriate hole cut in the centre of the basin, sealed by an o-ring and secured by a pvc nut so that the projecting side is internal to the basin, standing some 40mm above the floor and blocked when closed by a sink plug of appropriate diameter.

Dispersion

The whole sample is placed in a sample bowl, labelled, the sample bag retained to dry the pan concentrate, the bowl filled above the sample with rain water or dam water, stirred to facilitate dispersion of the clays, skimmed to remove flotsam and allowed to stand overnight. Rain water or distilled water is necessary to avoid flocculation of the clay fraction during sedimentation of the silt-size fractions. Rainwater caught for stock in earth dams is quite satisfactory for this purpose as the settling out of suspended clay leaves the water essentially de-ionized.

Clay separation

The soaked sample is stirred (with the hand, minus gold and silver rings!) and sieved into the panning dish to remove coarse material. The material on the sieve is rejected, and that in the pan deslimed with rainwater and the slimes decanted back into the sample basin, the process continuing until the water coming from the pan is clear following deformation of its contents with water. The contents of the basin is stirred, and after settling for about 20 seconds is decanted into the separating dish up to a level mark being 50mm above the level of the plug hole rim.

The level in the separating dish having been achieved either by additions of slimes from the pan or from further rainwater, it is set on a rack over the sample bowl, agitated by sweeping the hands back and forth across the bowl[1]. The material in the separating dish is allowed to stand for 60 seconds[2] and then the plug removed allowing the material still in suspension to be decanted back into the original labelled sample bowl. If the slimes contained so much silt that the level of the settled material is near to that of the plug hole, the decanted material is resuspended and the separation repeated to obtain a clean clay product[3].

The sample bowl containing the -10 micron fraction is allowed to stand overnight then the tape seal is removed from the drain hole and the water allowed to run to waste. The sample is then sun/air dried (simple most of the time in Central Australia, forced drying was necessary in Canberra), 50g packed in a kraft packet for despatch to the analytical laboratory and about 100g archived. Where it is found that silt has contaminated the sample, it can be trimmed off the bottom of the sedimented clay prior to despatch. Where the -10 micron fraction is dominated by material from oxic soils, flocs form into gels which are much more difficult to handle and dry than clay minerals which form oriented and cohesive aggregates. For this reason (and to maintain clean bucket chemistry) flocculating agents are not used

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[1] Stirring with a circular motion creates a cone of coarse sediment around the plug. When the plug is pulled to decant the still-suspended clay back into the sample bowl, silt may be drawn through with it, defeating the purpose of the exercise.

[2] According to my calculations all particles >25µm in diameter have sunk more than 50mm in 60 seconds, leaving about 50% of 10µm diameter particles in a suspension dominated by the 2µm and less diameter particles. I have been calling this product "the -10µm fraction". It commonly contains 15% - 20% superfine quartz which shows up well on x-ray diffractograms, making it analogous in composition (though not in chemistry) to marine shales.

[3] Sheet silicates commonly remain suspended with the clays and can be seen in the product, but as their cation exchange capacity is similar to that of kaolin, no attempt is made to remove them.

to hasten settling.

Panning

The deslimed sands from the overbank are panned, observed for gold, and the concentrate returned to the original sample bag to dry before storage.

Analysis

The whole clay-size fraction sample is digested in aqua regia, and aliquats drawn from this for three groups of analyses;

Au by solvent extraction/FAAS to 0.001ppm

Base metals by AAS

Arsenic, antimony, barium, iron, lanthanum, manganese, phosphorous, tin, tungsten, etc by ICPAES.

The single digestion keeps the cost down and allows multi-element analyses at a modest cost.

No panned concentrates have been assayed to date but over 2000 are in store for a possible future program.

RESULTS

Individual analytical batches show tight background population distribution for base metals and gold with clear anomalies.

The background populations commonly show a normal distribution of values except where several domains are present.

Multi-element anomalies cluster in adjacent catchments.

A calibration shift between different analytical batches for each metal often appears, requiring calibration before adding to the main data set.

Many anomalies have been located, but no potential orebodies have been identified to date.

ACKNOWLEDGMENTS

The data gathered in the Edwards Creek area and at Maud Creek is published with acknowledgement to and the permission of CRA Exploration Pty Ltd. Data which confirmed earlier conclusions was gathered for Bruce & Mules, Arltunga NT, whose contribution is also acknowledged.

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APPENDIX

The following -80 mesh samples were taken at three different times during 1979 - 1980 from adjacent sites at a junction on Maud Creek (Riddoch 1:100,000 sheet area) by different samplers. The catchment size is West Branch approximately 9 km², East Branch approximately 15km².

West Branch	600080	826262	822072
Cu ppm	10	26	50
Pb ppm	12	26	15
Zn ppm	22	100	65

East Branch	600081	826261	822071
Cu ppm	12	28	26
Pb ppm	5	24	5
Zn ppm	20	99	28

Figure 1. Locality map.

Figure 2. Stream sediment chemistry, Edwards Creek, NT.
(a) -180μm AAS copper.
(b) -10μm ICP copper.
(c) -180μm AAS lead.
(d) -10μm ICP lead.
(e) -180μm AAS zinc.
(f) -10μm ICP zinc.

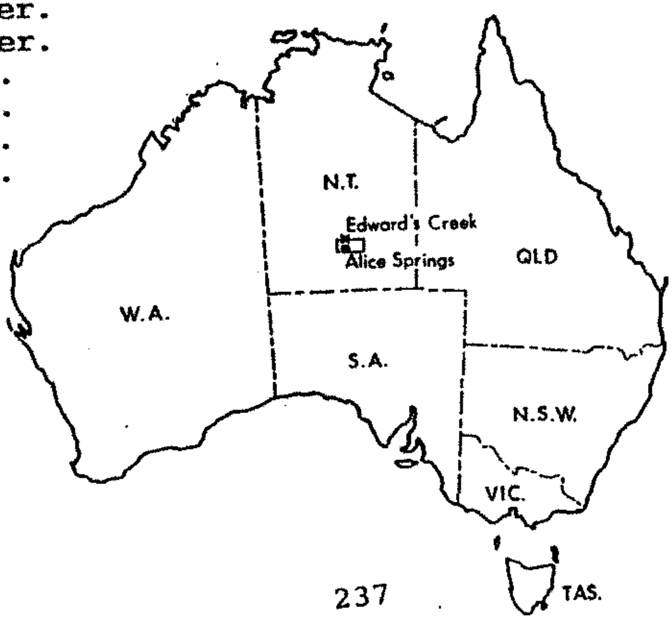
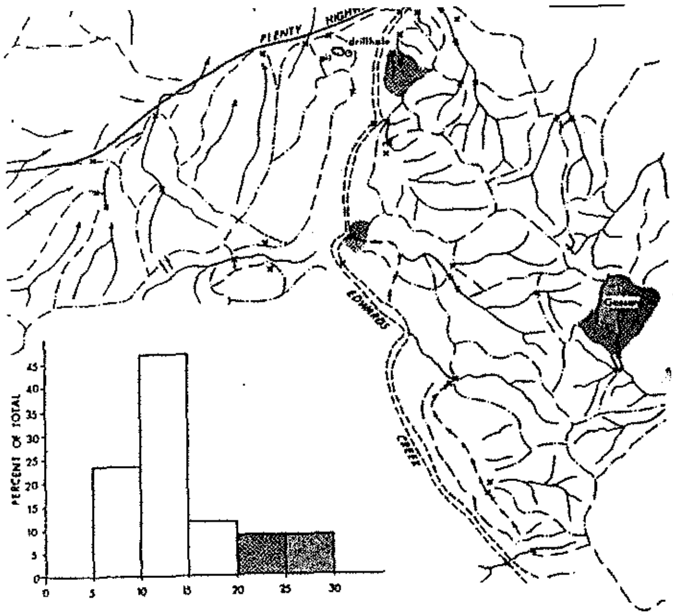
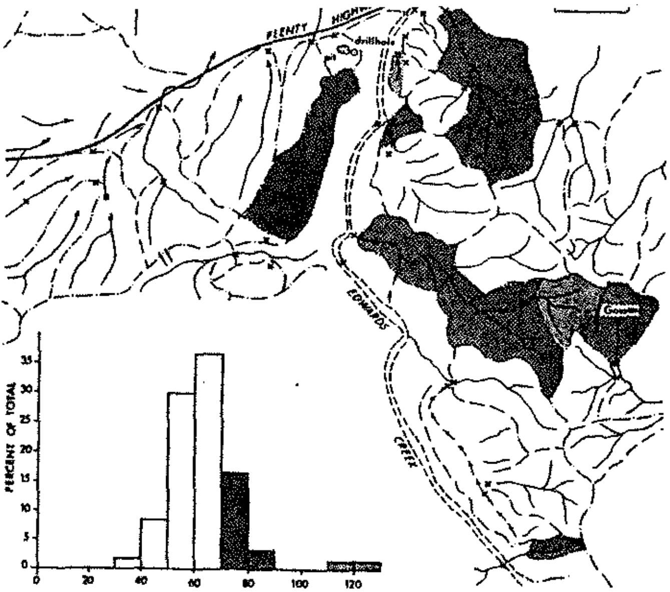


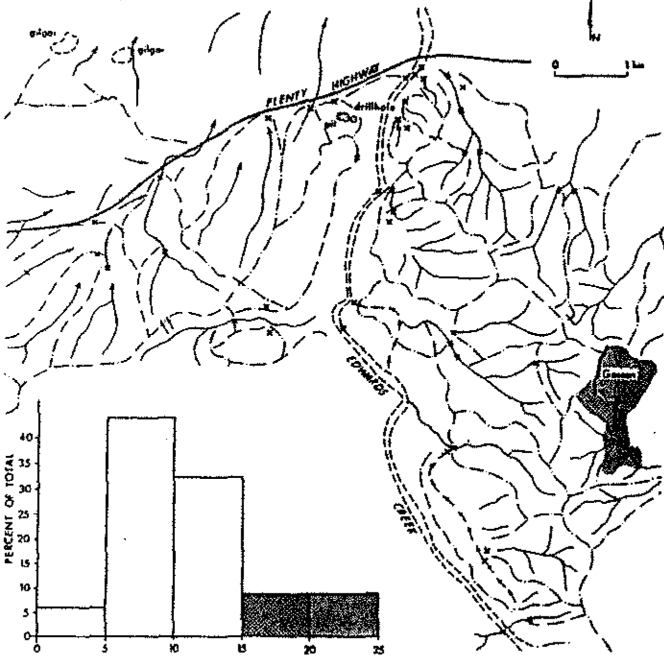
Figure 1. Locality map.



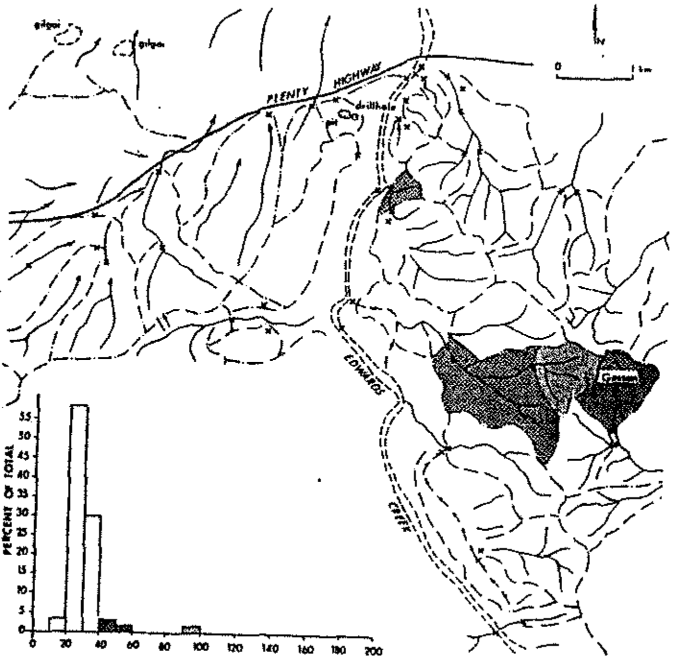
−180 μm AAS copper (ppm)



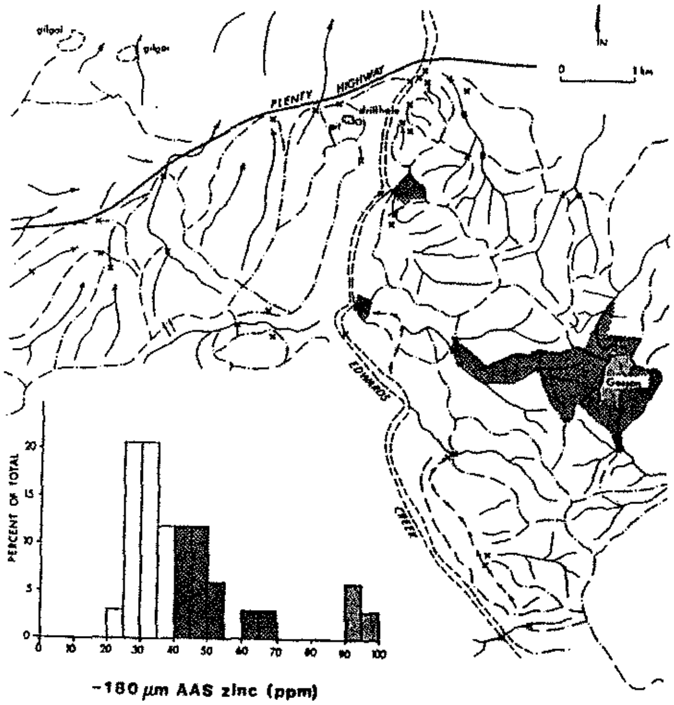
−10 μm ICP copper (ppm)



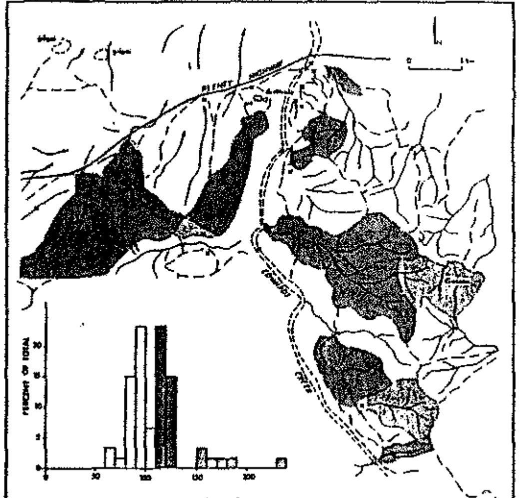
−180 μm AAS lead (ppm)



−10 μm ICP lead (ppm)



−180 μm AAS zinc (ppm)



−10 μm ICP zinc (ppm)

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COMPOSITION OF ORE-ASSOCIATED HALOES AND MECHANISMS OF THEIR FORMATION.

Geochemical haloes are widely used in geological practice. However, the successful use of geochemical data depends on our knowledge of haloes composition and mechanisms of their formation.

Usually the formation of ore-associated haloes is considered to be the result of interaction of hydrothermal solutions with the host rocks, while solutions move in interstice of fracture. Ore components are deposited in veins and are dispersed in host-rocks as well. That's why ore-associated haloes are often called haloes of dispersion. For example, uraniferous vein may be accompanied by the albitization halo with the increased content of uranium. In this case sodium and uranium are supposed to be introduced into the host-rocks by a solution from the fracture.

The filtration and diffusion are theoretically admitted as mechanisms of migration of elements into host-rocks. In fact the diffusion model doesn't always correspond to the real distribution of permeability and to differences in pressure. This model demands a considerable amount of filtrating solutions [1] and it doesn't explain reverse migration of separate elements [4](Fig.1).

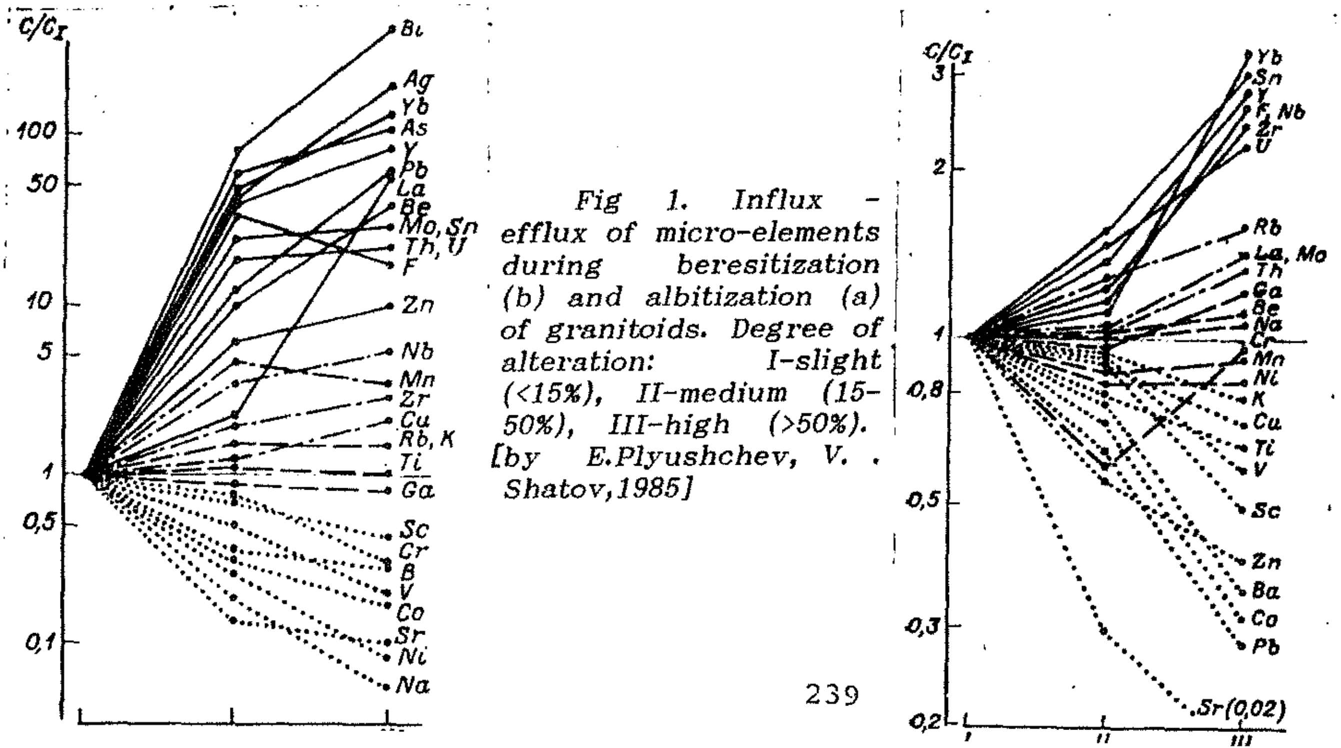


Fig 1. Influx - efflux of micro-elements during beresitization (b) and albitization (a) of granitoids. Degree of alteration: I-slight (<15%), II-medium (15-50%), III-high (>50%). [by E.Plyushchev, V. Shatov,1985]

The diffusion model is restricted by the speed of element diffusion:

$$l=\sqrt{D*\tau}$$

(l-depth of diffusion penetration, D - coefficient of diffusion, τ - time).

New data explaining the element migration in haloes have been received during the recent research of fluid inclusion in zone of ore-associated alteration.

The great amount of macrofaults as well as microdislocation is observed in ore-hosting tectonic zones. Many of these microfissures don't exceed an individual grain (Fig.2).Microfissures of such type are usually filled up with the same mineral.

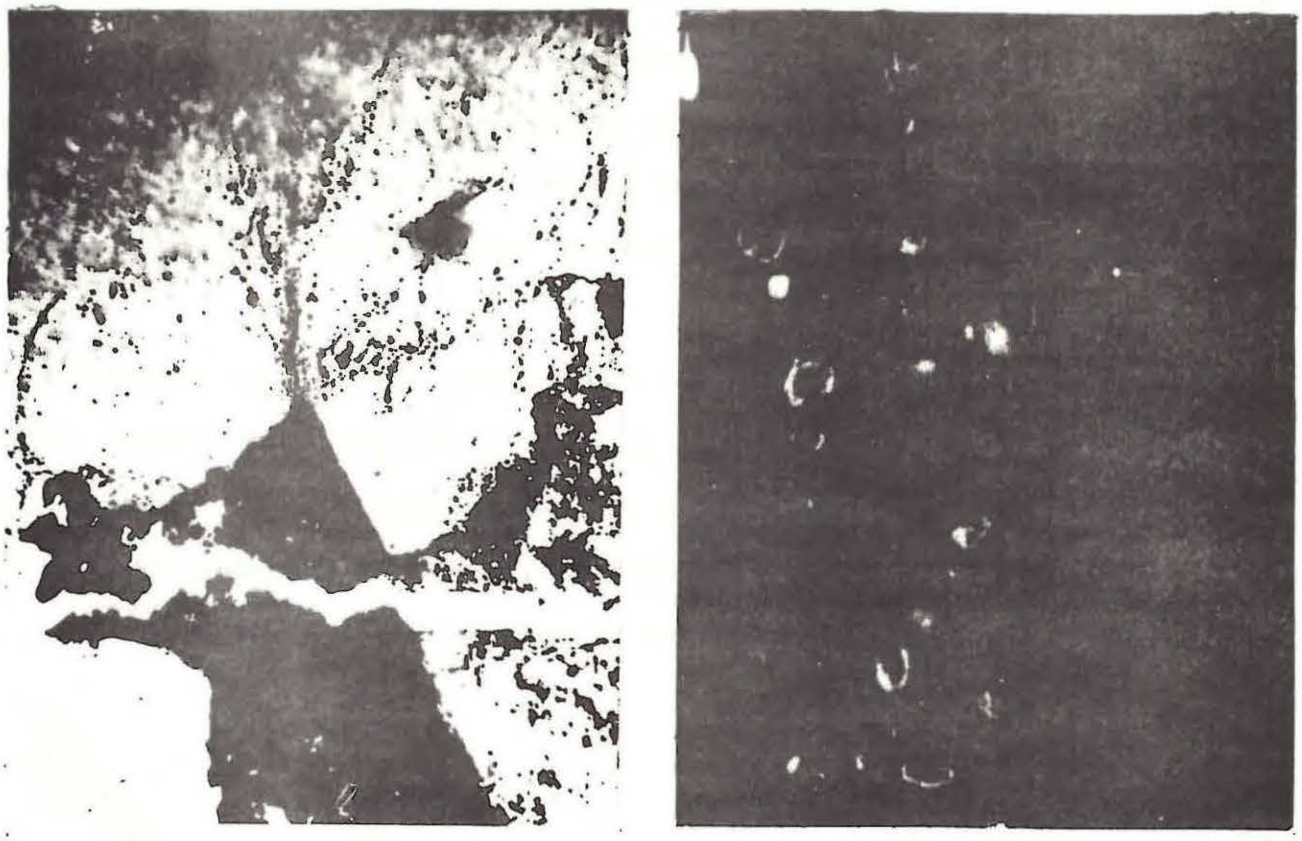

a b

Fig. 2. Microfissures (a) and secondary fluid inclusions in quartz of granite.

At the same moment pore solution is conserved in microinclusions. There are the secondary fluid inclusions in minerals. The more of this microfaults the more of secondary fluid inclusions [2](Fig.2a). Usually haloes with such type of inclusions are several times wider than metasomatic and geochemical ore-associated haloes. The amount of these inclusions increases towards ore veins.

Another tendency characterizes the gas component distribution in inclusions. Usually its concentration decreases towards the axis part of fracture zones [Fig.3].The partial pressure and total fluid pressure is lower in the axial parts comparing with the far-away parts of the halo. It means that the central parts of zones aren't the feeding but draining structures.

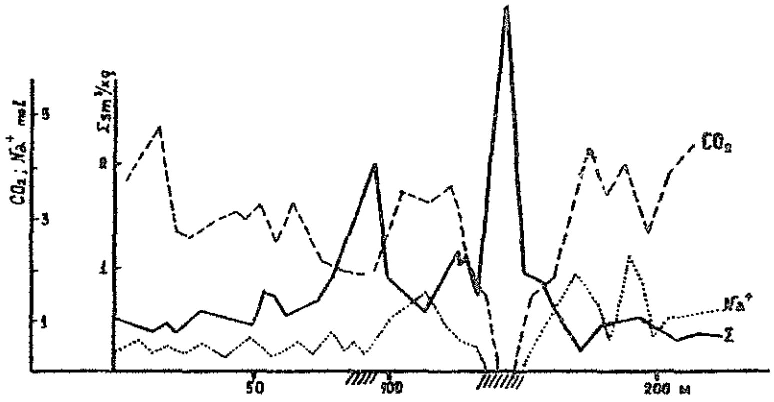


Fig 3. Fluid halo of rare metal albitites (Eastern Zabaikal'ye)

The analysis of another elements in fluid inclusions gives the supplementary data about the forming of ore-associated haloes.The concentration of sodium in albitization zones [Fig.3] is considerably less than in slightly altered host-rocks. The Cl concentration doesn't change significantly. In this case the albitization is connected with the migration of $NaHCO_3$ towards the axis, much more "opened", parts of geological structures. The degassing of CO_2 takes place in these parts, and the excessive sodium is bounded in albite.

Numerous determination of plagioclases composition in cross-sections [5] indicated, that the gradual increase of albite content in plagioclases begins far away from albitization zones. At the same time Ca is bounded in sphene, epidote and carbonate. Slight propylitization of rocks takes place and transforms up to albitization. This processes increases from periphery towards the center. Its intensity correlates with the amount of microfractures. Thus the formation of those albitization zones is connected with the redistribution of rock-forming elements. The oriented migration of Na takes place from the external metasomatite zones towards the internal ones. The whole process is connected with the mechanism of microfractures formation in rocks.

Usually a detailed sampling in ore-associated haloes reveals a rather nonuniform distribution of ore elements [Fig.4].Along with the high contents there one can see a group of samples which contain ore elements in considerably less amount than background.

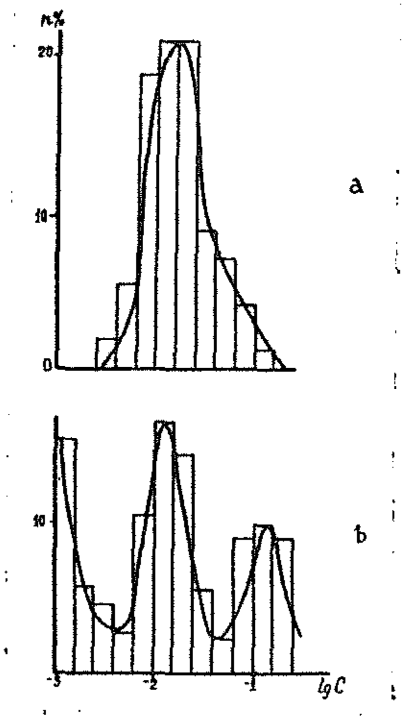
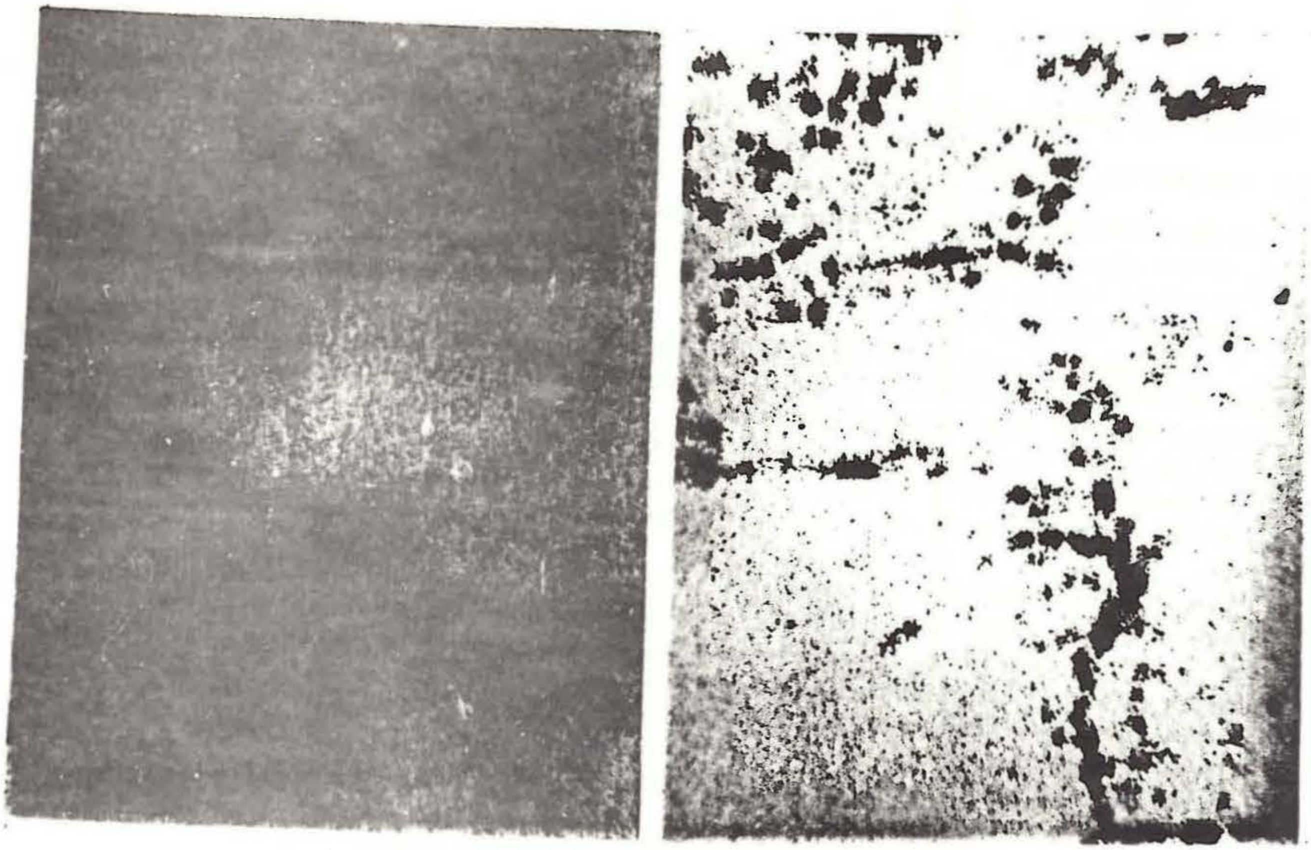


Fig. 4. Distribution of Zn in the rocks of Sumsarskoye deposit: a – background, b – ore-associated halo (according to S.W.Grigoryan, 1982).

Substantial non-uniform distribution is caused not only by input of ore-elements, but also by its redistribution. This phenomenon is noted also in far away overbackground haloes, which have got a special name of subbackground haloes. The average-values contents are equal to background contents [Cb], but their dispersion is more considerable. Defficiency of ore elements characterizes those subbackground haloes. The sample amount with Ci<Cb is larger than the sample amount with Ci>Cb. The mean contents of ore elements are lower than 20-30%, but sometimes 40-60%, than background contents. These zones have been found out in the deposits of U, Au, Sn, Pb, Zn, Cu, etc.

So, the formation of geochemical haloes can be connected not only with dispersion, but also with concentration of elements. The elements, that are disseminated in rocks.

The migration mechanism of collective recrystallyzation processes differs from the classic mechanisms of filtration and diffusion. The microdislocations play the determinative role in these processes. Any recrystallyzation is connected with the microredistribution of elements. The elements pass microdistances in pore solutions rather quickly by means of diffusion and microconvection mechanisms. Such mechanisms of element migration in ore-free tectonic zones lead to the alteration of elements microdistribution [Fig.5]. If there is macrogradients of chemical. potential the random micromigration becomes the oriented one. Modulation of micro- and macroforces results in the integral effect. This effect differs from the result of each forcer separately.



a b

Fig. 5. Distribution of traces of induced division of U in granite-gneisses (Eastern Zabaikal'ye): a -stable block; b - zone of faults.

We have called such a migration the translational migration [3], that is such a migration by means of which the transportation of object proceeds along the axis of translation. The model of translational migratión gives a good explanation to the geological and geochemical regularities of the composition of ore-associated haloes. This regularities aren't explained by the means of classic filtration and diffusion models.

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Ecological-geochemical estimate of condition of urban soils

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Human multilateral actions in nature have become so large-scaled, that they considerably affect the atmosphere, hydrosphere, biosphere and lithosphere. The Antropogenic period in the Earth's development characterized by humanity as the prominent geochemical and geological force has begun.

In the sourse of several decades enormous quantities of useful natural minerals,accumulated by nature for millions of years, have been evacuated from the lithosphere to the biosphere. Rare and dispersed chemical elements, concentrated in the deposits of useful minerals, were scattered within the biosphere. The process of enrichment of the biosphere and all landscape components is going only in one direction and is irreversible. The evolution of the biosphere geochemistry is taking place and man is the leading factor in this process.

Under the influence of anthropogenic activities the nature eco-systems are being substituted by the agrogenic and technogenic ones, which acquire new geochemical features. The most intensive alteration of environmental geochemistry occur in the technogenic eco -systems - in towns, urbanized areas, since in these sites the most active multiform large-scale antropogenic pressure on the landscape takes place:

Taking as an example large cities with great number of various industrial and municipal enterprises one can trace these main trend which seem to be extended to vast territories and to some extent to the whole biosphere.

The estimate of ecological-geochemical condition of urban landscape can be based on the study of chemical elements contents in soils, which accumulate material for the whole period of city's existence and reflect the processes of technogenic systems geochemical evolution, which were laid in the past, take place in the present and will occur in the future. Soils represent a geochemical shield of any landscape. They present the connecting link between all components of geochemical landscape and express the integral indicator of geochemical condition of the environment as a whole.

The surface and ground water, soil and atmospheric air are the most dynamic parts of landscape, being the reflection of quickly proceeding anthropogenic effects. Water and air flows can transfer the contamination substances over vast areas. They are the differential indicators of contamination conditions of the environment. Investigations of short-time effluents of elements occurring due to the anthropogenic factirs can be carried out by means of remote geochemical technique and apparatus. In the atmospheric air the registration of concentrations of elements, occurring in the forms of small gaseous components, clusters and aerosols is conducted by mean of techniques and apparatus, based ob the direct atomic absorption determinations of elements in the air layer as well as using lidar spectroscopy.

According to the results of ecological-geochemical mapping of mantle of soil of Leningrad one can trace the main trends of alteration of specific technogenic eco-system environment geochemistry. The specific character of technogenic change of microelement content of urban soils /table 1/ is determined on the basis of comparison of the statistical treatement data of more than 1000 soil samples analyzed /the sample are selected within the urban area/ with the local geochemical background /regional sampling/ as well as with clark contents of elements in the sedimentary rocks and soils.

It is clear from table 1 that the local background contents of the majority of technophile elements /Zn,Cu, Pb, etc./ are increased as compared with the clarks in the sedimentary rocks and soils, this effect being explained by the specificity of processes in the turf podzeol soil as well by the influence of global and mesotransfer contaminating substances. The average urban contents of wide range of elements differs from the clarks by one /Pb,Zn, Ba, Sr, Sn/ or two /Cu,Bi,Ag/ orders. The contents of Ba, Zn, Ni, Sn, Co in maximally anomalous areas show especially large excess over the clarks /by two - four orders/. The process of prevailing accunulation of technophilic elements in urban soils is described in fig. 1. As a result of technogenic action within the urban soils the global changes occur, leading to reconstruction of the typical geochemical association, characteristic of the region turf podzolic soils and the new specific association of chemical elements emerges, where most abundant are the technophilic elements, having low clarks. The process of unequal accumulation of various groups of elements in soils in accordance with their technogenic changes is given in fig. 2. The proper view of the rate of urban soils microelement content change can be obtained by computing the content of elements in soils of the same region at various time. For instance, for a time of approximately 40 years in the urban soils outside the limits of industrial areas, the content of Cu, Zn, Cd, Pb in the humic horizon of undisturbed soils have increased by one to three orders /table 2/.

Under the influence of technogenetic processes the initial uniform geochemical field, typical for certain geochemical province and corresponding to the regional landscape geochemical peculiarities, is transformed to the mosaic set of elements relatively small by size but variable in associations and their contents in technogeochemical anomalous fields /fig. 3/. The distribution of revealed technogenic anomalies over the city's territory is connected with the location of industrial areas, buried dumps of industrial and municipal wastes and corresponds to the age of city's region in accordance with the principe: the older is the region, the more changed are the soils. In the specific condition of Leningrad the geochemical field was found to be zonal. In the historical centre of the city, where the industrial enterprises have never existed, an area was disclosed, which is characterized by an average urban content of almost all elements. Around the historical centre the series of abnormal regions are located, which differ from each other by the associations of chemical elements as well by their concentration. They form a vast abnormal zone, confined to the former industrial outskirts and modern industrial construction sites. The average-urban and lower contents of the majority of elements were found to occur along the periphery of the ring zone, the distribution of elements coinciding with the modern new residential areas.

In technogenic soils, the natural relationships between pairs of elements-geochemical analogues, which are usually rigid in natural soils, are broken /table 3/. The imbalance of microelement contents in soils is being naturally transferred to the continguous mediums and has no regular pattern. The occurrence of "forbidden" geochemical associations, for instance, lithium, rubidium, calcium, tungsten an one hand and cobalt, nickel on the other seem to be an important peculiarity of technogenic landscapes.

Such geochemical parameters of urban environment, like excessiv and insufficient or deficient or imbalance of rare and trace elements may create a precondition for the occurrence of a wide range of human diseases, called microelementosis. Beside that there is a high rate of cancer expectancy, genetic and other kinds of human disorders. The state of health of the population, abundance of various diseases and the rate of mortality are considered to be the major criteria, to characterize the ecological situation in a city or an area. This is happening due to technological impacts on the biosphere which ignore the administrative and state boundaries and ecological processes occurring in all Earth's regions, where the anthropogenic activities take place. A decision has to be taken worldwide as soon as possible in order to solve the above mentioned problems. The development of such scientific branch as "technogenetic geochemistry" is therefore necessary and justified.

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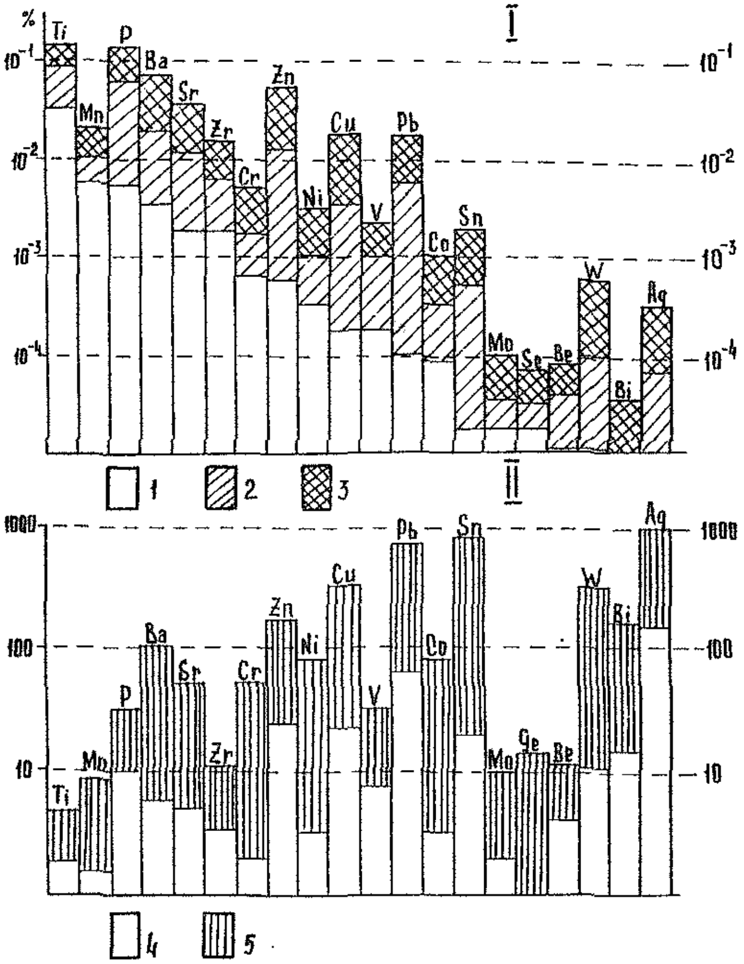

Fig. 1 - Comparative characteristic of element concentration distribution in urban soils

1 - background values of elements in wt %; 2 - mean urban contents of elements in wt %; 3 - low abnormal contents of elements in wt % /mean urban contents + standard deviation/. 4 - low abnormal contents vs background values / Ca_u/C_b /; 5 - low abnormal contents vs background values /Cla/Cb /.

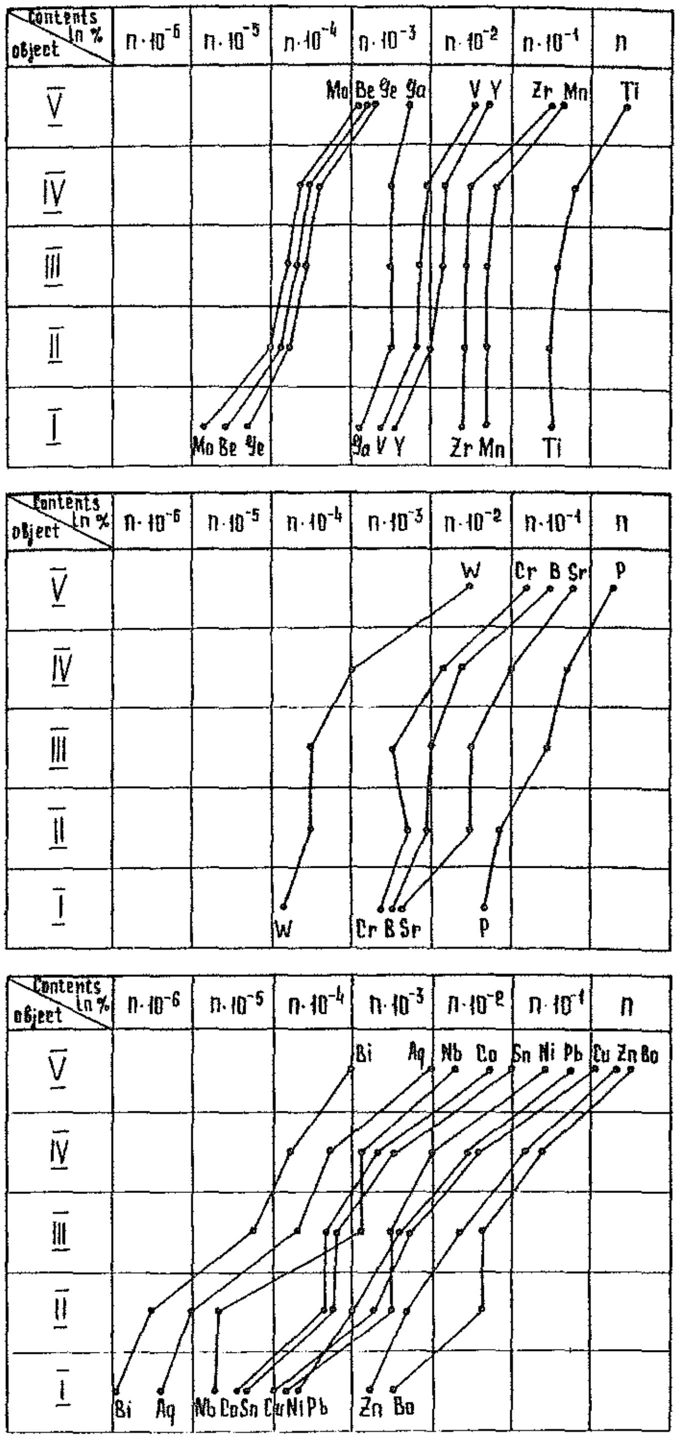

Fig. 2 - Distribution of mean contents of microelements in sedimentary rocks, natural soils and technogenetic /urban/ soils

1 - sedimentary rocks; 2 - world soils /clark/; 3 - regional soils /local background/; 4 - urban soils /mean level/; 5 - soils of urban anomalies.

CONCLUSION

The statistical distributions of elements are found to be lognormal with a bimodal or polymodal character.
Lithogeochemical and pedogeochemical maps showed clear anomalies that correspond to indices of mineralization.
The obtained geochemical associations caracterize the two principal types of Zn, Pb and Cu, As, Sb. mineralizations.
Geological and geochemical maps revealed the lithostructural control.
The technics of this prospection can be satisfactorily used for searching for such ore deposits in similar semi-arid zones.

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THE ROLE OF PATENT SYSTEM IN SOLVING ECOLOGICAL PROBLEMS CONNECTED WITH GEOCHEMICAL RESEARCHES

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Nowadays ecological problems has reached their crucial point on global scale. To solve these problems the efforts of all nations and non-traditional approaches are needed. One of them may be a purposeful ecological reorganization (ecologization) of patent law as well as the reorganization of international and national patent systems.

Scientific-technical progress and industrial society exert negative influence upon ecological systems responsible in the end for life on the planet. At the same time it is this progress that determines the positive development of human society and has the irreversible character. Hence the mission of international community and individual states is to ensure such a control of scientific-technical progress that would secure the highest harmonization of science technology or, at least, minimize technological impact on the environment.

Among different types of human activities inventive creativeness is the first and immediate source of scientific-technical progress and scientific discoveries and inventions are the decisive factors of this progress. Moreover, inventions are the product of not only man's imagination but of a state legal activities. It is the state that determines which technical decisions may be acknowledged as inventions. Only devices, substances, technologies, plants, cultures satisfying the criteria of patent ability which are introduced by a corresponding national legislation are considered inventions. Such criteria in the majority of countries are the world novelty of technical decisions, its evidence to specialists in a given field and industrial utility (usefulness). National and international patent departments examining international, national and foreign claims on the ground of the analyses of these criteria give out (or do not give out) protecting documents - patents. Patents, having state standing, guarantee their owners (inventors or, in many cases - firms) exclusive position on the market and, as a matter of fact, commercial future. It is inventions and patents that reflect technical ideas and tendencies of scientific-technical progress dominating at a given period of time, determine priority directions and most progressive world-wide acknowledged technical decisions, serve as a coordinating factor of world researches and developments. Inventions are somewhat like standards of scientific-technical progress.

But it turns out that many of these standards determining technical development of the world economy have destructive effect upon the environment. For example, inventions in the field of geochemical processes under the influence of ore mineralization oxidation bring about chemical and sanitary pollution of subterranean and surface waters , deterioration of biological qualities of general landscape on adjacent territories, infection of agricultural products.

REGIONAL GEOCHEMICAL MAPPING BASED ON THE HEAVY FRACTION OF TILL IN SOUTHERN FINLAND

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Regional geochemical mapping in Finland has traditionally been based on chemical analysis of the finest fraction of till. The south-western part of Finland has in addition been mapped by analysing the heavy fraction of till. The main purpose in using the heavy fraction is to widen our knowledge of the distribution of elements such as Au, As, W, Sn, Nb, Zr, La , Ce and Ba. The results of geochemical mapping from an area of 7200 km^2 in Pirkanmaa form the basis of this study. The Pirkanmaa area is located within the early Proterozoic (1.9 Ga) Svecofennian terrain and while dominated by granitoids, supracrustal schists, gneisses and migmatites are also abundant (Fig.1) In interpretating of the results, particular emphasis was given to Au because prospecting for Au has been active in the target area during recent years.

METHODS

Mapping was undertaken by systematically collecting 1 composite sample / 16 km^2 from a depth 0.5 m to 1.0 m. The heavy minerals of the samples (8 l) were preconcentrated in the field by panning and later further upgraded using heavy liquids (bromoform d = 2.89 g/cm^3) in the laboratory. The ferrimagnetic fraction was removed before analysis and the amount by weight of magnetite and other heavy minerals were parameters which have been used together with analytical data in interpretation. The analytical method adopted for the non-ferrimagnetic heavy fraction was energy dispersive X-ray fluoresence spectrometry (EDX) , with spectrophotometry for W and flameless atomic absorption (GAAS) for Au and As.

The data obtained showed distinctive characteristics: the statistical distribution of most elements was not normal, selection of elements was limited and element contents represented the concentrations within combined samples. Sampling, panning and analysis may also have caused some heterogeneity in the results. These restrictions affected the statistical method selected.

Correlation of parameters was studied based on both parametric and non-parametric measuring units (Henley 1981). Spearman's rank correlation coefficient was more suitable for these data than Pearson's product moment correlation coefficient. The non-parametric method allowed the data to be handled without manipulation. We preferred to study the heavy mineral data in original form, because during and screening some valuable information might have been lost, especially in the case of the most anomalous values which are of interest to exploration work. The internal configuration of the correlation matrix was studied by multidimensional scaling (MDS). MDS is an ordination (unfolding) method, which expresses a multivariate dataset as a two-dimentional scatter plot. This method is based on the Euclidean distances of vectors instead of angles between vectors as is the case in factor analysis (Schiffman et al. 1981). Measuring unit level by MDS is ordinal in this case and thus MDS is a more robust method than factor analysis. Statistical sofware used was SPSSX and MDS was performed by the ALSCAL- procedure.

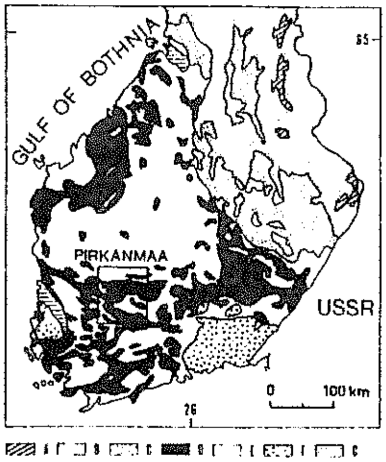

Fig.1. Location of the study area. Simplified geological map, after Simonen (1980). A. Archean greenstones B. Archean granitoids, C. Karelian schists, D. Svecofennian schists, gneisses and migmatites, E. Svekofennian plutonic rocks, F. Rapakivi granites, G. Jotnian sediments

RESULTS

Multidimensional scaling of the correlation matrix from heavy mineral mapping data from the Pirkanmaa target area revealed uniform elements association (A) of Ce, Fe, La, Nb, Rb, Y, and Zr (Fig.2). This is the most conspicuos feature of the data and shows that the host minerals of these elements have a distribution pattern resembling each other at a regional scale. Another general feature resulted, when the amount of magnetite and amount of non-ferrimagnetic heavy fraction were included as parameters (Fig.3). Multidimensional scaling revealed out significant correlation between these two parameters.

Areal distribution of the amount of magnetite and heavy fraction divided the study area into two geochemical provinces in an east-west direction (Fig.4). Element association A on the other hand discriminated the south-western part of the study area as a separate unit (Fig.5). These three provinces have been interpreted to form geochemical subareas that differed significantly from each other.

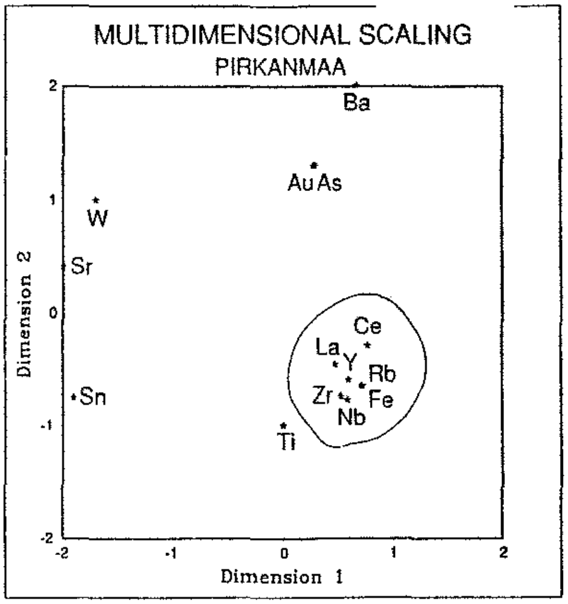

Fig.2. Configuration of Spearman's rank correlation matrix reduced on two dimensional scatter plot. Data comprises element contents in heavy fraction of till.

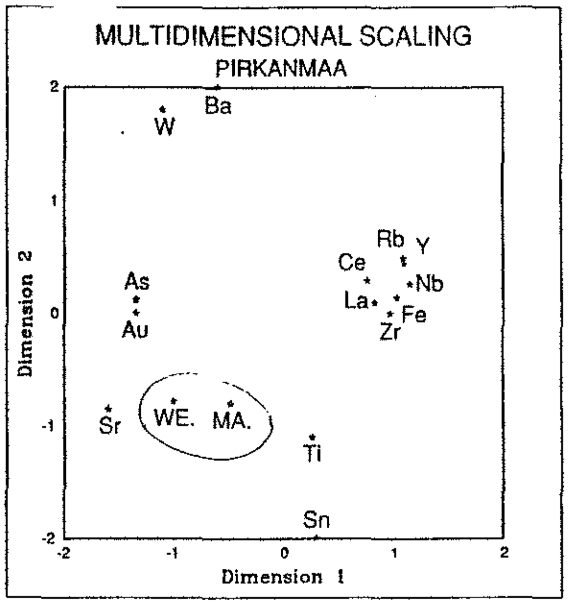

Fig.3. Configuration of rank Spearman's rank correlation matrix reduced on two dimensional scatter plot. Data comprises element contents in heavy fraction of till and the amount of magnetite (MA) and the amount of nonferrimagnetic heavy minerals (WE).

Distribution of gold

Prospecting for gold is active in the study area and thus the results of regional geochemical mapping have been interpreteded in this respect. Examination was done both by investigating the study area as a whole and within the above mensioned geochemical provinces. In the heavy fraction of till Au and As showed good mutual correlation (Spearman's rank correlation coefficient =0.31 n=415). Multidimensional scaling showed that correlation of Au and As is always positive both in the whole data and within the data for each geochemical province.

Integration of the results of heavy mineral mapping with geochemical mapping based on the fine fraction of till showed that Au and As in heavy fraction of till correlated positivly with Au and As in fine fraction (Au_f and Au_f) as well (Fig.6). Correlations between Au, As, Au_f and Au_f were positive within total area and in geochemical provinces(Fig.7). Examination of subareas revealed that some other elements can be used as pathfinders, where a particular subarea is concerned. For example in subarea I, W and Ba showed a close relationship with Au and As (Fig.8).

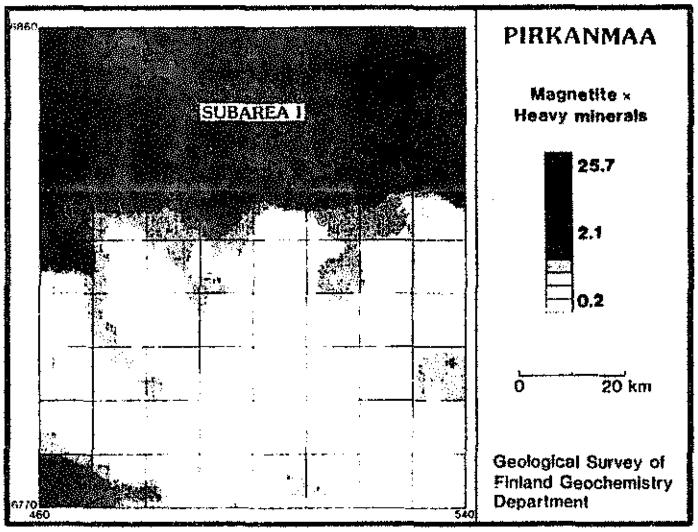

Fig.4. Division of the study area into two subarea on the basis of multiplied amounts of magnetite and heavy minerals in till.

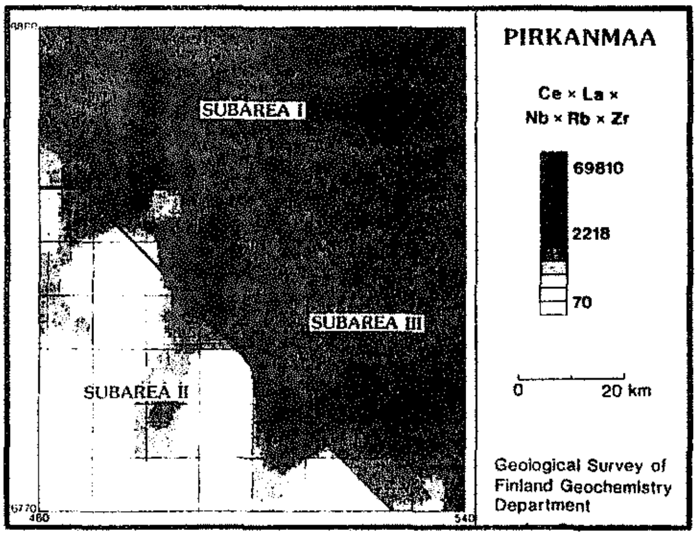

Fig.5. Division of the study area to subareas II and III on the bases of multiplied contents of Ce, La, Nb, Rb and Zr in heavy fraction of till.

	Fe	Nb	Rb	Sr	Ti	Y	Zr	Ba	Ce	La	Sn	W	WE.	MA.	Au	As	Au_f
Nb	.41*																
Rb	.27*	.40*															
Sr	.15	-.22*	.10														
Ti	.23*	.28*	.15*	.24*													
Y	.46*	.40*	.36*	-.12	.10												
Zr	.47*	.56*	.61*	.06	.39*	.41*											
Ba	.13	.13	.26*	.25*	.12	.23*	.15										
Ce	.47*	.29*	.44*	.23*	.37*	.59*	.65*	.38*									
La	.45*	.28*	.44*	.22*	.35*	.57*	.63*	.39*	.99*								
Sn	.06	.00	.08	.06	.03	.18*	.13	.11	.28*	.29*							
W	.03	.03	.12	.07	.02	.07	.06	.11	.03	.02	-.04						
WE.	.13	.30*	-.13	.61*	.29*	-.21*	-.04	.02	.23*	.21*	.04	-.10					
MA.	.35*	-.03	.10	.63*	.28*	.09	.28*	.11	.45*	.43*	.15	.03	.66*				
Au	-.11	-.07	.01	-.02	-.21*	-.11	-.11	.03	-.19*	-.19*	-.01	.06	-.11	-.10			
As	-.15*	-.12	-.03	.03	-.22*	-.07	-.17*	-.04	-.26*	-.26*	-.04	.15	-.16*	-.12	.31*		
Au_f	-.28*	-.07	-.06	-.45*	-.23*	-.06	-.19*	-.14	-.34*	-.32*	-.01	.09	-.43*	-.51*	.20*	.27*	
As_f	-.19*	-.07	.07	-.19*	-.16*	-.05	-.06	.06	-.19*	-.18*	-.05	-.02	-.24*	-.31*	.14	.08	.31 *

Fig.6. Correlation matrix resulting from Spearman's rank correlation coefficients of heavy mineral mapping data. Au and As contents in fine fraction (Au_f, As_f) are included.

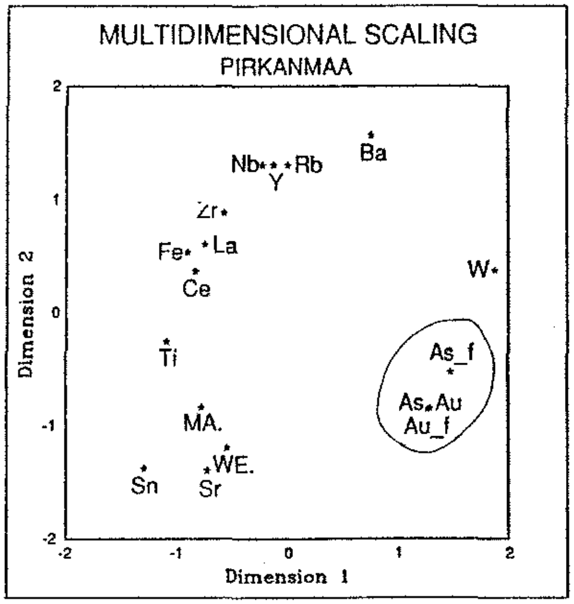

Fig.7. Configuration of Spearman's rank correlation matrix reduced on two dimensional scatter plot. Data comprises results of heavy fraction of till and Au and As (Au_f, As_f) contents in fine fraction of till.

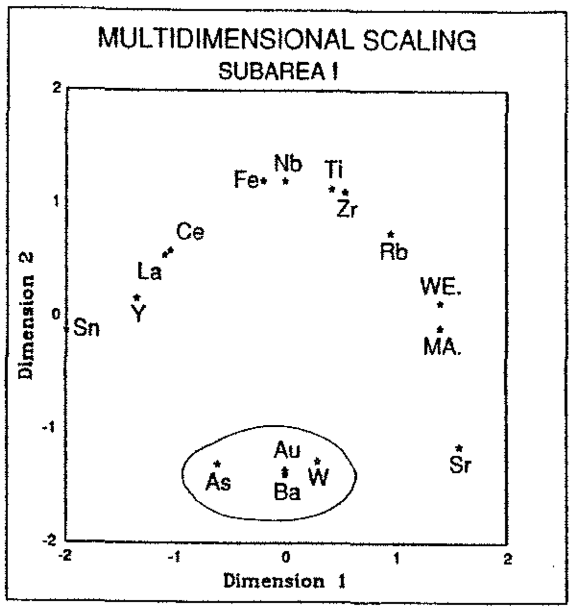

Fig.8. Configuration of Spearman's rank correlation matrix reduced on two dimensional scatter plot in subarea I.

In subarea II, W and Rb indicated gold potential areas but in subarea III only Au and As formed the geochemical Au association (Figs.9 and 10). The knowledge of pathfinder elements both increases information and makes the interpretation more reliable, because the distribution of Au is so erratic.

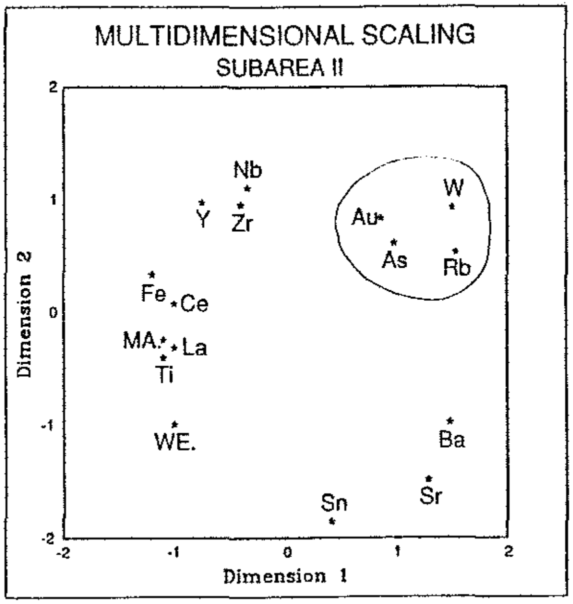

Fig.9. Configuration of Spearman's rank correlation matrix reduced on two dimensional scatter plot in subarea II.

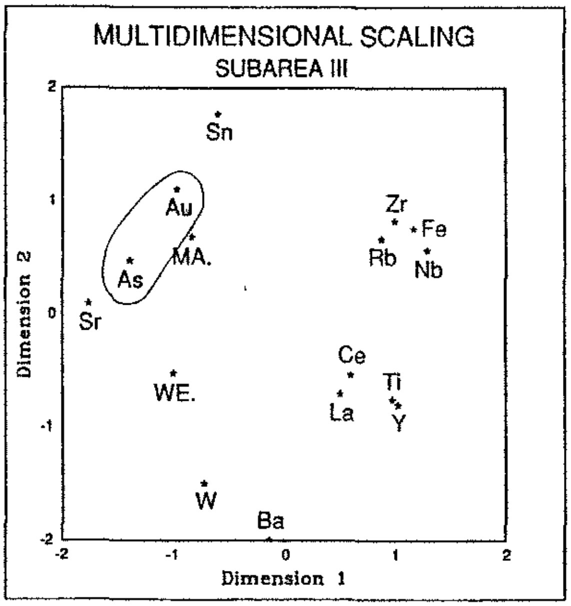

Fig.10. Configuration of Spearman's rank correlation matrix reduced on two dimensional scatter plot in subarea III.

The known economic Au deposits are located in subarea I - the old Haveri Cu-Au mine and Ylöjävi Cu-W mine, where Au was mined as by-product. The third economic Au-deposit and richest in Au has been found recently. The map derived from geochemical mapping data shows relationship with the new Au-potential targets indicated (Fig.11).

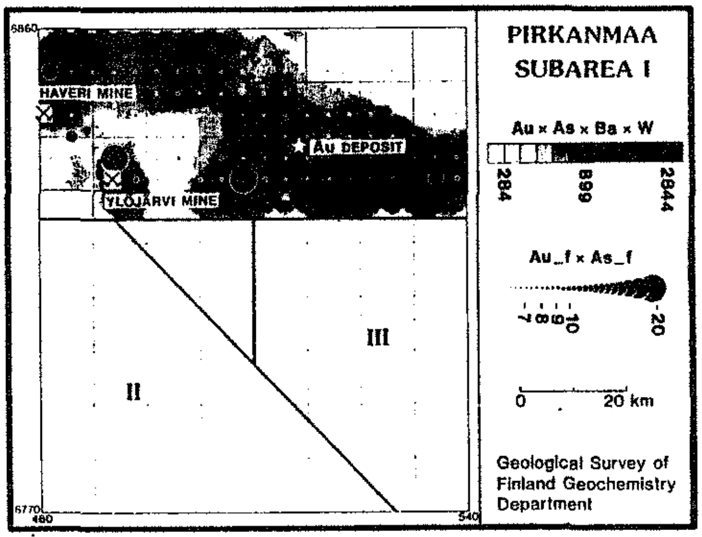

Fig.11. Grey tones resulting from element association indicating Au potential in heavy fraction of till. Symbols are Au x As contents in fine fraction till. Au =ln (Au+1), As =ln (As+1).

CONCLUSIONS

Multidimensional scaling based on Spearman's rank correlation coefficient has proven to be a recommendable statistical method for geochemical data. The method is non-parametric and allows the geochemical data to be handled without manipulation.

Three general features were discovered by examination of data from the total area. The amount of heavy minerals and magnetite show mutual correlation and elements Ce, Fe, La, Nb, Rb, Y, and Zr correlated with each other. The third general feature was good significant correlation between Au and As . Results of geochemical mapping based both on fine and heavy fractions of till gave a clear regional correlation between Au and As contents.
The correlation was positive both at the scale of whole study area and in individual subareas. More detailed correlations between Au and other elements were found by examing subareas separatly. Encouraging results were obtained in Tampere schist belt were W and Ba were used as indicator elements.

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CONDITIONS OF FORMATION AND MAJOR PARAMETERS OF DIFFUSIVE-DEFLUCTION SECONDARY DISPERSIVE HALOES OF THE SOVIET CARPATHIANS ORE DEPOSITS.

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The territory of the Soviet Carpathians belongs mainly to the European family of coniferous-broad-leaved landscapes of acid class of aqueous migration.It means,that typomorphic aqueous migrants here are hydrogen ions,typomorphic aeric migrant is oxygen,i.e., for given landscapes oxidizing conditions are typical.

The landscapes of a region form under conditions of low-mountain relief,medium-mountain relief and,to some extent,highland on rocks of various composition under conditions of temperate and cool humid climate and of low evaporation from soil surface,that causes a washing type of water regime of soils and their over-humidification.The quantitiy of atmospheric precipitation(800-1600mm per year) exceeds evaporation from the surface of soils 2,5 - 5 times,that causes their over-humidification and washing.

The large amount of precipitation and strong washing of soils determine very low general mineralization of surface and groundwater (0,03-0,2 g/l).In the field of development of the Carpathian flysch groundwaters of deluvial formations - are hydrocarbonaceous -calcic-magnesic and hydrocarbonaceous-chloridic-magnesic groundwaters.Groundwaters of deluvium in regions of development of metamorphic rocks of Upper Proterozoic-Lower Paleozoic are hydrocarbonaceous-chloridic-sulphatic-calcic-magnesic ones(in the composition of cations also often presents natrium.).

Certain dependence of groundwaters composition of eluvial-deluvial formations on composition of water-containing rocks gives evidence,that in chemism formation of these waters dissolution and exchange reactions with minerals of eluvial and deluvial formations play a certain part.

In composition of groundwaters anions ion HCO_3^- is constantly prevalent one,and among cations Ca^{2+} prevails almost constantly.Probably,the main process of formation of groundwaters chemical composition is the process of decay of organic materials:just ions HCO_3^- and Ca^{2+} come into solution during decay of organic materials in the largest quantities. According to the degree of hardness the waters under consideration are soft.Their reaction is neutral one or(in the field of metamorphic formations development) is sub - acid(pH = 6,0 - 6,5).

The existence of powerful zone of active water-exchange under conditions of mountain relief caused close consanguinity of ground- and surface waters and similarity of their chemical composition. The composition of surface waters weakly depends on bedrock composition of underlying water-containing deposits. In the composition of surface waters cations of the region Ca and Mg prevail constantly,sometimes potassium is also present in considerable amounts.In these waters hydrocarbonaceous ion prevails constantly;besides it, sulphate ion and chlorine ion present.

The reaction of surface waters of landscapes hydromorphic facies is neutral one (pH= 6,8 - 7,6),of transeluvial elementary landscapes is subacid one(pH = 5,5 - 6,0).

The formation of deluvial slope deposits in the region mountain-silvan landscapes a spontaneous motion of viscoplastic mass - defluction - plays a big part.The main forms of slope denudation are plane wash-off and solvent action of rain- and melt-waters.

For quantitative characteristic of denudation we have carried out calculations of moduli of hard(mechanical) and soluble(saline) run-off in landscapes of acid class of aqueos migration.

The denudation intensity of slope deposits of the region is characterized by value of annual layer(rate) of denudation (h) and its estimated on the basis of calculation of hard run-off modulus($_h$).The latter is calculated from long data about mid-annual water discharges of main rivers,and also about its mid-annual turbidity.According to our calculations and also according literary data the region is characterizes by high rate of the slope denudation:in different parts its annual layer of denudation is from 0,3 to 0,9mm/yr.

Relation of moduli of solid and soluble run-offs is estimated as 7 : 1.This relation characterizes a comparative role of lithochemical(mainly,mechanical) and hydrochemical(saline) forms of migration.

According to intensity of water-exchange and mechanical migration,almost all the geochemical landscapes of the region belong to landscapes of the third genus (according to classification of A.I.Perel'man,1966),i.e.,are characterized by vigorous water-exchange, sharp preponderance of slopes over watersheds (latter are not more than 15% of a territory),by preponderance of mechanical migration of dissolved matter.

In connection with abundant development of vegetative cover in the region the geochemical activity of a living matter presents itself larger.During decay of a vegetative fall in soils organic compounds and acids,which not only determine many physical-chemical conditions of the hypergene migration medium (pH,Eh,activity of sorption),but also directly come into interaction with element,liberating during rocks weathering and during mineralization of vegetative remains. In the region the part of organic acids is increased due to their limited participation in rocks weathering in connection with formation of protective organic-mineral films on surfaces of feldspar grains. Having no possibility to neutralize at the expense of silikates and alumosilicates decomposition,organic acids(fulvic and humic) are washed through a rock mass of loose deposits,causing leaching of secondary dispersion haloes of a group of metals from upper horizons of soils.

The formation of lithochemical residual secondary dispersion haloes of ore deposits in the region is clearly defined by semultaneous proceed of processes of mutual displacement of particles of deluvium,diffusion,defliction,slope denudation and by acid leaching of soils.Lithochemical streams of ore deposits dispersion are formed,mainly,under influence of defluction and slope denudation of residual dispersion haloes.

In the region modern deluvial and (more seldom) eluvial formations of ore-bearing rocks are mainly halo-forming medium.Experimental study of secondary dispersion haloes of the group of ore objects made it possible to establish domonant character in regions of diffusional-deflictional secondary dispersion haloes,which,according to their accessibility and manifestation in section of soils and deluvium,are opened to normal intensity, relaxed at the surface and closed (maximum impoverished and leached in upper part of a section of soils and deluvium). Expansion of diffusive secondary dispersive haloes is limited by area of development of autonomous eluvial landscapes and gentle,medio-slope landscadscapes of near-watershed part of slopes.

In structure of diffusive-defluctional secondary dispersion haloes 3 parts,differing in morphology and conditions of formation,are singled out: (a) upper,diffusive-deflictional(essentially diffusive one); (b) middle,deflictional and (c) lower,accumulative one.

The main features of haloes are:

- large elongation of haloes down the slope(Fig.1);
- unlike diffusive haloes,dimensions of proper deflictional component of halo decisively depend on length(extension) of a slope,but not on a scale of mineralization,that is why dimensions of halo area are,as a rule,large(Fig.1 - 2);
- the point C_{max}(maximum content of halo-forming element) of a halo is not always clearly marked;
- real halo displacement on slopes as to outcrop of ore body on the surface of the bedrock ranges from 50 - 60 to 200 - 350 m;
- in plan haloes have mantle-like character,but in section - ribbon-like one(Fig.1-4);
- the most extended part of a halo is its "train of a halo",within the limits of which vertical efficiency of a halo is not almost changed(Fig.5 - 6);
- in deflictional part of the halo content of element-indicators of polymetallic and other mineralization does not almost depend on depth of sampling.

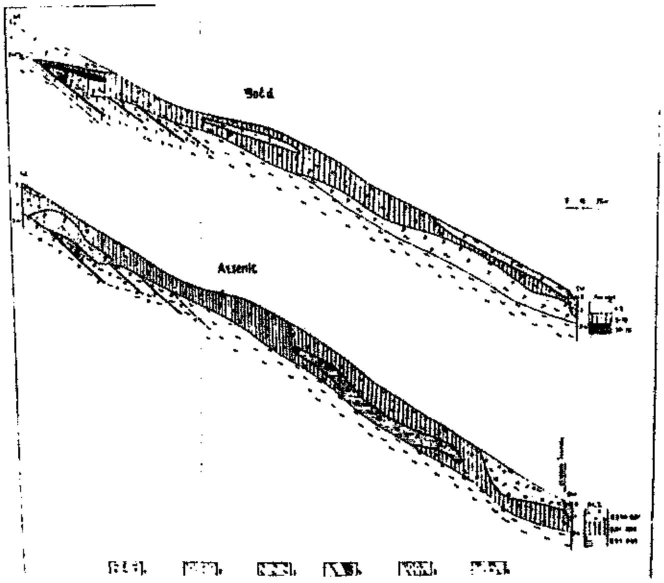


Figure 1.Vertical section of diffusional-defluctional secondary dispersion haloes of gold and arsenic gold ore body N3 o Banskoe ore manifestation.1 - soil-deluvial formations;2- alluvium;3-schists-quartz-chlorite-sericitic and quartz-coaly-sericitic;4-gold-quartzous veins; primary geochemical haloes: 5-gold(5-30mg/t),6-arsenic (0,01 - 0,1%).

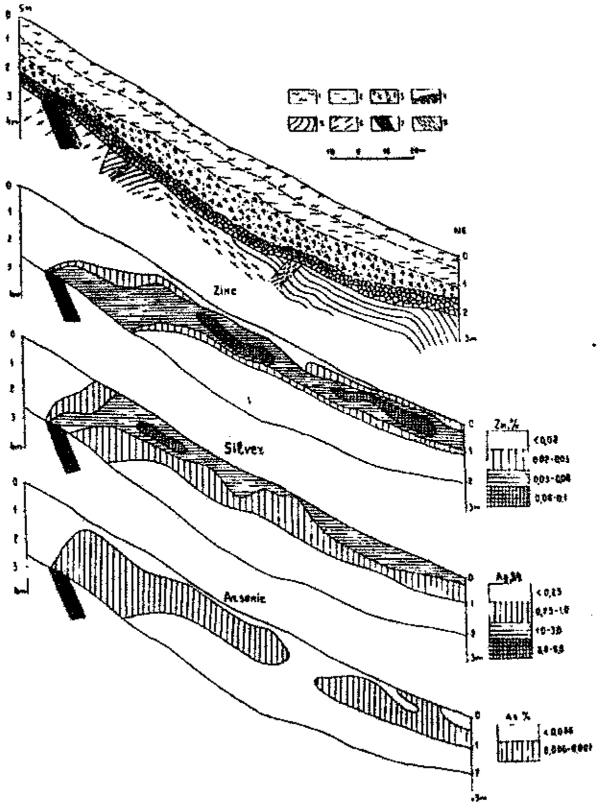


Figure 2. Vertical section of secondary dispersion haloes of zinc,silver and arsenic of Rakhovskoe ore manifestation of polymatals.1 - 4 -soil-deluvial formations: 1-loose loams of soils horizons A_1 and B,2 -clay of soil horizon BC,3 -gruss,rock debris with sandy loam,4 -rock debris and blocks;5 -metamorphic schists( ); 6 -granite gneisses( );7 -ore bodies;8 -zones of brecciation and mylonitization.

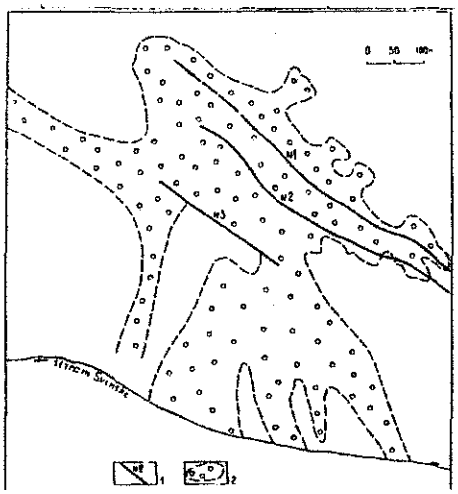


Figure 3.Secondary dispersion haloes of gold of Banskoe ore manifestation.1 - gold ore body;2-3 -secondary dispersion haloes of gold(5 - 70mg/t).

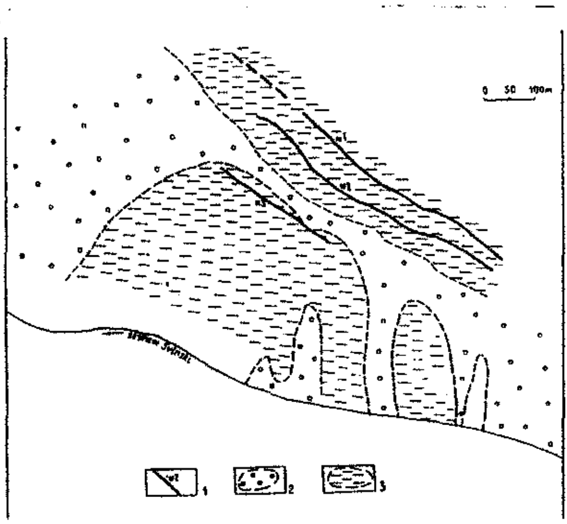


Figure 4.Secondary dispersion haloes of arsenic of Banskoe gold ore manifestation. 1 -gold ore bodies;2-3 -secondary dispersion haloes of arsenic:2 -0,006- 0,01%, 3 - 0,01 - 0,05%.

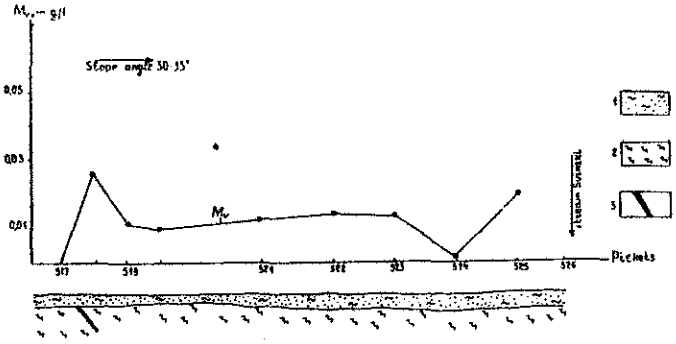
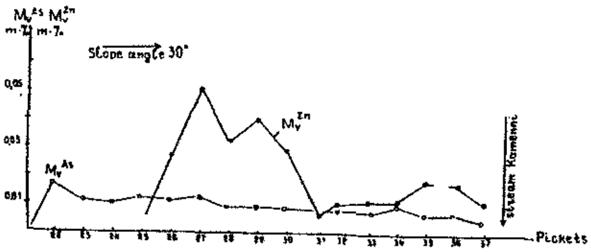


Figure 5. Plot of change of gold secondary dispersion haloes(M_v)vertical efficiency of ore body N3 of Banskoe ore manifestation.

Figure 6. Plot of change of zinc secondary dispersion haloes(M_v^{Zn}) vertical efficiency and of arsenic secondary dispersion haloes (M_v^{As}) vertical efficiency of Rakhovskoe ore manifestation.



The main parameters of diffusive haloes and formula of their calculation are well-known(Solovov A.P.,1985). As regards parameters of diffusive-defluctional haloes they are quite different and are not fully elaborated.The most important parameters of these haloes are vertical(M_V) and linear(M') efficiency of the halo.Taking into account the dual character of diffusive-defluctional haloes on the basis of Ploikarpochkin's V.V.(1976) formulae we suggest the following formulae of their linear efficiency:

$$M' = 2 \cdot M_V^{max} \cdot x \cdot \frac{h-h_1}{h^2} \quad ,$$

where M_V^{max} - maximum value of vertical efficiency of secondary dispersion halo;
x - distance of the halo section with M_V^{max} from watershed in meters;
h - thickness of loose formations in vertical section of the halo;
h_1 - depth of occurence of the halo from the surface,m.

Table 1.

Diffusive	Diffusive-defluctive
$M=\Delta x\left(\sum_{x=1}^{n} C_x - n\cdot C_\phi\right)$	$M=2\cdot M_V^{max}\cdot x\cdot \frac{h-h_1}{h^2}$
C_{max}	C_{max} - not always
σ, p, q	$M_V'=\sum_{1}^{m} C_i\cdot h_i$
γ, k	γ, k
$C_i=f(Z)$	$C_i \neq f(Z)$
$S_\alpha=0\div30m$	$S_\alpha=60\div350m$
on flanks of haloes $M_V' \approx 0$	on flanks of haloes M_V' = const
The shape of haloes in section:	
flabellate	ribbon-shaped

For the most widespread in the region open diffusive-defluctive secondary dispersion haloes(h_1=0) formulae is as follows:

$$M' = 2 \cdot M_V^{max} \cdot \frac{x}{h} \quad ,$$

The main parameters of diffusive-and diffusive-defluctive secondary dispersion haloes of ore deposits are in above Table.

All above-mentioned causes necessity of an additional stage of geochemical reconnaissance - the stage of detalization of revealed diffusive-defluctive haloes,which precedes trench sinking on haloes estimation.The task of this stage is the study of the vertical section of the halo on a slope with determination of value M_V^{max} and the position on a slope section of the halo with M_V^{max}.

Trench and ditch sinking is performed depending on point position on a slope with M_V^{max} of the halo and S - the value of halo's point C_{max} displacement with regard to the outcrop of the ore body on the surface of bedrock under given landscape-geochemical conditions.

Fulfilment of works of present stage of detalization of revealed haloes and employment of their indicated parameters will make it possible to increase essentially geological efficiency of prospecting (with semultaneous reduction in price) in the regions of development of diffusive-defluctive and defluctive secondary dispersion haloes of ore deposits. In addition wide employment (as an overtaking method) of lithochemical survey on stray fluxes as an overtaking method has a great importance: in the region under influence of defluction and slope denudation of secondary dispersion haloes of ore objects in proluvial and alluvial deposits of shallow channels form,mainly,open residual stray fluxes of normal intensity.The main features,determined by high rate of a slope denudation,by defluction and by diffusive-defluctive nature of secondary dispersion haloes,are following:

- intermittent("pulsed") character,caused by irregular washing and grading of a material,that is explained by sharp change of angles of a slope of a profile of stream channels and,mainly, by downpour character of atmospheric precipitation;
- hifh assessments of local coefficient of proportionality(k^{l}) between efficiency of lithochemical stray flux(p^{l}) and efficiency of outcrop of mineralization zone on the surface of bedrocks under cover of loose formations($P_{o.d.}$):

$$k^{l} = \frac{P'}{P_{o.d.}} = 1,4 - 12,0$$

- formation of redeposited part of a stray flux on the sections of manifestation of gravitatively sorptive geochemical barrier,that is explained by pronouncing of processes of deposition of this fraction of a proluvial-alluvial material and its sorption -mainly in near-mouth section of streams with slowed-up rate of their flow.

The present recommendations are applicable in search for ore deposits not only within the limits of the Soviet Carpathians,but also in another regions of the world with similar landscape-geochemical conditions of secondary dispersion haloes and stray fluxes formation. In the Soviet Union these regions are the Caucasian,Mongol-Amur and Sikhote-Alin' folded systems,separate regions of Altai-Sayanskaya folded system.

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EMPLOYMENT OF LARGE-SCALE LANDSCAPE-GEOCHEMICAL MAPS FOR INTERPRETATION OF GEOCHEMICAL ANOMALIES IN HUMID AND ARID LANDSCAPES.

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As a result of large-scale lithochemical survey in two regions of the USSR (Kuznetskii Alatau the south of the Western Siberia - and the Western Near-Azov region - the south of the Ukraine) the large group of lithochemical anomalies has been revealed. Their interpretation is given on the basis of maps of elementary geochemical landscapes to a scale 1 : 5 000 - 1 : 10 000.

In Kuznetskii Alatau humid south-taiga landscapes of aqueous migration acid class prevail. Depending on genesis of Quaternary deposits several species of elementary landscape are singled out: (a) ortho-eluvial; (b) neo-eluvial, and (c) eluvial-superaqueous. (Fig.1).

Ortho-eluvial south-taiga landscapes are formed on Lower Cambrian limestones, Middle Cambrian porphyrites and intrusive formations of Upper Cambrian-Lower Ordovician age. In their contours the thickness of eluvial-talus formations is 1 - 5 m.

Neo-eluvial landscapes are landscapes of flattened out divides and their near-divide parts. They are formed on Middle Quatrrnary - Upper Quaternary talus-proluvial deposits, arosed through redeposition of crust of weathering products. These deposits have diverse composition of clastic material, partly rounded.

Eluvial-superaqueous landscapes of acid gley class of aqueous migration are represented by small areas of swamped slopes. In a section of soils of these elementary landscapes the "gley" horizon, represenred by clays and loams of different colour with constant blue-grey tint, owing to compounds of ferrous iron, is marked. In gley horizon of soils an intensive aqueous migration of iron, manganese and other chemical elements may be observed.

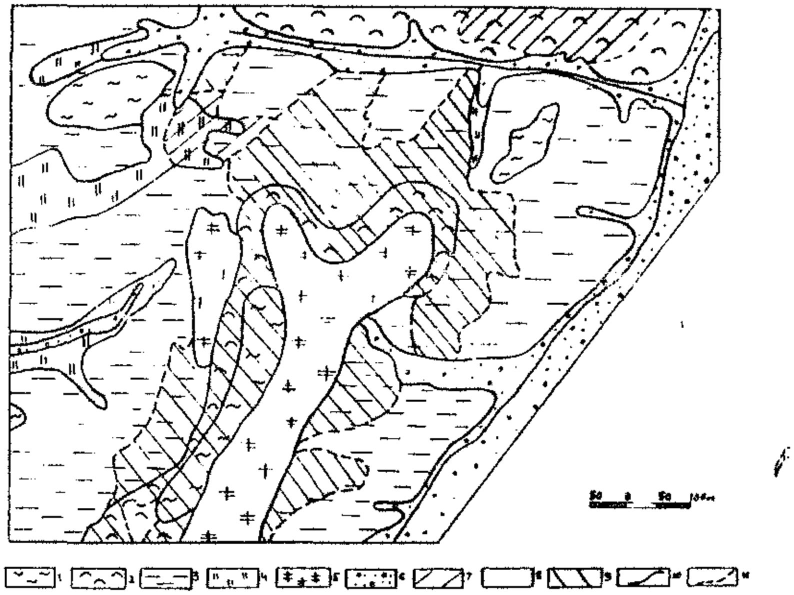


Fig.1. Landscape-geochemical map of the Belokamenskii area.

1-3 - south-taiga ortho-eluvial landscapes of acid class of aqueous migration: 1- autonomous eluvial; 2- medium-sloping transeluvial; 3- gently sloping transeluvial; 4-6 -south-taiga landscapes of acid gley class of aqueous migration: 4-eluvial-super aqueos; 5-neo-eluvial; 6- superaqueous; 7 - 8 -soilforming rocks: 7 -diabasic and andesitic porphyrites ($Є_2$); 8 -limestones ($Є_1$); 9 -granodiorites, diorites, gabbro ($\gamma\delta - \gamma Є_3 - O_1$); 10-boundaries of elementary landscapes; 11- geological boundaries.

Employment of large-scale landscape-geochemical maps to a scale 1 : 10 000 and of a larger scale made it possible to carry out classification of lithochemical anomalies with singling out of several genetic groups: (1) secondary dispersion haloes of gold-bearing mineralization zones;(2) rock anomalies;(3) technogenous anomalies;(4)anomalies on sorptive and gleyic geochemical barriers;(5-anomalies of neo-eluvial landscapes;(6)anomalies of eluvial-superaqueous landscapes(Fig.2).

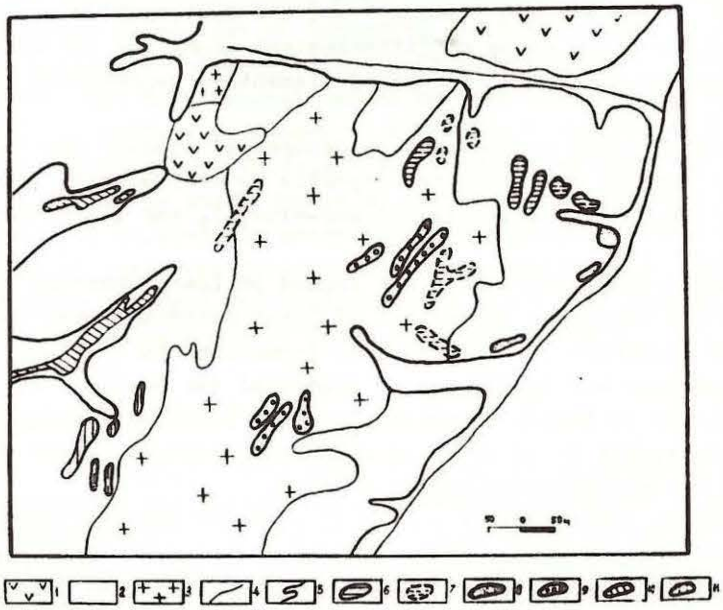


Fig.2. Hypergene lithochemical anomalies of the Belokamenskii area.

1 - diabasic and andesitic porphyrites($Є_2$);2 -limestones($Є_1$);3 -granodiorites,diorites,gabbro($\gamma\delta-\nu Є_3-O_1$);4 -geological boundaries;5 -contours of alluvial and proluvial deposits;6 - 7-rock anomalies: 6 - of nickel(200-300g/t);7 -of fluorine(1000g/t); 8 -technogenous anomalies of gold(0,02 - 0,7 symbolic units);9 -gold anomalies(0,01-0,7 symb.units),of silver (0,5 - 2,0 symb.units) of neo-eluvial landscapes;10- gold anomalies(0,03 - 0,05 symb.units),of silver(0,5 - 0,8 symb.units) in proluvial deposits(Q_{III-IV});11- secondary dispersion haloes of gold(0,01 - 0,05 symb.units),silver(0,7 - 2,0 symb.units), of bismuth(2g/t),corresponding to ore manifestation of gold.

The rock lithochemical anomalies are groups of hypergene anomalies of nickel(200 - 300g/t) and cobalt(70g/t),confined to fields of development of Cambrian-Ordovician gabbro and Middle Cambrian andesitic porphyrites.The features of rock anomalies are:considerable dimensions,spatial coincidence with geological formations of certain petrographic composition and specific(narrow) geochemical spectrum of anomalies,stipulated by all this.

Technogenous anomalies are established within the limits of superaqueous and mediosloping ortho-eluvial landscapes(on areas of their conjugation with superaqueous landscapes).Typical features of technogenous anomalies are their monoelementality,high contrastness and confinement to heaps and exhaust placers(Table 1).

Lithochemical anomalies on sorptive and gleyic geochemical barriers are confined to marginal zones of eluvial-superaqueous and ortho-eluvial landscapes of acid gleyic class of aqueous migration - on their conjugation with ortho-eluvial landscapes of acid class of aqueous migration. The group of hupergene lithochemical anomalies of molibdenum,fluorine,mercury and lead has been classified as amomalies of geochemical barriers.

Detailed landscape-geochemical mapping made it possible to single out lithochemical anomalies of gold and its elements-satellites(accessory elements) in neo-eluvial landscapes on Middle Quaternary - Upper Quaternary deluvial-proluvial deposits,originated by redeposition of the crust of weathering.Geochemical spectrum and intensity of hypergene lithochemical anomalies in indicated neo-eluvial landscapes are highly close to those in secondary dispersion haloes of gold-bearing mineralization zones.

Geochemical anomalies of eluvial-superaqueous landscapes are formed in deluvial-proluvial and alluvial-proluvial deposits, generated at the expense of redeposition of Upper Quaternary and recent eluvial-deluvial formations. Geochemical spectrum of these anomalies is reduced (gold, arsenic). These anomalies are characterized by significant productivities, anomality coefficients and indices of contrast range.

Both groups of landscape anomalies do not have connection with mineralization and are due to weak auriferousness of deposits, in which they had been developed.

Secondary dispersion haloes and its accessory elements have been revealed within the limits of autonomous eluvial and gently sloping trans-eluvial landscapes on eluvial-deluvium of various thickness. Singling out of secondary dispersion haloes, perspective for gold mineralization, was carried out on the basis of geochemical indices of zoning of mineralization (V), areal productivity of haloes(P) and their coefficients of residual productivity(k). Estimation of a group of the secondary dispersion haloes made it possible to reveal two zones of ore mineralization.

Geochemical landscapes of the Western Near-Azov are para-eluvial landscapes and belong to dry-steppe landscapes of neutral (calcic) class of aqueous migration. The thickness of loose deposits, overlying ore-bearing formations, is 80 - 100m. The most widespread species of elementary geochemical landscapes of the region are: (a) autonomous eluvial and gently sloping trans-eluvial landscapes with ordinary black soils, forming on Quaternary loess-like loams; (b) eluvial-accumulative gently sloping landscapes on alluvial black (chernozem) soils; (c) trans-eluvial landscapes on shallow black (chernozem) soils, forming on Lower Neogene deposits(Fig.3).

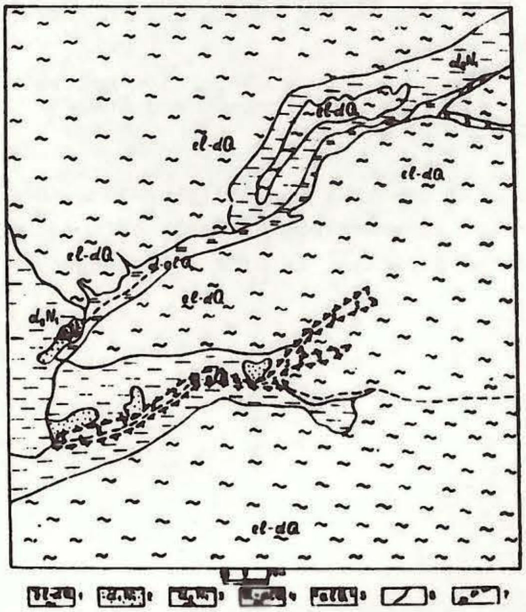


Fig.3. The map of elementary landscapes of the Novopoltavskii area.

1 -autonomous eluvial and gently sloping trans-eluvial landscapes with chernozem soils, forming on Quaternary loess-like loams; 2 -trans-eluvial landscapes on talus (deluvium) of kaolin sands of Poltava Neogene suite; 3 -gently sloping trans-eluvial landscapes on low-powered chernozem soils, forming on Poltava suite deposits; 4 -eluvial-accumulative landscapes; 5 -superaqueous landscapes; 6 -boundaries of elementary landscapes; 7 - geochemical barriers.

Buried superimposed secondary dispersion haloes are typical for two former species of elementary geochemical landscapes .Within the limits of trans-eluvial landscapes,forming on Lower Neogene deposits,open superimposed secondary dispersion haloes of buried carbonatite minemalization have been established.They are represented by contrast complex haloes of lanthanum,cerium and barium,which develop directly over large bodies of carbonatites on a level of horizons B and BC of soil-eluvial formations(Fig.4).The revealed secondary dispersion haloes represent hypergene neogenesis on sorptive,evaporative and oxygenous geochemical barriers.

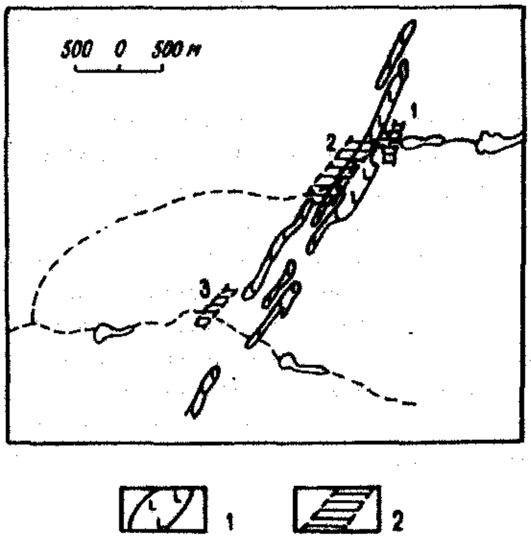


Fig.4. Secondary superimposed lithochemical dispersion haloes of lanthanum,cerium and barium in Neogene deposits of the Poltava suite.

1 - carbonatites;2 - dispersion haloes of lanthanum (50 - 200g/t),cerium(60 - 1 000g/t),barium (500 - 1 500g/t).

The fulfilled works give evidence that forestalling large-scale landscape-geochemical mapsing makes it possible to increase substantially efficiency of geochemical search for ore deposits,including buried deposits(in arid landscapes).

Geochemical soil and rock surveys in search for tin in the Eastern Erzgebirge, Saxony

by Werner Pälchen, Günter Rank, Birgit Harpke

Introduction

Tin mineralizations of the Erzgebirge region are known since Middle Ages, when exploitation began at small placer deposits near Krupka (Graupen) in its Eastern part. Some deposits were in exploitation for several hundert years until today on the German as well as on the Bohemian part and became international types of tin deposits, as the stockwerk of Altenberg, the bed-like bodies (fletzes) of Cinovec cupola or the veins of Ehrenfriedersdorf. In the period after the Second world war many efforts were done to ensure the raw material base for the isolated national economy of Eastern Germany. In this connection great exploration activities for tin too were led in the Saxonian Erzgebirge. Whereas in the former times the exploration was carried out mainly by special geological mapping in connection with technical works as prospecting trenches and boreholes in the nearest vicinity of known deposits and occurences, in the last exploration period from the middle of seventies up to now a whole complex of geological, geophysical and geochemical prospecting methods was applied to ore fields of several hunderts of square kilometers in area.

1. Geological and metallogenic situation of the Eastern Erzgebirge

The Erzgebirge Mts belong to the Saxothuringian zone of European Hercynides at the northern border of the Bohemian massif. The geological framework of the tin deposits of Eastern Erzgebirge is formed by paragneisses of the East Erzgebirgian and Pressnitz groups of Upper Proterozoic (PR 3) and by mica schists and phyllites of Cambrian. In late Variscan time (Upper Carboniferous to Permian) an intense multiphase acid magmatism occured (granites, rhyolitic dykes, ignimbritic rhyolites, granite porphyry). Emplacement of magmatic rock bodies was controlled by fault structures of different directions, mainly NNW-SSE and NE-SW. Some of old fault directions were rejuvenated while late Mesozoic to Cenozoic development of this region, when Cretaceous clastic sediments of the Saxon-Bohemian basin and Miocene alkali basalts were formed.

Tin mineralization is spatially and genetically connected with subvolcanic granitic intrusions of the so-called Younger intrusive complex (TISCHENDORF 1989). These small granitic cupolas have a multiphase internal structure. In the most occurences two series can be distinguished: an earlier sequence of protolithionite to Li-siderophyllite bearing porphyritic mikrogranite and an younger sequence of zinnwaldite bearing albite granite. Albite granites form either small cupolas in the inner parts of the intrusion bodies of the earlier granite sequence (so-called "Inner granite", e.g. Altenberg, Sadisdorf) or overlap the older phases as an uppermost shell (e.g. Cinovec, Schenkenshöhe Falkenhain).

Tin mineralization mainly belongs to the greisen types of quartz-cassiterite formation. With each intrusive phase of granites an independent mineralization with somewhat different mineral association is connected. Pre albite granite greisens are mostly stockwerks of small veinlets of dark greisen with low contents of Cu, As and W, whereas the post albite granite greisens are light, more homogeneous in structur and show higher contents of W, Rb, Li, Nb and Ta.

2. Geochemical methods

Exploration activities for new tin mineralizations in the Eastern Erzgebirge were focussed on the ore field Altenberg-Dippoldiswalde. This area was contoured on the basis of distribution of known deposits and mineral occurences, but also by means of results of previous regional stream sediment geochemical survey and heavy mineral panning (PÄLCHEN & OSSENKOPF, 1989) of the whole Erzgebirge - Vogtland region. Taking into account succesful experiences of similar explorations in other parts of the Erzgebirge, as principal method of geochemical prospecting was chosen soil survey. In cases, where outcrops of primary rocks are rather seldom or entirely absent, whereas an autochthonous soil cover overall is present, this method is generally favoured for detail geochemical prospecting (PÄLCHEN et al., 1989). As recommended by Soviet authors (e.g. SOLOVOV, 1987) the sampling density was 100 samples per km^2 corresponding to the scale 1:25 000. Sampling was carried out by spade from the subsoil, i.e. the B-horizon in brown soil or podsol respectively the G-horizon in gleyish soils. Samples were taken commonly at 20 to 40 cm depth, in swamped localities at 80 cm and deeper. After drying the soil samples, altogether about 25 000, were analysed for Ag, B, Ba, Be, Bi, Co, Cu, Li, Mn, Mo, Nb, Pb, Sn, Ti, V by emission spectrography. The elements As,W, Zn (by X-ray fluorescence spectrometry) and F were determined in a reduced number of samples. Analytical accuracy was checked by international standard samples TB, GnA and GM of Central Geological Institute Berlin (GDR).

The main steps of data handling were

- univariate statistics of each element for
  - graphical documentation on monoelement maps, scale 1:25 000
  - determination of lithology-related background values

  - calculation of lithology-related contrast coefficients (elimination of geochemical specialization)
  - definition and localization of anomalies
  - quantitative and qualitative valuation of tin anomalies
- multivariate statistics for
  - definition of characteristic element associations (original data, contrast coefficients)
  - calculation of factor scores
  - plotting of factor score maps for the main factors (mineralization, lithology).

3. Results

3.1 Distribution of tin mineralization

The mean values of the total sample population show as expected the predominant influences of mineralization and lithology on the secondary geochemical field (Table 1). Eliminating the effect of mineralization the modes of all elements in soil samples are in near correspondence with regional Clarkes of the Erzegebirge region (PÄLCHEN et al., 1987). Calculation of lithology-related local background values on the basis of selected data population confirm this establishment for the lithological units, e.g. paragneiss. Increased tin values of soil samples 30 ppm in areas, where Schellerhau granite massif and other small granite cupolas appear at the recent surface, emphasize their geochemical specialization and affiliation to the Younger granite complex.

By means of factor analysis could be established some very stable element associations. The association Sn-Bi-Mo± Be±Li±Cu±W±As±F is typically for tin mineralizations of greisen formation in Eastern

Erzgebirge. It appears not only as the strongest factor in selected populations of mineralized areas, but is also clearly expressed in the complete data collective. It is very remarkably, that boron, a stready constituent of tin associations in the Middle Erzgebirge (Ehrenfriedersdorf), in the Eastern Erzgebirge is enttirely absent. In areas with sulphide mineralization the element association Pb-Ag with Cu, Zn, As appears as separate factor. The association Ti-V-Mn-Co unites more basic components of lithology. Increased factor scores reflect amphibolites and amphibole schists, intercalated in paragneisses, mica schists and phyllites of Upper Proterozoic and Cambrian. Beside confirmation of known occurences of basic rocks there are also new indications with regard to the existence at all or to the intensity of their appearance. High values of this factor in connection with increased content of Nb characterize occurences of Tertiary alkali basalts. The association Nb-Li-Be is typically for outcrops of younger granites. The elements U, Th and K, determined by aerogamma spectrometry and included into interpretation of soil geochemical data, form also a very stable association. Its independence of all other elements seems to be caused by other effects and influences, as vegetation and moisture of upper floor.

Areal distribution of tin mineralization is indicated by tin anomalies as well as by anomalies of the element association Sn-Bi-Mo-Cu in the factor score map. Concerning the monoelement tin map two variants are to be distinguished: map of original tin contents and map of contrast coefficients. For prospecting tasks the first mentioned map has a serious disadvantage, because the anomalies are originated not only by mineralization but also by effects of geochemical specialization. Calculating contrast coefficients (CC) on the basis of lithology-related local background this ambiguity can be eliminated. The maps of these contrast coefficients of tin and of the factor score map of tin association on the basis of the contrast coefficients of the elements are very similar and confirm each other. All further operations were carried out only for such "purified" anomalies. In the investigated area were contoured 15 tin anomalies, most ot them corresponding to known tin deposits or occurrences (Fig. 1). New indications appear especially in the northwestern part of the ore field, in the vicinity of the villages Reichstädt and Obercarsdorf near Dippoldiswalde (anomalies A,B). Primary nature of these anomalies in meantime is verified by follow-up studies, by which the existence of cassiterite in rock samples and its relation to veinlets of chloritic greisen was pointed out.

The well-known relation of tin mineralizations to granites of the Younger intrusive complex in the Erzgebirge is also reflected in the studied area. A comparison of the distribution of tin anomalies with the configuration of granite surface shows, that the tin anomalous areas can be divided into two main groups:

1. Tin anomalies immediatly in the exocontact zone of granites or near to the hidden granite surface are characterized by the typical element association Sn-Bi-Mo±Be±Li±Cu±W (anomalies D to O). Among them are the anomalies of known deposits and tin ore occurrences (Altenberg K, Zinnwald L, Sadisdorf D, Schenkenshöhe E).
2. Tin anomalies far from the known or suggested by geophysical data granite surface show labil and weak correlations of tin with other elements, especially with Cu, Zn, Pb, Ag (anomalies A,B,N,P).

Anomaly C (Niederfrauendorf) displays features of both groups.

3.2 Valuation of tin anomalies

Following recommendations and experiences of Soviet authors, for the above-mentioned tin anomalies the areal productivity (P) was calculated, i.e. a measure of the intensity of a given anomaly, expressed in m^2 %. As figure 2 shows, the anomalies of the first group have in general an increased tin content and higher areal productivities.

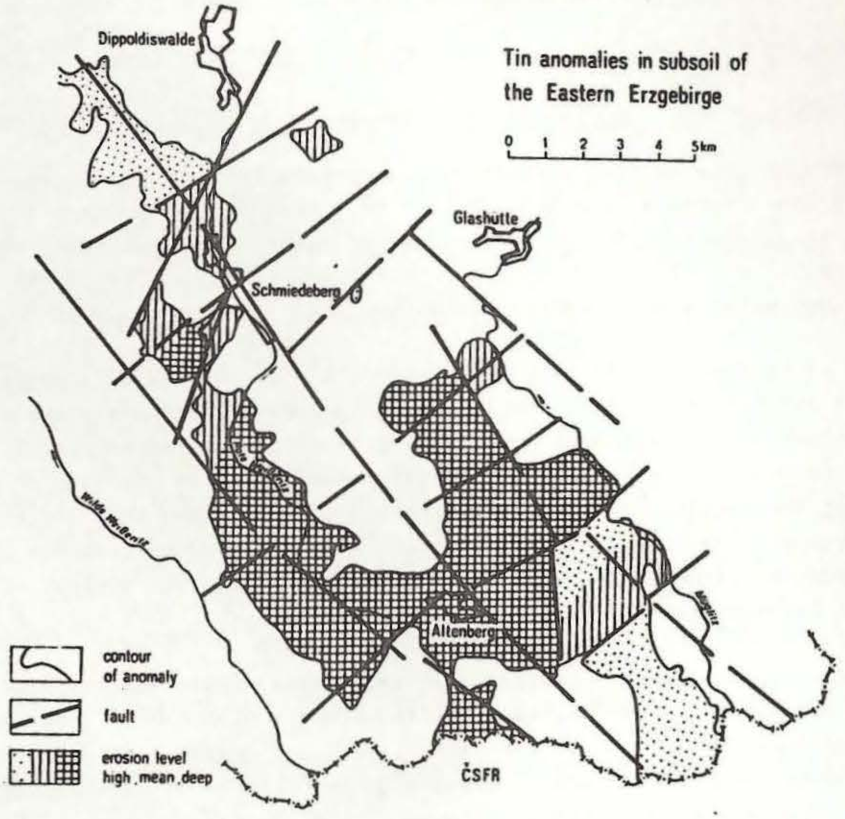
Other essential feature of quantitative valuation of secondary geochemical anomalies is the index of zonality. Introduced by Soviet geochemists on the basis of intensively investigated mineralogical and geochemical zonality of hydrothermal ore bodies, in its strong sense it is only calculable for primary geochemical haloes. However, with some care it can also be applied to secondary geochemical anomalies (GRIGORJAN & MOROZOV, 1985). Considering results of geochemical investigation of primary haloes in some tin occurrences in the Eastern Erzgebirge and the generalized zonality sequence of elements in hydrothermal mineral deposits (GRIGORJAN et al., 1983) the following subdivision was used

- supraore elements: Cu, Zn, Pb, Ag
- subore elements: Mo, Bi, W, (li).

On this basis 12 different zonality indexes were calculated (e.g. Cu x Pb x Zn/Mo x Bi x Li; Cu x Pb x Zn/Bi^2 x Mo etc.) and normalized to unity. Mean (median) index of zonality ($\bar{z}$) is plotted against areal productivity and mean tin content.

Accepting the general model of vertical geochemical zonality and supposing the comparability of studied anomalies may be concluded, that mineralizations, represented by geochemical anomalies with low indexes of zonality are deeper eroded than such with increased values of this index. This establishment corresponds with known geological facts. Apparent deviations in meantime are solved in favour of geochemical prediction (anomaly F, Hegelshöhe). Due to the close relation between tin mineralizations and Younger granites it also means, that anomalies with low z-values are nearer to the granite surface than such with higher quotients. The acceptance of this generalized model also includes, that for neighborhood geochemical anomalies with very different indexes of zonality an essential influence of post mineralization (postgranitic) faulting is to be assumed. Comparing these results with other geological and geophysical observations, a mosaic of relative upthrown and downthrown blocks cam be constructed.

Only such anomalous vareas may be recommended for further tin exploration, which are deeply eroded.
These results show, that by means of geochemical prospecting in subsoil, may be received important indications for the distribution and intensity of hydrothermal mineralization and their erosion level too. It helps to focuse the follow-up exploration to the most promising objects.



Tin anomalies in subsoil of the Eastern Erzgebirge

REGIONAL GEOCHEMICAL RECONNAISSANCE OF THE LA PARAGUA RIVER DRAINAGE, VENEZUELA

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INTRODUCTION

The purpose of this work is to analyze the distribution of Cu, Zn, Rb, Sr, Y, Zr, Nb and Au in fine-grained drainage sediments of a part of the drainage area of the La Paragua river, Venezuela. The work is a part of a larger project that intends to cover 400.000 km^2 of the Venezuelan Guayana Precambrian shield with regional geochemical prospecting, using several sample types.

The area describeal in this work /about 7000 km^2/ is covered by tropical wet jungle /Escandón and Pasquali, 1987/ and inhabited by around 1000 people the area suffered no contamination, and since it has no roads it is considered remote. Travelling within the area is done by canoes with or without outboard motors. Because of the few outcrops typical of the results of tropical weathering processes and the difficulty in locatign them, the basic geological knowledge of the area is based on sections studied during the dry seasons along the major streams . This situation is typical of most of the Venezuela Guayana Shield.

Two Proterozoic geological provinces are recognized within the study area: Cuchivero, which is dominated by acid volcanism, with abundant pyroclastic rocks and minor lava flows, and together with some basic lava flows; and Roraima, which is dominated by sub-horizontal quartz sandstones, arkoses, conglomerates of fluvial origin, with minor acid volcanics and diabase sills /Moreno, et al., 1985/.

A small and discontinous mining activity for placer gold and diamonds was supported in the area.

The La Paragua drainage area has served as the basis of several geochemical studies which have been useful in the selection of sample types, chemical elements, analytical methods and sample density of this work.

In this work a comparison is made between two types of samples; the first taken in the field as deposited by the stream, and the second seived, starting from material coming from a mixture of energy environments. In all cases the minus 230-mesh fraction was analyzed.

The variation in concentration of each element within a sample site is compared with the analytical error and the variation between the sites. The types and density of anomalies detected are discussed.

METHODS

Samples of fine sediments were collected during the dry season /November - April/ in such a way as to represent all rivers of order 6 and larger. Some samples of rivers of order 4 and 5 were also taken. Rivers of order 1 were taken from topographic maps derived from aerial photographs 1:50 000, and have a drainage area that averages 0,35 km^2.

The drainage area of rivers of order 2,3,4,5,6,7,8 and 9 are found to be 1,7, 2.9;7,35; 370;1900;9400 and 45000 km^2 respectively (Escandón and Pasquali, 1987).

The area was covered by samples taken at one sample site for each order-6 river to ensure a uniform coverage at that level. Samples from lower-order rivers were taken where the logistics of the collection traverse allowed. Some order-6 streams could not be reached because of lack of navigability of a few larger streams in which they drain; this occured mainly within the Roraima province where mountans with flat tops have typically large rivers with falls and long stretches of rough water. The actual overall sample site density was one site per 130 km^2.

Fine-grained deposited samples /D/ were taken collecting material deposited in low-energy environments as mud, either dried up or submerged. This type of material commonly includes mostly clay-size and silt-size particles, although at times it includes fine sand-size particles. Finegrained sieved samples /T/ were obtained by sieving the field material deposited in higher-energy environments.

At each collected site of stream order 6, or higher, three subsamples of each type were taken in order to study the within-site variation. Samples were stored in plastic bags, dried at 70% C, sieved through stainless steel sieves, and the minus 230-mesh fraction analyzed.

Cu, Zn, Rb, Sr, Y, Zr and Nb where analyzed by X-ray fluorescence, using a Kevex instrument with a Si /Li/ detector, Rh tube and Ti, Fe, Ge, Ag, Sn and Gd secondary targets. Analytical errors which include sample preparation, electronic variations, and counting statistics are respectively of the order of 5,4,6,6,4,5, and 6 per cent, determined as coefficients of variations CV = σ/X x 100. Reference samples were constructed using three matrices detected in three major rivers and the addition-of-standard method.

Gold was determined by atomic absorption after roasting a 50-g sample, aqua regia attack, and extraction in methyl isobutyl ketone. The lower limit of determination of the method is 0,01 ppm, and typical errors are of the order of 15 percent of the concentration present.

RESULTS AND DISCUSSION

Table 1 summarizes analytical results obtained for sample types D and T. It shows the average values for the elements considered in samples that are not considered anomalous for the particular element; the CV of these values, the average CV for within-site subsamples is based on 54 sites.

Average concentrations of elements together with their respecive CV may be taken as a background indication for the whole region for these types of materials. The averages of CV for within-site subsamples are useful in establishing the likely concentration differences required in these types of samples to detect slight anomalies, or differences between drainage areas. In general the concentration of an element has to be at least 15 per cent higher, or lower, than the corresponding concentration in another drainage area before a true difference may be inferred; although this value varies with the element and the type of sample used.

Sample types D and T are similar but not identical. Cu, Zn, Sr, Zr, and Nb have higher average values in sample type T while Rb and Y are higher in sample type D. These differences, specially for Zr, indicate that care should be taken in treating both sample types as a single population, or else anomalies may be created or eliminated artificially.

Anomalies were detected using the following criteria:

1. Concentration of an element higher than $\overline{X}$ + 2; 2. coincidence of two or more higher than average concentrations of elements at one site; 3. higher, or lower, elemental ratios /$\overline{X} \pm 2\sigma$/, such as Rb/Sr; and 4. sequence of higher, or lower, values of concentration of one or more elements /X, $\overline{X}$/ in tributaries on one bank or both banks of main rivers.

Samples D and T give rise to similar but not identical anomalies, and in certain cases give rise to anomalies that are not geographically coincident.

In the area of 7000 km^2 30 anomalies of the four types /using the above criteria and all elements except Au/ were found, or one anomaly per 240 km^2. Commonly anomalies of the first three types group into anomalies of type 4, which in turn are generally accompanied by broad anomalies /high values/ in water conductivity easily detected in the field. These larger anomalies are of the order of 300 km^2, and six of them have been found in the area under study. Additionally 38 Au anomalies were found.

As a result of this type of regional geochemical reconnaissance attention may be profitably directed towards 25 percent of the area under consideration where anomalies of known nature have been detected by using several criteria.

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TABLE 1

AVERAGE CONCENTRATION OF ANALYZED ELEMENTS /ppm/ IN SAMPLE TYPES D AND T /$\overline{X}$/, WITH THEIR AVERAGE VARIATION COEFICIENT /CV $\overline{X}$/ FOR THE WHOLE POPULATION /140/; AND AVERAGE VARIATION COEFICIENT /CV/ FOR WITHIN-SITE SUB-SAMPLES BASED ON 54 SITES. ANOMALOUS VALUES /$X_2 > \overline{X} \pm 2\sigma$/ HAVE BEEN EXCLUDED, EXCEPT FOR THE CALCULATION OF CV VALUES

ELEMENT	Cu	Zn	Rb	Sr	Y	Zr	Nb
$\overline{X}$ /D/	25	67	85	35	63	1040	28
$\overline{X}$ /T/	30	77	83	41	53	1440	31
CV $\overline{X}$ /D/	24	19	21	29	21	22	25
CV $\overline{X}$ /T/	30	21	20	22	25	46	26
CV /D/	18	10	10	12	10	12	12
CV /T/	8	10	12	14	16	12	10

GEOCHEMISTRY OF F, Sr, TR AND U IN PHOSPHORITES OF THE EAST BALTIC PHOSPHORITE BASIN

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GENERAL REMARKS

The East Baltic phosphorite basin lies sublatitudinally as a narrow, 600 km long and 60 km wide stripe of land along the southern coast of the Gulf of Finland /Phosphorite-bearing ..., 1979, Fig. 1/. The northeastern and western margins of the basin have not been established. In the north its geological boundary has been destroyed by Post-Ordovician denudation, the present boundary roughly coincides with the clint escarpment represented by Cambrian-Ordovician rocks and running along the southern coast of the Gulf of Finland. In the south the basin is delimited by thinning out of phosphorite-bearing sediments.

Phosphorite-bearing sediments, the so-called Obolus sandstone /Öpik, 1929/ are assigned to the Tremadoc Pakerort Stage /Lower Ordovician/ /O_1pk/. They lie subhorizontally /inclination 2÷4 m/km to the south/ on the erosion surface of quartzose sandstones of the Lower Cambrian Tiskre Formation /$Є_1$ts/ constituting the basal layers of the Ordovician. The Obolus sandstone is overlain by metalliferous kerogenous black shale argillites and aleurolites known as Dictyonema shale, also belonging to the Pakerort Stage /Petersell et al., 1981; Pukkonen, 1989/, or by glauconitic sand and siltstones of the Arenig Leetse Formation /Lower Ordovician/ /O_1lt/. The thickness of Obolus sandstone increases westwards reaching 10-14m, in places 22 m /Fig. 1/.

Obolus sandstone is represented by horizontal - and crossbedded siltstones and crossbedded siltstones and fine-grained, sometimes medium - to coarsegrained sandstones, in places containing Dictyonema shale interbeds. Characteristic are dark, often brown or almost black valves or their fragments /skeletal detritus/ of inarticulate brachiopods /obolids/, extremely variable in number. In some areas of tens, more rarely of hundreds square km, the amount of skeletal remains, seldom obolids exceeds 10-15% and reaches 50-70% of the rock mass in the layers of 0,3-1,0 m and more in thickness. Such areas comprise all well-known phosphorite deposits of the East Baltic basin: Maardu, Toolse, Aseri-Saka, Narva, Kingissepp, etc., also new perspective areas south of Maardu, south Kingissepp, etc. and undoubtedly the unique Rakvere deposit. Although the P_2O_5 content is low in phosphorites of these deposits ranging from 3-4% to 15-20%, rarely more, and P_2O_5 resources do not exceed 30-60 million tons, the exploitation of these deposits is economically expedient as phosphatic shells /detritus/ can be concentrated easily.

Economical significance of the East Baltic phosphorite basin increased considerably with the discovery of the unique Rakvere deposit containing P_2O_5 resources of about 1 milliard tons.

Phosphorites of the East Baltic basin are composed of phosphatic minerals with terrigenous component. The former are represented by obolid shells or their fragments /detritus/ composed of phosphatic minerals of the fluorine-carbonate-apatite group, rarely with hemogenic phosphorite interlayers. Films of the latter sometimes surround also quartz grains /Raudsep, 1984/. P_2O_5 content in phosphatic shells and their chemical composition are rather stable in the basin area /Table 1/.

Terrigenous component contains 70-90% and more of quartz and up to 10-15% of

Table 1.

Chemical composition of Obolus shells and their fragments in wt % (Geologia ..., 1987).

Compounds	Deposit Maardy	Toolse	Rakvere dark material	 light	Azeri	Kinginsepp
P_2O_5	34.66	33.85	35.37	37.11	34.59	36.80
MgO	0.21	0.45	0.63	0.67	0.47	-
Fe_2O_3	1.59	2.45	3.15	1.17	3.47	-
SiO_2	-	3.16	0.79	1.17	0.64	-
Al_2O_3	-	0.31	0.51	0.46	0.73	-
CaO	50.58	47.56	50.21	52.34	49.78	51.91
CO_2	-	3.41	3.46	3.68	3.57	3.50
Na_2O	-	0.89	0.54	0.47	0.61	-
K_2O	-	traces	0.10	0.10	0.10	-
S total	-	1.53	1.20	0.20	2.66	-
H_2O	3.38	5.98	3.07	3.21	3.39	-
FeS_2	3.20	-	3.36	0.21	4.46	-
SO_3	1.26	-	0,47	0.32	0.27	-
number of analyses	1	12	6	12	15	8

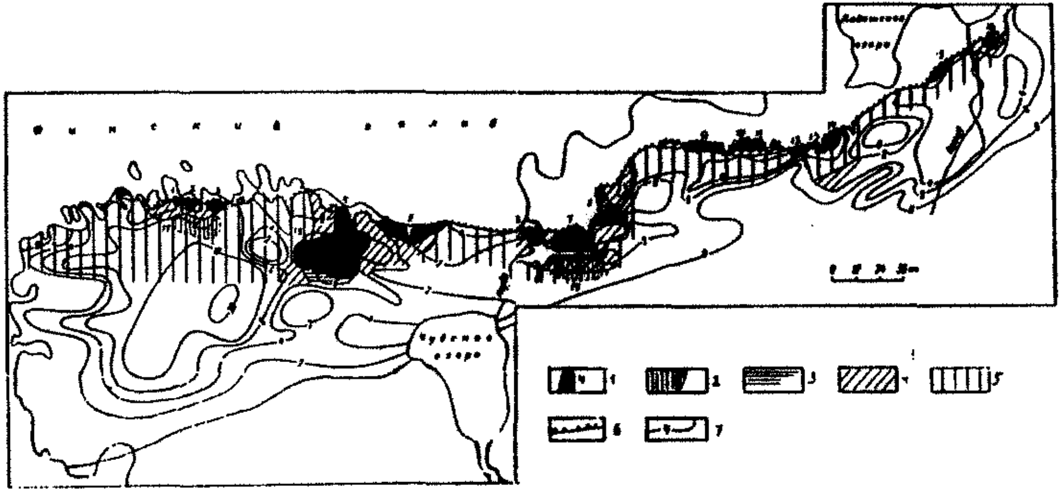

Fig. 1 - Map of distribution of phosphorite deposits in the East Baltic phosphorite basin.
1 - phosphorite deposits (1=Iru, 2=Maardu, 3=Tsitre-Valkla, 4=Toolse, 5=Aseri, 6=Naeva, 7=Kingsepp, 8=Kolotovsk, 9=Gladinsk, 10=Krasnoselsk, 11=Dudergolfsk, 12=Fedorovsk, 13=Popovka, 14=Uljanovsk, 15= Chaplinsk, 16=Volhovsk, 17=Maardu-South, 18=Rakvere, 19=Kinginsepp-South), 2 - areas of economic ores: 2-5 with P_2O_5 up to 9 % (3), up tp 6 % (4), up tp 3 % (5), 6=fault, 7 - isopachite of phosphorite-bearing sediments.

feldspar, glauconite grains and mica scales. Also rare or single grains of zircon, tourmaline, apatite, monazite, xenotime, iron and titan minerals, also rock-forming minerals of the baltic shield. In separate areas there are found scare grains of galenite, sphalerite and chalcopyrite. In places phosphorites are weakly to strongly dolomitized. In the latter case the dolomite content in phosphorite cement reaches 5-10% and more whereas phosphorites turn into relatively solid rock where phosphatic obolid shells are difficult to concentrate. Carbonates come from the Ordovician carbonate rocks lying on phosphorites and glauconitic sandstones. "The water, leaching carbonate rocks, permeates into Obolus sandstone where carbonates are separated from the solutions and fill empty spaces between sand grains and, first of all, cracks in the rock" /Phosphorite-bearing ...,1979/, p. 66/.

Phosphorites of the East Baltic basin are characterized by the increased F, Sr, REE, also U content /Mineev, 1974; Petersell p. 1986/. These elements belongs to phosphatic minerals in isomorphic way forming an obligatory geochemical load in these. They concentrate together with phosphatic minerals and in phosphorite concentrate considerably exceed the clarke of sedimentary rocks. In the chain phosphorite-fertilizer-soil-biosphere or utmost importance is to establish the occurrence of there elements in phosphorites, first of all in phosphatic minerals.

According to commercial significance the above elements are divided into two groups. Simultaneous extraction of F, Sr and U from phosphate concentrate not only cleans fartilizers of harmful elements but also allows to cover their deficiency in the industry. Although the resources of REE are sufficiently big, the incrasing demand for them and high-quality complex reworking of phosphatic raw materials alloww to consider phosphorites as an additional potential source for REE, in any case for the countries lacking their own RE raw material /Altschuler et al., 1967; Mineev, 1974/.

METHODS OF THE STUDY

F, Sr, TR and U, also other trace elements were determined in laboratory duplicates of core and technological samples collected during prospecting for phosphorite deposits. Monofraction of the phosphatic shells and skeletal detritus was separated from the same samples only from nonshattered geological duplicates. The analyses were performed by means of widely-used methods of chemical, X-ray spectral, X-ray spectrochemical, neutron-activization, chemical fluorine-selective electrode and X-ray fluorescent analyses /Methods ....1979/ in the laboratoties of IMGI, IMFRE and Geological Survey of Estonia. Preciseness of the analyses meets the standard required by the USSR Ministry of Geology /Otras ...1986/.

Isotopic analyses of oxygen and carbon were carried out in the laboratory of IGEM of the UkrSSR Academy of Science and by the joint Soviet-Polish enterprise "Balto-Teriva". The isotopic ratios weredetermined with mass-spectrometry MI-$_{1}$20$_{1}$ B according to standards SMOW /$18_{O}/16_{O}$=0,1993/ and PDB /$12_{C}/13_{C}$= 88,99/ /Žukov, 1982/. Preciseness of analyses is ± 0,3 ‰ and ± 0,4 ‰, respectively.

DISTRIBUTION OF F, Sr, REE AND U IN PHOSPHORITES

As was said above, F, Sr, REE and U occur and are concentrated mainly in phosphatic valves and skeletal detritus of obolids; together with P they form a distinctly defined positive geochemical association. These elements are characterized by highly positive correlative relations /Table 2/. Due to this the distribution of F, Sr, REE and U generally corresponds to the areal as well as vertical distribution of P_2O_5 in the phosphorite area. Yet, depending on the total content of phosphatic minerals in phosphorites, there are observed considerable differences in the sections contaning any of these elements.

Fluorine. The F content in phosphatic layers of the East Baltic phosphorite-bearing area is greatly variable ranging from 0,27% to 2,07% and exceeding the clarke of sedimentary rocks by 6 to 41 times. Vertically the F content is even more variable ranging from 0,24% to 2,28%. Areal distribution of F in phosphorites in the section of the deposits almost completely coincides with that of P_2O_5. Its maximum content was recorded in the epicentral part of the basic ore body of the Rakvere deposit, minimum content in the marginal parts of the phosphorite deposits /Fig. 2/.

The F/P_2O_5 ratio is very stable in this large area. The F content is similar to that of P_2O_5. It does not depend on the absolute P_2O_5 content in phosphorites and fluctuates only slightly, from 0,082 to 0,098. The correlation coefficent between F and P_2O_5 is high, positive, in separate deposit sections nearing 1. The coefficient of content variation of F and P_2O_5 is rather high - 39-64%, the coefficient of their ratio variation, however, is only 10-16% /Fig. 3, Table 3/.

Strontium. The Sr content in the phosphorite layers of the basin is unequal and also greatly fluctuating ranging from 380 to 3250 g/t. It exceeds the clarke of sedimentary rocks by 7.2. times Vertically in the section of the phosphorite layer the greatest Sr content is up to 3600 g/t /Fig. 2/.

Areal distribution of Sr in phosphorites generally coincides with the distribution of P_2O_5 in phosphorite deposits. The correlation coefficient of P_2O_5 and Sr is high by positive nearing to 1 /0,97/.

The Sr/P_2O_5 ratio in this area is stable but somewhat more changeable than by fluorine ranging from 107 to 165 /Fig. 3, Table 3/. It has been noted that in the layers of the epicentral part of the main ore body of the Rakvere deposit the Sr/P_2O_5 ratio tends to decrease inconsiderably with the incrase in the total content of P_2O_5 in the ore. This is also evidenced by the negative correlation between P_2O_5 and the Sr/P_2O_5 ratio in this area.

Lanthanoids and yttrium $/TR_2O_3/$. The mean TR_2O_3 content in the phosphorite layers of the phosphorite basin is also uneven, ranging from 358 to 842 g/t and exceedint the clarke of the sedimentry rocks by up to 4,1 times. Vertically in the sections studied the TR_2O_3 content fluctuates in the same limits /Fig. 2/.

Areal distribution of TR_2O_3 in phosphorites only in sections of separate deposits roughly coincides with that of P_2O_5. The absolute TR_2O_3 content is the greatest in the Toolse deposit, the lowest in the main ore body of the Rakvere deposit, in Kabala and Assamalia localities and in the Kingissepp deposit.

Everywhere in the studied deposits P_2O_5 and TR_2O_3 are in positive correlation. The correlation coefficient between these components, however, is considerably lower as compared to F and Sr ranging from 0,618 to 0,936.

The TR_2O_3/P_2O_5 ratio in phosphorites of the basin is greatly variable ranging from 26 to 93 by separate layers, in the sections of different boreholes even more /Fig. 3, Table 3/. The variation coefficient of the ratio TR_2O_3/P_2O_5 is changing laterally, high, in the Kabala and Assamalla localities exceeding the variation coefficient

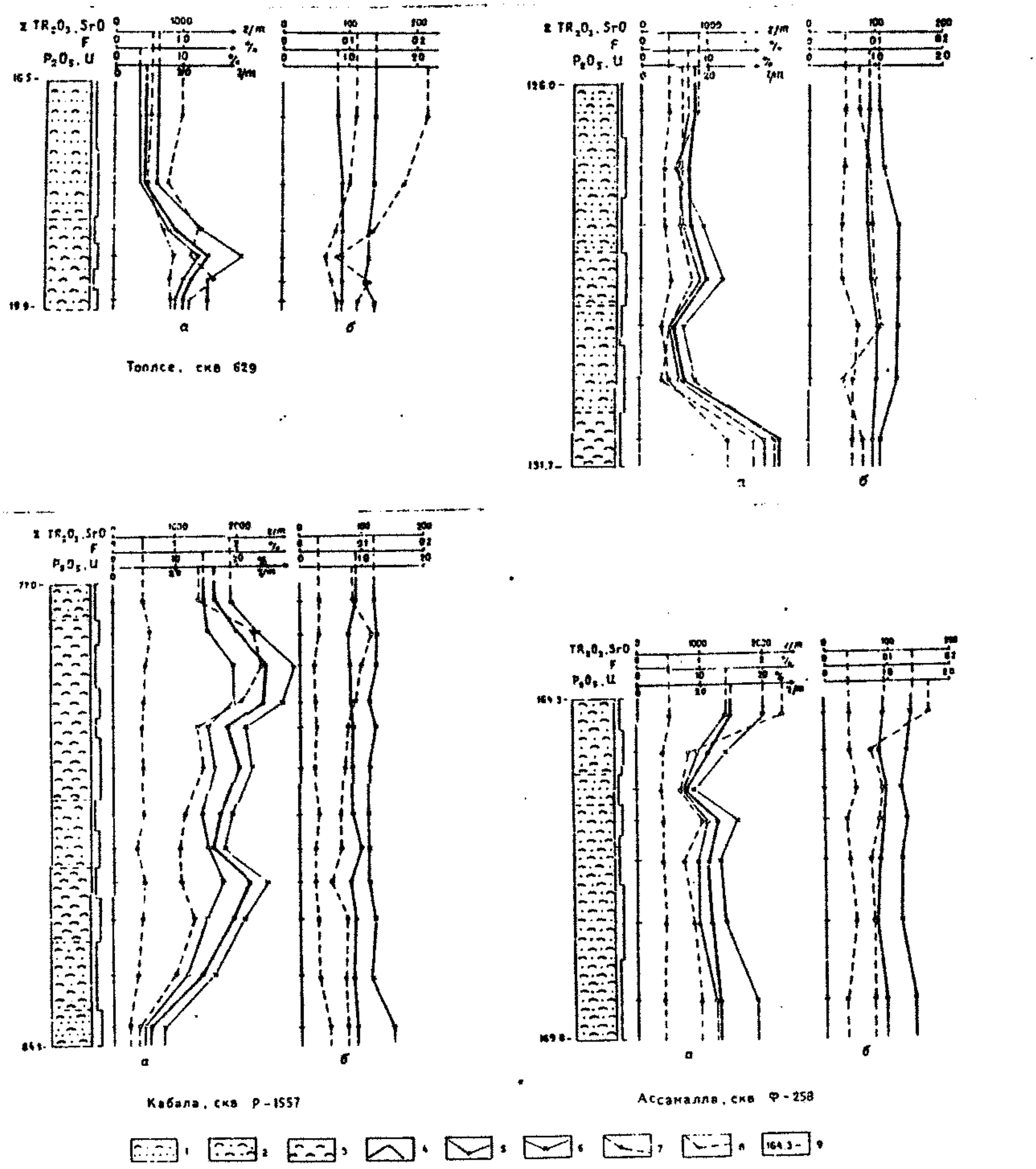

Fig. 2 - Geological-geochemical section of phosphorite from Rakvere phosphorite-bearing area.

1 - 3 phosphorite (1-detritidal sandstone, 2-detritical sandstone, 3-detrite); 4 - 8 distribution graphs (a) and P_2O_5 ratio (b): 4-P_2O_5, 5-F, 6-Sr, 7-TR_2O_3, 8-U); 9-depth (m).

Table 2.

Statistical parameters and matrix of linear correlation coefficients of selected elements

Deposit Toolse

	P_2O_5	MgO	Fe_2O_3	FeS_2	F	Sr	REE	Y_2O_3	$\frac{F}{P_2O_5}$	$\frac{Sr}{P_2O_5}$	$\frac{REE}{P_2O_5}$	$\frac{Y_2O_3}{P_2O_5}$
P_2O_5	-	.395	-.086	-	.978	.969	.936	.935	-.161	-.240	-.780	-.668
MgO	.359	-										
Fe_2O_3	-.086	-.119	-									
FeS_2	-	-	-									
F	.978	.343	-.123	-								
Sr	.969	.322	-.116	-	.990							
REE	.936	.391	-.117	-	.961	.984						
Y_2O_3	.935	.346	-.137	-	.959	.961	.984					
$\bar{x}$	9.98	0.31	1.32	-	0.89	1376	774	181	0.091	142	83	20
S	5.99	0.058	0.61	-	0.51	782	309	79	0.012	18	20	4.8
V	60	19	46	-	58	57	42	44	13	13	24	24

$n = 29$
$r_{99} = \pm .437$
$r_{95} = \pm .317$

Section Ragavere

	P_2O_5	MgO	Fe_2O_3	FeS_2	F	Sr	REE	Y_2O_3	$\frac{F}{P_2O_5}$	$\frac{Sr}{P_2O_5}$	$\frac{REE}{P_2O_5}$	$\frac{Y_2O_3}{P_2O_5}$
P_2O_5	-	.563	.288	.383	.987	.967	.914	.903	-.221	-.352	-.521	-.500
MgO	.563	-										
Fe_2O_3	.288	.667	-									
FeS_2	.383	.644	.956	-								
F	.987	.558	.271	.371	-							
Sr	.967	.609	.260	.349	.956	-						
REE	.914	.533	.196	.270	.924	.866	-					
Y_2O_3	.903	.552	.205	.276	.912	.842	.975	-				
$\bar{x}$	9.61	0.54	1.09	0.91	0.88	1059	496	119	0.093	117	56	14
S	6.10	0.39	0.70	0.80	0.55	597	280	71	0,009	28	14	3.8
V	64	73	64	89	63	56	56	60	10	24	25	28

$n = 43$
$r_{99} = \pm .366$
$r_{95} = \pm .264$

Section Assamalla

	P_2O_5	MgO	Fe_2O_3	FeS_2	F	Sr	REE	Y_2O_3	$\frac{F}{P_2O_5}$	$\frac{Sr}{P_2O_5}$	$\frac{REE}{P_2O_5}$	$\frac{Y_2O_3}{P_2O_5}$
P_2O_5	-	-.397	-.443	-	.994	.978	.618	.805	-.114	-.212	-.585	-.505
MgO	-.397	-										
Fe_2O_3	-.443	.370		-								
FeS_2	-	-	-	-								
F	.994	-.389	-.452	-	-							
Sr	.978	-.437	-.497	-	.975	-						
REE	.618	-.499	-.538	-	.617	,652	-					
Y_2O_3	.805	-.535	-.467	-	.803	.869	.864	-				
$\bar{x}$	13,46	1.64	1.36	-	1.22	1792	450	124	0.088	128	38	10
S	7.06	2.06	1.04	-	0,63	944	107	34	0.014	31	19	4.4
V	52	127	83	-	52	53	24	27	16	24	51	43

$n = 22$
$r_{99} = \pm .492$
$r_{5} = \pm .360$

Table 2 - continuation

Section Kabala

	P_2O_5	MgO	Fe_2O_3	FeS_2	F	Sr	REE	U	$\frac{F}{P_2O_5}$	$\frac{Sr}{P_2O_5}$	$\frac{REE}{P_2O_5}$	$\frac{U}{P_2O_5}$
P_2O_5	-	-.006	-.483	-.267	.968	.976	.692	.862	-.334	-.441	-.606	.370
MgO	-.006	-										
Fe_2O_3	-.483	-.178	-				n = 43					
FeS_2	-.267	-.274	.844	-			$r_{99} = \pm.366$					
F	.968	-.089	-.537	-.298	-		$r_{95} = \pm.264$					
Sr	.976	-.038	-.537	-.234								
REE	.692	-.055	-.280	-.099	.670	.671						
U	.862	-.160	-.146	-.099	.832	.883	-.643					
$\bar{x}$	14.40	0.77	0.97	0.31	1.25	1621	440	20	0,088	114	37	1.4
S	5.80	0.74	0.68	6.44	0.48	628	128	11	0.013	19	21	1.3
V	40	96	70	141	0.39	39	29	52	15	16	56	93

Table 3.

Contents of F, Sr, REE and U in phosphorites and their concentrates

deposit, basin	%	g/t									References
	P_2O_5	F	Sr	TR_2O_3	Y_2O_3	U	$\frac{F}{P_2O_5}$	$\frac{Sr}{P_2O_5}$	$\frac{TR_2O_3}{P_2O_5}$	$\frac{U}{P_2O_5}$	
	Shellitic phosphates										
Maardu South	10.07	0.98	1114	756	-	17	0.097	111	75	1.7	Petersell et
Toolse	9.98	0.89	1376	774	181	28	0.091	142	83	2.8	al. 1986
Assamalla	13.46	1.22	1792	450	124	16	0.088	128	38	1.2	-"-
Ragavere	9.61	0.88	1059	496	119	13	0.093	117	56	1.4	-"-
Kabala	14.40	1,25	1621	440	130	20	0.088	114	37	1.4	-"-
Azeri-Saka	7.42	0.70	875	487	122	25	0.094	118	66	3.4	-"-
Narva	8.21	0.76	1006	460	104	47	0.093	123	56	5.7	-"-
Kingisepp (technolog. sample)	5.57	0.61	873	327	90	24	0.109	150	59	4.3	
	Grained phosphorites										
Karatau	29.4	2.70	1740	780	-	-	0.092	59	27		Bliskovskyj et
Phosphoria (USA)	30.5	3.1	780	1500	760	90	0.103	26	49	3.0	al. 1983
Morocco	33.1	3.7	1830	1300		100	0.112	55	39	3.0	-"-
Syria	26.1	2.9	1450	1100		80	0.113	55	42	3.1	-"-
North Australia	35.6	3.4	354	1650	774	78	0.095	9.9	46	2.2	-"-
	Concentrates of phosphorites										
Maardu	24,29	1.83	2350	1357	368	42	0,076	97	56	1.7	Petersell et
Toolse	27.50	2.55	2600	2000	480	52	0.093	95	73	1.9	al. 1986
Assamalla	30.01	2.88	2750	1265	285	32	0.096	92	42	1.1	-"-
Ragavere	30.12	2.90	3100	1600	380	42	0.096	103	53	1.4	-"-
Kabala	29.15	2.67	3100	604	122	38	0.092	106	21	1.3	-"-
Kinginsepp	27.96	2.72	3450	1700	432	49	0.097	127	60	1.8	-"-
Apatity (conc.)	38.57	2.59	11900	8080	420	10	0.067	308	209	0.3	Mineev 1974

of TR_2O_3 content. The analysis of the TR_2O_3/P_2O_5 ratio has shown that these values are the greatest in the Toolse deposit, the lowest in the epicentral part of the main ore body of the Rakvere deposit /Fig. 3/. Areally, as well as along the section, the TR_2O_3/P_2O_5 ratio decreases relatively with the increase in the P_2O_5 content in phosphorite. P_2O_5 and TR_2O_3/P_2O_5 are everywhere in distinctly negative correlation. For clearing up the nature of this phenomenon, the TR_2O_3 content was studied in monofractions of the phosphatic shells of obolids collected from the ore of Assamalla area containing P_2O_5 from 11,85 to 25,90%. The results of the analyses are given in Table 4 and Fig. 4. In a similar way they show that the TR_2O_3 content in monofractions of obolid shells decreases with the increase in the total number of phosphatic shells or detritus /P_2O_5/ in phosphorites. This is noted also by the study of TR_2O_3 content in phosphorite concentrates obtained from the ore with different P_2O_5 contents. It is clearly seen that the higher is P_2O_5 content in ore, the lower is the TR_2O_3/P_2O_5 ratio in phosphorite concentrate whereas the F/P_2O_5 and Sr/P_2O_5 ratios remain stable. This regularity allows to suggest the following:

- the water of the paleobasin, subjected to phosphate accumulation was deficient in TR_2O_3 and crystal framework of obolid shells in their growth stage was not completely filled with these elements;

- accumulation of phosphatic shells generally took place "in situ". They were not moved noticeably in the course of sedimentation.

Spectrum of TR is monotypical and unchangeable in the whole area.

Y_2O_3 in TR_2O_3 makes 19-28% and does not depend on the absolute P_2O_5 content in phosphate ore /Table 3/. Among Ln 16± 3% are made up by La, 35± 4% by Ce. The most concentrated in the clarke of sedimentary rocks are always Eu, and Tu, the least concentrated - La and Yb, particularly Lu. The spectrum of lanthanoids is monotypical and rather persistant throughout the whole basin serving as a regional geochemical parameter /Table 5/.

Phosphorites of the Baltic basin are characterized also by the increased /13-47 g/t/ U content exceeding the clarke of sedimentary rocks by up to 10 times and more. Although the distribution pattern of U in phosphate ore generally, coincides with that of P_2O_5, there are noted considerable deviations. The U content is risen in the phosphate ore of the Narva deposit and lowered in the basic ore body of the Rakvere deposit. The U content, also the U/P_2O_5 ratio are the highest in the upper part of the section, especially immediately below the Dictyonema shale. Towards the base these values are decreasing unevenly. U and P_2O_5 are in positive but often fused correlation. This is mostly caused by 3 ways of occurrence of U in phosphate ore. The greatest part of U is concentrated in obolid shells or detritus. By means of f-radiography it was established that the distribution of U in them is uneven and increases in the areas enriched in ferric hydrates and pyrite. A part of U contents with the increased clarke come from the interbeds of metalliferous Dictyonema shale in phosphorites and an in considerable part from micas and accessory minerals. In the process of concentration from two last forms U falls into mud or tails. This concerns most of all Toolse, Aseri-Saka, Narva and Kingisepp deposits.

As compared to some of the larger basins of grained phosphorites of the world /Table 3/, phosphorites of the East Baltic basin contain 2-3 times less P_2O_5 and only

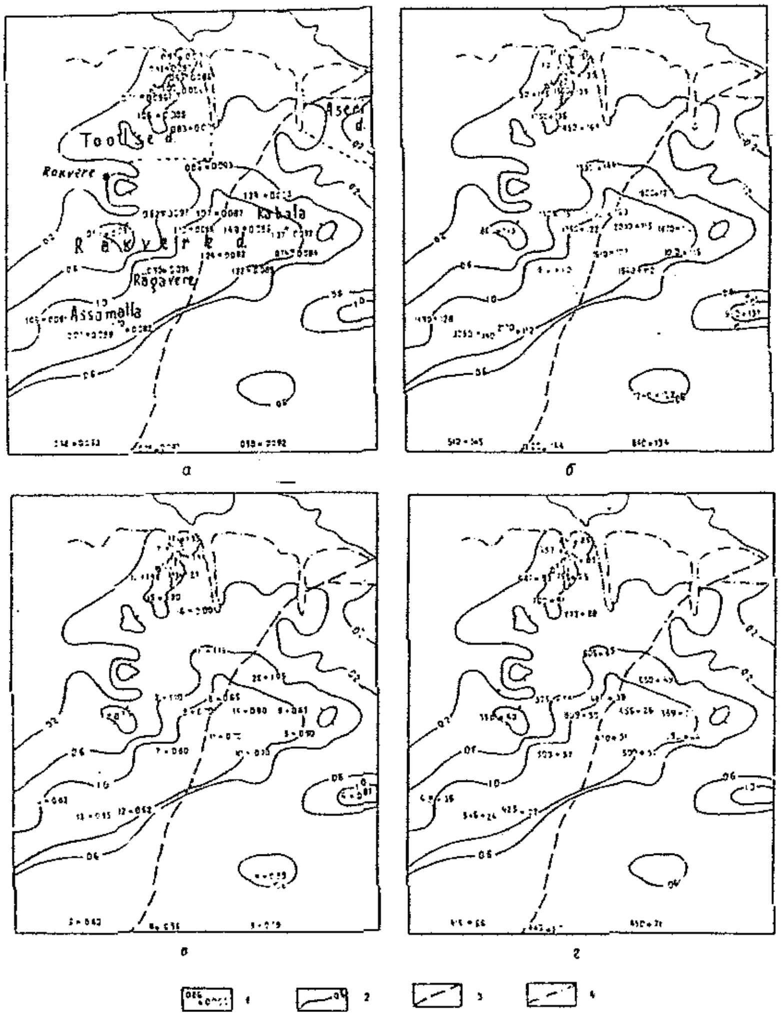

Fig. 3 - Contents of F (a), Sr (б), TR_2O_3 (b) and U (r) in the phosphorites of Rakvere phosphorite-bearing basin.

1-drill hole (left - medium content, right - relation to P_2O_5), F - in %, Sr, TR_2O_3 and U - in ppm; 2 - line of isoproductivity P_2O_5 in tons/m^2; 3 - Aseri fault; 4 - north boundary of the phosphorite basin.

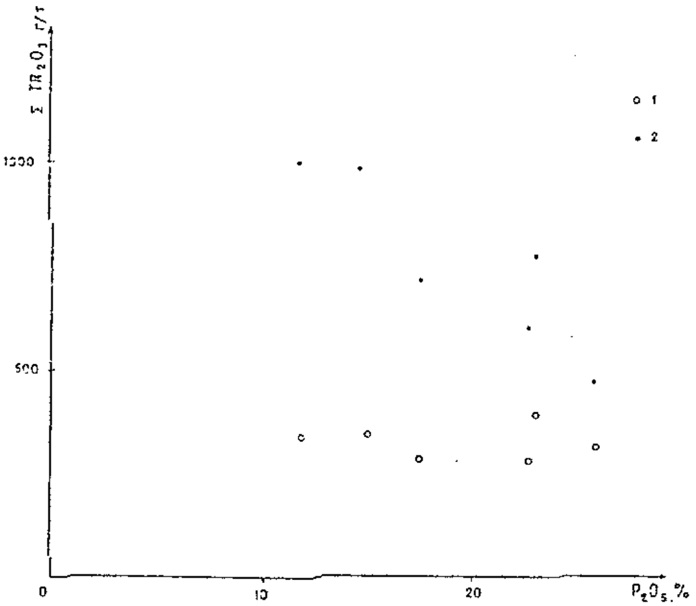

Fig. 4 - Relationship between lanthanides content in the Obolus shells and P_2O_5 contents in the ore of the Rakvere deposit (Petersell et al. 1986).
1 - contents of lanthanides in phosphorites; 2 - contents of lanthanides in obolid shells from corresponding ores.

phosphate concentrates can be compared considering the P_2O_5 content. The concentrates differ from compared grained phosphorites in the increased Sr contant and in the decreased U, F, also Cd contents /Loog, Petersel, 1990/.

ON THE SOURCE OF THE ORE MATTER

Shelly phosphorites constitute an independent ore formation of specific genesis and paleogeographical conditions of accumulation. As a rock, phosphorites are composed of two main components of different genesis - sand - and slit-sized allochthonous quartz and biogenic phosphatic shells and skeletal detritus of inarticulate brachiopods. Other minerals - clayey, accessory, etc. are not rock-forming. Local increase in dolomite content in evidently a more recent as compared to accumulation of terrigenous minerals and phosphatic shells.

One of the most complicated and yet unsolved problems is the source of P,F, Sr, REE and U and other trace elements. Undoubtedly these elements have concentrated in obolid shells due to their increased content in the paleobasin in the form of solutions, capacity for isomorphism of growing phosphatic obolids with respect to above trace elements, paleoecological etc. conditions. They prove that as compared to the mean content of these elements in the inorganic part of living organisms /Vinogradov, 1954/, phosphatic shells of obolids are enriched in the average with U - by 100 times, F - by 102 imes, Y - by 35 times, Fe - by 4.4. times, P - 3,4 times and Sr - by 2,5 times /Petersell 1986/.

From the afore-said it can be concluded that, apart from P, the F content and generally also the Sr content were high everywhere in the paleobasin and they completely filled the crystal framework of shells during their growth even in the phase of their maximum accumulation.

Concentration of TR and U in phosphorites depends on their areal distribution, as well as on the absolute content of phosphatic minerals in phosphorite. Occurrence of regular TR/P_2O_5 and U/P_2O_5 ratios and stable TR spectrum in phosphorite evidences that phosphatic shells were not transported and displaced noticeably in the paleobasin during the growth stage and life of brachiopods, also in the process of sediment accumulation. Undoubtedly the paleobasin was deficient in TR and U and the crystal framework of obolid shells in their growth stage was not filled with these elements even in the area of the Toolse and Kingissepp deposits where the content of these elements is the highest. The TR spectrum is persistant throughout the whole basin area and obolid shells show no concentration of any of them. The Ln spectrum in phosphorites differs greatly from that characterizing ocean water, but also from the average spectrum of sedimentary rocks and lithosphere /Table 5/.

The isotopic composition of oxygen in phosphatic shells coming from the epicentre of the greatest ore body of the East Baltic basin /Rakvere deposit/ shows /Table 6, Fig. 5/ that oxygen of obolid shells is lighter as compared to that of above-lying carbonate rocks. Considering the isotopic composition, it remains between oxygen of intrusive and carbonate rocks, it is rather similar to oxygen from apatite of gabbro-diorites, of rapakivi-granite-anorthosite formation. In the section of the phosphorite layer $\delta^{18}O$ fluctuates from +12,6 to +16,6‰ and grows fairly rapidly in the lowermost part of the phosphorite layer from +12,6 to +15,7‰ . If the fluctuations of $\delta^{18}O$ are caused by temperature changes in the paleobasin, it takes place in the interval of about 0-20-24°C. By this, accumulation of phosphates started by increased water temperature in the paleobasin, which in turn, was higher than the temperature of carbonate sediment accumulation.

The isotopic composition of C coming from cement dolomitizing the same ore body /Fig. 5, Table 6/, shows that, as compared to $\delta^{13}C$ of carbonate rocks in general and of phosphorite overburden in particular, it is also lighter, persistant and resembles the isobopic composition of subsurface carbon and carbonate of the Kovdor deposit. Rather similar to it is $\delta^{13}C$ of carbon from hemogenic phosphorite of the Narva deposit. The isotopic composition of pyrite sulphur from the underlying Tiskre sandstone of the same section /Table 6/ and from the overlying Dictyonema shale /Petersell, 1987/ is also of subsurface character.

Simple calculations have proved that P with increased clarke makes up 1,5 - 2 milliard tons, F - 250-380 million tons, Sr - 26-44 million tons, TR - 10-20 milllion tons and U - 0,2-0,4 million tons in phosphorite-bearing deposits of the East Baltic basin. The transportation of such an amount of P and other elements into the basin by surface water during sediment accumulation is unrealistic. Neither could it be considered as upwelling, in the water of which there should be other element ratios than in the ocean, first of all of Ln.

The above factual material allows to suggest the flow of subwater hydrothermes from deep springs into the East Baltic phosphorite basin at the peroid of phosphorite accumulation, enriched in P, F, Sr, TR, U, Fe and other elements. This inflow took place in the platform activization zone of the northwestern part of the Russian Plate in the stage of the Caledonian orogeny. One of such wide zones of Caledonian activization proceeds along the East Baltic phosphorite basin from Hiiumaa Island in the west through Kohila, Uljaste up to Narva reservoir and farther in the eastern-north-eastern direction. It can be traced by disturbances in bedding of the surface of the crystalline basement and in the bedding of the sedimentary rocks, often by helium anomalies in water, also by lineaments in areo-and cosmic photos. In West Estonia this is evidenced by subsurface faults in the crystalline basement, along which dislocation of the surface "M" up to 2-4 km took place /Bulin, 1978/. In the east it coincides with the Volhov zone of subsurface faults /Kapta, 1981/.

These subwater hydrothermes caused the formation of specific short-term paleogeographical conditions in the paleobasin favourable for anomalous massive appearance of poor and monotonous fauna of inarticulate brachiopods, shells of which were composed of minerals of the fluorine-carbonate-apatite group. Highly significant was also the incrased U content in the water. The most probable sources of hydrothermes were deep springs opening during the Caledonian tectonic activization, which were genetically connected with evolutionary Proterozoic subplatform magmatic hearths of granitoids and gabbroids of anorthosite Rapakivi formation. The Proterozoic representatives of this formation in the distribution area of East Baltic phosphorite-bearing deposits are characterized by distinctly increased positive geochemical association of P, F, Sr, REE and U /Petersell, 1986/ and by the Ln spectrum similar to that of phosphorites /Table 5/.

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Table 4.

Contents of P_2O_5 and REE in phosphorites and Obolus shells of the Assamallask deposit

borehole No	depth of bulk samples in m	phosphates P_2O_5 %	phosphates REE g/t	Obolus shells P_2O_5 %	Obolus shells Sr g/t	Obolus shells REE g/t	Obolus shells Yg/t	$\frac{Y}{REE}$
F-258	164.3	14.72	342	36	4650	980	261	27
	166.0	17.49	281	36	5000	710	174	25
	168.0	11.89	340	36	4750	1000	253	25
F-255	154.6	23.20	398	36	4100	710	158	22
	156.3	22.82	292	36	4650	600	166	28
	157.6	25.95	302	36	4850	470	166	31

Table 5

Concentration of lanthanides in phosphorites of the Pribaltijsky phosphorite-bearing basin

type of sample	number sampl.	P_2O_5 %	REE %	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
				REE composition wt %													
phosphorites	4	7	0.027	16.1	37.1	5.27	18.7	5.20	1.23	7.47	0.72	4.75	0.82	1.71	0.32	0.83	0.14
	5	8-15	0.052	17.3	36.4	5.14	18.8	4.98	1.22	6.66	0.79	4.34	0.85	2.40	0.39	1.40	0.25
	3	16-22	0.081	15.7	37.3	5.33	19.5	5.00	1.20	6.87	0.77	4.03	0.75	1.97	0.31	1.13	0.22
concentrates	2	29	0.145	17.9	37.6	4.75	19.5	4.60	1.15	4.60	0.80	4.20	0.85	2.25	0.35	1.20	0.20
							Deposit Rakvere										
Obolus shells from phosphates with: 11.85-17.66 wt % P_2O_5																	
	3	36	0.090	17.3	35.7	4.67	18.7	4.47	1.13	6.50	1.03	5.07	0.93	2.80	051	1.00	0.19
22.82-25.95 wt % P_2O_5																	
	3	36	0.J59	17.4	33.6	4.50	18.1	4.83	1.20	7.27	1.13	5.73	0.98	3.17	0.59	1.13	0.25
							Deposit Maardu										
concentrate	1	26.0	0.130	17.0	35.4	4.7	19.9	4.9	1.1	5.2	0.9	5.0	1.0	2.8	0.5	1.4	0.2
							Deposit Kingisepp										
concentrate	1	28.2	0.150	16.4	39.3	4.2	20.2	4.1	1.5	6.9	0.5	3.4	0.4	1.5	0.3	1.2	0.2
clarke of sedimentary rocks (A.P.Vinogradov 1962)				27.6	35.4	3.45	15.9	4.49	0.69	4.49	0.62	3.11	0.69	1.73	0.17	2.07	0.48
clarke of sea water /A.P. Vinogradov 1962)				34.5	15.5	7.13	9.72	4.49	1.31	7.13	-	8.68	2.61	7.13	1.19	5.95	1.19
granitoids and intrusive rocks of rapakivi formation of North Estonia g/t				188	365			19		4	2.3					7.5	1.1

Table 6

Isotopic composition of carbon and oxygen in phosphorites of the Rakveresk deposit

depth in m	content wt % P_2O_5	content wt % Fe_2O_3	$C_{carb.}$	$\delta^{13}C_{carb.}$ ‰	$\delta^{34}S_{pyrite}$ ‰	$\delta^{18}O_{shells}$ ‰	rocks
93.0-93.2			10.33	-0.9			dolomitized carbonate
94.7-94.9			13.44	-1.1			dolomite
95.9-96.1	2		0.26	-10.7			glauconitic sandstone
96.1-97.2	25.25	1,74	3,22	-6.8			dolomitized phosphorite
98.3-98.8	14.33	1.17	3.20	-6.9			-"-
100.2-101.1	7.58	0.56	1.57	-6.6			-"-
101.8-102.6	2.82	0770	2.76	-8.3			-"-
103.6-104.6	7.38	0.92	2.74	-7.9			-"-
104.8-105.0	1.0		0.96	-7.5			dolomitized sandstone
87.2-87.4			1.19	-7.9	-2.7		dolomitized and pyritized sandstone
87.6-87.8			2.84	-8.7	-2.7		-"-
91.1-91.6	16.99	2.09				+16.6	phosphorites
91.6-92.4	17.10	1.21				+15.6	-"-
92.4-93.0	19.50	1.54				-	-"-
93.0-93.6	21.20	1.98				+13.5	-"-
93.6-94.7	22.10	1.11				+15.7	-"-
94.7-95.9	8.72	0.45				+16.6	-"-
95.9-96.9	12.27	0.50				+16.1	-"-
96.9-97.5	16.90	0.60				+15.7	-"-
97.5-97.9	21.07	0.83				+14.5	-"-
97.9-98.2	5.39	0.88				+12.5	dolomitized phosphorite

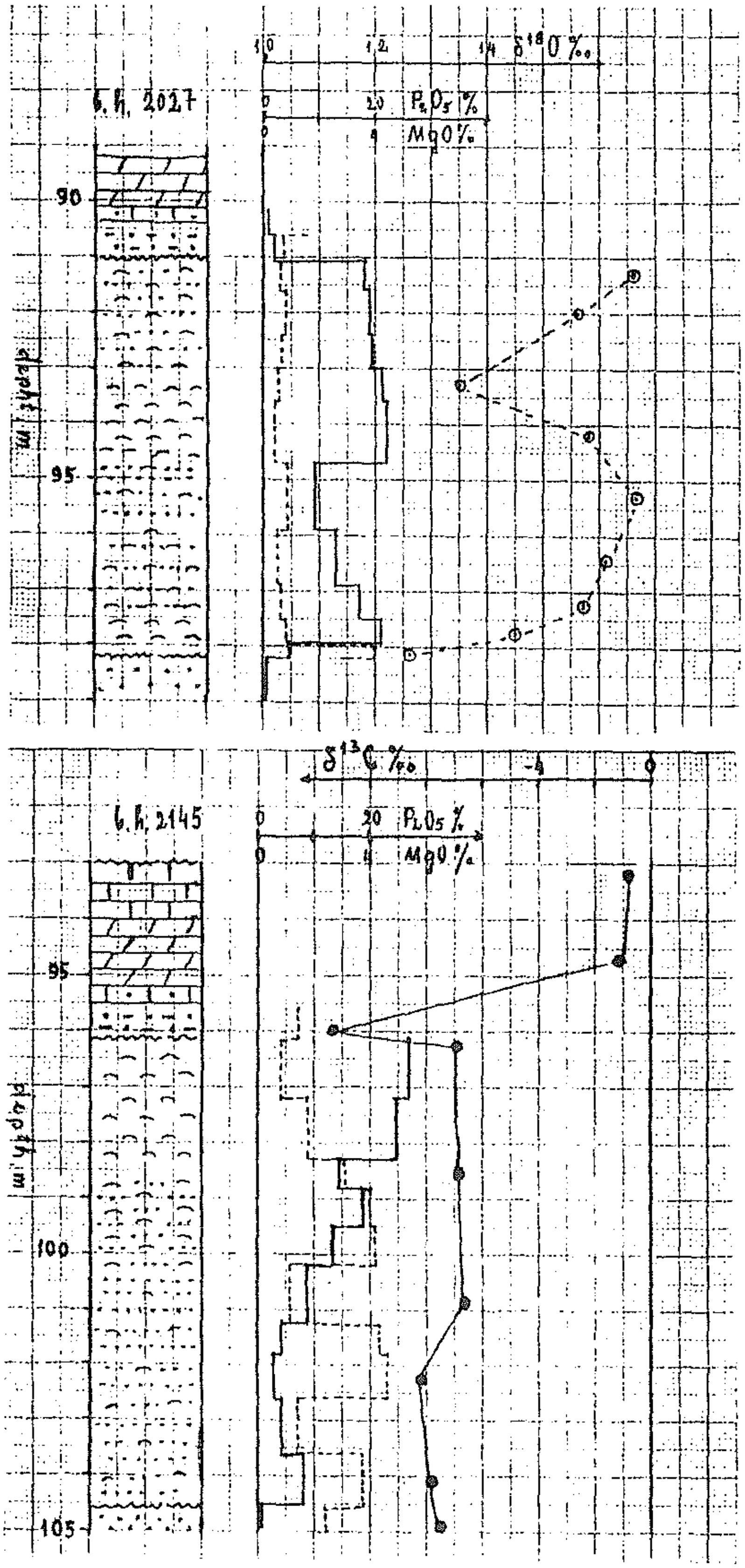

Fig. 5 - $\delta^{13}C$ of carbon from matrix cement dolomitizing the ore body and $\delta^{18}O$ of oxygen from phosphatic shells (see table 6).

ON THE MODE OF OCCURRENCE OF ZINC IN GLACIAL TILL AND ITS APPLICABILITY TO THE USE OF HEAVY MINERAL GEOCHEMISTRY IN THE SEARCH FOR ZINC ORES

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Introduction

Economically, the most important zinc-bearing mineral in zinc ores is zinc sulphide, or sphalerite, which is readily decomposed in a surficial, oxidizing environment to release zinc ions into the circulating water. In glaciated terrain, till samples taken from deep down near the bedrock surface, often below the groundwater table, can contain glacially dispersed primary sphalerite (Peuraniemi, 1982). Since it is the fine fraction rich in phyllosilicates and secondary iron hydroxides that is most often analyzed in till geochemistry, the hydromorphically dispersed zinc can also be identified.

On the other hand, heavy mineral geochemistry, in which the samples are usually taken from the surficial part of the till, is not regarded as a reliable means for searching for zinc or other sulphide ores. It is widely believed that the glacially dispersed sphalerite has been decomposed in the oxidizing surficial parts of the till deposits during postglacial times.

Most research dealing with the mode of occurrence of zinc in glacial till has employed only partial extraction methods (cf. Rose, 1975; Cole and Rose, 1984; Cardoso Fonseca and Martin, 1986).

Results

The present survey deals with the mode of occurrence of zinc in four areas in Finland (Fig. 1) where anomalous zinc concentrations have been encountered in the surficial parts of the till. Both chemical analyses and mineralogical determinations are used here to resolve the mode of occurrence.

Figures 2 and 3 show the distributions of Zn and S in heavy mineral till concentrates in the Sadinharju sub-area of Yliklimlnki. The northwestern corner of the area, which is anomalous only for Zn, is higher, dry ground, while the central part, where a Zn-S anomaly occurs, is moist and boggy. The anomalous till contains a large amount of unweathered sulphides such as sphalerite, pyrite and chalcopyrite (Figs. 4 - 5).

The reason for the preservation of sulphides in the till is that the area is flat and the groundwater table high, so that also the surficial parts of the till are quite moist in places and postglacial weathering has not totally destroyed the glacially dispersed sulphides.

In the Leteensuo area, where quite a neat fan-shaped Zn anomaly occurs in the heavy mineral till concentrates (Fig. 6), no Zn mineral phase has yet been found but the mineralogical investigations are still going on. As Table 1 shows, the Zn-anomalous samples contain also high Fe and Mn values.

Fig. 1. Location of the survey areas.

The interpretation is put forward that glacially dispersed sphalerite has been decomposed and the liberated zinc ions have immediately become bound to Fe-Mn hydroxides (cf. Cole and Rose, 1984; Nikkarinen et al, 1984).

A zinc anomaly in the surficial part of the till in the Saajanmäki area (Fig. 7) led to the discovery of a sphalerite mineralization. Some sphalerite was also found in the heavy fraction of the till samples, but some had evidently been decomposed, generating secondary iron sulphate, melante-

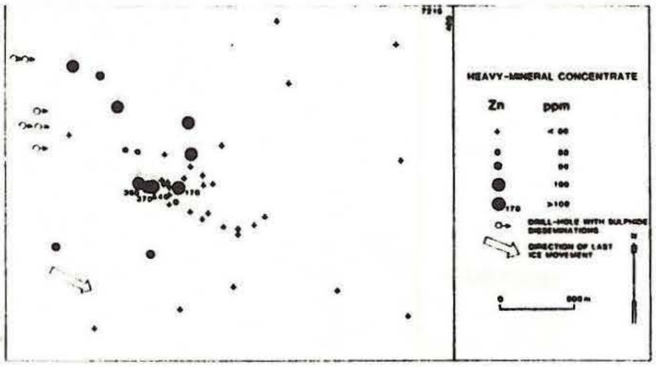

Fig. 2. Zinc contents in the heavy mineral concentrates of till at Sadinharju.

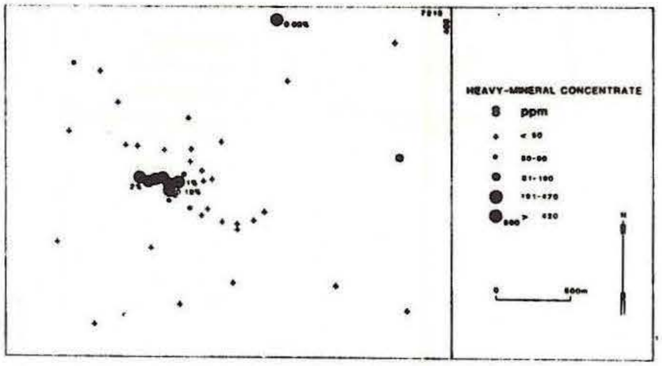

Fig. 3. Sulphur contentents in the heavy mineral concentrates of till at Sadinharju.

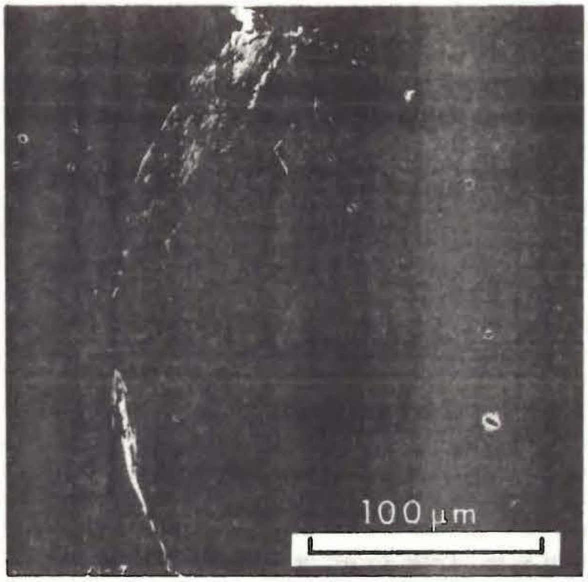

Fig. 4. A prismatic sphalerite grain from till at Ylikiiminki. SEM. secondary electron image.

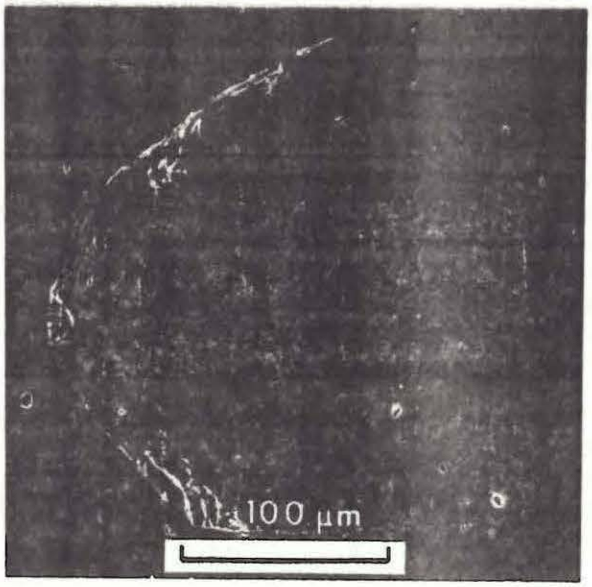

Fig. 5. Sphalerite grain from till at Ylikiiminki A typical cleavage pattern of sphalerite is clearly seen. SEM, secondary electron image.

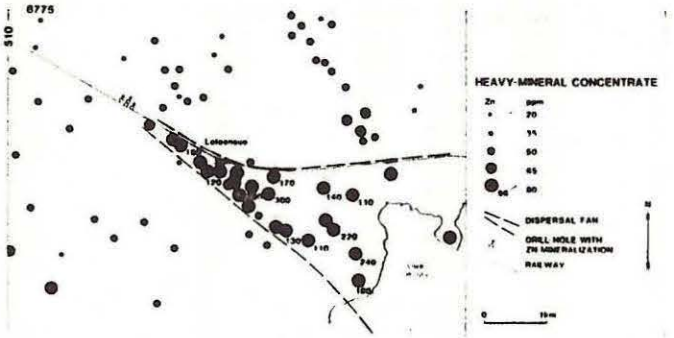

Fig. 6. Zinc contents in the heavy mineral concentrates of till at Leteensuo

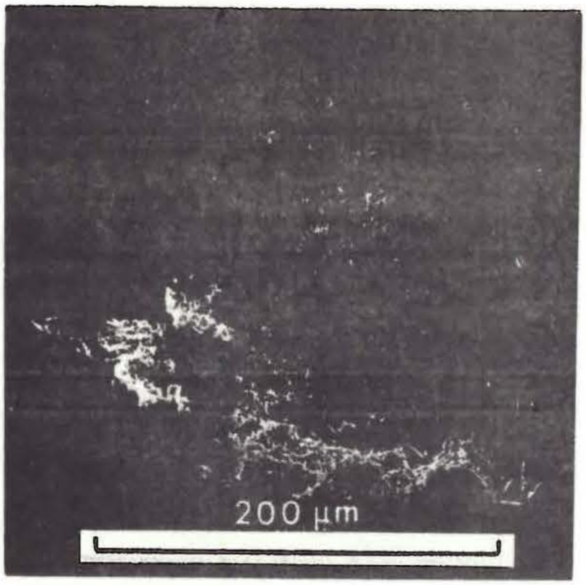

Fig. 8. Two light spots are melanterite grains resting on weathered silicate grain from till at Saajanmäki, SEM, secondary electron image.

rite $FeSO_4 \cdot 7H_2O$, as a result. Melanterite can still contain some zinc in its lattice. The heavy fraction also contained another rare iron sulphate, szomolnokite $FeSO_4 \cdot H_2O$. Sulphates occur as yellow flakes and encrustations on the surface of the other minerals (Fig. 8).

Heavy mineral till samples from the Kataloistenjärvi area (Fig. 9) show a distinct Zn anomaly. The samples contained no sphalerite, as shown by the low S content in the chemical composition (Table 2).

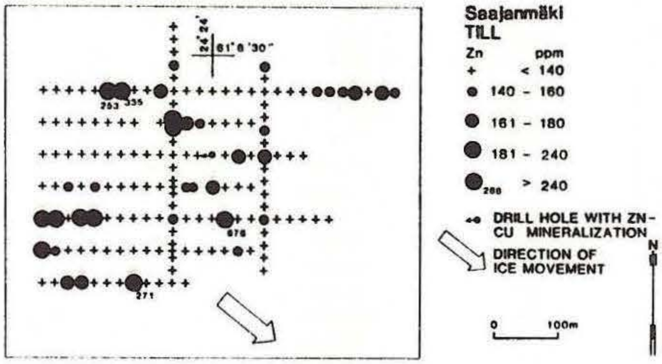

Fig. 7. Zinc contents in the heavy mineral of till at Saajanmäki.

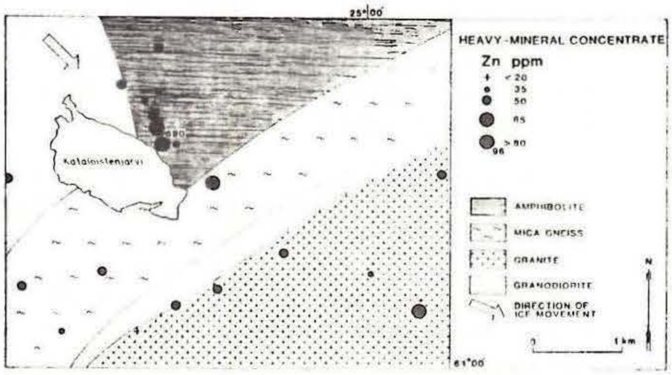

Fig. 9. Zinc contents in the heavy mineral concentrates of till at Kataloistenjärvi.

The anomaly was found to be caused by a green, entirely fresh mineral identified as a zinc spinel, gahnite $ZnAL_2O_4$, which usually occurs in connection with sulphidic zinc ores, so that it can be regarded as an important indicator mineral (Figs. 10).

The sulphide-bound metals Zn, Cu, Pb, Ni, Co should generally also be analyzed in regional heavy mineral surveys, and if anomalous concentrations are found it may be rewarding to look into the mode of occurrence of these metals.

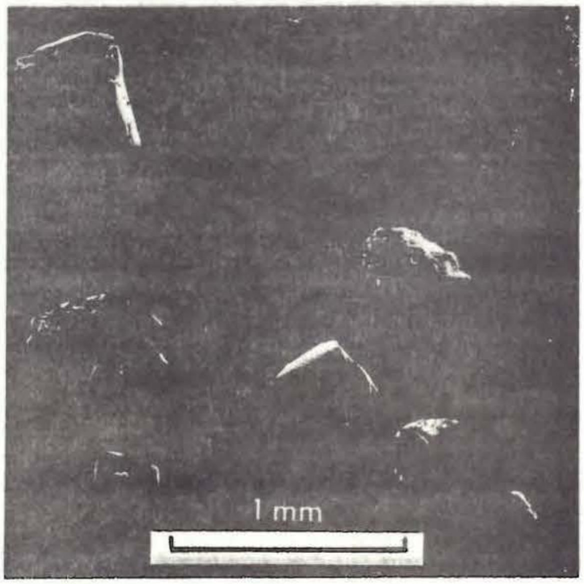

Fig. 10. Seven gahnite grains from till at Kataloistenjärvi. SEM, secondary electron image.

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Table 1. Chemical compositions of three heavy mineral samples at Leteensuo.

		Sample 276	Sample 278	Sample 5349
SiO_2	%	64.22	63.87	69.25
Al_2O_3	%	13.14	13.41	11.62
MgO	%	1.44	1.61	1.48
CaO	%	2.44	2.17	2.78
Na_2O	%	1.76	1.54	0.14
K_2O	%	1.13	1.15	1.04
Fe_2O_{3tot}	%	13.46	14.03	11.19
MnO	%	1.41	1.36	1.13
TiO_2	%	0.73	0.68	1.17
P_2O_5	%	0.15	0.10	0.10
S	ppm	70	50	60
V	ppm	50	60	120
Cr	ppm	60	70	100
Cu	ppm	0	10	10
Ni	ppm	20	20	20
Co	ppm	10	10	10
Zn	ppm	240	140	300
Pb	ppm	20	20	20
Mo	ppm	0	0	0
Sn	ppm	0	0	0
W	ppm	0	0	10
U	ppm	0	0	0
Th	ppm	10	10	20
Ta	ppm	0	0	10
Nb	ppm	10	10	20
Zr	ppm	190	150	220
Ba	ppm	230	240	230
Sr	ppm	140	120	120
La	ppm	0	0	0
Ce	ppm	30	10	60
SUM	%	99.99	100.01	100.03

Table 2. Chemical and mineralogical composition of the heavy mineral sample 5107 with the maximum Zn content at Kataloistenjärvi.

Chemical composition		Mineralogical composition
SiO_2	69.88%	quartz
Al_2O_3	12.74%	plagioclase
MgO	1.66%	microcline
CaO	3.51%	amphibole
Na_2O	2.79%	chlorite
K_2O	1.76%	mica
Fe_2O_{3tot}	5.96%	ilmenite
MnO	0.28%	almandite
TiO_2	0.96%	haematite
P_2O_5	0.12%	gahnite
S	140ppm	scheelite
V	110ppm	rutile
Cr	10ppm	zircon
Cu	10ppm	
Ni	30ppm	
Co	20ppm	
Zn	690ppm	
Pb	30ppm	
Mo	10ppm	
Sn	10ppm	
W	30ppm	
U	0ppm	
Th	50ppm	
Ta	0ppm	
Nb	20ppm	
Zr	450ppm	
Ba	340ppm	
Sr	270ppm	
La	60ppm	
Ce	190ppm	
SUM	99.95%	

NEW LOCAL PREDICTION METHODS APPLIED TO ORE DEPOSITS UNDER EXPLORATION BASED ON MINERALOGIC-GEOCHEMICAL DATA

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Leading mineral producing countries are currently building up their non-ferrous and precious metal reserves due to investigation and exploration of deposit deep levels and flanks. Therefore, a further development and improvement of deposit local prediction methods, including mineralogic-geochemical methods, offers great opportunity today.

Estimation of ore content by mineralogic-geochemical methods is based on the study of ore and its endogenic aureole zoning. However, despite the zoning common for the majority of deposits, complicated relationship between zoning and geologic structural peculiarities of ore occurrences may often lead to low results in conventional geochemical investigations.

Our experience of working on several deposits as well as the analysis and revelation of the most efficient conventional geochemical forecast methods call for the improvement of the aforementioned methods. We suggest the possible trends to be followed in future:

- general study of ore zoning scale of different geologic structural levels: deposit - ore zone - ore body - ore column, etc.;
- overall study chemical element spatial differentiation at the contact of ore body and metasomatite;
- general study of ore and aureole mineralogic-geochemical zoning together with mineral impurity elements zoning.

The zoning character interpretation calls for the differentiation of bulk concentrations of ore- and aureoleforming elements into the components, that meet the definite mineral form requirements. The author has been involved in the investigations of the aforementioned problems while working on hydrothermal deposits (gold, tin, etc.). In the process of local mineralization forecasting, within the limits of the deposits under study, the activity is aimed at two interrelated goals:

- search for and evaluation of uncovered ore bodies and their geochemical aureoles;
- estimation of possible vertical extention of mineralization (through the deposit).

At present, the process of the geochemical anomaly evaluation often requires the calculation of multiplicative zoning coefficient. The principal methodological evaluation techniques should involve a system approach to a deposit structure. Taking in consideration the abovementioned approach, any deposit consists of several different-scale ore formations - deposit, its sections, ore-bearing zones, ore bodies, ore columns, etc., which are characterized by the corresponding aureole fields.

Considering discrete and irregular nature of marker elements distribution in host rocks, the method of testing results smoothing by means of sliding "window" was used for reliable delineation of their aureoles. The "window" size was determined accordintly to the size of the corresponding structural level. It permits identification of the aureole field regular component. This method provides delineation of space persistent, contrast, continuous aureoles and evaluation of their features. Within the wide range of aureole-forming elements two groups of them are the most prominent: 1 - group of aureoles with distinct zonal structure at all hierarhic levels; 2 - group of various-scale ore formations aureoles with qualitative differences in structure and zonation.

Besides, for the first element group the following quantitative features in zonal structure of different-scale aureoles were identified:

- ore formations scale increase (from ore columns to deposits as a whole) is accompanied by down the dip decline of zoning coefficient variation gradient. The gradient of zonation coefficient variations for some ore bodies is five-tenfold over the gradient of whole deposits.
- limits of zoning coefficient variations of various scale formations are relatively constant and depend only on the number of elements composing the zoning coefficient.

The identified features permitted to work out method of potential ore content estimation for deposit deep horizons. This method is based on graphic model which represents down the dip variations of zoning coefficient of various-scale ore formations. Assess of mineralization distribution depth is based on correlation of zoning coefficients, determined for aureoles of various-scale ore formations.

Of no less significance while deposit prospecting and exploration is ore content assess. Over 50% of mines and holes originally expose poor in ore content sections of ore bodies. Thus, ore column prediction based on poor intersections data is of vital importance. For the sake of recognition of possible geochemical criteria of rich and poor mineralization differences, ore-forming elements behaviour in ore bodies and near-ore metasomatites was studied. This was based on detail testing of a number of sections which revealed ore bodies at different levels. The chosen sections expose ore columns and poor, ordinary segments of ore bodies at their different levels.

Detail three-dimensional study of ore-forming elements behaviour within ore bodies and near-ore metasomatites permitted elaboration of estimation method of mineralization ore content. This method is based on ore content geochemical model, main features of which are the following:

- column upper parts and flanks are marked by constant predominance of super-ore elements (Ag, Pb, Zn, etc.) over near-ore metasomatites in ore bodies;sub-ore elements (As,Co, W, Sn, etc.), on the contrary, prevail within near-ore metasomatites.
- under-level zones of ore columns are characterised by constant predominance of sub-ore elements in ore body and of superore elements in near-ore metasomatites;
- in poor or ordinary segments of ore bodies main ore-forming elements content prevails over near-ore metasomatite one.

Thus, we may conclude that there is a certain relation between ore-forming and associate elements distribution in cross sections of ore bodies and mineralization scale. The described model provides both the assessment of erosional section levels within ore bodies and the prediction of ore column presence within their limits.

Presently geochemical methods of ore potential evaluation are developed and being most widely applied for bulk concentrations of guide elements in ores and haloes. The interpretation of the zoning nature and consequently the improvement of geochemical methods can't be achieved without subdivision of bulk concentrations. of ore- and halo- forming elements into components corresponding to definite mineral forms they occur in. Therefore the ores and haloes mineralogical-geochemical zoning study should be carried out alongside with that for the impurity elements in minerals forming these materials. We suggest that zoning of elements in minerals, and particularly of impurity elements, not always corresponds to the geochemical zoning of ores and haloes typical for the particular deposit and possesses some specific features. The most distinct regularities were revealed while calculation of mineral balance for each element in ores of separate horizons of this or that different deposits.

The generalized distributional model of vertical zoning in minerals for ore-forming and assessory elements includes the following:

- the degree of dissemination decreases in mostly sub-ore minerals and increases in mostly super-ore ones upwards relative to the position of study mineral within the zoning series for elements occurring in ore predominantly as their own mineral forms (such as Sn, As, Cu, Pb, Zn, etc.);
- for the impurity elements (In, Cd, Co, Ti, etc.) the degree of dissemination within other minerals increases upwards if the predominant host-mineral is a sub-ore and decreases if it is a super-ore one;
- the relationship between geochemical zoning within ore bodies and the characteristic features of the elemental spatial distribution in minerals suggests that if some element has its own mineral form, the accumulation of the mostly sub-ore elements and the decrease in quantity of the super-ore elements in upward direction within geochemical zoning series take place.

The above model explains the previoustly known cases of the so-called "reversed" zoning. One of the practical applications of this model for the assessment of ore body delineation is the usage of medium-ore or "continuous" minerals, the impurity elements' zoning of which is the most pronounced. Moreover, this model can be used for the development of the most efficient ore processing schemes for the ores mined at different horizons.

GEOCHEMICAL FIELDS OF MULTILEVEL CONVECTIVE METALLOGENIC SYSTEMS

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Abstract

It has been explained that evolution of ore-forming systems having a rank from ore district to local orebody is appeared by means of multilevel convective mechanism. A vast set of multilevel convective are-forming system (MCOS) features is studied. It is shown that all members of MCOS have a ringlike zonality of initial (or transformed) physico-geochemical fields.

The practical important peculiarities of MCOS are: 1. the self-governing coordination of the junior members into a contour of the elder ("mother") cells; 2. the consequent evolution of ore-concentrating processes from productivity rocks of ore districts to individual orebodies; 3. the polar zonality of cells for each rank; 4. the applying of A.P.Solovov's principle of geochemical and geometrical similarity to the identical members of any rank ore-forming structures.

Introduction

All applied at present features don't guarantee revelation of promising ore. In the purpose of the more proved solving it can be to turn to notions of system and to use additional information about evolution of ore-forming processes, which contains in the shape and structure of physico-geochemical fields. Real geological bodies are centres of such fields. The aim is to cross from analysis of separate anamalies to investigation of independent are-forming systems wholly,

We'll choose ore district as the object of study. It occupies intermediate position in the ore hierarchy between metallogenic zone and ore knot. Every one is characterozed by distinctly discrete distribution of ore mineralization hereat allotments of the more enriched ore have decreased sizes one after another. Usually such areas are limited rather roughly extensity of ore deposition decreases irregularly to their periphery, shape of targets is isometrical etc.

It must be natural factors, if ore-forming systems possess natural (genetic) hierarchy really, these factors determine wholeness of system and its regular structure.

The convective model of metallogeny

Realization of modern ore-genetic schemes supposes specialization of an accumulation process beyond the bounds of each ore formation. All schemes of metallogeny are based on admission of long existence of stable thermodynamic conditions both in leaching and in deposition zones.

Peculiar importance of convective model consists in fact that all rest of schemes can be reduce to it, so far convective heat-and-mass transter is universal way of transformation of heat flow into translational movement, providing temperature balance in the system. Convective cells are presented in constructions of many eminent geologists, the recent convective cells were studied directly in zones of recent riftogenesis on the oceab floor (Rona, 1984).

Experimental investigations of fluid systems into thermogradient or density-stratified environments were shown (Letnikov and Jatnuev, 1986 etc.) that efficiency of this mechanism is provided by combination of cells belonging to different Self-ordered Benar's cells are an ideal example arising on heating of sufficiently viscose liquid. These structures are more profitable on the hand of thermodynamics - liquid raises to surface on the centre of cell and lowers at borders.

It is necessary to note that at present convective models were used only for qualitative description of separately taking deposit. By convection of fluid the only last episodes in evolution of ore-forming systema were explained - development of ore bodies. However one-level convective process couldn't to be reason of self-ordered ore substance through natural hierarchical systems.

There is not any limit to apply the convective model for all levels of self-coordination of substance. Nevertheless, there are cells arising by means of hydrothermal solutions. These cells have most spreading and very important meaning. It is ascertained (Masalovitch and Ovtchinnikov, 1983) about ten special points, where physical characteristics of water solutions are changing due to polymorphism of water in vast interval of temperatures and uneven change of its molecular groups. It is occured the possibillity to describe natural hierarchy of ore system by the help of this temperature zonality in water structure. Take into consideration that such ore system has features of ore district.

The convective removal of heat answers some simple requirements: 1. an open system with heat sources under battom or within; 2. a plane layer of mobile fluid that viscosity rapidly increases at decreasing of temperature; 3. a great excess of the adiabatic gradient; 4. an autocatalyous exchange of mobile fluid there are reverge communications of intermediate states too.

The well regulated structure of physico-geochemical fields (power centre is alone but identicalt dimension cells of following rank are several) reveals in such parts of lithosphere where third and fourth conditions are carried out. The power sources are: the gravity differentiation of lithosphere, nidus and linear geodynamics processes. magmatic centres of different ranks and so on. A lamination of lithosphere is generally acknowledged and a stratification of fluid is founded on the polymorphism of water. Determined for the last years fundamental principles of self-coordination (Prigogine, 1989) may be to realise only in unlinear systems. There are autocatalytic reactions having a reverse communication in these systems, securing regime of auto-oscillations around its current equilibrium. Synchronization within million of chemical reactions is arising from these systems and such processes are essence of ore origin.

It is possible to restrict myself to quoted above arguments to benefit of oscillating regime of fluid (transfer upward with heating and falling down with cooling), but it is necessary to discover autofluctuations into both polar parts of ore systems - in mobilization zones of ore matter and within ore deposition ones - for the comprehension of ore-accumularion role of convection. Leaching may be to identify with creating of numerous hydro-and aquacomplexes, using hydroxil-ions or water moleculеs as ligand. A water by high temperatures becomes a direct partner of chemical reactions. There are partial disturbance the convey complexes in deposition zone, appearing by such spontaneous way at the time of regrouping of water molecules, namely - composition exchanges of circulating fluid oscillate near some current equilibrium.

The development of self-regulated ore systems is determined by long entrance of energy from external environment. It's adaptation of productive ore system as regards to environments, placing it. Long living tectono-magmatic systems completely correspond to such condition.

Upper half-sphere of any cell is zone of deposition. There is establishing alkaline conditions, because dissociation of alkalines is passing more intensively than dissociation of acids at the temperature falling of (Naumov and Dorofeeva, 1975). Disintegrating hydrocomplexes and little by little rebuilding aquacomplexes bring their contribution to rise pH of environment.

There are predominatory acid conditions in the under half-sphere resulting at the invertion of these reasons during rise of temperature, therefore mobilization of substance is carried out here. Step-discrete character of springing up and transformation of aquacomplexes has importance in both zones. Besides, water on high temperatures is promoting to increase of chemical reactions speed and it is creating conditions for intergraine movement of fluid on pellicular surface or for diffusion of ions across lattice of minerals. It is forming vacncies on partly breaks of bonds, for example Si-O-Si into silicates (Rubie, 1986).

The heating of containing rocks brings to their thermal discompression and, in consequence of it, to growth of permeability by 10000-100000 times (Tauson, 1983).

Ore objects acquire reliably determined characteristic signs both in section and in plan. Analysis of its essentially raises trustworthiness of prognosis and search of profitable ores.

Specific features of convective ore systems

Productive systems possess the polar zonality in the form of separating zones for all studied elements. These zones situated on the apposite parts of vertical diameter of cell. The reasons of this effect is thermo-physical characteristics of fluid components and clarkes of elements in containing rocks, which define macrocomposition of mobile phase. Therefore polar zonality of structures belonging to various ranks is formed by own sets of elements (tables 1-3).

There are development of ore elements leaching as the result of "thermal sliding effect" (linear analogue of convection) in the contacts of vein's bodies becoming in the upper part of all cells or telescoping under them. Such are the "rod" veins of many gold-bearing deposits. Pulsaring halt-opening of fractures, taking away mechanical tensions in the upper part of cells (the result of rock's breaking up in deposition half-sphere) accompanies convective systems of any rank, even the very local, connecting for example with dikes. Often ore veins are forming into fractural systems, inheritedly developing from the early stage of ore-concentrating processes. These bodies are multistage formations, in which not only various associations and generations of minerals (elements), but and different correlations of lots of accumulation-mobilization are coincided. Every section of halo is corresponded to individual diagram.

It is ensured from qualities of considered model, that all members of ore-forming system have a special zpnality in primary or transformed values of physico-geochemical fields. In plan this type of zonality is near to concentric one. Contours of structures of overy rank are forming arched zones of falling contents of centrifugal indicators, and centres of these cells are isometrical blocks of rising contents of centripetal indicators. Packing of clusters (in contour of mathernal senior member of system, the nearest to them) is compact. Due to different erosion of separate blocks it is possible not only compact, but and discrete accomodation of unequal, although as before isometrical, cells.

The number of cells may be evaluated by facts about discretions of geological objects. For example, according to V.V.Piotrovsky (1964), concentric dislocations of earth crust have the next steady typosizes: 3, 10, 30, 100, 300 km, therefore in the boundaries of structure 7-9 junior clusters are packed up the most conveniently.

All multilevel ore-forming systems have one-type structures showing in the form of circular external zones of physico-geochemical fields and in the form of relatively local allotments of internal zone. Fragments of concentres together with the radial tectonic breaks are composing framework of endogenous systems. Contours of clusters are allotments of leaching aspecially intersifying during contacts of cells. Therefore surface of accumularion half-sphere at the recent level is transformed by junior clusters into mosaic field of physical properties, distributions of element contents, composition of metasomatites etc. However every cell is characterized by external broad ring of rising meanings, formed by periphery clusters. There is internal circle of rising meanings in the contours of central clusters and intermediate circle of falling values - on perimeter of central and periphery clusters contact.

The indicators of favourable ore systems

Productivity of the investigated fields depends on plenitude or recycling structures collestion in the contour of ore district. Ore resources within tested area (in recent payable condition) are excepted independently on presence ore-mineralization occurrance if any system level is reduced. Concentrating takes place one after another on the complication of system (according to our data, enrichment in the cells of adjacent ranks for the gold-quartz manifestations - about 10 times, for the stratiform polymetallic ores - up to 3-5 times). Sucsessive increase of the useful component depends on the initial start level exceeding over clarke (there is not revealed a profitable oreformation on the territories with poor clarkes), on individual characteristics of elements and long existence of each kind of cells.

As the result of multilevel ore-forming convection the every system's member is acquiring polar geochemical zonality, which formed by own set of elements. This quality can be used for appraisement of erosional opening of accumulation half - spheres at all members of hierarchyc system. Besides considerated model grounds completely principle of geochemical and geometric similarity formulated empirically by A.P.Solovov (1985) and gives possibility for its spreading on all suitable members of ore-forming structures.

At the study of recycling systems necessity of examination and the evaluation of all geochemical anomalies falls away, because search signs becomes not separately, let it be bright, but zonal structure of physico-geochemical fields. Only the whole data totality represents complete character of objects: the field of petrogenic elements (macrolevel of cut; correlation between mobilization and deposition areals), distribution of volatile (contours of structure) and ore element (the number of concentration levels, the erosional cut of boides etc.).

We considered common peculiarities of lithospharal substance concentration in usedul mineral accumulations, and in this sense, multilevel recycling is universal for majority of endogenous deposits.

Basic conclusions

1. There are common features of ore-forming systems which are identified with structures of central type having a well-regulated packing of daughter's clusters.

2. Ore-concentrating structures have mosaic-cellular construction of physical, geochemical, metasomatical fields. Qualities both of periodicity in distribution of allotments with high and low contents and, especially, of the polar zonality of central and periphery indicators are showed in these fields and in morphostructural evidences too.

3. Zonal system of multilevel geochemical fields is similar to geometrical system of self-organized ore structures by convective model. And this may be signify verification of such scheme.

Thus, structural analysis of joint prospecting data is effective way of formalization and ampping of multilevel ore objects. Using of consecutive number of levels of description and mapping are began by high clarke elements, and finished by elements of ore complex. There is change of information signs between levels, and this is supposed by many exsamples from prospecting practice.

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Table 1. Shape and composition of multilevel convective ore-forming systems (on the data for gold, rare metals, vein-polymetallic and stratiform polymetallic deposits)

Metallogenic divisions	The characteristical signs		
	Area, sq.km	Diameter, km	Depth of power source, km
Ore region	10^4-10^5	100-300	100-120
Ore district	10^3	30-40	to 50
Ore knot	10^2	10-20	to 25
Ore field	10^1	3-5	to 10-15
Ore deposit	1	1-2	to 5-7xx/
Ore body2	0,1	0,3xx/	to 2-3x/

x/ except nearsurface deposits, xx/ including the halo

Table 1. - Continued

Metallogenic divisions	The thickness of deposition zone, km	
	Centrifugal elements	Centripetal elements
Ore region	to 609Al, Si)	to 50 (Na,K)
Ore district	to 30 (Na, K)	to 25 (Ca, Mg)
Ore knot	to 15 (Ca, Mg)	to 10 (Fe, Ti, Mn)
Ore field	to 7 (Fe,Ti,Mn,Rb,Sc)	to 5 (Sr, Ba,Cr,Ni,Cs)
Ore deposit	to 3 (Sr, Ba,Cr,Ni,Cs)	to 2 (Li,Ag,Tl,Zn...)
Ore body	to 1,5 (Li,Ag,Tl, Zn...]	to 0,3 (Main component)

Table 1. - Continued

Metallogenic divisions	Emanation halo	Geomorphological expression
Ore region	F, Cl	Co-operation of large lineaments with large concentres, cryptomorphic formations
Ore district	CO_2,Hg,H_2O	The ring structures of central type: the ones - arches, banks, etc.
Ore knot	P,S,J,Hg,CO_2	the other ones - big domes, depressions, kalders...
Ore field	J,S,Hg,CO_2,CH_4	the another ones - small domes, funnels, structural lobes...
Ore deposit	Hg, J,Br...	Combination of small linear and small ring structures
Ore body	-"-	-" -

Table 2. Geological features of ore-forming systems

Metallogenic divisions	Number of cells in preceding rank	Geological expression
Ore region	Individually	Formational and magmatic complexes
Ore district	7-9	Groups of geological formations, abyssal batholites
Ore knot	7	Geological formations, mesoabyssal intrusions
Ore field	7	Horisons, areals of big hypoabyssal intrusions, volcanic structures.

Ore deposits	5-9	Strata, layers, subvolcanic beds, dikes
Ore body	to 30	Lenses, chutes, stockworks, veins.

Table 2. - Continued

Metallogenic divisions	Metasomatism	Modes of occurrence of useful component
Ore region	Areals of regional metasomarism (subalkaline propylites, feldspatholites, and so on)	Fluid inclusions, organic matter, amorphous paticles at the interstices of layered minerals
Ore district	- " -	Main rockforming minerals (adsorption on the planes of microfractures)
Ore knot	Fields of local metasomatism (hydrothermal quartz rocks, biotite rocks, greisens, beresites and so on)	Mineral impurites (isomorphous minerals, own microminerals at the defects of lattice)
Ore field	-"-	Early generations of own minerals, sulphides of another metals
Ore deposit	Fields of wallrock metasomatism (propylites,alkali9 spathites, argillizites and so on)	Late generations of own minerals
Ore body		Laters generations of own minerals

Table 2. - Continued

Metallogenic divisions	Zonal distribution of fluid inclusions
Ore region	The lateral xonality (from early NaCl + F, Cl and H inclusions, through hydrocarbonate - Na + clorid - Na + Cl, J, H, carbon dioxide to hydrocarbonate- Ca, Mg + J, H, carbon dioxide and methane)
Ore district	
Ore knot	The concentric lateral and vertical zonality of the temperature and of inclusions phase (gas, gas-liquid + carbon dioxide, water, salt-brine)
Ore field	
Ore deposit	The multistage vertical zonality of the temperature and of the phase
Ore body	The multistage vertical zonality of the temperature

Table 3. Geochemical features of ore-forming systems

Metallogenic division	Structure of geochemical field	Statistical reflection
Ore region	Isometric block-strip areals of unhomogeneous Si, Na,K distribution possessed the higher clarke of ore element	An increased mean content of are elements
Ore district	Close packing up isometric blocks that possess the polar zonality of Na, K (periphery), Ca, Mg, Fe (centre); emanation haloes of F, Cl, Hg, water; ore element haloes in hard extracts; asonal ground waters	An increased mean content and dispersion

Ore knot	Close packing up circular haloes of Fe,Ca,Mg (periphery), of rare alkalines and Sc (centre); emanation haloes of P,J,Hg, carbon dioxide; ore elements haloes in soft extracts; macrocomponent anomalies in waters; lithogeochemical anomalies in stream sediments (indicating a formational specialization)	High values both of mean and deviation. The right asymmetry of macrocomponent frequency distribution
Ore field	Concentric zonality of next associations; Rb, Cs, Sc, Ti, Mn (periphery). Sr,Ba, Cr,Ni (centre); frequency anomalies of high contents of main ore component; gaseous haloes of S,J, Hg, carbon dioxide and methane; a combination both of local hydro- and lithogeochemical anomalies of ore element	A left-asymmetry polymodal histograms
Ore deposit	A lateral and vertical polar zonality of Sr, Ba,Cr, Ni (remote zone) and Li, Ag, Tl, ore element (near zone)? gaseous Hg, J, Br-haloes; combination of main ore-element anomalies; association of leaching and deposited haloes within main ore-element field	A rough left asymmetry of histograms. The steps on the resource curve.

Ore body	A vertical zonality of universal set; anomalies of main ore-element; the gaseous Hg-haloes	A payable level of main ore-element contents

BASELINE GEOCHEMICAL MAPPING USING LAKE SEDIMENTS[1]

P. J. Rogers[2], J. A. C. Fortescue[3] and J. G. Ogden[4]

INTRODUCTION

Lake drainage systems cover large parts of the Canadian landmass. For this reason lake sediments have been used extensively during the past 15 years as a medium for mineral exploration or resource appraisal geochemical mapping (Hornbrook, 1989). Grab samples of lake sediment provide large multielement geochemical databases well suited to mineral exploration purposes (Rogers and Chatterjee, in press). These grab samples may lack stratigraphic detail, however, and when mineral resource appraisal and geochemical baseline information is desired from lakes, sediment cores are required. Lake sediment is perhaps unique as a mapping tool as it defines both spatial and temporal aspects of the catchment's landscape evolution. Indeed, lake sediment has been likened to a mass storage device for historical geochemical data derived from the catchment (Ogden et al., 1988). Geochemical data from lake sediment cores may be used (1) for geochemical mapping, (2) in pollution studies and (3) in investigations of global climatic change. If lake sediment cores are used as a medium for geochemical mapping such mapping may relate to anthropogenic input of elements during the past few hundred years and/or to material laid down prior to the advent of modern man in lake catchments of interest.

These sediment cores are of two kinds: 'short cores' (30-40 cm long), which usually include sediment laid down during the past 200 years, and 'long cores', which penetrate the entire organic layer at the bottom of a lake and are usually 3-5 m long. Short cores are used in acid rain studies to trace the pH history of lakes during the past 200 years using geochemical and diatom inferred pH methodologies (Fortescue, 1984, 1985). Lake sediment long cores include material laid down since the last Ice Age and can be used to describe the geochemical, palynological and diatom history of lake catchment areas.

RESULTS

Data from Ontario and Nova Scotia (Fig. 1) demonstrate that spatial correlations and temporal markers from lake to lake can be established by these methods. For example, a ragweed (Ambrosia Spp.) pollen layer in Ontario and a Plantago Spp. pollen layer in Nova Scotia (Figs. 2 and 3) have both been used extensively to date the chemical stratigraphy of lake sediment cores collected from these areas.

Our lake sediment core case histories also describe at least four types of Canadian acid lakes. Some of these lakes are naturally acid and others have become acid due to acid rain, pollution and/or environmental degradation. The geochemistry of post-Ambrosia environmental disturbances has been noted from lakes near smelters in Ontario and from the post-Plantago layer at Chocolate Lake, Nova Scotia. Dramatic increases in baseline metal values (e.g. by Pb due to automobiles, Cu due to modern plumbing, V due to home heating oil, etc.) are observed in most lake sediment cores (Fig. 4). Cores from some Nova Scotia lakes include a geochemically distinct 'backhoe' horizon caused by accelerated bedrock weathering due to excavation and construction activities in catchment areas about 40 years ago (Ogden et al., 1988). Certain elements can also be used as time and spatial or ballistic markers. For example Ni, Cu, U, Br, As, Sb and Co have been found useful in Ontario (Fig. 2) and Al and Zn at Soldier Lake in Nova Scotia (Fortescue, 1986; Ogden and Rogers, 1988).

All post-glacial lakes in central and eastern Canada show an increased organic content with time from ca. 10,500 to 9,000 radiocarbon years before present (RYBP). This increase is a consequence of decreased soil erosion and increasing vegetation as post-glacial warming permitted a re-establishment of closed boreal forests (Fig. 5). In Nova Scotia, lake sediment cores record a distinct climatic change to a warm, dry maximum at ca. 3500-5500 RYBP, the xenothermal interval. Reduced precipitation and runoff during this time lowered flushing rates and increased organic sedimentation. The possible effects of future global warming can be inferred from such data on previous periods of global warming recorded in long cores.

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CONCLUSIONS

Lake sediment short and long cores provide a means to establish both a spatial and temporal baseline datum for geochemical mapping. Short cores may provide detailed evidence for increased acidification and/or input of elements due to man's activities during the past several hundred years. Long lake sediment cores, taken from all ecological zones in the world, would provide unique spatial and temporal information pertinent to the preparation of a world geochemical map.

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FIGURE CAPTIONS

Figure 1. Location map showing study areas in Eastern Canada.

Figure 2. Biological and chemical stratigraphy from Nawa and Sudbury.

Pollen Stratigraphy

1. Decrease in Picea pollen at end of Spruce Zone
2. Increase in Betula pollen at end of Spruce Zone
3. Minimum in Picea pollen at end of Birch Zone
4. Peak in Pinus and minimum in Abies pollen at end of Birch Zone
5. Decrease in Betula pollen at end of Birch Zone
6. Decrease in Pinus pollen at end of Pine Zone
7. Increase in Abies pollen at end of Pine Zone
8. Increase in Betula at beginning of Birch and Spruce Zone

Geochemical Stratigraphy

1. Peak of calcium at end of Spruce Zone
2. Minimum for copper at end of Spruce Zone
3. Maximum for copper just prior to end of Birch Zone
4. Increase in calcium at end of Pine Zone
5. Decrease in copper at end of Pine Zone

Figure 3. Biological stratigraphy from Chocolate Lake showing the Plantago layer. Note increase of halophilic diatoms due to winter road salting practices.

Figure 4. Chemical stratigraphy from Chocolate Lake showing post war constructional activities in catchment with (a) As-Fe-Mn-Al increases (b) Zn-V-Pb increases (c) Ba-B-Co increases and (d) anomalous Ni-Cu peak.

Figure 5. Diagram to illustrate post glacial increases in organic material as afforestation of catchment proceeds, Five Islands Lake near Halifax, Nova Scotia.

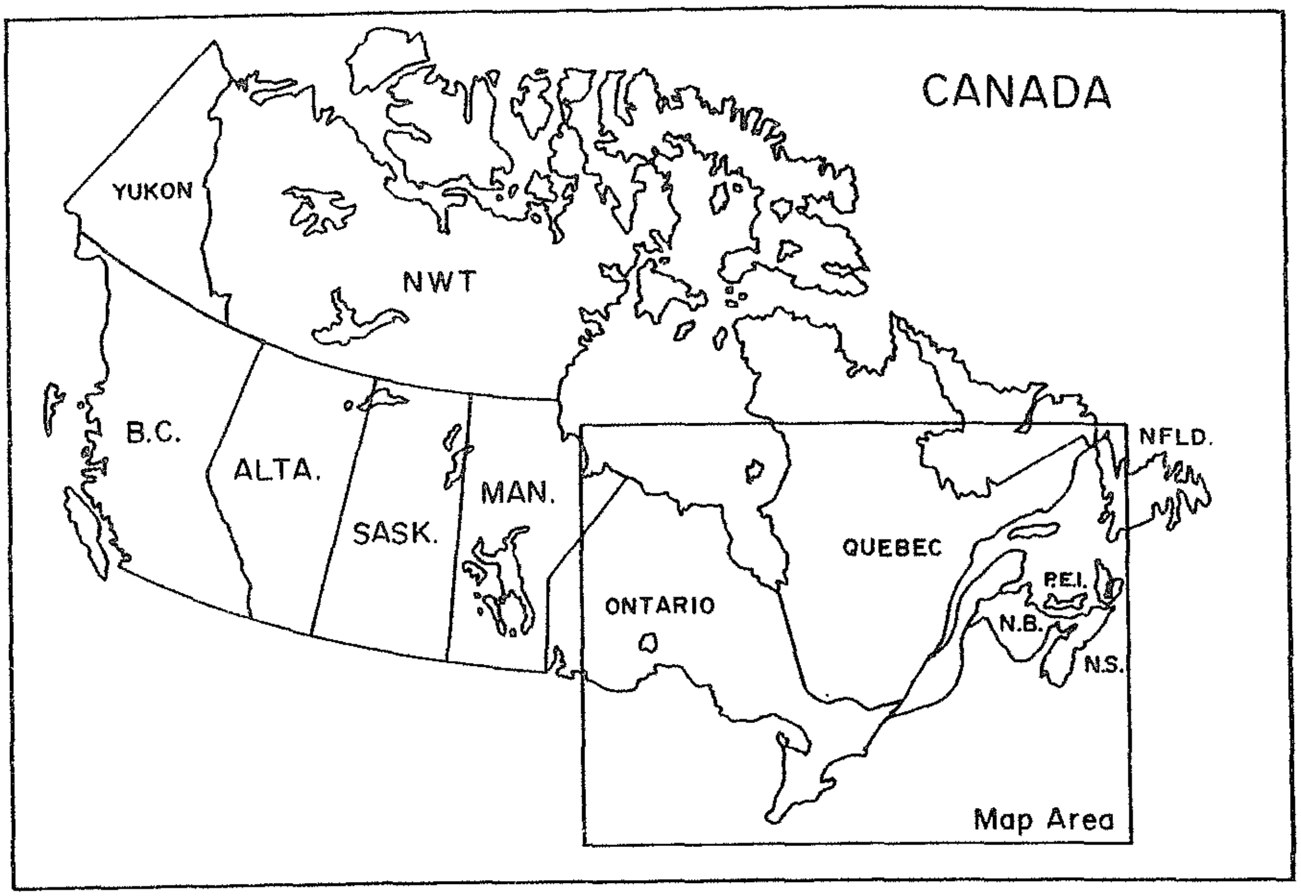


Figure 1 a.

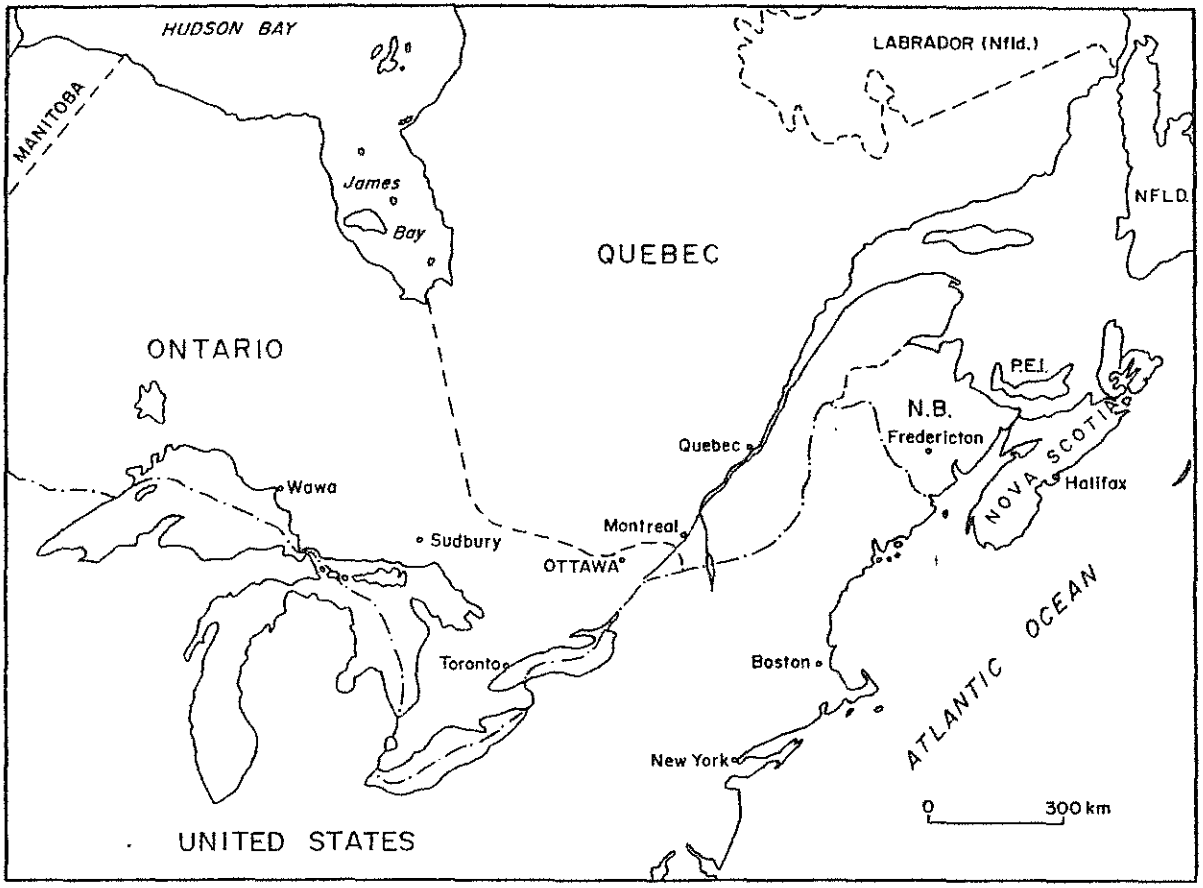


Figure 1 b.

BIOLOGICAL AND CHEMICAL STRATIGRAPHY
Wawa and Sudbury

Figure 2.

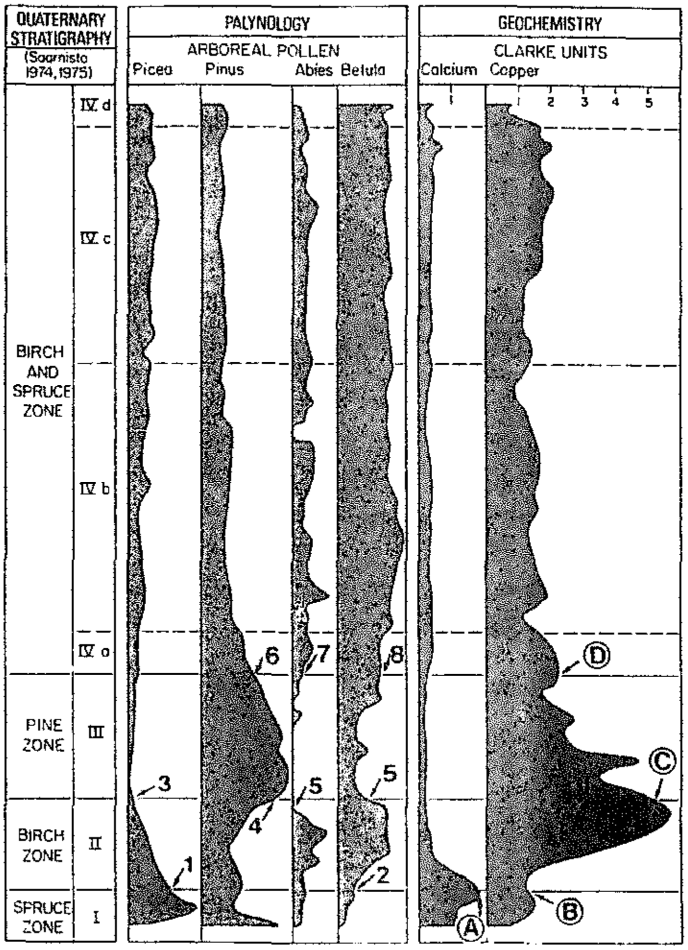
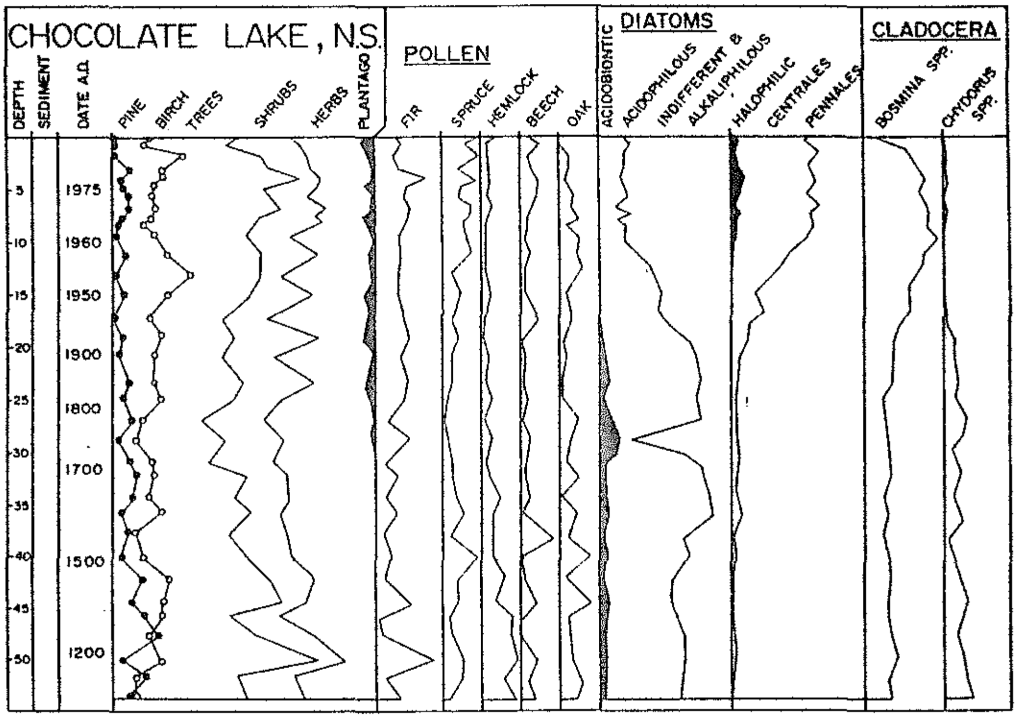


Figure 3.



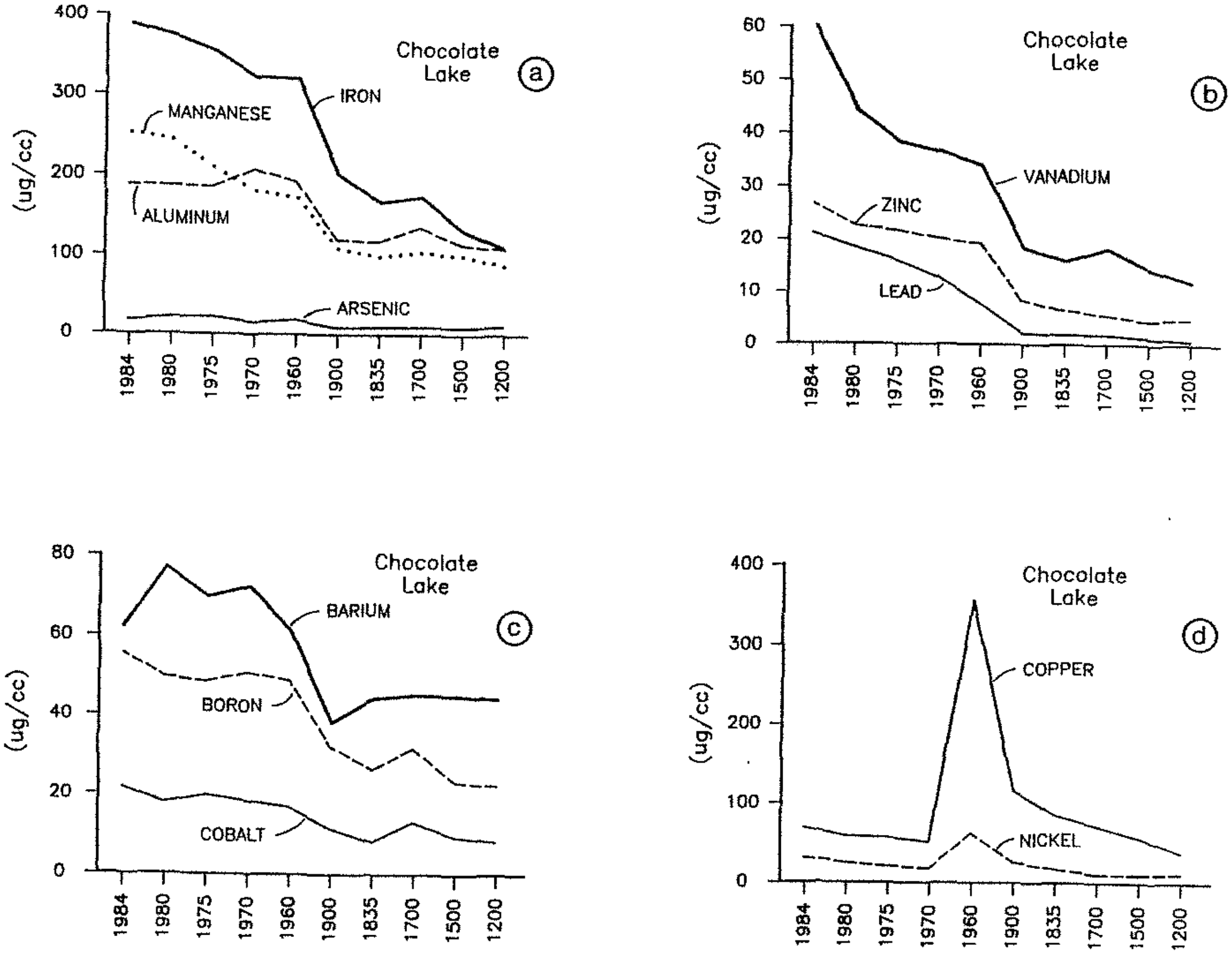


Figure 4.

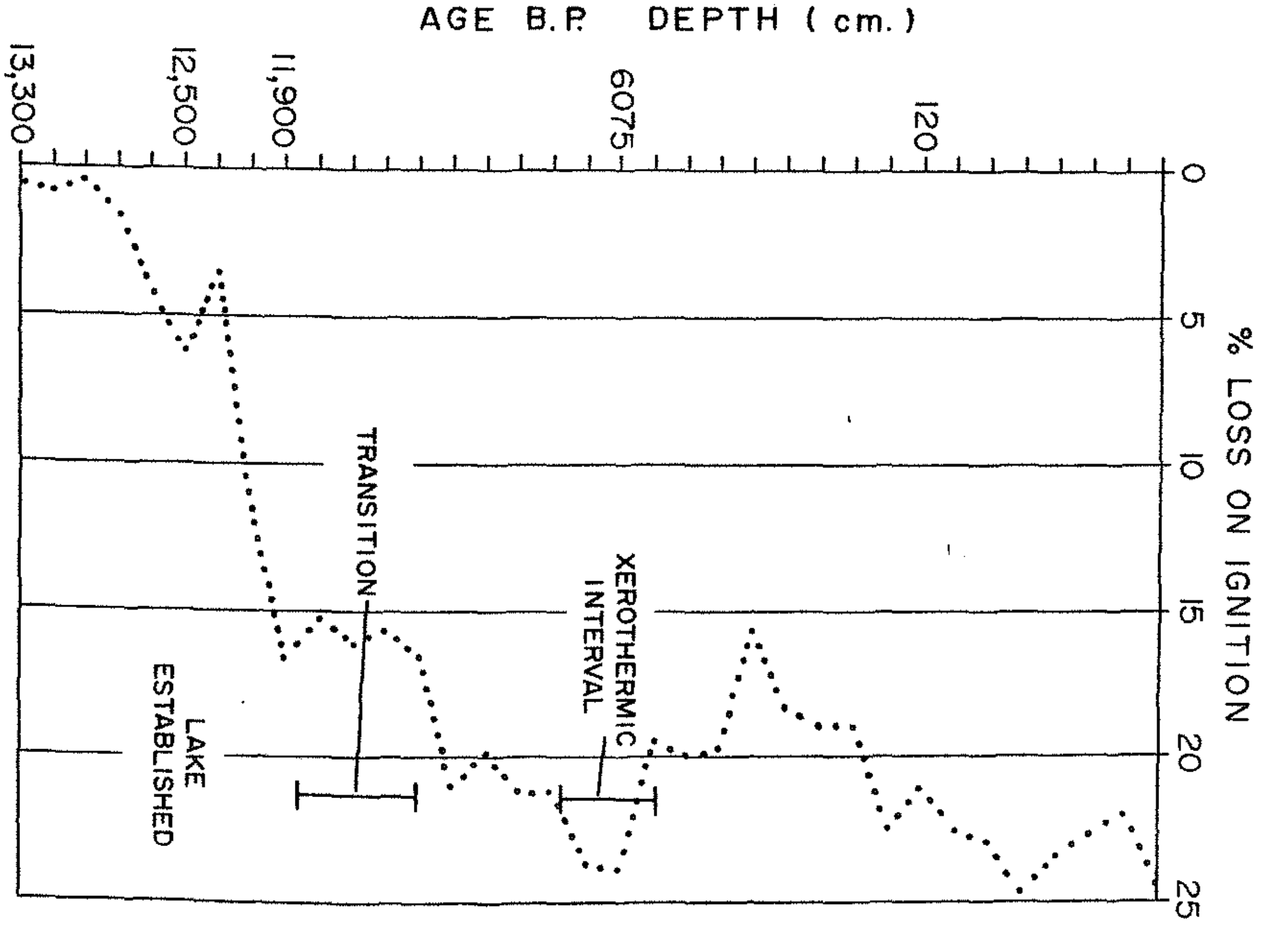


Figure 5.

GEOCHEMICAL BACKGROUND: IMPLICATIONS FOR ENVIRONMENTAL GEOCHEMISTRY IN NOVA SCOTIA, CANADA

P. J. Rogers[1] *and J. G. Ogden III*[2]

INTRODUCTION

Since the early 1950s exploration geochemical surveys have been carried out on a variety of surficial materials in Nova Scotia (Fig. 1). To date most of this effort has been directed exclusively at resource potential applications with the intention of stimulating development in the mineral sector of the economy. During this exploration phase an extensive geochemical database has been collected. A traditional mineral producer, Nova Scotia has a high population density sharing a relatively small area. This demographic reality exacerbates a land use issue often represented as a conflict between the desire for a clean environment versus the need to generate wealth from the abundant mineral resources of the province. The impact of mineral development on the landscape and quality of life is an important environmental issue in North America and especially Maritime Canada.

Most geochemical exploration activity has concentrated on stream or lake drainage systems by sampling sediments and(or) surface waters. Lake and stream catchment basins are important repositories of geochemical information concerning the composition and characteristics of their drainage areas. Modern drainage systems can be considered as mass storage devices (Ogden et al., 1988) which contain the 'geochemical genetic code' for each catchment. The extension of the catchment basin concept to exploration geochemistry (Bonham-Carter et al., 1987) forms a bridge to environmental geochemistry. This paper will consider studies of a number of catchment basins in Nova Scotia.

One of the principal aims of exploration geochemistry is the estimation of geochemical background to define threshold levels and indicate anomalies. Recognition of 'natural' background levels in surface materials of various elements is needed to define baseline element levels and principal controls and to monitor changes in the ecosystem. Widely different element levels can be found in stream and lake systems. It is possible to define various natural and imposed geochemical controls present in stream and lake drainage systems. Principal geochemical factors governing background levels include catchment lithology, chemical mobility, and dispersion and dilution of metals during transport. pH is one of the most active geochemical factors and also the one most readily affected by imposed external loading such as from acidified rainfall. To estimate the pH effect on heavy metal mobilities, background levels and vector properties of these metals in natural systems must be elucidated.

RESULTS

Catchment basin analysis (CBA) has been used to characterize background for 1500 stream sediment and water samples from the Cobequid Highlands (Fig. 1) . Background is modelled for element concentrations in stream sediment as a function of the areal proportion of map units occuring within each catchment basin. Step-wise regression uses areal proportions of mapped units as independent variables to model geochemical background for Cu, Pb, Zn, Ag, Fe, Mn, Ni, Co, As, Hg, U and Mo in sediment and U, F and pH in water for each of 65 mapped lithologic units. Calculated background levels for each map unit are given as weighted means for each element (Fig. 2). The model thereby determines a measure of the association between the geology and surficial geochemistry. Volcanic and granitic units of the central upland core have much higher background levels for most elements when compared to other units. After subtraction of background the residual variance of catchment basins (Fig. 3) reveals areas of anomalies, which as elevated concentrations could be seen as potential hazards in terms of heavy metal content. The CBA model also distinguishes variance due to scavenging by Fe and Mn and pH effects on the mobility of elements such as U, Mo and As. Catchment basin plots for these elements clearly outline the pH response in terms of the underlying geology.

We call attention to, and illustrate, two important properties of limnic systems:

(a) Catchments with definable sub-watersheds can show distinctive biostratigraphic and geochemical

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signatures throughout the lake basin. We describe Soldier Lake, Halifax County, Nova Scotia (Ogden and Rogers, 1988) which has a hydrogen ion [H^+] gradient from distinct sub-watershed units ranging from 0.7 μeq L^{-1} (pH 6.2) to 102.3 μeq L^{-1} (pH 2.99). Mass balance studies (Ogden and Machell, 1985) indicate retention (presumably by deposition) of 33% of Al, 63% of organic C, and 85% of Fe entering the lake. Outlet pH values of 4.6 (25.1 μeq L^{-1}) imply neutralization of 38% of the [H^+] entering the lake. We show the presence of distinct geochemical and biostratigraphic (diatom) domains related to water chemistry, independent of regional (allocthonous) pollen deposition (Fig. 4).

(b) Sediment cores from three connected lake basins in the St. Margaret's Bay area, Halifax County, Nova Scotia, which have shown substantial acidification, with pH values from 6.0 to 6.3 in 1979 and from 4.8 to 5.6 in 1987, reveal four goechemically (and biostratigraphically) distinct horizons or zones:

(1) Initial (ca. 12,500 RYBP (Radiocarbon Years Before Present)) high energy meltwater deposition of coarse (sand and gravel) sediment including a large proportion of extra-catchment materials, with little or no organic matter.

(2) A silt to clay transition horizon (ca. 11,500 RYBP) with very little organic carbon and very low hydraulic permeability (Ogden, 1986), which effectively seals an initial catchment geochemical signature unaffected by biological modification.

(3) A mid-postgalcial period of warm/dry conditions (3500-5500 RYBP) of reduced hydraulic throughput, increased organic production, and longer water residence times which provided increased opportunity for organic/inorganic geochemical interaction.

(4) A post-colonization period of increasing anthropogenic influence, land disturbance, and changing atmospheric geochemistry.

In the St. Margaret's Bay area, development and construction activities have been primarily limited to the Five Island Lake catchment area, and are mostly residential and seasonal cottage developments. A number of new residential developments are currently under way in this watershed and may be expected to change both runoff and water quality as development pressures continue to affect many of the present hydrogeochemical parameters. With increasing acidification we infer the development of geochemical deposition domains in these lakes in future, similar to those described for Soldier Lake.

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FIGURE CAPTIONS

Figure 1. Location map showing study areas of study, Cobequid Highlands stream sediment survey and Soldier and Five Islands Lake near Halifax.

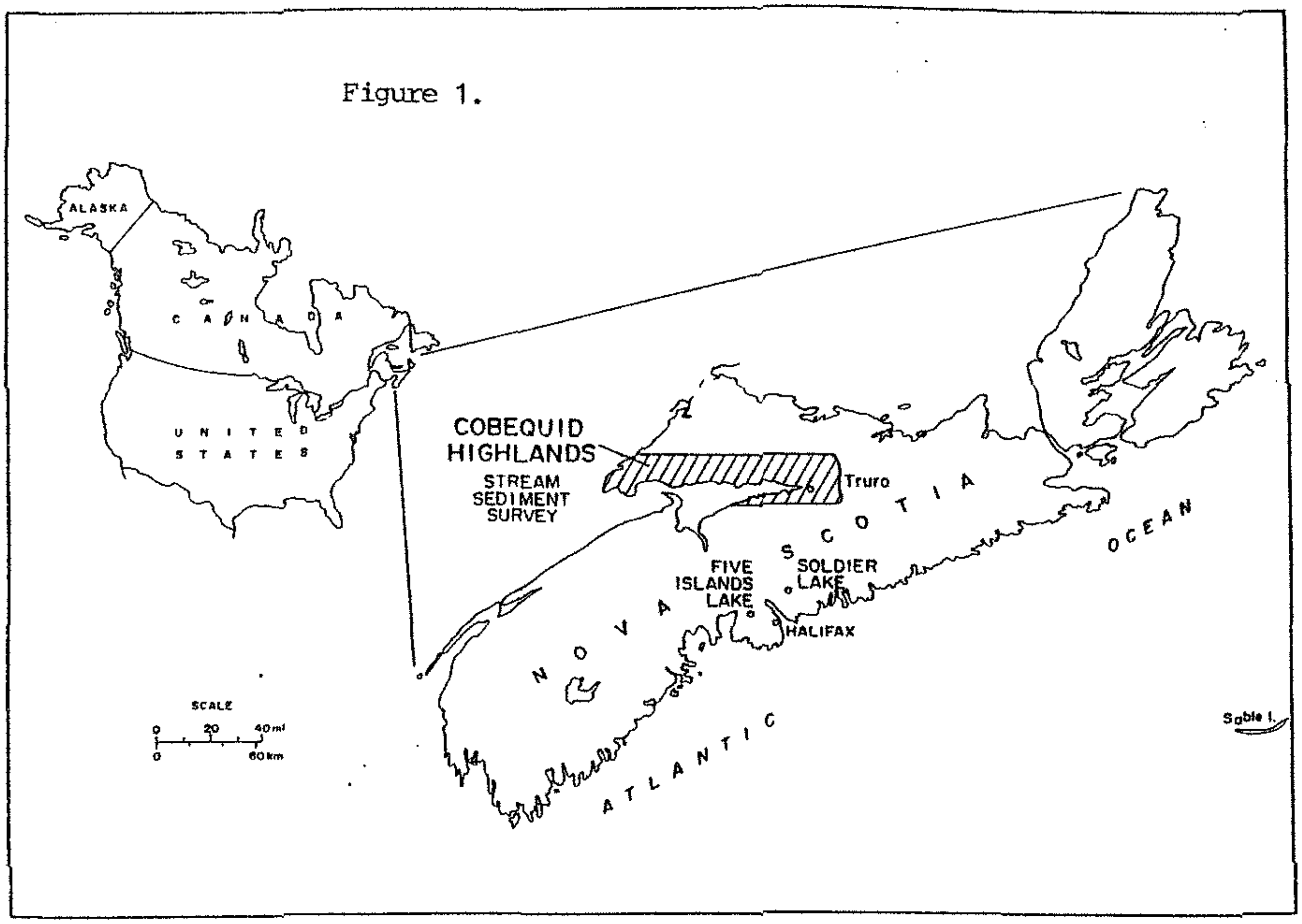
Figure 2. Diagram illustrating the amount of variance explained by the two principal geochemical factors (from Bonham-Carter *et al.*, 1987).

Figure 3. Example showing residual values plotted as a theme filling for each stream catchment basin, in this case principal component scores (Cu-As) (from Rogers *et al.*, 1986).

Figure 4. Soldier Lake, Halifax County (a) showing sampling stations and (b) effect of pH gradients on mobilities of Al, Fe and Zn in the lakes/sediment interface.

Figure 5. Five Islands Lake borehole showing changes in As, Rb, Ba and U with Xenothermic Interval indicated by 'bulge' of element values.

Figure 1.



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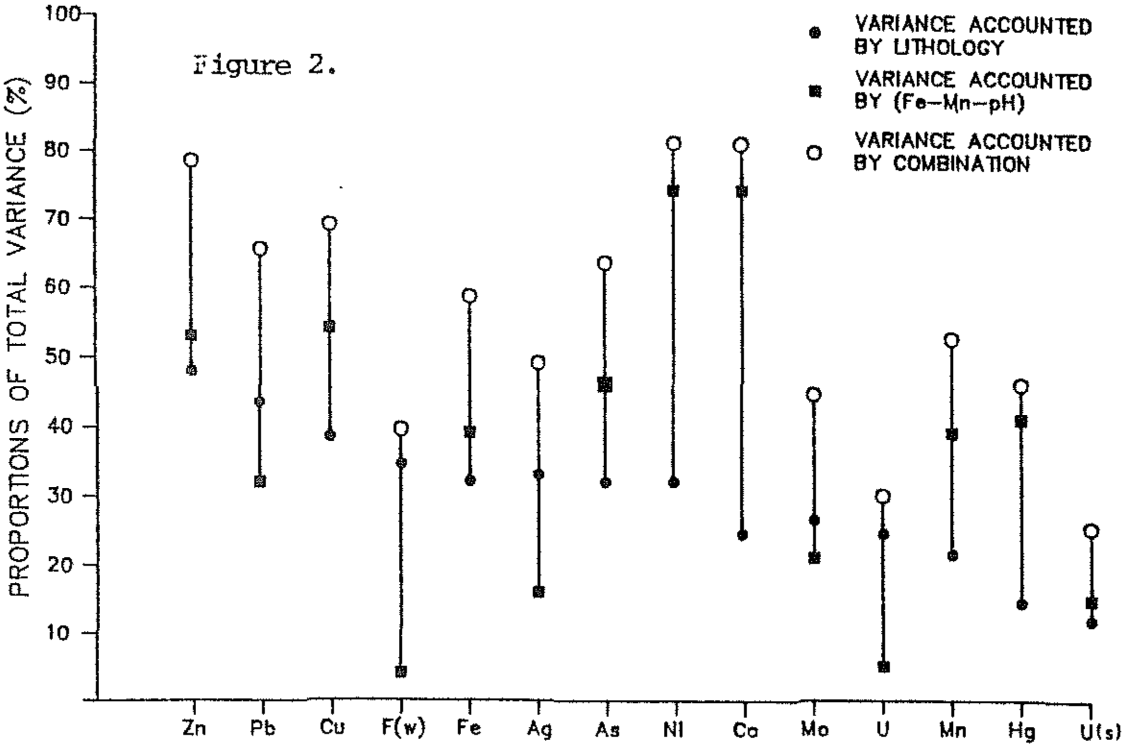

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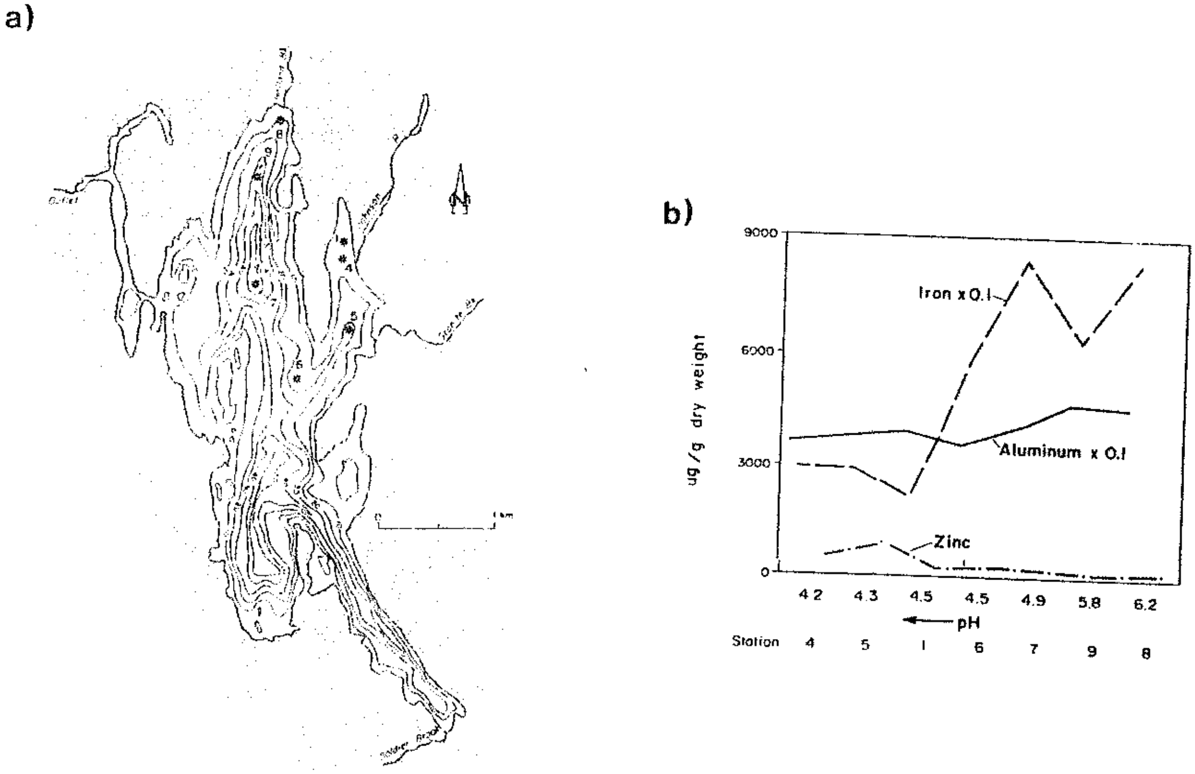

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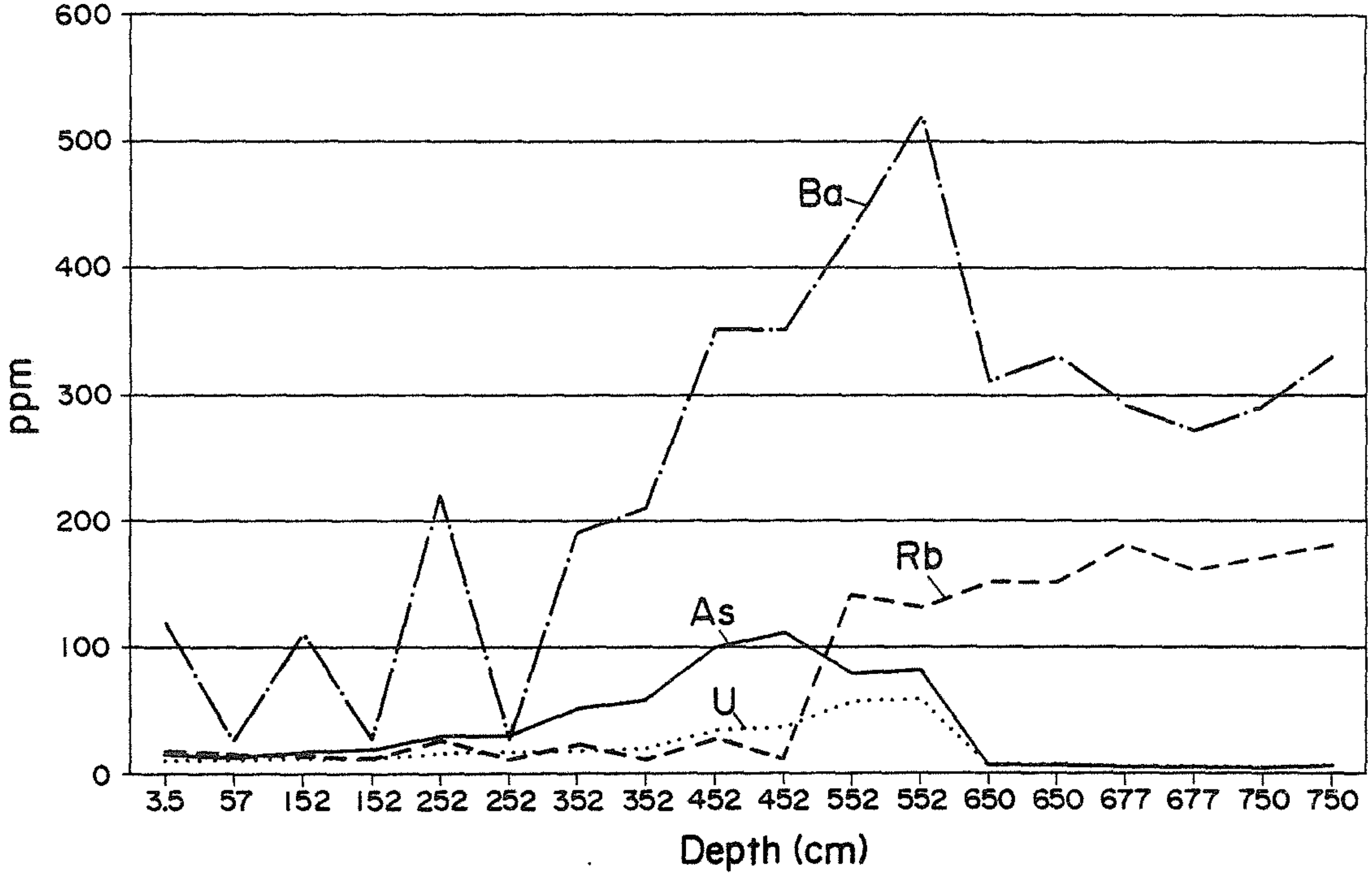
600
500
400
300
200
100
0
ppm
Ba
Rb
As
U
3.5
57
152
152
252
252
352
352
452
452
552
552
650
650
677
677
750
750
Depth (cm)

Figure 5.

Hierarchy of systems in exploration geochemistry.

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A system approach determined by the break of system into components is the major principle of a scientific method of recognition where from all the concepts and principles system. A system analysis allows the evaluation of the complexity of geochemical systems, their hierarchy levels and multidimensional set of indicators characterizing these systems and necessitates a single-level correlation. However, the system levels resulting from processing are often inconsistent with natural levels of the matter order, hence, there is an inconsistency between theoretical models and natural regular features. A subjectivity in selecting original data and the definition of the problem determine the unambiguity of their solution. The author has constructed a technological scheme for a geochemical forecast structure. It is based on the metrological assessment of all stages of work starting from data acquisition to their interpretation, sequence of stages and combination of methods, hierarchy of the whole exploration process with due attention to methodology and philosophy. Each cell of the technological scheme can be developed into a lower level scheme. A set of such different-level scheme consists of: - prediction strategy; - data processing; - tasks to be solved with the aid of geological data processing packages of application programmes PGD OS; - classification with consideration for coordinates. Along with an hierarchy of schemes as well as within their limits an hierarchy of involved systems can be evaluated. It is noteworthy that the system properties is not just a sum of constituing elements but are characterized by new qualitative indicators, i.e. by their origin. The origin of systems depends primarily on methods of their formation based on certain concepts and principles and allowing to outline an adequate hierarchy of levels depending on the system's complexity and their combination within independent, intersecting and overlapping space.

Out of the upper-level systems, the systems of views, data acquisition, analysis and preparation for analysis, data processing and interpretation appear to be the most important. All of them can be quantitatively characterized only through the system of quality estimation; this is indirectly expressed by analysis results for this purpose; the metrological support package is realized in the PGD system.

Views determine the system of space in which they are realized, and the system of methods with the aid of which they can be expressed. Therefore, the presentation of raw data depending on redistribution of elements in the entire matter or its part, proportional changes relative to constituents by the formation of haloes and flows is reflected in content, concentration, and contrasting features. The interpretation of systems of views and interrelation are determined by raw and converted data representation. With due account for this statement we pose a question of three philosophies in applied geochemistry as a missing link in theory of geological recognition. The low-level systems transform methods, principles, concepts into technologies and models. The resulting models can be inadequate to natural processes and reflects their different parts depending on the data representation. The system's properties strongly affect a set of applied methods which in turn emphasizes new properties of a system resulting in its improvement; the study of the system's hierarchy in view of the reflection of natural features should occupy a certain place in exploration geochemistry, othewise its advancement will be impossible. The upper-level systems, being unknown, thus preventing geochemical methods from application, are the first to be studied. Unlike other geochemical methods, a mineral component can be recognized as a reference for determination of element content for hydrochemistry and biochemistry fairly unambiguously.

The use of concentration philosophy in the form of the regional clark of the hydrosphere / ICH/ is at variance with main processes of water solution formation not taking into account the mineral part and stating a concurrent income of all components. Therefore, it cannot be recommended for geochemical concepts and premises. In case of phytogeochemistry the situation become more complex due to the presence of plant species and their separate parts differing in sorption capacity. Alluvium silty fraction forming a small part of the bulk composition in the presence of disturbing objects is rich in sought elements. The concentration of metals in silty fraction is proposed to be proportionally recalculated to the entire sediment and then estimate their proportion in bulk composition of sediment metals, i.e. to using contrasting features based on the assessment ion-soluble discharge to characterize the flows. The use of contrast ranges /with respect to the content in unaltered rock, clark, median, weighed average, etc./ and different dimentionless indicators, in particular, multiplicative, derivatives of concentrations and contents for complex systems predetermines proportional changes of these indicators in different natural media. The philosophy of gradation was used for the development of a technique for multielemental mapping of concentrations, gradations and contents. However, it should be stressed that only data with media with undirectional processes of halo and flow formation can be generalized. The model system is determined certainly not only by raw data representation but by methods of their conversion and continuity and discrete pattern. However, it is possible to state that whenever contents on factor diagrams are used for bedrocks, the ore-generating trend becomes evident whereas whenever median gradations, with respect to rock types, are used there is a trend showing how the products of the process affect the enclosing strata. Therefore, when doing geochemical prospecting within deposits it may be reasonable to apply the gradation philosophy and philosophy of contents for small scale works. In any case it is necessary to do a corectly evaluation of the relationship between the philosophy used and reflected in initial representation of original data and natural features. Otherwise one and the same processing may provide quite different results and respective recommendations.

The application of one or another philosophy is determined by researcher's views, traditions and capacities of the analysis. The recalculation of results from one representation into another become possible if necessary parameters are available. This has been done for complex systems in independently overlapping space in the North Siberian nickeliferous region.

Of the upper-level systems, it is reasonable to discuss a system of matter acquisition not tackling the sampling technology. The data collected apart from the evaluation of its representativeness and sufficient amount should reflect anisotropy of the geochemical field /if any/, and answer the question whether spatial relation or class is a critical factor for the given field. For this purpose, the model of an incidental casting of a net with changing size of a mesh which makes possible the assessment of peculiar features of a geochemical field at different scale of works and taking into consideration all the discussed classes of objects which fell in the net mesh; meshes not filled with classes are evaluated statistically from individual characters and from integral characteristics. Such an approach has been implemented as a simplified version when the coordinate field is broken down into cells according to the scale of works and to evaluate invariance under computing origin sliding is performed. A different representation of raw and converted data can be used.

It should be noted that systems of the next level of importance in methodology of the geochemical forecast are tightly interrelated samples and indicators which are considered relatively in three- dimentional coordinate and multidimentional indicator space which in turn can be independent, overlapping, intersecting and this should be accounted of all subsequent levels. The data processing allows to increase its generalization level and possible type recognition. The sequence of steps in search for deposits is as follows:

1. Evaluation of the efficiency of processing methods of geochemical data realtive to detecting of a deposit
2. Consideration of a set of geochemical approches followed by the evaluation of each,
3. Chice of a set of applied mathematical methods,
4. Evaluation of the quality of geochemical data,
5. Elucidation of the succession of element association in deposits, primary and secondary haloes, and dispersion flows,

6. Comparative assessment of separate sites and of the area potential.

Prevision is made for each step for a certain hierarchy of systems and the prediction problem itself can be considered at different levels. However, other options may be used along with the hierarchy of systems.

Thus, the prediction methodology is a structurally complex system frame whose loading on elements are determined not only by their number and connection between them but by the structure of the frame itself. When the frame is filled with a certain knowledge about system properties it takes shape of a finished building and the role of its machines is played by the lower-level systems processing principles and methods into technologies and models.

Software for the technology of metallogenic forecast

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of the World Ocean, Leningrad, USSR.

The package for processing of geological data /PGD/ is based on the model principle and realized on computers of single series /SS/ and IBM PC. PGD contains a large set of service programs /sorting, conversion, merging, selection, normalization, centring, and tabulation/. Many of them can use matrix with vacancies containing vacant values which can be filled with special program. Realized was a set of statistical programs starting from computation of elementary statistics /of mean, dispersion, standard, coefficients of variation, asymmetry, kurtosis, range/; evaluation criteria od their difference /Pearson's test of fit, Student's t-test, Fisher's variance ratio, Abbe number, Barlett and Rao tests and the like/; pair, multi-fold /after Yu.K. Burkov/ and partial correlation; computation of regression, discriminant functions, different versions of regression factor analysis. A substantial group of programs related to hierarchical and non-hierarchical clustering of initial data are to be obtained in "sliding windiw" mode.

There is a group of programs which perform a large set of petrochemical conversions /of coefficients, atomic ratios, virtual composition, indexes of basicity of rocks and minerals/. Programs intended to study the structure of geophysical fields work with data using uniform rectangular grids. Therefore, there is a program for conversion of any data in such grid. Naturally, all parameters obtained can be schematically represented and mapped.

The system envisages built-in programming aids allowing compilation of subprograms for a user by employing any algorithms as well as all-purpose procedures permitting to vary some parameters of functional programs and including programs prepared for computers SS without changing internal structure of the programs. Data can be transmitted to any system both by external representation and by the presence of system interface.

PGD was used as a basis for the development of technological schemes of tasks to be solved with its aid, of processing of geochemical data, classification with regard to coordinates. All the schemes are realized as job batches characterized by a certain sequence and priority.

The processing consists of blocks of accumulation, convolution and mapping of data accounted for cyclic approximation to optimal result:
1. Based against background of high and low clarks of concentration, the formation of a given type of deposit is determined. Informative typomorphic indicators are chosen using a primary knowledge or factor analysis on the model example. Therefore, models of ore provinces, districts, zones, fields, deposits aquire a primary importance. A rank of a model is determined by a scale of works and a necessary depth of knowledge, by a set of geochemical methods. In case of several ore assemblages, characters of each are recognized and their joint effect on a geochemical field is evaluated. Apart from typomorphic characters of ore assemblages, associations of indicators above ore and above intrusive halo. The task of the first block is the formation of sets of initial indicators and their conversion for different representations of initial data and various interpolation models. The extrapolation models are realized to a much lesser extent because of the absence of clear theoretical statements on many issues, but the processing scheme of the second block is accounted for check procedures of such statements.

The emergence properties of the system include dispersion and the presence of "exclusiveness". The exclusiveness approach was proposed by M.S. Sadikov /1972/ as a technique of geochemical search for deposits determined by their effect on a geochemical field not requiing the presence of reference objects and realized on the basis of the principle of uniqueness. The approach is based on the fact that these ore objects differ from all the rest occuring in the area and on the fixation of the difference in geochemical fields. The regression factor analysis which till recently was the final objective of the study is considered now as a procedure for conversion of initial data for their futher processing; the analysis was used as a model to realized the approach. The authors are the first to consider factors as independent random events whose joint probability of given outcome can be predicted. Hence a possibility of establishment of beforehand /before the experiment/ and a later /after the experiment/ probabilities and evaluation of the correlation between them which allows establishing of a regular pattern of the disscused events. The exclusiveness approach enables the recognition of unique objects which we identify with a deposits. The notion exclusiveness and superordinariness reflect the positive and negative specialization of disturbing object characterized a level and order.

A large number of processing methods available at present is based on evaluation of communication measures /correlation analysis/,and on check of their stability and communication means /regression analysis/.

2. The second block performs a multistep convolution of data, each step of which increases the level of community. Provision is made for the transition from individual to general and at higher level of community back to individual. All this enables to obtain quite new results by means of a common statistical apparatus: calculation of statistics, correlations, regressions. We can provide three examples: primary material - histograms - similarity matrix - factorization - histogram groups - groups of initial specifiers; primary material -correlation matrices according to rock type - matrix of homogeneity of correlation coefficients - factorization - group of specifiers reflecting different attitude of the ore-generating process - factorization based on groups of specifiers - similarity matrix /congruence/ - factorization; primary material - statistics and correlation with respect to all values - without anomalous values - anomalous values. Hence there appear models reflecting different aspects of natural processes. These premises can be complicated due to additional cyclicity or due to output at each step in individual samples.

The task of the researcher is to adjust the model to a certain situation, to evaluate the potential of the area for this purpose, to use a large set of numerical characteristics of geochemical fields of a specific area and scale, the latter defines the representativeness of original data.

3. Similarly to the second block it is necessary to differetiate between the syn- and epigenetic components and to determine their interrelation. This is used as a basis for automated mapping of data to reflect the intense zones of element association redistribution. Of principle is the classification accounted for coordinates and mapping of exclusiveness fields of the second and third order. For this purpose the authors have developed two techniques of multielemental mapping: extreme situations and concentrations, contrasts, contents. An attempt has been made to plot on a single base-map of spatial-temporal regular features and results of different geochemical methods to decrease the amount of details of a map. The analysis of the maps obtained is an integral part of the forecast technology.

The classification accounted for geographic coordinates is a new step towards the understanding of natural phenomena. The maps of classes is a quantitative leap as compared to the classification of specifiers and subsequent plotting of the data obtained on the topographic base-map. Both hierarchical and nonhierarchical procedures when classes are sampled from a complete set of partitionings and when concurrently several centers of clusters are sampled and objects are being assigned to them, followed by redistribution of both. The recognition of classes has been done mainly using the first three factors from typomorphic characters of deposits which allows us to better evaluate initial specifiers and to avoid the scale effect. A different representation of initial data makes possible to obtain diverse models reflecting variety of natural processes. The classification incorporates three options to take account of coordinates:

1. Preliminary factorization accounted for coordinates followed by clusterization into a

fairly large number of classes and their grouping according to factors only from specifiers and subsequent mapping.

2. Preliminary partitioning with respect to coordinates into a fairly large number of clusters followed by step-by-step agglomerative procedures using the first three factors allows us to obtain a small number of classes close to a given one. When clusters based on coordinates are obtained, they can be used for averaging of factors and by means of average file to continue clusterization up to the required number of classes projecting the values obtained for the entire data array. Unlike the hierarchical procedures of clusterization, the above nonhierarchical procedure is much faster, the partitioning based on ordered standard deviations as they decrease and on a specifier with maximal deviation.

3. Classification of data using potential functions approach accounted for coordinate weight and specifiers. The effect of the field on a particular point is determined by a sum of exponential functions of distances to remaining points normalized and centered with respect to all indicators. Net potentials in points reflect a typical pattern of each object. The program performs a successive classification of objects using their most typical features accounted for coordinates only on the first step. The time of run being quadratically dependent on the number of objects; it could be excessively large for big massifs, despite the fact that the nodes procedure is realized in the program, the processing time is beyond reasonable. To better use the advantages of the third option, the authors have proposed the algorithm of sequential typization of sorted data arrays allowing to decrease the processing time by about three orders forming uniformity vector during one file scan with variable sliding window. For the third option two other models based on data conversion into the regular grid; in case of the first model, only initial characters are converted into the regular grid, they are used for factorization, then depending on the volume of the information aither classification is made or the data are preliminary averaged with respect to cells corresponding to a certain scale of works followed by the distribution of data to the entire file; the second model converts factor values into the regular grid with subsequent classification.

If factors of some amount of initial characters which can be expressed in contents, concentrations and contrasts are taken as specifiers, then the complexity of the problem stated becomes evident. If we know now to a certain degree how to solve such tasks it is only owing to computer technologies allowing standardization of the tasks proper and their solution.

The development of the type packages of processing makes provision for the uniformity of geological objectives aimed at the metallogenic prediction study. The recognition of uniformity in geological objects is the basis for their successful study because a special processing procedure cannot be developed for each particular case.

THE SIMULATION OF GEOCHEMICAL PROSPECGING ON A PERSONAL COMPUTER

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The simulation system permits to realize the search-prospecting process, preserving the succession of actions of a geologist and at the same time decreasing the duration of the process from several months or years to minutes and hours. The model territory perspectives can be evaluted irrespective of the size and orientation of the search net, with analytical data being accurate. Making use of this system a researcher is able to correct his hypotheses and optimize the search methods whereas a student or a production worker have the possibility to accumulate an experience in carrying out combined prospecting, to analyse and correct their mistakes.

The technical base of the system is a personal computer of IBM PC type. The information base is represented by the bank of the model territories perspective from the point of wiew of discovering minerals deposits of definite geological-commercial types.

Representation of the information base of the system can be get from the Table:

Sign	Gradations
The deposit	lead-zinc .... molybdenum .... gold ...
The geological-commercial type	i-skarned .... 4-stratiform ... 5-veined
The size	i-occurrence ... 2-small ... 3-medium-large deposits
The erosion level	i-top ... 2-central ... 3-bottom
The secondary dispersion halos type	i-open ... 2-partially over lapped ... 3 close

The note: Only the part of connection is shown.

The creation of models is realized in the dialoque with a personal computer. Look at the screen i listing.

The Screen i Listing

```
WORK PROGRAM WITH THE MODEL FOR
SIMULATION SYSTEM OF GEOCHEMICAL PROSPECTING

Creation of the model ......................................................1
Correction of the model ....................................................2
Disk recording of the model ................................................3
Disk reading of the model ..................................................4
Examination of the model ...................................................5
Listing of the model .......................................................6
Graphic approximation of geological map ....................................7
```

At present, the model territories are used, which are perspective to the detection of the polymetallic stratiform, copper-molybdenum hydrothermal stockworking, molybdenum-tungsten skarned, gold-ore-quartz-sulphide deposits and others. Taking the opportunity, we invite those who are interested to take part in the formation of a model bank using your own materials.

Representation of the kinds of the simulation works is given by the screen 2-6 listing.

The Screen 2 Listing

```
SIMULATION OF GEOCHEMICAL PROSPECTING

MAIN MENU


SAMPLING OF DISPERSION TRAINS .........................................................1

SAMPLING OF SECONDARY DISPERSION HALOS ................................................2

DETAILED PROSPECTING WITHIN LIMITS OF DISCOVERED HALOS ................................3

DATA PROCESSING ........................................................................4
```

The Screen 3 Listing

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SAMPLING OF DISPERSION TRAINS


Streams sampling of 3rd and more high orders .......................................1

Streams sampling of ist-2nd orders by end samples ..................................2

Streams sampling of ist-2nd orders in whole ........................................3

Slopes examination with sampling of eluvium-deluvium
for chemical analysis ..............................................................4

Panning ............................................................................5
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The Screen 4 Listing

SAMPLING OF SECONDARY DISPERSION HALOS

Traverse sampling /profiling/ 1

Geological examination of the location 2

Panning 3

The Screen 5 Listing

DETAILED PROSPECTING WITHING LIMITS OF DISCOVERED HALOS

Traverse sampling /profiling/ 1

Trenching 2

Pit sampling 3

Well sampling 4

The Screen 6 Listing

DATA PROCESSING

Survey quality evaluation 1

Establishing of background and anomalous contents 2

Diseprsion trains productivity evaluation 3

Secondary dispersion halos productivity evaluation 4

Data smoothing for weak anomalous detecting 5

Erosion level of ore zone evaluation 6

The simulation of all prospecting stages takes not less then three days work including 10 to 12 hours spent at the personal computer. The game elements of the system are: projecting with the aim carrying out geochemical works at any stage, their realization, data processing and iterpretation, making and defending accounts in accordance with the works done.

As the training software the simulation system is used during the students' study, qualification rise of field geologists and specialists' examination.

As the tool of the imitation modelling it is successfully used, in making the choice of the step of the spectral analysis quantification, in the account of dimensions of the geochemical survey net, in the rational complex control of prospecting signs of the ore metallization.

By finishing the software of the geophysical methods the system also gets the integration function of the geochemical-geophysical methods of different deposits prospecting.

To get an additional information about the system you may contact the authors:
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GEOCHEMISTRY OF EPHEMERAL STREAM SEDIMENTS IN THE SOUTHERN-MOST PART OF ISRAEL

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Introduction

The National Geochemical Mapping Project of the Geological Survey of Israel was initiated with the aim of sampling and analysing stream sediment and bedrock througout the country. The purpose of the geochemical sampling program is: (1) to examine the behaviour of major and trace elements in relation to the source rocks; (2) to locate possible concentrations of mettalic minerals; and (3) to produce stream sediment geochemical base maps. The data obtained are being incorporated into a computerized data base which allows graphical and statistical processing of the data. The results presented hereafter are from the Elat area sub-project which was accomplished recently, covering an area of about 200 sq.km.

Generalized Morphology & Geology

The southern-most part of the Negev Desert in south Israel, located along the western margin of the Dead Sea transform (rift), is a typical arid, rocky desert, with an avarage annual rainfall of ca. 50 mm. All streams are ephemeral (wadies), characterized by a steep gradient due to the abrupt height difference across the rift's margin. Flash floods occurring at irregular intervals, frequently years apart. Soils are absent and rock exposures are fresh. Stream sediments consist of an immature mixture of very coarse- to very fine-grain size material. Ancient river terraces are present along the banks of allmost all major and many of the minor wadies.

The southern part of the area is dominated by diversed Precambrian crystalline rocks, while the northern part is typified mainly by platform carbonate sediments of Upper Cretaceous to Eocene age (see Fig. 1).

The Precambrian outcrops represent the northern exposures of the Arabo-Nubian shield which is part of the Pan African terrain. The area was structurally reshaped in the late Cenozoic by rifting and regional doming (Garfunkel, 1980) which ultimately resulted in the present exposures as a series of "blocks" ("massif" in Bentor, 1961), each of which is geographically isolated and, to a degree, is relatively homogenous geologically. The oldest units present are metamorphic rocks - pelitic schists, amphibolites and gneiss - which occur in the Elat and Roded blocks. The quartz diorite which dominates the Roded block is considered to have formed by anatexis. Eyal et al. (1990) dated the age of the metamorphism at ca. 800-820 Ma. Other rock types outcroping within the Precambrian blocks are alkali granites, rhyolitic flows and pyroclastics, basalts and a wide variety of dyke rocks. A gabbro and a monzonite to granodiorite association occurs only in the most northern Timna block.

The sedimentary sequence in the studied area is devided into five main groups:
a) Yam Suf Group (220m) represents a platform accumulation of mainly subarkosic sandstones during the Cambrian. b) Kurnub Group (200m) - mainly Lower Cretaceous quartz arenites, deposited on a regional erosive unconformity. c)Judea Group (380m) - comprises thick platform carbonate sediments deposited during Upper Cretaceous. d) Mount Scopus and Avdat Groups (150m) - a sequence of chalks, chert, marls and shales deposited on the Arabian platform from the Senonian to Late Eocene. Uplifting which took place at that time led to the development of continental conditions in that area.
e) Conglomerates, river terraces and alluvium, from the Miocene to recent, are included in the Dead Sea Group. In the Arava valley its thickness reaches several thousands meters.

There are no known metallic ore deposits in the Israeli Precambrian terrain. Minor copper mineralization is fairly widespread throughout the area and is more abundant in the Timna block. The Timna Cu/Mn deposit is hosted mainly in the clastic unit of the Lower Cambrian Timna Formation (Segev & Sass, 1989).

Sampling and Analytical Methods

Previous works (Bugrov, 1974; Zeegers et al., 1985) demonstrated that mechanical dispersion plays a significant role in metal mobility (secondary dispersion) in arid areas. Zilberfarb and Bogoch (1974) found that in mineralized areas within the Precambrian terrain in the Sinai Peninsula, the anomalous halo for copper is ~300m and for molybdenum only ~200m. These limited dispersion trains are apparently largely the result of masking by barren diluting material. Another important factor in considering sample density in the present survey was that gold was among the important elements targeted for exploration. Thus the well known nugget effect had, at least in part, to be addressed. Based on this knowledge, an orientation survey of the Timna block (Beyth et al., 1988) and on the sampling program within the precambrian terrain (Bogoch et al., 1990), it was found that at least 3-5 samples/sq.km are required for this type of terrain.

A total of 780 samples were collected, each original sample weighing ca. 30 Kg. Screening to <1 mm had been carried out at the sampling site and further screening to minus 100 mesh was accomplished at the laboratory. Out of this fraction, 500 mg of the sample was sintered with Na-Peroxide and analysed for major, minor and most trace elements using ICP-AES (total of 30 elements). Synthetic solutions were used for calibration and Scandium served as an internal reference, substantially reducing short-term variability. Arsenic and antimony were analysed using hydride generator. Gold determination was carried out on 20 gm samples using AA, after roasting, aqua regia digestion and treatment with MIBK and HCl. Natural standard reference materials were analyzed routinely, using the same procedures.

Results and Discussion

The results obtained by the sampling, analytical and the data processing methods establish, for many of the trace elements, a distinctive reliance between the geochemistry of stream sediments and the outcroping source rocks.
Generally, the content of all trace elements (excluding Pb) is higher in wadi sediments derived from the precambrian terrain. A statistical summary of the results is given in Table 1.

The **transition elements** (Cu, Ni, Co, Cr, Zn, V, Mn) show increasing contents (in wadi sediments) from sedimentary terrain through granites and rhyolites, diorites and intermediate to basic metamorphics, to gabbro. The Timna block exhibits the highest values of copper content in the wadi sediments, which are considered to relate in part to widespread, hydrothermal copper mineralization in the area, and in part to the abundance of basic ignous rocks which generally contain >100 ppm Cu. The geochemical behavior of chromium, nickel, vanadium (and to a lesser extent that of manganese and cobalt) is similar. It is strongly associated with mafic minerals and spinels, and is henced enriched in mafic rocks. The aerial distribution of these elements in the Israeli Precambrian is nearly identical, and the samples with high values all derive from the gabbros of the Timna block and the diorites of the Roded block. Since **zinc** tends to occur in similar abundances in rocks of most compositions (~100- 200 ppm), a fairly even distribution of the values is actually reflected in the geochemical maps. The occurrences of the 98%-ile Zn values in the Timna and Roded blocks possibly relate to mineralization features. **Yttrium and the REE** (La, Ce, Eu, Yb) contents can be directly related to the source rock, with higher values in alkali feldspar-rich rocks. Anomalous REE values were encountered south to Elat, in an area built of white to pink granite, crossed by acid and intermediate dykes with minor pegmatoid occurrences. **Gold, Arsenic & Antimony**: close to 97% of the wadi sediments samples measured for gold were below the detection limit of ~10 ppb. Almost all samples containing >30 ppb Au are located in the Roded block (Fig. 2), and are related to defined gold mineralization occuring in a number of geographically closely spaced anomalies. High values of As and Sb (up to 120 and 5 ppm, respectively) are located in the very same localities (Fig. 2). Few samples of wadi sediments draining sedimentary terrain around the Timna block contain up to 50 ppb Au. The reason for this enrichment cannot at present be surmised. Apparently all of the **Barium** high values can be related to the presence of barite mineralization, mainly in the form of veins, some of them ~1000 m long (Bogoch and Weissbrod, 1986). As mentioned previously, the **lead** content in samples derived from the sedimentary terrain, especially around the Timna block, are significantly higher than those derived from the precambrian terrain (Fig 3a,b). This is due to the presence of a lead/manganese mineralization cotaining coronadite within the Lower Cambrin Timna Formation. However, if only the "Precambrian" samples are treated (Fig. 3c), the geochemical map reveals distinctive anomalies of lead in the Timna and Roded Precambrian blocks; the latter is due to the presence of Pb-arsenates coexisting with the Au ore bodies.

Factor analysis (R-mode) carried out on log-transformed major and trace element data yielded 5 main factors explaining 70% of the variance. These factors can be largely explained on the basis of the mineralogy of the stream sediments as well as the probable source rocks.

Factor I (30% explained variance) - Y, La, Ce, Yb, Ti, Fe. This factor suggests concentrations of heavy minerals such as monazite, zircon, sphene and ore in the samples.

Factor II (17%) - Cr, Ni, Mg.; indicative of ferro-magnesian minerals and spinels (source rocks - mafics).

Factor III (10%) - Mn, Pb, Co, Ba, Cu.; represents the cambrian ore mineral assamblage in the area.

Factor IV (7%) - Si(+), Ca & Sr(-).; this "miror" factor represents the partition between samples derived from the Precambrian terrain and those from the sedimentary terrain.

Factor V (6%) - Eu, Sb, V, As.; indicates the samples derived from the As-Sb-Au mineralization localities.

Conclusions

Based on the reported survey and on the orientation survey in the Timna block (Beyth et al., 1988), the following conclusions can be drawn:

1. The effective sampling density in rocky deserts is greater at least by a factor of 2 than that required in temperate climates. Thus, 3-5 samples per sq.km would yield a high confidence level in interprating the geochemical data. With this sampling density and sample grain size (minus 100 mesh), it was found that several elements were extremely sensitive to mineralization phenomena, both known and previously unknown. The latter include (a) As-Sb-Au anomalies in the Roded block; (b) Cu- anomaly in the western part of the Amram block; (c) La-Ce- Yb anomaly in the Elat block.

2. The analytical techniques employed are rapid, accurate and reproducible. The combination of major and trace elements determinations in wadi sediments is a valuable aid in relating trace elements to their source rocks and to specific host minerals.

3. When dealing with an area built of extremely different rock types (e.g.: carbonates vs igneous), data treatment should be carried out very cautiously in order to avoid masking of significant anomalies.

4. The "classic" pathfinder elements for gold (As and Sb) would have led to the same discoveries without direct analyses for gold.

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Table 1: Statistical summary of stream sediment analyses (N=778).

	min.	max.	mean	median	standard deviation	no. of samples below limit of detection
%						
SiO_2	12.5	97	51.8	52	13.6	-
Al_2O_3	2.1	15	7.1	7	2.8	-
Fe_2O_3	0.5	19.4	3.8	3.6	2.5	-
CaO	0	50.3	16.2	14.5	8.3	-
MgO	0.2	8.6	2.6	2.5	1.1	-
TiO_2	0.12	4.9	0.7	0.6	0.4	-
P_2O_5	0.1	1.4	0.3	0.3	0.1	33
ppm						
As	1	120	6.7	4	12.5	6
Ba	36	9900	567	580	655	-
Be	0.3	6	1.5	1.4	0.8	-
Ce	6	300	60	55	31	-
Co	1	208	17	14	13	21
Cr	10	963	93	72	90	29
Cu	3	10000	99	59	379	-
Eu	0.1	2.9	0.9	0.8	0.5	212
La	10	201	33	30	17	-
Mn	68	9000	792	720	669	-
Mo	1	75	7	5	7	565
Ni	5	285	42	32	34	125
Pb	1	1000	49	30	92	41
Sb	0.1	5	0.4	0.3	0.4	392
Sr	26	1998	326	316	140	-
V	20	288	75	65	35	-
Y	9	129	28	26	13	-
Yb	1	15	2.8	3	1.5	-
Zn	12	290	78	75	36	-
ppb						
Au	10	990	168	50	278	733

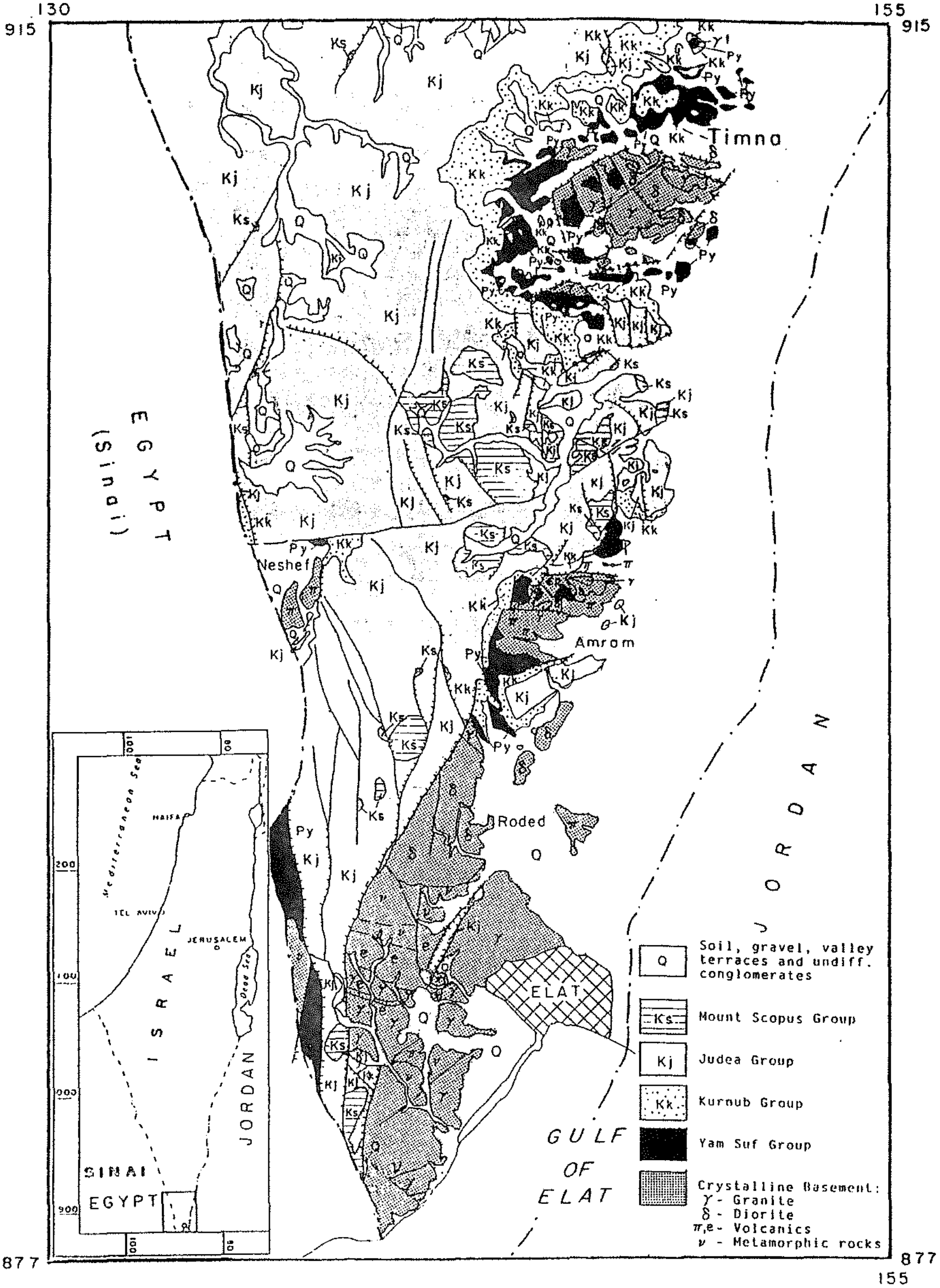

Fig. 1: Location and geological maps

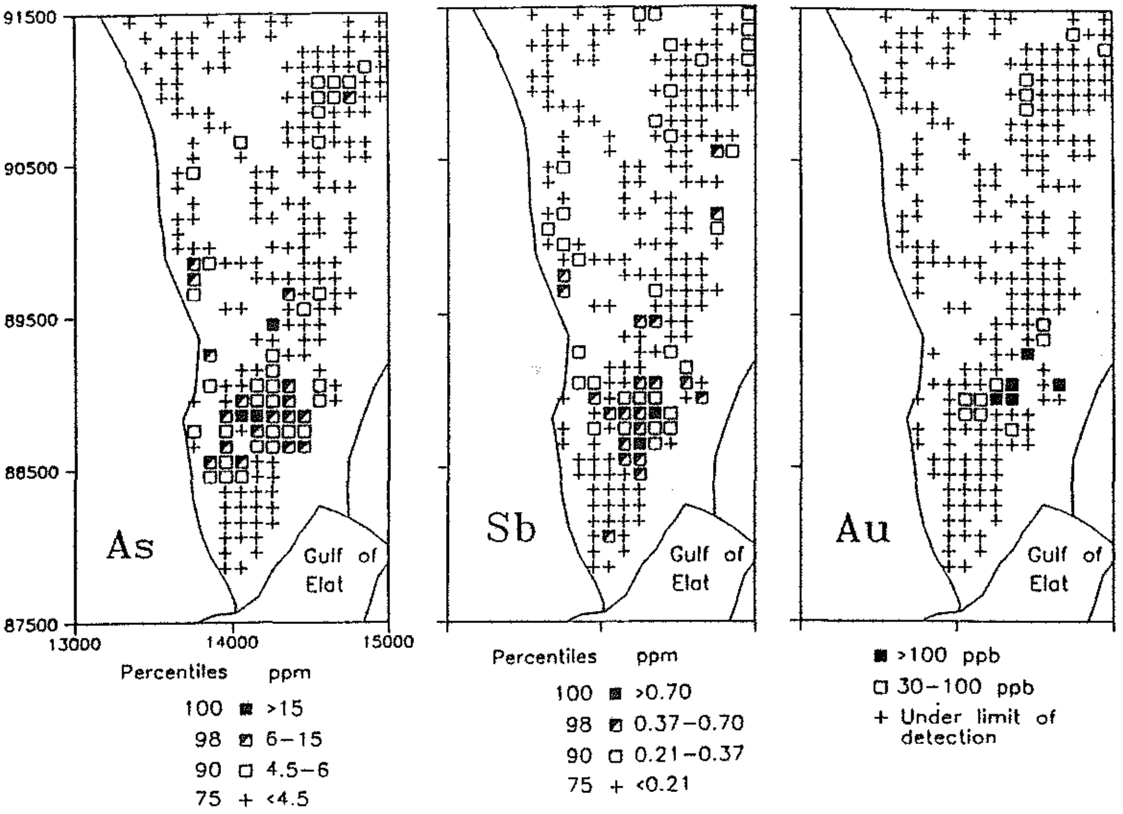

Fig. 2: Geochemical maps of As, Sb and Au. Every graphic symbol represents average content within a 1X1 km square.

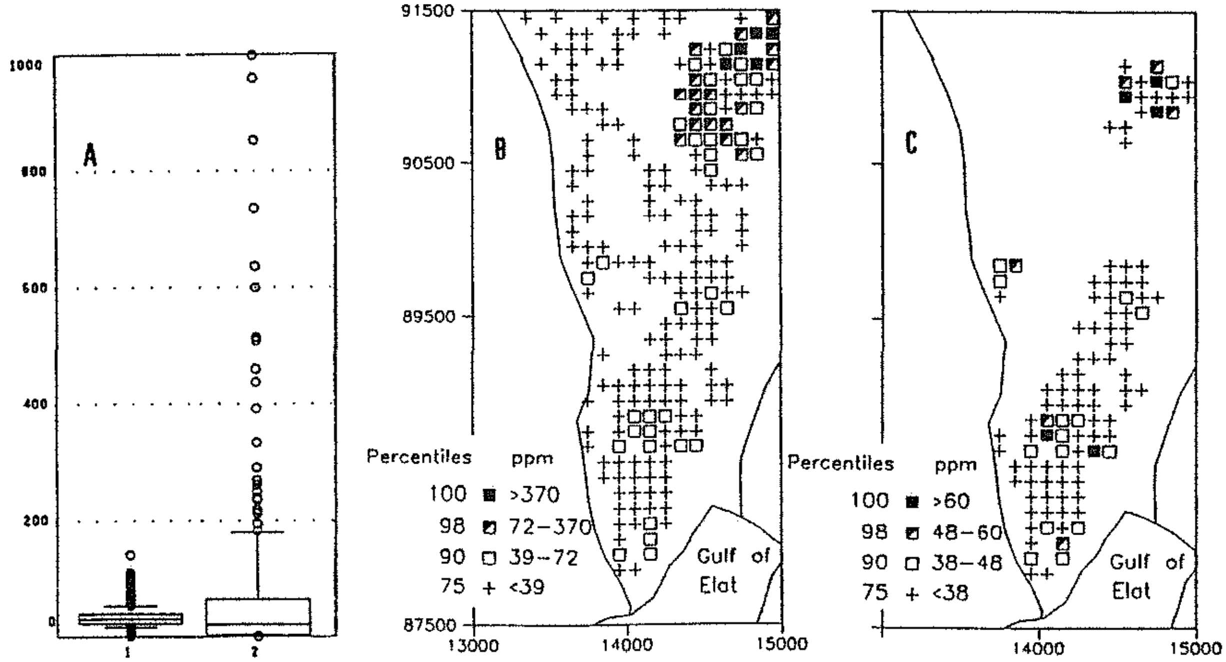

Fig. 3: a) Box plot of Pb content (ppm) in stream sediment derived from Precambrian terrain [1] and sedimentary terrain [2]. b) Geochemical map of Pb. c) Geochemical map of Pb - Precambrian terrain.

GEOCHEMISTRY OF RARE AND TRACE ELEMENTS IN SEDIMENTARY COVER OF YOUNG PLATFORMS

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The paper characterizes the general pattern of distribution and combination of rare and trace elements, revealed in the course of geochemical mapping and the study of reference geochemical section in occurence areas of the sedimentary cover of young platforms and zones of their tectonic (tectono-magmatic) activation. Special emphasis is placed on the role of syngenetic and superimposed (epigenetic) proceses in the formation of the geochemical background, geochemically specialized rock complexes, accumulation of rare and trace elements and revealing the potential ore-bearing areas and provinces. Such an approach to systematization and generalization of geochemical information is an integral part of regional geochemical analysis, developed by the school of geohemists from VSEGEI A.A. Smyslov, V.K. Titov, E.V. Plyushchev, G.M. Shor et al.

The object of studies were the geochemical features of the Mesocenozoic mantle of the Central Eurasian young platform (as understand by R.G. Garetsky 1972) comprising the Scythian Turan and West Siberian plates, divided by the Central Kazakhstan young shield. The Central Eurasian platform is bounded by the largest Earth's crust stuctures, i.e. East European and Siberian ancien platform, epigeosynclinal and epiplatform orogenic areas (Fig.1).

Young platforms, as a independent object of geochemical (and metallogenic) analysis, have been studied during the last decades in connection with prospecting for iron, manganese, bauxites, titanium placers, rare and trace elements, petroleum, hydrocarbon and other gases.

The distribution pattern of rare and trace elements in the cover of young platforms is associated with the evolution of processes, mainly of the sedimentary cycle.

The geochemical background of rare and trace elements is mainly formed in the process of lithogenesis taking place under different paleogeographic and paleoclimatic conditions.

Lateral geochemical zonation of background contents of rare and trace elements is subordinate to the lithological facies, and paleogeographic and paleoclimatic conditions.

A conrincing example can be the distribution of uranium and thorium in the generalized facies profile on the Turan plate (Fig. 2). Excluding rock complexes, specialized in organic matter (carbonaceous clays and marls) with elevated concentrations of certain rare and trace elements, among, them uranium it is seen that thecontent of uranium and thorium from the continent to the lagoon and from the continent to the coastal, and further to the shallow and deep parts of the sea is decreasing.

The facies zonation is associated with the distribution pattern of rare and trace elements groupings in the Upper Cretaceous - Paleocene and Eocene clays of the southern West Siberian Plate, which, in the direction of facies zonal change, are characterised by replacement of groupings of chalco-lithophile and chalco-sidero-litophile geochemical types by those of chalco-siderophile and lithophile types (Fig. 3). Iron ore mineralization, revealed in this region, occurs in the area where fields with the chalco-sidero-lithophile and lithophile geochemical rock specialization are recorded.

The vertical zonation in the distribution of rare and trace elements, associated with the impact of lithological facies and paleoclimatic (landscape-geochemical) conditions, can be considered using the example of evaluation of geochemical features of rocks on the eastern margin of the Turan Plate (Table 1).

The formation of the geochemical habit of the Rhaetian-Middle Jurassic rocks was strongly affected by an intense weathering during thich epoch, which resulted in a marked depletion of sillstone-clay rocks in rare and trace elements of the siderophile and chalcophile groups.

In the course of subsequent erosion of the shield and development of marine transgression in the eastern Turan Plate, the role of rare and trace elements of the siderophile group was still more decreased.

Generally, on the Turan Plate, as well as in its eastern part, there is a decrease in siderophile properties of geochemical associations up the section, which characterizes its vertical geochemical zonation. In the West Siberian Plate, in this direction (up the section) an increase in the siderophile character is recorded. Its maxima are confined to the Late Cretaceous-Paleocene and Oligocene rocks.

A special place in the course of formation of vertical zonation is taken by geochemically specialized formations, containing sorbents, concentrators and precipitators of rare and trace elements, i.e. coals, lignites, peats, bitumens, phosphates, iron and manganese oxides and carbonates, aluminium and silican oxides and sulphides, determining the geochemical specialization of geological formations.

The formations specialized in organic matter of a petroleum origin are exemplified by the strata of biogenic marine rocks enriched in sapropel (to 40 - 50 %) and with high concentrations of a number of rare and trace elements, i.e. molybdenum, copper, nickel, vanadium, tungsten, selenium, tellurium etc., tens and hunderds, and for certain elements (selenium, tellurium, rhenium, molybdenum) thousands of times exceeding their clarke contents in the lithosphere (Table 2). Among such specialized complexes on young plates are: Bazhenovo Formation and its equivalents in the Upper Jurassic - Berriasian on the West Siberian Plate; the Eocene and Oligocene-Miocene bituminous clays and marls on the Scythian -Turanian Plate. The continental equivalents of marine biogenic formations are lacustrine bituminous clays of the activated margin of the Turan Plate and adjacent inner depressions of the recent Tien Shan orogen.

A broad spectrum and high background of selenium, rhenium. tellurium, molybdenum, tungsten and other rare and trace elements are due to similar conditions of emplacement and a slight influence of the specific character of lithogenesis in space and time. The predominant position of certains elements in natural associations is determined by the forms of their association with concentrators. The composition of prevailing rare and trace elements in continental equivalents of marine biogenic rocks is much narrower (molybdenum, sulphur, silver, boron, rare earths etc.) and it is due to the influence of the features of lithogenesis in specific lacustrine paleobasins.

The role of endogenic factors in the formation of geochemical specialization in bituminous rocks can be recorded as a definite geochemical correspondence between the Triassic sedimentary-volcanic strata and rocks of the Bazhenovo Formation, revealed in the course of studies on the Tomsk geochemical section (Shor, Spiridonov et al. 1983).

Geochemically specialized rock complexes can be the source of metals in exogenic epigenetic and "hydrothermal" ore formation. According to A.G. Luzanovsky and E.F. Poshekhonov (1979), a close position in the Mesocenozoic section of a number of exogenic sheet - infiltration deposits and the occurence areas of the Eocene oil shales, and a similar spectrum of accompanying elements point to a possible role of the redistribution of metals.

Redistribution and accumulation of rare and trace elements in the mantle of young platforms is associated with activity of different types of underground water with migration of petroleum and diverse gases.

Oxygen-bearing underground water of meteogenic origin in marginal parts of young platforms, in the areas of adjoining post-platform orogens, under arid climatic conditions, ensures the supply of rare and trace elements from water-enclosing rocks. Of practical interest are the accumulations of rare and trace elements confined to closure of ground and stratal oxidation zones formed by oxygen-bearing waters. At the boundary of wedging of stratal oxidation zones, selenium, molybdenum, vanadium, rhenium, scandium and uranium, which are actively migrating in underground water, are accumulated (Fig. 4, Shor et al. 1988). There is a gold and rare earths accumulation.

Therefore, the boundary of wedging of oxidation zone is the critical factor of natural separation of rare and trace elements and represent the first level of their accumulation in hypergenetic and catagenetic zones.

The activity of oxygenfree metal-bearing water can be associated with vanadium, nickel, cobalt, copper, zinc and lead accumulations (to 2.5 - 9 clarkes) recorded in the Jurasic - Upper Cretaceous sandstones of local anticlinal structures in the southern and, particularly, southeastern West Siberian Plate in the area of intense infiltration washing by underground water flows developed from the Kuznetsk Alatau and Eastern Sayan. Apparently, as presumed by I.N. Ushatinsky and O.G. Zaripov (1978), the source of rare and trace element can be petroleums and this accumulations of elements proeeded in the zone of a former water-petroleum or gas-water contact. This points to the destruction of the previously existed hydrocarbon accumulations.Irrespective of the type of source of rare and trace element and with regard for the known evidence of their accumulation in connection with transformation of hydrocarbon deposits in a reducing environment, the latter can present one more level of the natural separation of rare and trace elements in the catagenetic zone, associated with the activity of oxygen free underground water of a predominantly meteogenic nature. In the territory of the West Siberian Plate the Tobol-Ket geochemical province is distinguished, characterized by a chalco-siderophile specialization and a former oil and gas province. It occurs between the West Siberian oil and gas province proper and the geochemical province of the suborogenic belt with a chalco-litophile specialization (Fig. 5).

Thus, the infiltration activity of underground water, shown up in artesian basins affected by post-platform orogenic area, results in significant changes in background contents of rare and trace elements in permeable rocks and ensures the formation of regional geochemical zones of their evacuation, supply and accumulation in an oxidizing environment after iron (sorption on limonites), at the boundary of oxidizing and reducing environments and in a reducing geochemical environment.

Infiltration activity of underground water shows up under conditions of artesian basins. It is recorded that widespread under such conditions are the processes of clay dehydratation, carbonate dissolution, decomposition of dispersed organic matter, abiogenic reduction of sulphates and many other not adequately studied processes. In the course of these processes are supplied a significant amounts of water from clays into sandy reservoirs, hydrogen sulphide and carbon dioxide accumulations form.

Z.Ya.Serdyuk, A.A. Rozin (1969), B.A. Lebedev, G.B.Aristova et al. (1976) associates the complex of epigenetic rocks alterations with a series of neocrystallizations, i.e. with a carbonatization,kaolinization, chloritization of micas, formation of zeolites, with carbon dioxide migration in the West Siberian Plate mantle. According to G.N. Perozio (1967), the accumulation of strotium (up to 120 clarkes), manganese (up to 24 clarkes) and barium (up to 10 clarkes) is due to the epigenetic carbonation.

In downwarping artesian basin there are regional shows of clay dehydratation process. According to A.M. Blokh (1968), A.A. Kartsev (1978), water released from clay is noted for a highly agressive character. According to N.V. Kholodov (1983), most actively dissolved are copper, nickel, lead, molybdenum, germanium, iron, manganese contained in carbonate minerals, i.e. rare and trace elements similar to those accumulated under a reducing environment, under conditions of intense infiltration water exchange,not connected with stratal oxidation zones.

Discussing the problems cennected with squeezing of water from clay (elision water exchange) one cannot but present the notion of D.S. Korzhinsky (1947), E.T. Degens et al. (1971), according to which during water migration through the clay filter the effect of filtrational separation of various constituents can be observed. Such a regional separation can present the third level of rare and trace elements accumulation in the catagenic zone.

An intense redistribution of rare and trace elements can proceed in the area where the infiltration and exfiltration hydrogeological regimes adjoint.

The marginal parts of young platforms adjoining post-geosynklinal orogens (i.e. Cheleken, Gaurdak, Tadjik Depression, Fergana etc.) are interesting in this respect.

The use of geochemical information on rare and trace elements during regional metallogenic analysis and prediction of mineral deposits ensues from their revealed space-time distribution pattern.

The use of data on rare and trace element concentration to solve a number of general geological problems:

1. subdivision of stratigraphic section;
2. providing basis for the types of lithogenesis;
3. judgement about facial-paleogeographic conditions of sedimentogenesis;
4. assessment of the tectonic setting of sedimentogenesis;
5. structural zonation of the territory particularly in connection with the neotectonic activation and orogenic processes;
6. assessment of climatic conditions of continental strata emplacement;
7. separation of geological formations with a nomal and anomalous distribution of rare and trace elements and revealing the emplacement features of geochemically specialized rock complexes;
8. revealing of a possible role of the endogenic factor during sedimentogenesis.

Geochemical information is widely used to solve the ecological problems connected with an assessment of the influence of natural and technogenic factors on the environment.

Main conclusions from the work accomplished are as follow:

1. Space-time distribution patterns of rare and trace elements in the young platform mantle was established. It was shown that their background concentrations are formed in the course of lithogenesis proceeding under different paleogeographic and paleoclimatic settings. The latter are associated with the lateral and vertical zonation in the distribution of their associations.

2. A specific place in the vertical geochemical zonation is taken by rock complexes specialized for sorbents, concentrators and precipitators of rare and trace elements. They can be the sources of ore substance in exogenic epigenetic and "hydrothermal" processes (with a participation of heated water).

3. Two levels of natural separation of rare and trace elements in hypergenetic and catagenetic zones are associated with the development of infiltration processes resulting from activity of oxygen-bearing and oxygen-free undergroundwater,predominatly, of a meteogenic nature. One of the levels is confined to boundaries of the oxidation zones wedging. The second one -to alteration centres of hydrocarbon deposits.

4. Local accumulations of rare and trace elements, confined to channels of underground water hydraulic connection, are associated with shows of exfiltration proceses, resulting from activity of fracture-vein water and carbon dioxide supplied from the basement or subsided horizons of the plate mantle. Squeezing of pore water from clay can be associated with formation of the third level of regional accumulation of rare and trace elements in the catagenetic zone due to the filtrational separation effect in the course of water migration through the clay filter.

5. Geochemical information on rare and trace elements can be used not only for the purposes of regional metallogenic analysis and prediction of mineral deposits, but also to solve various geological and ecologicals problems.

Table 1

CHARACTERISTIC RARE AND TRACE ELEMENT ASSIATIONZ
IN SANDSTONES AND CLAYS OF THE EASTERN TURAN PLATE

Type of structures	Age	Rare and trace elements associationz			
		$K_K \leq 5$		$K_K \geq 1$	
		Clays	Sandstones	Clays	Sandstones
Resent orogen	N_2 - Q	(Ni,Mn) (Sn,Li)	(Cr,Co,Ni,Mn)(Zn)(Sn)	(Pb) (Th,Ba,U,Y)	(Pb) (Ba,Mo)
	N_1	(Mn)	(Cr,Co,Mn) (Zn) (Li, Be,Sr,Th)	(Ti)(Pb)(Sn,U,Y,Mo)	(Pb,Cu) (Mo,Y,Nb)
Platform	P_2	(Mn) (Be,Sr)	(Mn) (Ba,Sr,Be,Th)	(Ti,V) (Cu,Zn,Pb) (Sn,U, Mo,Zr)	(Cu,Zn,Pb) (Y,Zn,Sn, U,Mo)
	P_1	(Mn) (Be,Ba,Sr)	(V,Cr,Mn) (Ba, Sr,Li,Th)	(Ti) (Cu,Pb,Zn) (Zr,Y, Sn,U,Mo)	(Cu,Pb) (Sn,Y,U,Mo)
	K_2	(Mn) (Zn) (Sr)	(Y,Cr,Co,Mn) (Zn) (Li,Sr,Th)	(Cu) (Sn,Zr,Y,U)	(Cu) (Y)
Epigeosynclinal low-amplitude orogen	T_1 - J_2	(Ti,Y,Cr,Co,Ni,Mn) (Cu,Zn) (Mo,Nb)		(Th,Y,U)	

Note. Kk is given on the basis of relation to rare and trace element contenls in the Earth is crust, after A.P.Vinogradov, 1962.

Table 2

CLARKES OF RARE AND TRACE ELEMENTS CONCENTRATIONS IN YOUNG PLATFORM ROCKS, OVERSATURATED IN ORGANIC MATTER

Stratigraphic position		$n \cdot 10^3$	$n \cdot 10^2$	$n \cdot 10^1$	$n \cdot 10^0$	$n \cdot 10^{-1}$	$n \cdot 10^{-2}$
Jurassic, Volgian, and Haterivian, Bazhenovo and Tutleim formations (bazhenovites)			Se	Copr, As, Mo, Ag, Sb	Sc, V, Co, Ni, Cu, Zn, Y, Cs, Ba, Eu, Yb, Hf, Pb	B, Tl, Cr, Mn, Fe, Ga, Rb, Sr, Zr, La, Ce, Sm, Tb, Ta, Au	
Lower Eocene. Suzak stage (turanites)		Se, Te, Re	Mo, W	Copr, V, Ga, Ge, Sr, Ag, Cd, S, P	Fe, Co, Ni, Cu, Y, Ba, La, Pb	Sc, Ti, Cr, Mn, Zn	
Middle and Upper Eocene. Kum Hozizon ets. Kum Horizon ets. (turanites).		Se, Te		Copr, S, Sr, Mo, Ag	V, Fe, Co, Ni, Cu, Ga, Y, Ba, La, Pb	P, Ti, Cr, Mn, Zn, Zr	Ge
Oligocene and Miocene. Maikop series (Caucasites)		Te, Mo	Se	Copr, TR	Ti, P, V, Sr, Ni, Co, Pb, Cu	Cr, Ba	
Miocene. Serafimov Formation	tien - shanites			Bi	Ag, Ba, Sr, Sn, Mo, Nb, Y, Sc, P, Copr	Cu, Zn, Pb, Zr, V, Cr, Ni, Co, Hg, Ga, La, Ce, Ti, Fe, Mn.	
Miocene. Chul - Adyr Formation				Mo, S	Tl, Sr, As, Fe, Copr	Ga, Mn, V, Cu, Ni, Cr, Ba	
Miocene - Pliocene			B, Ag	Y	Mn, Ni, V, Ti, Cu, Zr, La, Co, Mo, Ce, Sn, Nb	Ba, Ga, Fe, Cr, Pb, Zn, La	

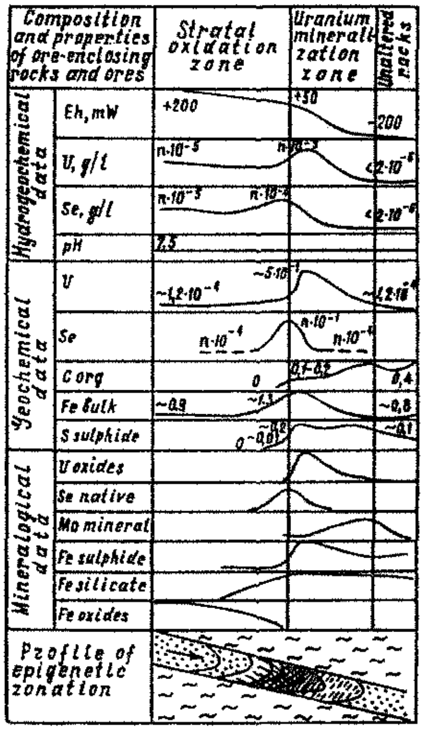

Fig. 4 - Distribution of rare and trace element accumulations in exogenic epigenetic deposits associated with stratal oxidation zones, depending on hydrochemical and geochemical environment (after M.F. Kashirtseva 1970).

1 - ore-enclosing rocks; 2 - imprevious strata; 3 - uranium ores: a - rich, b - common; 4 -molybdenum mineralization; 5- selenium mineralization; 6- movement direction of stratal water; redistributing ore concentrations.

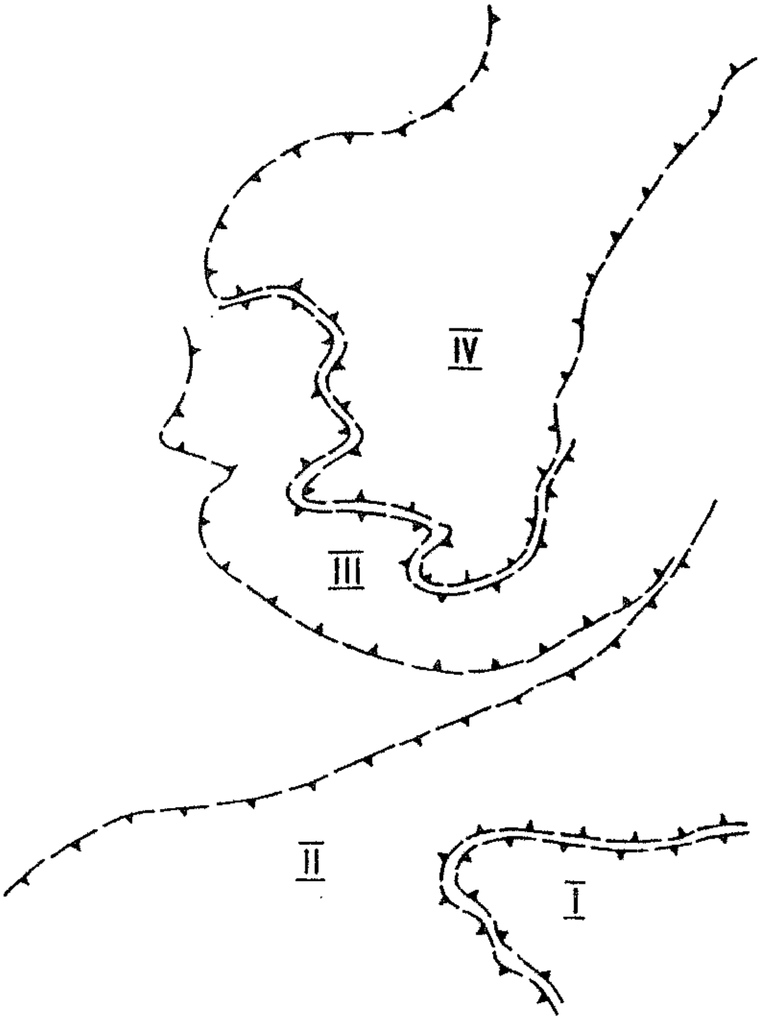

Fig. 5 - Geochemical zonation of the Mesocenozoic mantle in the West Siberian Plate.

I - IV - Geochemical provinces with chalco-lithophile specialization:

I - Altay_sayan orogen;

II - near-orogen belt of the West Siberian Plate, with chalco-siderophile specialization;

III - Tobol-Ket;

IV -West Siberian oil and gas province.

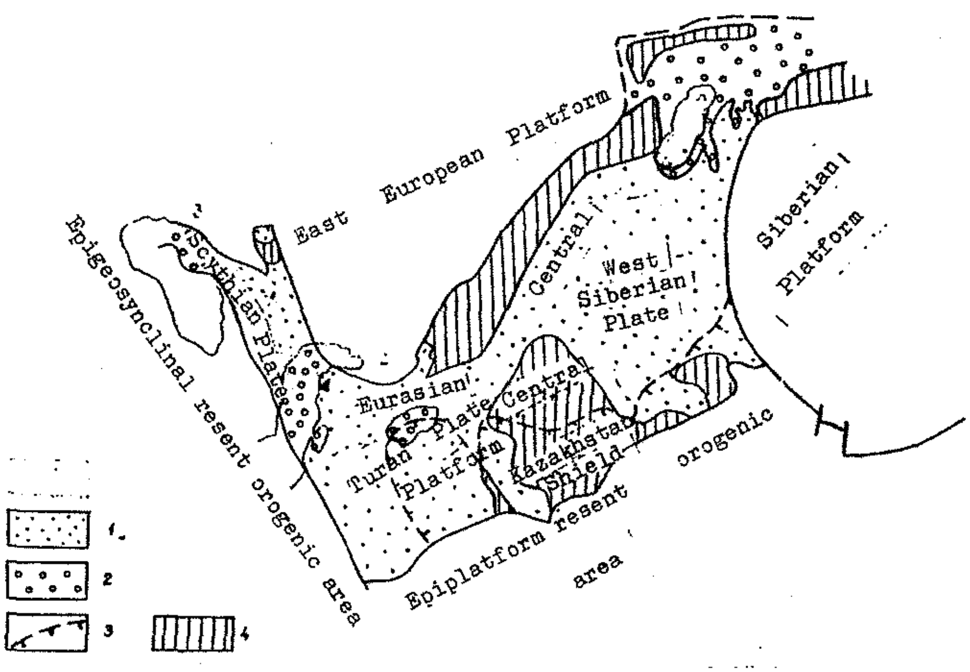

Fig. 1 - Central Eurasian young platform (after R.G. Garetsky 1972, supplement by G.M. Shor). 1-2 - occurence area of platform mantle: 1 - on continents; 2 - under sea level; 3 - external boundary of hydrogeological structures; 4 - basement rock exposures.

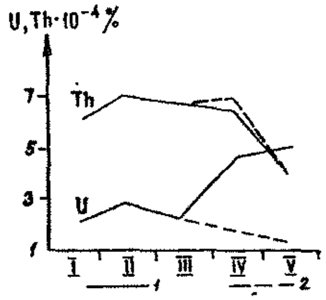

Fig. 2 - Mean uranium and thorium contents for paleogeographic settings of the Turan Plate. 1 - rocks with elevated uranium content included; 2 - this kind of rocks excluded.
I - IV - paleogegrafic settings: I - lagoon; II - continent; III - coastal pyrt of sea; IV - shallow sea; V - deep sea.

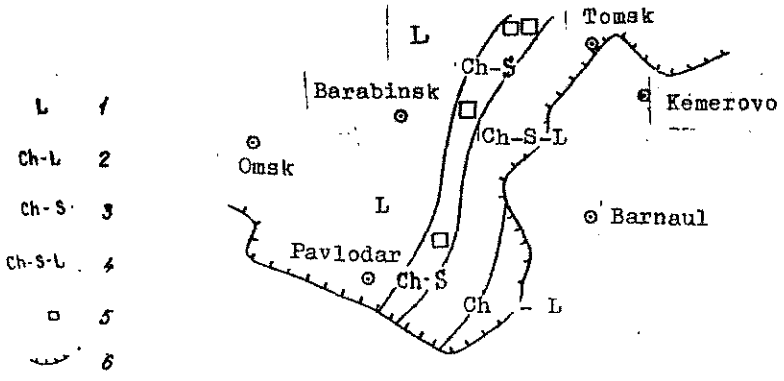

Fig. 3 - Distribution of rare and trace element associations in the Late Cretaceous-Eocene clays of the West Siberian Plate.
Geochemical specialization of rare and trace elements: 1 - L - lithophile; 2 - Ch-L - chalco-lithophile; 3 - Ch-S - chalco-siderophile; 4 - Ch-S-L - chalco-sidero-lithophile, 5 -iron ore mineralization;6 - bondary of occurence of the Late Cretaceous-Eocene clays.

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APPLICATION OF CYANIDATION TO GOLD EXPLORATION IN GLACIATED TERRAIN, BRITISH COLUMBIA, CANADA.

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INTRODUCTION

Gold content of exploration samples is usually determined instrumentally, after fire assay or *aqua regia* digestion, or directly by neutron activation. These methods are all suitable for analysis of assay tonne (approximately 30 g) or smaller samples. However, sampling statistics suggest that, because of the scarcity of gold particles in even anomalous samples, such samples can be too small to give reliable results (Clifton et al, 1969; Nichol et al, 1989).

Subsampling reliability can be improved by analyzing larger samples. Therefore, following Huffman et al (1967), there has been renewed interest in use of cyanidation, a process used for about one hundred years to recover of gold from its ores, on exploration samples (Fletcher and Horsky, 1988). Because gold is extracted from a bulk sample some users, particularly in Australia, refer to this approach as BLEG - Bulk Leach Extractable Gold (Sharpe 1988). However, there is little published data on the effectiveness of cyanidation in extraction of gold from exploration samples. This paper accordingly presents preliminary data on its application to soils and glacial till downice of a gold deposit in southern British Columbia, Canada.

DESCRIPTION OF STUDY AREA

The Nickel Plate Mine, a 2900 tonne-per-day open pit operation in the southern interior of British Columbia, is a gold bearing skarn related to intrusion of Jurassic diorites into limy sediments of the Upper Triassic Nicola Group (Ray et al, 1988). Gold occurs as blebs, generally smaller than 25 μ, associated with arsenopyrite in tabular bodies of garnet-pyroxene skarn.

The mine site is in the subalpine zone (elevation 1700 m) close to the southern limit of the Thompson Plateau. During the last glaciation the Cordilleran ice sheet, moving south-southwest in the vicinity of the mine site, deposited a stony basal till from less than one to several meters in thickness. The region now has an arid climate with warm, dry summers and cold winters. Soils are principally eutric brunisols and orthic gray luvisols with carbonate cemented C horizons.

METHODS

An earlier geochemical survey outlined an anomalous zone, delineated by gold concentrations exceeding 100 ppb in B horizon soils, extending up to 2 km downice of the mine (pers. comm., I. Thomson). Sampling involved hand pitting and collection of 10 kg samples from soil horizons along five lines across the eastern part of the anomalous zone (Fig. 1). Additional till samples were collected in sections along the road that bisects the study area.

Representative subsamples were wet-sieved to obtain the -212 μ fraction for determination of gold by fire assay-atomic absorption. Results were then used to select typical soil profiles for size fraction studies. These involved wet sieving to obtain the -420+212, -212+106, -106+53 and -53 μ fractions followed by preparation of a heavy mineral concentrate (SG >3.3). All size and density fractions were weighed and their gold content determined by fire assay-atomic absorption. Subsamples (30 g) of the -53 μ fraction were treated by cyanidation using a one hour bottle-roll with a 0.25 % cyanide solution. Dissolved gold was then extracted into MIBK-Aliquat 336 and determined by flame atomic absorption. Gold remaining in the residue from cyanidation was determined by fire assay-atomic absorption.

RESULTS AND DISCUSSION

Gold concentrations show a systematic decrease from proximal to distal sites (Fig. 2 and 3). However, results along lines are extremely erratic and show no systematic trends (Figs. 4 and 5). Fifty five duplicate analyses also showed considerable scatter with several points outside the +/- 50 % error limits (Fig. 6). Size distribution studies show that more than 60 % of the gold is finer than -53 μ (Table 1). Most of the remaining gold can be attributed to a few particles, in the -212+53 μ heavy mineral fraction, that probably account for the poor duplicate analyses and erratic along-line results.

Although the total gold content of each size fraction is rather similar, the proportion contributed by the heavy mineral fraction increases from less than 50 % in the -420+212 μ fraction to more than eighty percent in the -106+53 μ fraction (Table 1; Fig. 7). Sibbick (1990) attributes this to glacial abrasion and comminution releasing fine gold from its matrix. By extrapolation, roughly 80 % of the gold in the -53 μ fraction should be present as free gold and thus amenable to extraction by cyanidation.

As predicted about 80 % of the total gold content of the -53 μ fraction is extractable by cyanidation from B and C horizon soils (Table 2; Fig. 8). However, in three of the six profiles studied, appreciably lower proportions of the total gold are extracted from A horizon soils. The A horizon soils contain 1.67 to 5.60% (average 3.46%) organic matter compared to 0.39 to 3.64% (average 1.90%) in the subsoils. Lower and more erratic recovery of gold from A horizons is therefore tentatively attributed to the well-known ability of organic matter to reduce dissolved gold. This is the basis of the carbon-in-pulp process for metallurgical recovery of gold from cyanide solutions.

With respect to exploration, results indicate that fine gold in the subsoil is amenable to cyanidation. Trends from proximal to distal sites are the same as in the fire assay data and local anomaly contrast, taken as the ratio between average gold values at proximal and distal sites, is roughly the same as for total gold content. Cyanidation is thus a viable alternative to fire assay for analysis of the -53 μ fraction of soils in the vicinity of the Nickel Plate Mine provided that A horizon material is avoided.

CONCLUSIONS

Roughly eighty percent of the gold in the -53 μ fraction of subsoils is extracted by cyanidation and anomaly contrast is comparable to that obtained by fire assay-atomic absorption. Recovery of gold from A horizon soils is low.

ACKNOWLEDGMENTS

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Table 1: Average gold content (ppb) and average contribution (%) of different size and density fractions to total gold content (n=7 for proximal and distal sites).

Site	Size fraction (microns)			
Au (ppb)	-420+212	-212+106	-106+53	-53
Proximal	257	339	448	405
Distal	35	53	82	70
Contrast	7.3	6.4	5.5	5.8

Contribution (%)	-420+212		-212+106		-106+53		-53
	L	H	L	H	L	H	L+H
Proximal	4.5	7.4	3.2	9.9	1.9	10.9	62.2
Distal	3.9	0.9	4.6	4.7	2.9	7.4	75.5
Contrast	1.2	8.4	0.7	2.1	0.7	1.5	0.8

L = S.G. < 3.3; H = S.G. > 3.3

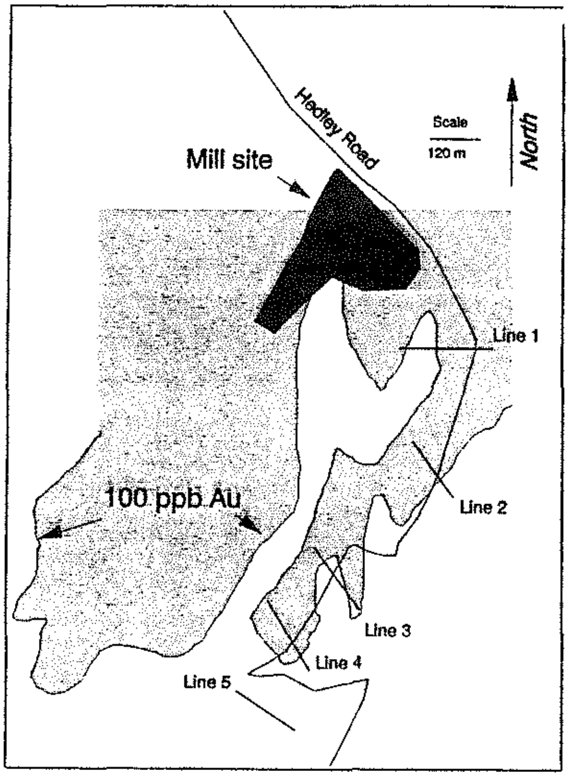
Table 2: Cyanide extractable gold in the -53 micron fraction.

Site/ Horizon	Au (ppb) cyanide	Au (ppb) residue	Au (% extracted)
Proximal			
A	90	45	66.7
B	450	145	75.6
C	350	105	76.9
A	95	145	39.6
B	130	115	53.1
C1	370	115	76.3
C2	510	145	77.9
Intermediate			
A	<15	20	27.3
B	145	35	80.6
C1	145	35	80.6
C2	145	35	80.6
A	145	35	80.6
B	80	15	84.2
C1	175	45	79.5
C2	110	65	62.9
Distal			
A	<15	20	27.3
B	65	15	81.3
C	<15	5	60.0
A	30	5	85.7
B	110	40	73.3
C1	80	15	84.2
C2	130	25	83.9
Averages			
Proximal	362	125	72.0
Distal	80	20	76.5
Contrast	4.6	6.3	0.9

Proximal = Line 1; Intermediate = Line 3;
Distal = Line 4 (Figue 1)

Figure caption

Figure 1	Location of soil traverse lines and the original (100 ppb contour) geochemical anomaly, Nickel Plate Mine, British Columbia.
Figure 2	Variation of gold content of soil horizons from Line 1 to Line 5. Data for all horizons except the LFH is for analysis of the -212 μ fraction. Error bars are one standard deviation.
Figure 3	Variation of gold content in the -212 μ fraction of till along the Hedley Road.
Figure 4	Gold content of soil horizons along Line 1. All data except LFH horizon based on analysis of -212 μ fraction.
Figure 5	Gold content of soil horizons along Line 4. All data except LFH horizon based on analysis of -212 μ fraction.
Figure 6	Duplicate gold determinations on the -212 μ fraction.
Figure 7	Contribution (%) of the heavy mineral fraction (SG > 3.3) to the total gold content of each size fraction.
Figure 8	Cyanide extractable versus total gold content for -53 μ fraction of soils.



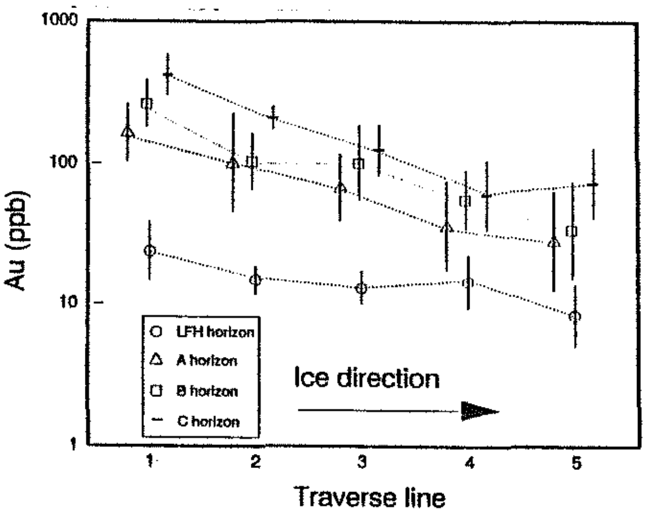


Figure 2.

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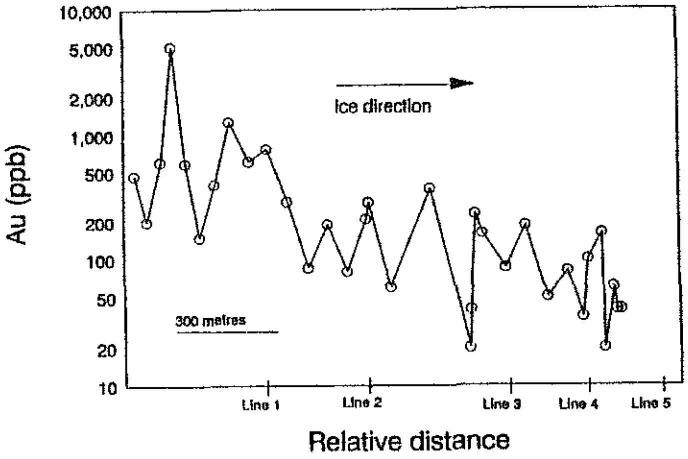

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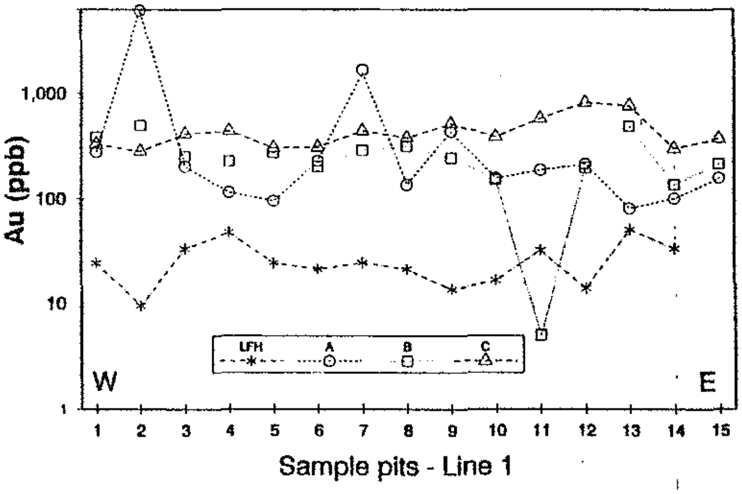

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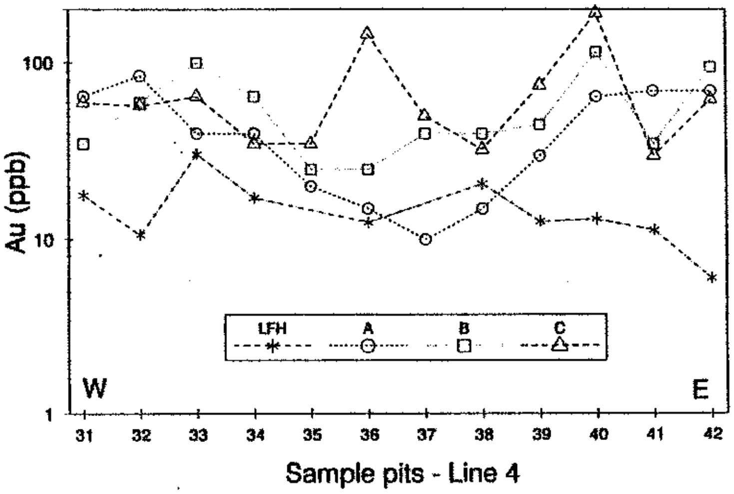

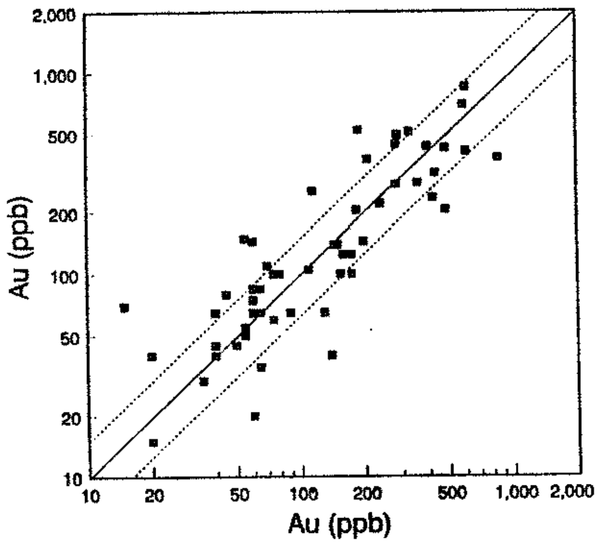

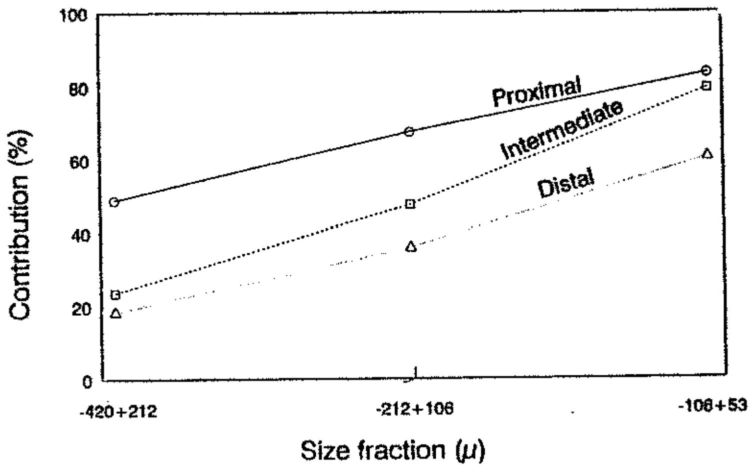

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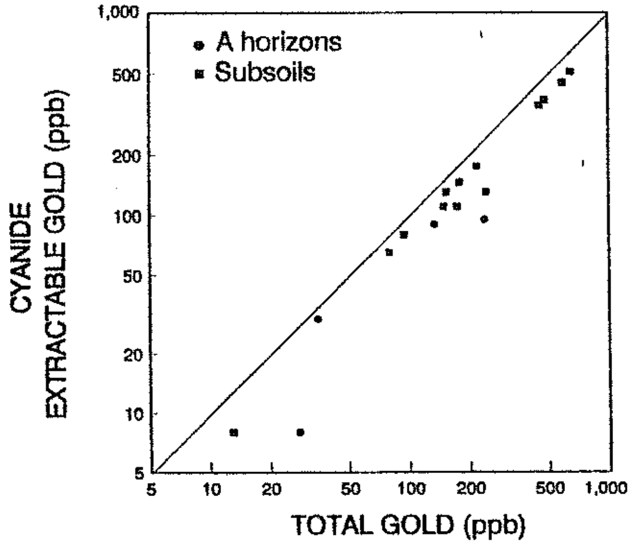

GEOCHEMICAL MAPPING OF RARE-METAL ORE KNOTS OF MOUNTAIN-STEPPE REGIONS IN MONGOLIAN ALTAI

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The present article concerns the results of investigations, aimed at applying the data of geochemical survey from the stream sediments in geological mapping and mineralization prospecting in the mountain-steppe regions of the Mongolian Altai. Geochemical works were done in two ore regions (the Kyzyl-Tau and Khaldzan-Buregteg). The tungsten and the associated rare-metal mineralization of these regions are related to the granitoid magmatism.

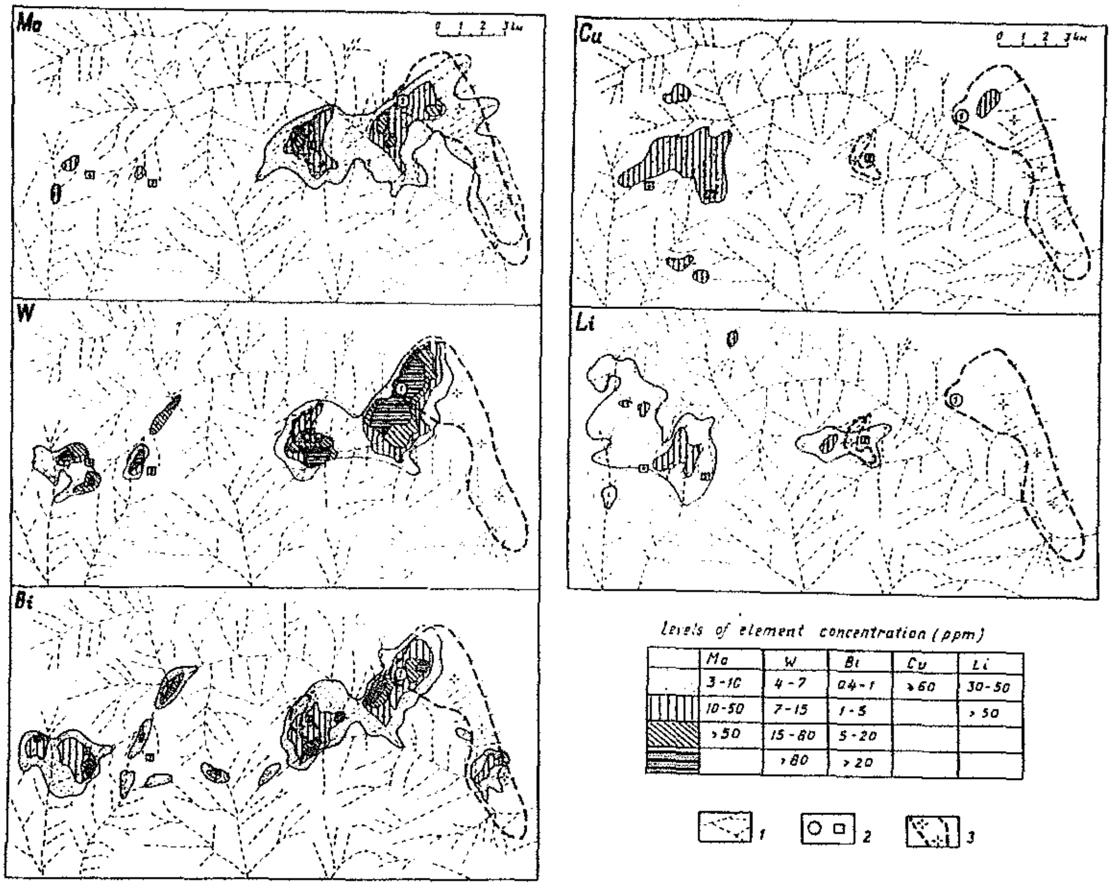
The Kyzyl-Tau ore knot is composed of sand schists and acid volcanics, broken by the Paleozoic Kyzyl-Tau granite and leucogranite intrusion (Fig.1).

Fig.1. GEOLOGICAL SCHEME OF THE KYZYL-TAU ORE KNOT

1 - recent proluvium deposits, gravel, scree debris, sands, loams;
2 - leucogranites of the final phase of the Kyzyl-Tau intrusion: a - fine-grained porphyry-like; b- medium-grained;
3 - amphibole fine-medium-grained porphyraceous granites of the Kyzyl-Tau intrusion;
4 - biotite granites of the main phase of the Kyzyl-Tau intrusion: a - medium-grained porphyraceous; b - coarse-grained;
5 -sphene-biotite granites of the main phase of the Kyzyl-Tau intrusion:a - fine-medium-grained porphyraceous; b - coarse-grained;
6 - micro-grained granites, microgranite-porphyries of the Altai intrusive complex;
7 - ryolites; 8 - dacites; 9 - gabbro-diorites of the Kobda intrusive complex; 10 - sandy schist sequence, aleurolites, sandstones, rare conglomerate interbeds; 11 - ruptive dislocations.

The geochemical survey from the stream sediments was done in the latitudinal strip, which includes the granite Kyzyl-Tau massif on the east and stretches in the western direction for 20 km. The sampling area involves several localities with quartz-tungsten-sulphide mineralization. They are the Kyzyl-Tau deposit and the Burat and Tsinkuk ore occurrences. The area of the survey from the stream sediments totals about 280 sq.km. The survey grid from stream sediments in sampling all ephemeral streams was 500×250-150 m. The samples were collected from the depth of 10-20 cm, the 1,5+ 0,25 mm fraction was analysed. The bedrocks of ore-bearing intrusions, ore formations and the rocks, hosting mineralization were sampled by point specimens as well as by cross sections. The samples were analysed for a wide number of elements via the atomic emission spectrometry (AES) through the evaporation from the electrode channel.

Figure 2 represents the results of geochemical survey from the stream sediments of the **main** indicator. elements in the Kyzyl-Tau ore knot.



Levels of element concentration (ppm)

	Mo	W	Bi	Cu	Li
░	3-10	4-7	0.4-1	>60	30-50
▥	10-50	7-15	1-5		>50
▨	>50	15-80	5-20		
▤		>80	>20		

Fig.2. The fields of W, Mo, Bi, Cu, Li anomalous concentrations of geochemical survey from stream sediments of the Kyzyl-Tau ore knot. 1 - scheme of sampling of ephemeral streams; 2 - ore objects (1 - Kyzyl-Tau, 2 - Burat, 3 - Tsinkuk, 4 - the Western Zone); 3 - outlines of granite massifs.

Geochemical specific features of the granites from the Kyzyl-Tau massif are reflected in the anomalous fields of molibdenum (Fig.2). The massif is mapped by these fields with high precision despite the survey from the stream sediments and semi-quantitative analysis. Alongside with this, anomalous fields of molibdenum possess the evident complicated pattern: on the one hand, they correspond to the heightened background of molibdenum concentrations in granites of the massif and on the other hand they show the areas of hydrothermal molybdenite mineralization. In the northern part of the massif the more intensive haloes of molibdenum correspond to the areas of molybdenite mineralization in the south-western part of Kyzyl-Tau leucigranite dome (molybdenite stockwork) and on the whole area of endo-and-exocontact rocks of the Burat satellite dome. Within the Tsinkuk ore region, molybdenum haloes are insignificant by size and intensity.

In contrast to Mo, anomalous fields of other elements reflect only the areas of hydrothermal mineralization. Intensive tungsten haloes are evident in all regions of wolframite-quartz mineralization, the more extensive haloes occur in endo-exocontact zones of ore-bearing leucogranite domes of the final intrusion phase (Fig.2. the Kyzyl-Tau deposit N1, the Burat ore occurrence N2) but more local haloes are present in the Tsinkuk region (N3) and in its Western Zone (N4).

The above investigations indicated high indicator value of bismuth. Its vast intensive haloes show the regions of wolframite-quartz and molybdenite mineralization more detailed as compared to tungsten haloes. The scheme of bismuth haoes (Fig.2) displays that they outline the ore zone of sublatitudinal strike, which stretches from the Kyzyl-Tau deposit to the Western Zone of Tsinkuk region.

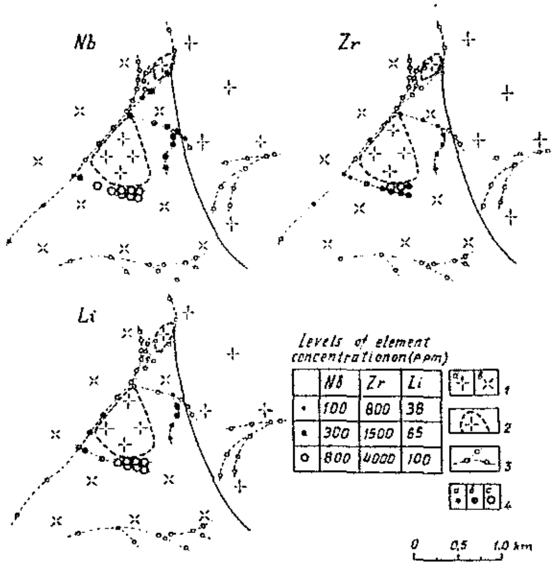
Weak copper anomalies are probably connected with the sulphide component of wolframite-quartz veins, which markedly increases in less eroded Tsinkuk region. The ore veins of this region contains pyrite, chalcopyrite and other sulphides. General overlapping of the copper haloes and vast low-contrast Li anomalies indicates that the last ones correspond to the areas of hydrothermal propylitization-sericitization of acid volcanics and schists, which host ore bodies. It was already mentioned in literatures sources, devoted to the primary dispersion haloes from different hydrothermal deposits.

So, the considered anomalies of the stream sediments indicate the rare-metal speciality of the intrusive Kyzyl-Tau system (Kozlov, Goreglyad, 1989) as well as the connection of mineralization with leucogranite domes of the final phase. The anomalies of granites and the imposed hydrothermal mineralization coincide within these domes. The above data show the vertical zonation of the haloes, which is associated with increase of sulphide mineralization on ore bodies at the removal from the dome roof of the ore-bearing granites. The molybdenite mineralization is associated with the granite contact zone. The analysis of halo zonation shows that the mineralization of Tsinkuk region and its Western Zone is associated with hidden dome prominences of the ore-bearing leucogranites. This conclusion is also confirmed by geochemical data on the fine-middle-grained granites of the dyke from the Tsikuk region. These data are identical to ones on rare-metal leucogranites of the Burat dome.

As for mineralization forecast, the data of the geochemical survey from the stream sediments indicate the promising potentials of the Tsinkuk region (N3) and the Western Zone (N4). Due to low erosion of the ore bodies from these occurrences, the hiddenn mineralization, which is similar by scale to the Kyzyl-Tau deposit, may be supposed here.

Thus, the geochemical survey from the stream sediments in the ore Kyzyl-Tau region may be applied not only for prospecting but also for geological mapping. So, the results of the survey show, that in bad outcropping it may applied in mapping not only the rare-metal granites, but also the fields of acid effusive rocks and sand-schist ones, which are different by heightened concentrations of Mo, Sn, Pb and Ti, Cr, Co, Zn correspondingly.

The fitness of geochemical survey from the stream sediments for geological mapping of granitoids is confirmed by the results of the works on the Khaldzan-Buregteg massif, which locates in the central part of the Western Mongolia (Fig.3).



	Nb	Zr	Li
•	100	800	38
●	300	1500	65
○	800	4000	100

Fig.3. GEOLOGICAL SCHEME OF THE SOUTHERN OUTCROP OF THE KHALDZAN-BUREGTEG MASSIF

1 - alkaline granites (a) nordmarkites (b)
2 - rare-metal alkaline granites;
3 - sampling scheme of proluvium deposits;
4 - levels of anomalous concentrations.

The massif which mainly contains alkaline granosyenites-nordmarkites was discovered and studied by the joint Soviet-Mongolian geological expedition of the USSR Acad.Sci. and the Mongolian Acad.Sci. (Kovalenko et al.,1989). A small (0,85 sq.km.) intrusive body of the alkaline rare-metal granites, possessing abundant niobium-rare-earth-zirconium mineralization (pyrochlore, fluorine carbonates of rare earths, elpidite, hyttensite) occurs within this massif. Elpidite and hyttensite form rocks. Due to the specific features of the mineral paragenesis, the alkaline granites do not produce zirconium placer. Therefore, the investigations of the character of stream sediment anomalies, which are related to these massifs, are interesting. So, the standard geochemical survey from the stream sediments (scale 1:50 000) with sampling the channel stream sediments of the well developed dry valleys and their large tributaries, was done within the nordmarkite massif on the area of 30 sq.km.

Figure 3 demonstrates, that the alkaline rare-metal granites are distinct among the background nordmarkite field by the high anomalous concentrations of Zr, Nb, Hf, Ce, La, Li, Y in the samples of the channel stream sediments, which are located within the massif and near its exocontacts. So, the rare-metal granites are appropriately mapped by the points with anomalous concentrations of the above elements.

Thus, the above examples indicate, that the the dispersion flows of the temporary torrents are extremely shortened and they maximally preserve geochemical specific features of bed rocks and mineralization. Due to this, the geochemical survey from the stream sediments possess the high sensitivity and show appropriately the ore objects as well as the geological boundaries of the rock fields, which are marked by the heightened concentrations of the typomorphic elements (rare-metal granites, ultramafic rocks, etc.). It permits the geological survey from the stream sediments to be applied for large scale geological mapping.

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GEOCHEMICAL FEATURES OF PROSPECTING AND FORECASTING APPRAISAL OF ORE MINERALIZATION RELATED TO RARE-METAL GRANITES

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At the present time it is stated that rare-metal ore mineralization of the considered type is spatially and genetically related only to the definite geochemical type of leucogranites, that is rare-metal plumasite granites /RPG/ /Tauson, 1977/. These granites are studied in details over the different regions of the world /Tichendorf, 1970, 1973, 1977: Aubert, 1971; Lameyre, 1973; Howkes, 1974; Stemprok, 1974, 1979; Burnol, Autran, Bornici, Geffroy, 1974; Moore, McMahon, 1977; Rundkwist, 1977; Koval 1975; Troshin, 1984; Kozlov, 1985, etc./.

Despite some regional compositional variations this geochemical type of the granites is characterized by a series of stable petrographical features distinguishing it from the other types of leucogranites. Thus everywhere these granites are characterized by the molecular excess of Al_2O_3 over $CaO+Na_2O+K_2O$, lowest basility, femicity, Sr and Ba low contents and on the contrary hihgtened settled content of characteristic granitophilous elements.

Geochemical criteria of appraisal of the potencial ore content of leucogranites are generally established. The levels of mutual concentration in the rock of a definite set of characteristic guide elements including Li, Rb, F, Sr and Ba are considered to be such criteria. Based on this proposal using the system of three-dimensional diagrams /in Li+Rb, F, Sr+Ba coordinates/ the perspectives of ore content in leucogranites are considered for many regions /Kozlov, 1985/. But practically especially turning to the large-scale levels of investigations some problems arise in successfull application of the criteria. First of all the most geochemical criteria are of different values and the observed type of granites are characterized by extremely large facial variations resulted in the considerable redistribution of the material. Thus degased facies of orebearing granites are often practically similar in the content of such common guide elements as Li and F not only to the complexes of low ore content but to the ore free ones as well. And what is much in the late differentiates of the latter some concentrations of the elements are observed. More over recently it is stated that the hightened levels of Li and F concentrations are not always the indicators of ore productivity of RPG, since together with Li-F type the ore-bearing RPG with low content of the elements up to the clark lower ones are widespread. The later are presentad by low fluoric and poor lithium varieties of ore-bearing RG of muscovite-albite composition with the wide spectrum of selectively developed rare-metal mineralization: Sn-Ta /Abu-Dabbab, Egypt; Zabaikalie/; Be-W, Be-Ta, Ta-W-Sn /Primorie, Zabaikalie, Mongolia/.

The problem of prospecting and forecasting appraisal of ore mineralization related to RG consists of the wide range of aspects the most important of which are:

1. To reveal the most reliable and analytically simple indicators of geochemical typification of leucogranites with distinguishing of RPG type showing the potencial rare-metal mineralization. Within Phanerozoic midland mobile zones where they are most widespread and among abundant series of polygenic granitoids /differentiates of ultrametamorphogenic and basaltoid series, polygenic granitoids of calc-alkali series/ RPG type is distinguished with diffilculties only after a complex of geochemical studies is carried out.

2. To establish geochemical criteria of ore productivity of the different types of ore-bearing RG. This problem is the most actual one for revealing poor lithium and low fluoric types of ore-bearing RPG, first of all the muscovite-albite composition. Appearance of the rocks is similar to that of the orefree aplites, albitites of endocontact facies of granites. A certain geochemical criteria of ore mineralization are absent.

3. To carry out the methods of revision of the superdome aureoles for appraisal of ore productivity of nonderoofing domes and revealing ore-bearing exocontact metasomatites.

4. To solve the problem of express and sensitive analytical base for a series of characteristic ore and indicator elements not only in laboratories but in natural conditions as well.

Geochemical preconditions

The basis for the considered variants of the prospecting and forecasting appraisal methods of rare-metal ore mineralization retated to RG serves the geochemical developments obtained during long-term petrochemical, geochemical and mineralogical studies of intrusive formations of the West branch of Mongolo-Okhotsky folded region where the Mesozoic magmatic processes are completed by productive rare-metal ore genesis. A concept of the presence of correlated system in magma genesis developed during the period of Mesozoic stage of tectonic magmatic atvivization /TMA/ for a given region and resulted in formation of a series of appropriate intrusive complexes and related ore minaralization is considered to be one of the basic concept. RFG origin is related to the final stage of origin of the obtained ore magmatic system chemically represented by the compositional disсret-successive series of the rocks from alkali gabbroids to plumasitic leucogranites. Directivity in the evolution of chemical composition of the systems is confirmed by a common trend of development and by the absence of miscibility gap in compositional fields constructed in factor coordinate space reflecting the main petrogenic processes /fig. 1/. Analysis of the structure of multidimentional analytical data using petrochemical composition plus the content of indicator elements Li, Rb, Sr, F is carried out by the method of main components of R-factor analysis /Syritso, 1989/.

The fact of the presence of unique magmatic system with successive chemical evolution constructs the basis for revealing the geochemical indicators of its development. Investigations show that the leading tracer that is the most reliable and informative indicator of the degree of development of a given intrusive system and the measure of its preparation for ore genesis is considered to be the levels of mutual concentration of only the two elements Rb and Sr in the rocks /Syritso, et al., 1989/. These elements are characterized by the multidirectional tendention of their behaviour in magmatic fractionation processes, by significant contrast of the contents differing up to three orders for Rb and four orders for Sr. They are less than other elements subject to emanation redestribution and analytical studies are not difficult for them. The latter is very important for solving the applied problems. The obtained data allow to recommend the method of Rb-Sr indication for solving some problems: carrying out formational and metallogenetical analysis and thus appraisal of potencial ore content and geochemical typification of granitoids including leucogranites hardly recognized by other methods. Some of these granitoids are perspective for prospecting for rare-metal and tin-tungsten ore mineralizations, estimation of manifestation intensity of postmagmatic metasomatosis processes. Often it can be considered as indirect criterion of the degree of concentration of a series of rare elements.

In coordinates of correlation of the element contents the succession in stages of origin for intrusive formations in TMA zones of the considered region is regularly traced /fig. 1/. Concerning the considered problem the most interesting is the fact that leucogranite compositional fields in all the considered complexes are practically not overlapped. It is important because the types of granites are practically not distinguished by petrochemical data. Geochemical criteria of their distinguishing are not simple. The possibility of correct application of geochemical criteria also fails due to the small time interval less than 100 m.y. of the whole intrusive system origin.

Four fields of biotite leucogranites are distinguished in fig. 2. They have polygenic nature accompanied by principally different ore potencial. The II- field is a critical interchamber differentiate of calc-alkali granitoids /Schkhtaminsky complex/. Ing this region molybdenum and gold associate with it the III field corresponds to leucogranites. According to the composition they are intermediate members in a series of calc-alkali granitoids to RPG /Oldonsky complex/. The rocks of this complex are the model examples of limiting productive granites. This type of granitoids is the most complicated for large-scale prospecting and forecasting appraisal works as they are often marked by appreciable concentration of rare-elements developing the illusion of ore productivity. The IV field represents the compositions of leucogranites of RPG geochemical type. Practically all the rare-metal mineralization of the region /Kukulbeisky, Asakan-shumvolsky complexes/ is related to this type. The V- field includes compositions of granitoids of ultrametamorphogenic nature /Borshevochny complex/ with ore productive potencial of rare-metal mineralization of pegmatite type.

As shown in fig. 2 RPG fields within a series of the considered rocks is characterized by the highest Rb content / 350g/t/ and the lowest one for Sr / 200g/t/. It is most compact one compared to the other fields despite the large area of the considered region and the presence of the different structural formational zones. This confirms the choice reliability of the suggested indicator elements.

Analytical data on Rb and Sr content in the known ore-bearing RPG massifs show the possibility to suggest that concentration levels of Rb 600 g/t and Sr 50 g/t are the guide features on ore productivity. This universal parameters can serve for estimation of ore productivity of RG of the different parageneses from lithionite-amazonite-albite to low fluoric and poor lithium muscovite-albite with varying rare-metal mineralization.

At the same time it should be mentioned that the contents of such traditional guide elements of rare-metal ore genesis as Li and F vary within the wide limits in the different paragenic types of RG. That is why these elements cannot serve as the universal indicator of the ore material concentration. With some approximation they only are considered as indicators for Li-F type tantalum-bearing RG. The studies show that for RG of lithionite-amazonite-albite composition the level of rubidium concentration /but not of lithium and fluoride ones/ is the most reliable indicator of the tantalum content. Statistical treatment of geochemical material for the known RG massifs of the considered type over the world shows that the most intensive and reliable correlation with low value of the dispersion characterizes Ta-Rb bonds exclusively /fig. 3/, being less clear for Ta-Li and Ta-F bonds. For a series of granitoid rocks of the considered region correlation coefficient of the Ta-Rb bond is +0.86, while for RPG sampling is practically equal to unity /0.96/. Ta-Li and Ta-F bonds have 0.73 and 0.68, respectively. The revealed dependence creates the prerequisites for development of indirect method of tantalum concentration estimation upon rubidium content. Determination of the latter is not difficult for analytical methods even in the natural occurrence /Syritso et al., 1988/. Such a possibility exists only for lithionite-amazonite-albite RG type. As it is shown in fig. 4 the correlation of Rb-Ta bond is absent /the C field/. The same applies for ongonites /the B field/.

As it is known the ore mineralization related to RG is limited not only by concentration of the ore material directly within the granite massif. As a rule it has a zonality and it is complex. This results in multistage localization of the morphologically different bodies and their metallogenic specialization. More generally for Li-F Rg type this zonality is the following: orebearing RG dome /Ta-Li/ -- endo-exogreisen deposit /W, Sn, Be/--quartz-ore veins and dykes of the outer areas of superdome zone /Sn, W, Be, Bi/. In the presence of a smaller erosion shear /up to 300-400 m/ the existence of nonderoofing dome is confirmed by the areas of specialized dyke "swarming". Their nature of orebearing complex is confirmed using Rb-Sr indication method /Syritso et al., 1989/. The levels of Rb and Sm mutual concentrations permit to estimate the degree of metasomatic alteration of the rock as well, that often indicate the concentration of ore material /fig. 5/ and thus may be used in sorting out of the ores /Syritso et al., 1989/.

Conclusions

On the basis of the above mentioned the succession of the prospecting works on rare-metal ore mineralization is the following:

1/ Geochemical typification of leucogranites with revealing of RPG and appropriate distinguishing of the perspective massifs on the basis of the proposed Rb-Sr indication method. Successful obtaining of the stage is possible if the different-scale maps in Rb and Sr content coordinates are developed and based preliminary on the data of marker massifs and deposits if the latter are presented on the considered area.

2/ The detailed study of RPG massif that is delimitation of the territory with optimal levels of Rb and Sr concentrations /Rb 600 g/t, Sr 50 g/t/.

3/ For lithionite-amazonite-albite granites preliminary prospecting works on tantalum during expedition can be carried out on the basic of analytical method of indirect tantalum concentration estimation upon rubidium content /Syritso et al., 1988/.

For effecient realization of the above mentioned geochemical developments the corresponding analytical data were established. For the last years the complex problem of express and highly sensitive analytical method of determination of the considered rare and quide elements in laboratories and natural conditions is carried out on the basis of programming complex for X-ray-radiometric and X-ray spectral analysis /Korobeinikova, 1984/. As a whole the considered complex of geochemical and appropriate geophysical developments serve as the basis for construction of the mobile geochemical laboratory equipped by the complex of nuclear geophysical instrumental techniques. In expedition conditions this laboratories can work out the prospecting problems and forecasting appraisal of rare-metal mineralization /Syritso, et al., 1988/.

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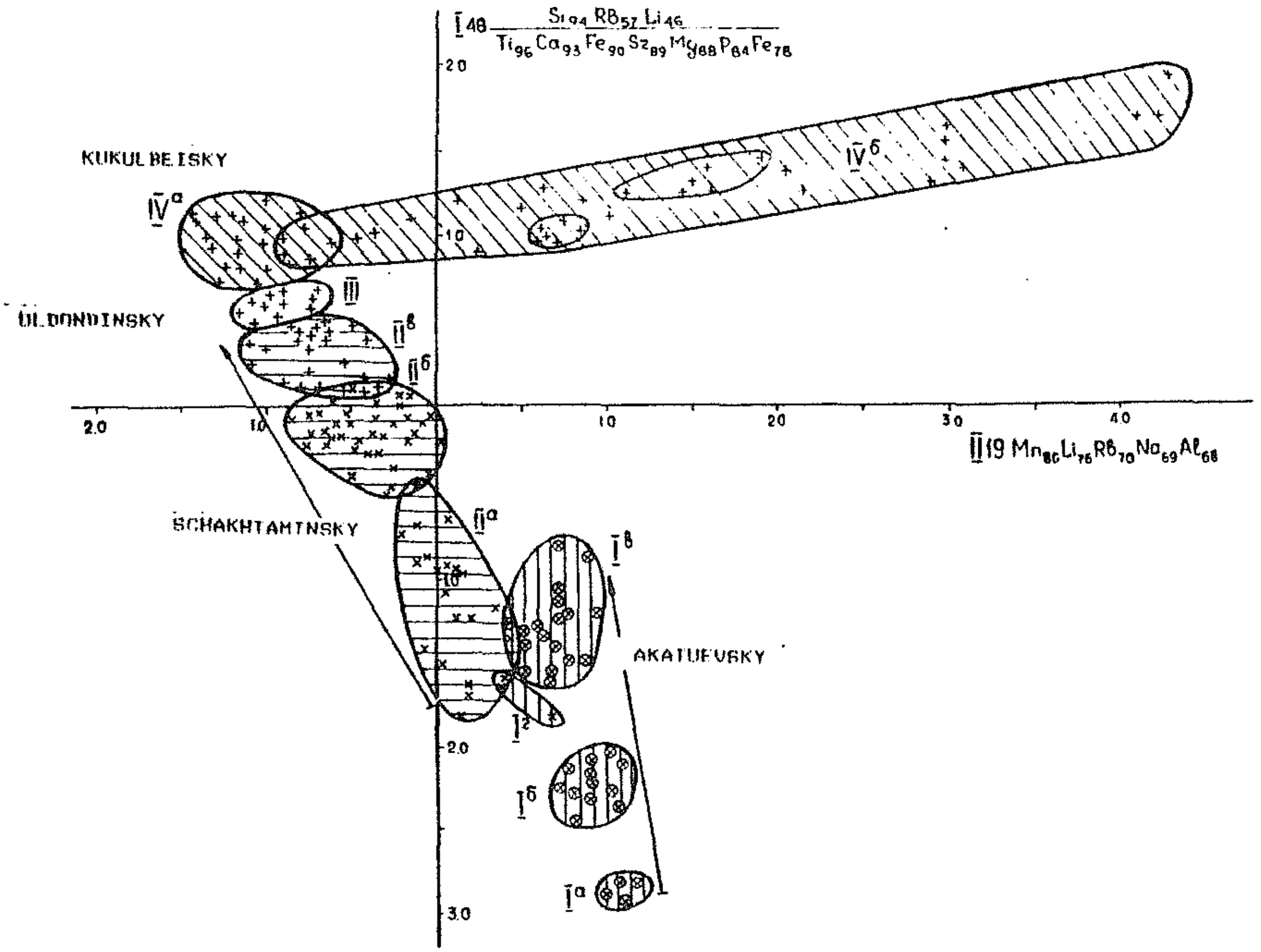

Figure 1. Factor diagramm on composition of the rocks of Mezozoic intrusive system, Eastern Zabaikalie

It is carried out on the basis of 330 petrochemical analyses and more than 1500 determination of rare alkali elements, fluoric and strontium. The field of rocks composition: 1-Akatuevskyj komplex /a-essexites, b-gabbro-monzonites, c-syenites, d-diorites/; II-Schachtaminskyj komplex (a-diorites, b-granodiorites, c-granito-adamelites):III-Aldondynskyj complex - amphibole-biotite granites; IV-Kukulbeiskyj complex (a-biotite leucogranites, b-rare-metal plumasitic leucogranites); V-Sretenskyj complex (a-granosyenites, b-granosyenite-granites, c-biotitic granites).

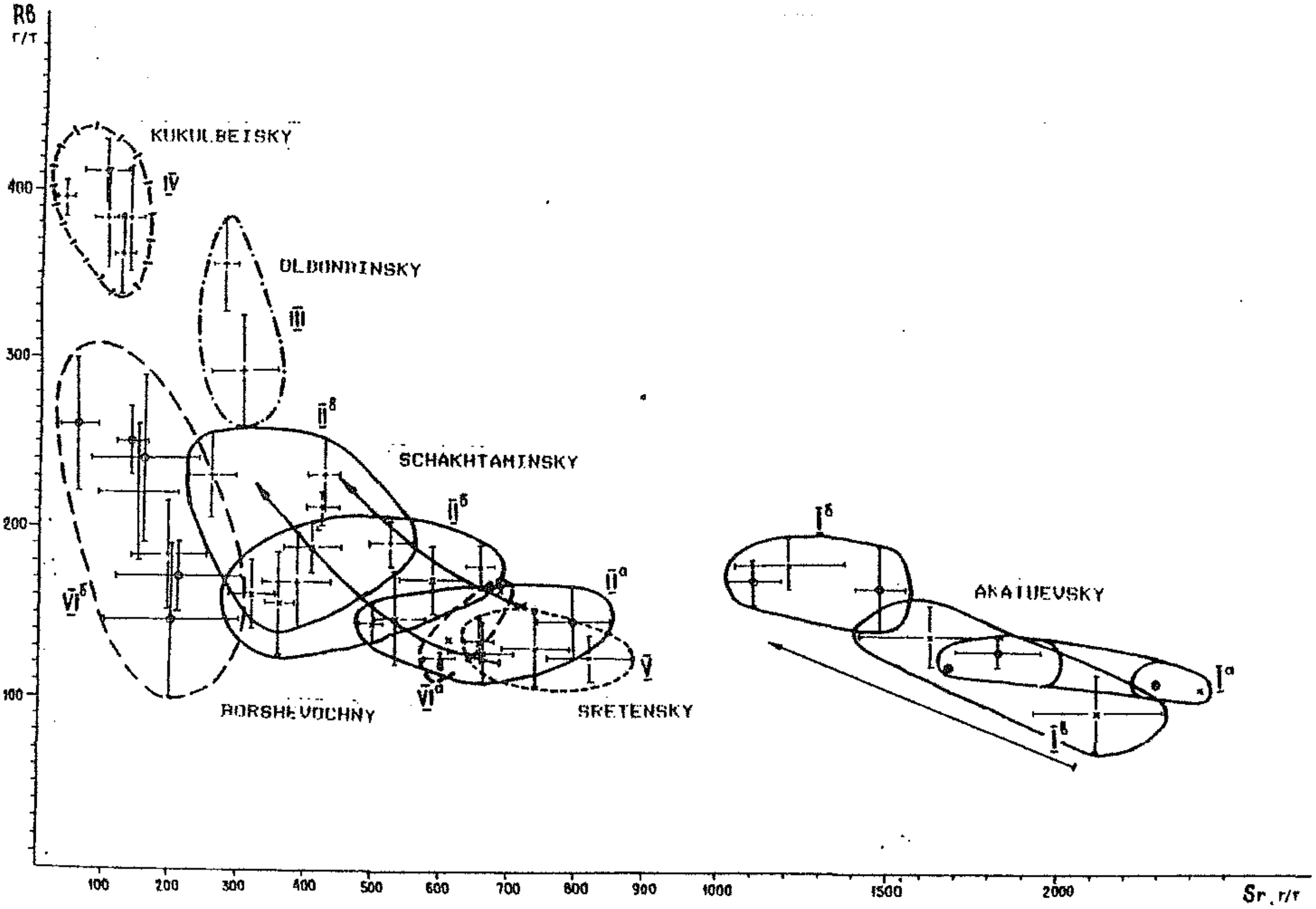

Figure 2. Localization of compositional fields of Mezozoic intrusive complexes, Eastern Zabaikalie, in coordinates of Rb and Sr concentrations.

Compositional fields of the rocks: I-V the same as in fig. 1; VI-Borshevochnyj complex (a-granodiorites, b-biotite granites).

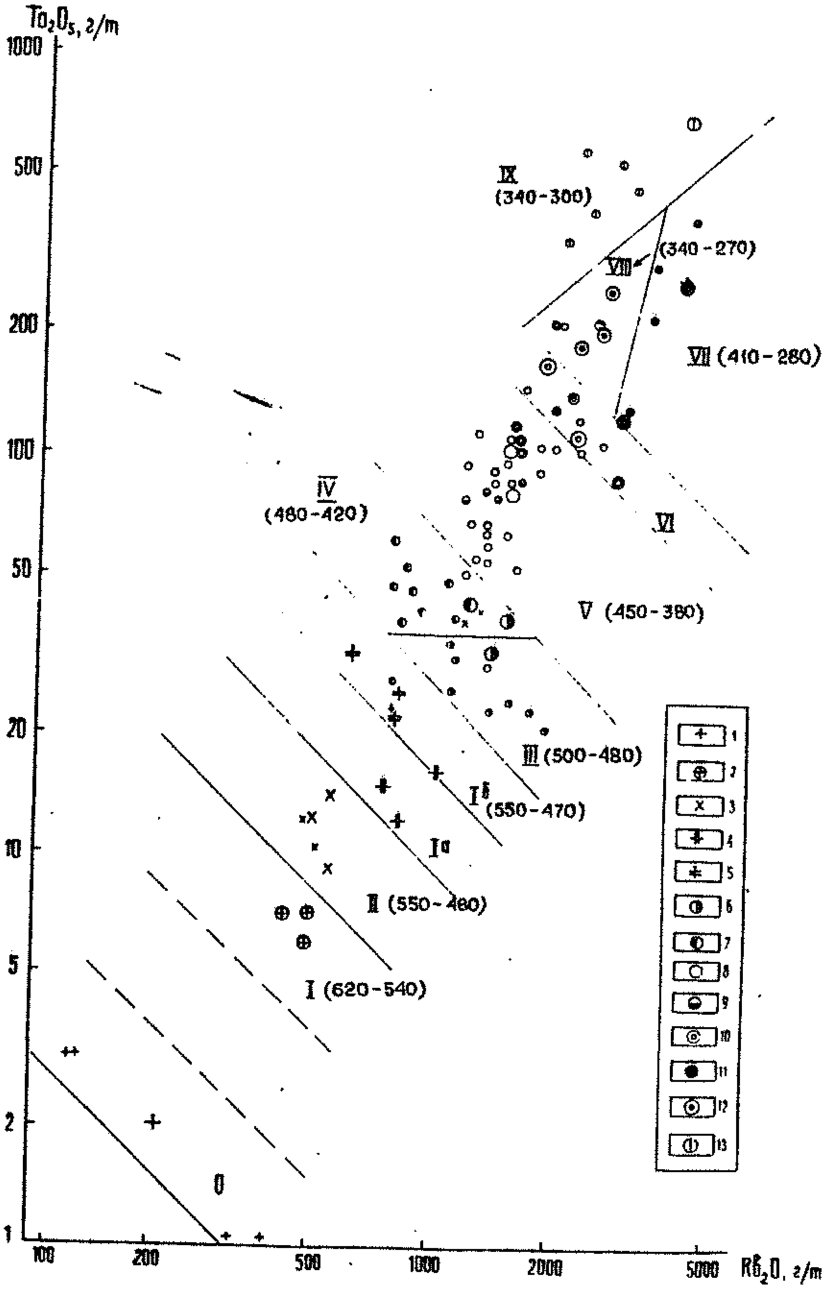

Figure 3. Correlation of Tantalum and Rubidium contants in the vertical section of lithionite-amazonite-albite RG complex.

Roman numerals and symbols correspond to the separate zones of a section from the lower levels (biotite granites - I) to greisen endo-exocontacts) VIII-IX). Temperatures of origin for zone are in parantheses (Syritso et al., 1981).

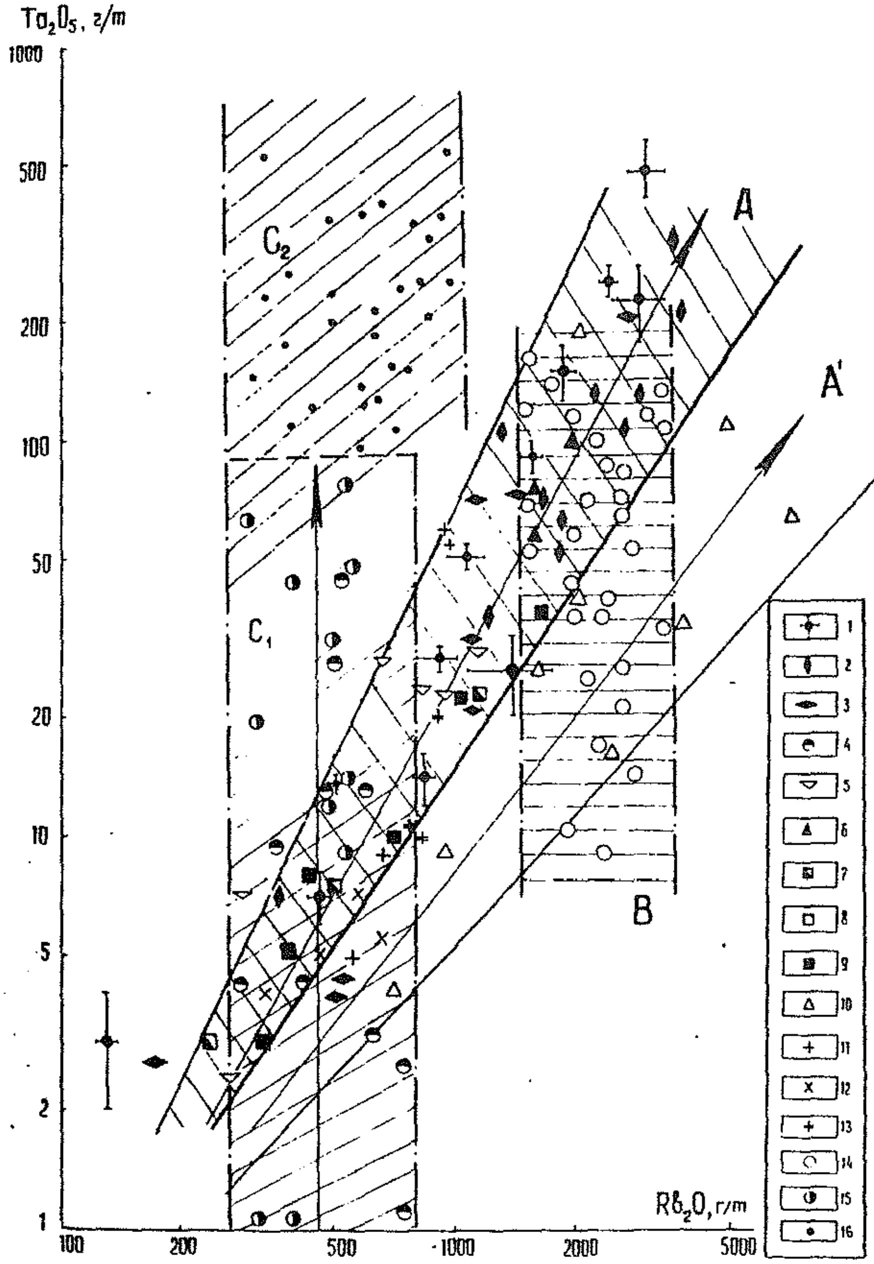

Figure 4. Correlation of Tantalum and Rubidium contents in RG of different types: A-lithionite-amazonite-albite type (Zabaikalie, Kazakhstan, Pamir, Mongolia); A^1-Cínovec; B-ongonites (Mongolia,Zabaikalie); C-muscovite-albite type; C^1-tungsten-bearing (Zabaikalie), C^2- tin-tungsten-bearing (Abbu-Dabbab, Egypt).

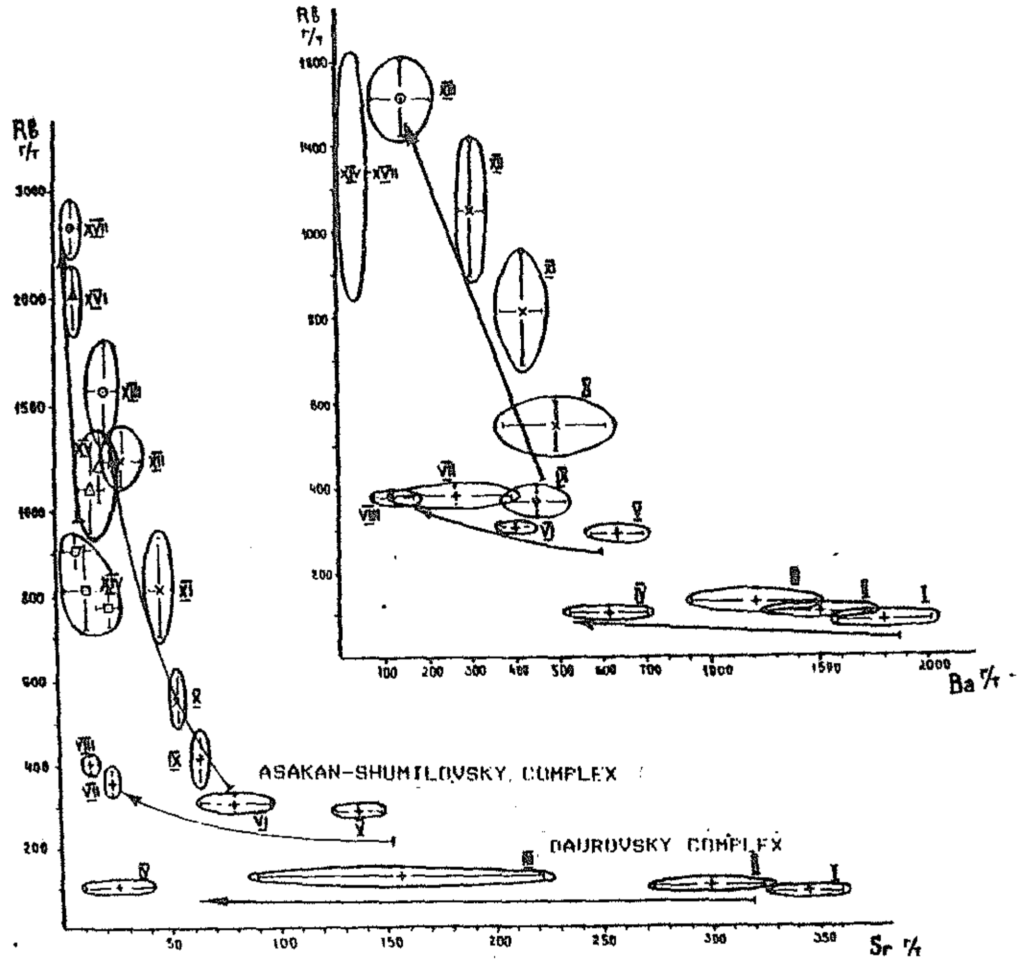

Figure 5. Variations of Rb-Sr and Rb-Ba contents in granites and metasomatites of Asakan-Schumilovsky region.

Daursky geosyncline (ore-free) complex: I-IV; Asakan-Schmilovsky activizating ore-bearing complex: V-VIII:greisen. granites and greisens: IX-XIII; phase of ore productive lithium-fluoric granites and greisens: XIV-XVII. Cursors shown the developing trends of intrusive and metasomatic systems.

CRYOGENIC HALOES OF GOLD DEPOSITS IN BALD MOUNTAIN TAIGA LANDSCAPES OF SIBERIA

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Migration and formation of gold haloes in gold-bearing regions of bald mountains-taiga landscapes of cryogenic zone of Siberia are reviewed in the publications by Taisaev /1982, 1983, 1988, 1990/, Taisaev and Plusnin /1984/, Taisaev, Konstantinova /1988/.

The salt haloes are formed in the cryogenic zone within ore fields /Melnikov, Ivanov, Makarov 1988, Taisaev, Konstantinova 1988/, whis is marked by well-pronounced electrochemical oxidation-reduction reactions /Melnikov P.I., Melnikov V.P., Tsarev 1989/ responsible for redistribution of chemical elements and their concentration on geochemical barriers including gold. This is indicated by concentration of gold as a thin films of gold in ice veins of gold ores /Boule 1951/.

We studied the cryogenic haloes of gold-quartz and gold-sulphide deposits. They are located in bald mountains and taiga landscapes of median ranges and high plateaus. The continous permafrost is 200 to 500 m thick. The average annual temperature varies from -5 to -8.5 °C. In dissected median range the cryogenic weathering crusts of crystalline schists and gneisses of the Archean-Proterozoic age produce vast fields of block seas and taluses. The solifluction covers, the products of their cryogenic weathering, are widely spread on high plateaus on the black schist rocks. The watersheds of mountains are covered by lichen and lichen-moss tundra. The lower part of slopes and bottoms of river and glacial valleys are covered by thin forest of larch and birch trees and shrubs combined with marshes.

The gold-quartz sulphide-poor deposits are confined to faults in crystalline schists and gneisses of Archean-Proterozoic. The mechanical Au haloes are derived in the gryogenic zone of desintegration of gold veins with an intense release of coarse gold /size -2.5 to 0.1 mm, Taisaev 1990/ from quartz. Formation of Au haloes is related to oxidation of gold containing sulphides. The sulphide gold horizons are located in black schists of the Vendian and Paleozoic. They show a cryogenic zone of oxidation of sulphate-oxide profile 3 - 5 m thick. Along with major minerals /pyrite, chalcopyrite, pyrrhotine, galena, sphalerite, gold/ this zone contains hydrogaethite, goethite, jarosite, gypsum, melanterite, malachite, azurite/. In winter time, in the cryogenic zone of fissured sulphide ores, the soluble salts of metals with interstitial water are transported to the surface.

An intense frost desintegration of quartz and oxidation of sulphides occur at cryogenic weathering of significantly fissured quartz-gold veins. The veins are often transformed in ice detritus - stone - sand formations. The content of free coarse gold in the active layer above vein outcrops achieves 30 - 50 % of its total amount. The near-surface residual concentration of gold, i.e. eluvial haloe/placer/ takes place where the gold content is 2 - 5 times higher than in primary ores /fig. 1/. The formation of such haloes is related to an active release of free gold in the zone of vein crvogenesis and removal of fine products of weathering, fine and soluble gold. Continuously derived residual eluvial concentrations of gold are the source of alluvial placers with an active cryogenic transfer along the slopes. It should be particularly mentioned a conjugate series of eluvial, slope and alluvial mechanicla haloes and placers. The gold bearing sediments are formed in corriers and flooded glacial lakes. The gold-enriched clay formations, ferous hydroxides and soluble gold of cryogenic zone are readily transferred by supra-permafrost waters.

In bald mountains gold is accumulated in lithophylic lichens growing on gold bearing rocks. The lichens assimilate gold directly from rocks. Its content varies from 1 to 3 ppm.

Snow plays a destructive role in gold quartz deposits and is important for gold migration. The bald mountains are marked by well-prononnced nivelation /snow weathering/ of ore gold zones affected by snow cover under conditions of freezing and melting. In the glacial period, nivation causes formation ofcomies and reveal deposits. Nivation of ore zones is particularly intense near firn basins. It should be noted thet snow erosion is also significant, i.e. fine products of cryogenic weathering of ore are washed out and transported from the slopes in the bottom of correiers. Hg, Zn, Cu, Pb, Ni, Co and Au acumulate in snow in the ore deposits /Jonasson, Allan 1972, Pogrebnyak, Tatyankina, Tolochko 1979/. The snow cover is a peculiar cryogenic barier, concentrating ore elements, of ascending migration from the cryogenic zone of deposits. The elements are supplied into thawing waters from snow. These waters leach gold from an active layer of deposits and their lithological haloes. Thawing waters participate in formation of suffosion haloes. The content of gold in melt-waters of the deposits sudied achieves 0.0x - 0.x ppb. Thus, snow accumulates ore elements, provides the frost weathering of ores from which melting snow waters carry out solid and soluble products of weathering.

On the rock-stream slopes of river valleys and corriers of ore gold deposits the clastic material is transported along cryogenic slopes, the pocesses of mechanical suffosion are widespread /Taisaev 1982/. The boundary of the rocks-stream slope, i.e. the foot /lake/ is regarded as the mechanical barrier forming at a sharp loss of the water flow velocity /fig. 1/.

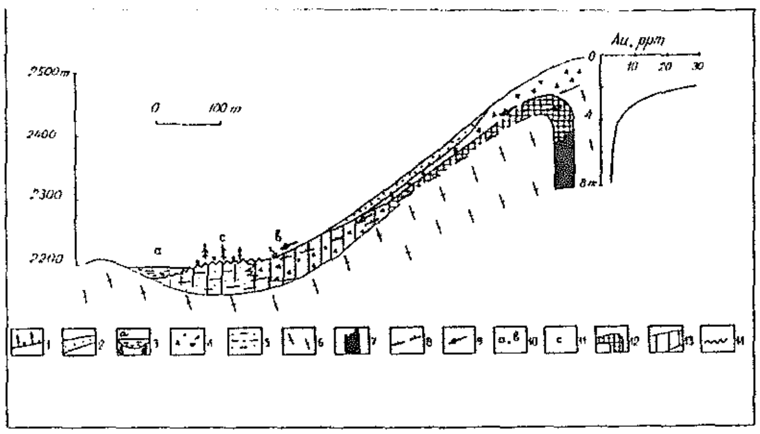

Fig. 1 - Cryogenic haloes of gold-quartz deposit in glacial corries.
1-surface biocenosis; 2-snow cover; 3-corrie or cirque lake /a/ and spring /b/; 4-block slopes and taluses; 5-lake silts; 6-crystalline schists A-PR_2; 7-gold-quartz vein; 8-upper per,afrost boundary; 9-evacuation of fine and soluble gold; 10-water haloes in lake /a/ and springs /b/; 11-biogeoch. haloes; 12-residual halo; 13-gold in lake silts; 14-geoch. barriers.

On the mechanical barrier, the basic amount of suspended ore material is removed from slope waters, the suffosion gold haloes and gold-bearing lacustrine silts are formed. An active suffosion removal of fine material and gold from the veins on the slope intosifies a residual concentration of coarse-grained gold above its exposures. Fine-grained gold is dominant in gold-bearing silts and suffosion haloes /Taisaev, Prokopchuk 1986, 1990/. The mechanical differentiation of gold according to size takes place on the rock-stream slope.

The hydrogeochemical anomalies of quartz-gold deposits related to thawing, rain and supra-permafrost waters, occur at the foot of rock-stream slopes and on the bottom of corriers. The coefficient of water migration of gold /K_{Au}/, estimated from A.I. Perelman /1975/, varies from 50 to 200. Gold belongs to mobile elements in the oxidation medium. The lacustrine silts, suffosion debris and overlying soils possess salt anomalies of Fe, Cu, Zn, Pb and Au. The latter are easily revealed by application of artificial sorbents and in plants.

The salt gold haloes are characteristic of soils nad of an active layer of the cryogenic zone of gold-sulphide ores. They are formed at oxidation of gold-bearing sulphides. The content of gold in water achieves 0.0x - 0.x ppb. The coefficient of water migration /K_{Au}/ varies from 100 to 400. The water anomalies of gold are the indicators of gold-bearing zones for 12 - 15 km. The salt haloes of gold of buried mineralization are found in plants. In places of solifluction cover development the ore zones are reflected by the gold anomalies /0.0X - 0.X ppm/ in lichen /Taisaev, Konstantinova 1988, fig. 2/.

The soluble forms of gold are related to the biogenic and sorption accumulation of gold. The vegetation of bald mountain-taiga zone actively obsorbs gold. The coefficient of biological sorbtion of gold /A_{Au}/, calculated from A.I. Perelman /1975/ in bald mountains on the corrier range from 50 to 500 in lichen and moss, from 100 to 1000 in currents, rhododendron, while in subtreeless mountain-taiga in the foot of rock-stream slopes the vary from 20 to 200 in the bark of larches, in the branches of creeping cedar, alders. Such a significant coefficient A_{Au} in the bald mountains and taiga possibly reflects the intensity of cryogenic mobilization and concentration of soluble gold. In ore gold deposits, gold is accumulated in animals /Taisaev 1988/.

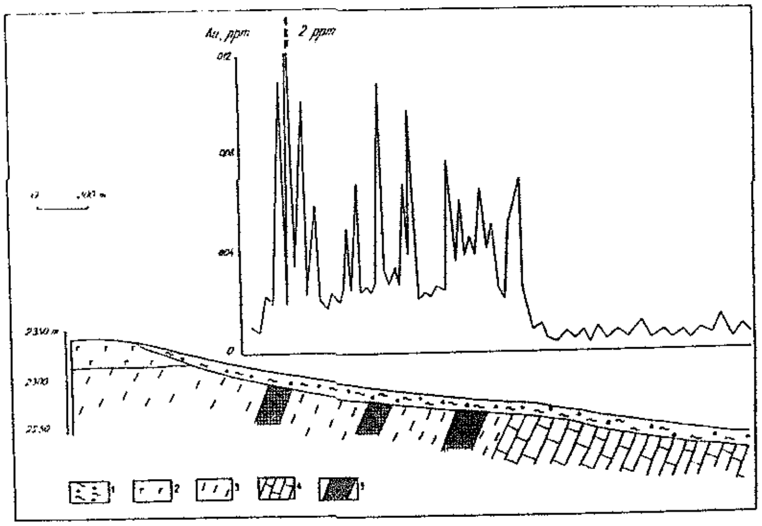

Fig. 2 - Distribution of gold in lichen /reindeer moss/.
1-solifluction Q_{III+IV}; 2-basalts N; 3-metamorphic black schists PZ_1; 4-carbonate series; 5-gold-bearing zones.

Gold is well sorbed by ferrous sediments in marshes, peat bogs, lacustrine silts and suffosion debris. the clarks of concentration vary from 10 to 100. On the boundary of rock-stream slope-peat bogs the oxidized waters with the increased gold content with gley setting The gold reduction is possible. Such gold anomalies /0.0X - 0.X ppm/ occur on the margins of peat bogs conjugate to rock-stream slopes. In the cryogenic zone of sulphide gold ores the gold concentration is significant /0.X - X ppm/ in residual limonite ores and clays. They mostly contain fine gold /3 - 9 /. In the rock-stream slope such gold forms suffosion haloes. Near such deposits the ferruginous sediments of river marshes are enriched in gold /0.0X ppm/.

Thus, in the ore gold fields of bald mountains-taiga landscapes gold is concentrated on the mechanical, sorptive, gley and biogenic barrier.

The lithochemical and biochemical stream of gold /Taisaev 1988/ are derived in the rivers of gold ore deposits /Taisaev 1988/. Gold is supplied in plants from weak aqueous solutions and contrasting lithogeochemical haloes with fine and soluble gold. The concentration of gold in plant ash achieves 0.0X - 0.X ppm. The regions of mountain glaciation are characterized by glacial stream sediments of gold and gold-gearing sediments of flooded water reservoirs /Taisaev 1986/.

CONCLUSIONS.

In the bald mountains-taiga landscapes of dissected median ridges and high plateaus at cryogenic weathering of gold ore deposits there form lithochemical /mechanical and salt/, water and biogeochemical haloes of gold. At gold-quartz vein deposits, when free gold particles being released, the mechanical gold haloes /eluvial, slope, suffosional, gold-bearing lacustrine silts/, stream sediments and placers are formed. On the rock-stream slopes, gold is differentiated according to size. The local contrasting aqueous and biogeochemical haloes of gold occur near these deposits. In formation of mechanical and aqueous haloes of gold of particular significance is snow /nivation, snow erosion and melting water/.

The salt /lithochemical, water and biogeochemical/ and residual sorptive haloes of gold in limonite ores are derived from sulphide gold deposits. Gold is concentrated on geochemical barriers: mechanical, sorptive, gley and biogenic.

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GEOCHEMICAL MAPPING OF PRIMARY AND SECONDARY SETTINGS IN ORE-BEARING REGIONS

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Since the number of easily discovered deposits noticeably decreased and existing methods of assessment of geochemical anomalies are not effective enough, the theoretical and practical methods for geochemical prospecting in present conditions should consider the features of formation of endogenic and exogenic geochemical fields of concentration (GFC) of the entire ore-magmatic system. They reflect successively developing processes and contain necessary information on their features, trend and scales. The analysis was based on the theory of geochemical fields of concentration and classification formulated by Tauson (1977, 1979, 1983_1, 1983_2, 1988).

The area studied covers the southern part of the Balagychan-Sugoy trough (Northeast, USSR). This is a great magmatogenic intrusive-domal uplift, formed in the Upper Cretaceous, in the place of intersection of deep faults. The geological structure of the region consists of two stages. The lower stage represents the Triassic-Jurassic terrigenous deposits, the upper stage -magmatic formations unites in volcano-plutonic complexes of the Upper Cretaceous age: early diorite-andesite and late rhyolite-granite. The acid effusives, subvolcanic intrusions, nevadite bodies, leucogranites of the Pjostrinsky intrusive massif are referred to the latter.

The ore mineralization is due to pneumatolitic and hydrothermal processes. The first process is responsible for formation of tin-rare-metal mineralization while the second one for formation of numerous zones of dispersed sulphide-polymetallic mineralization, silver-polymetallic and tin-silver polysulphide ores. The endogenic GFC revealed within the intrusive-domal ore-magmatic system from the source of ore substance are paragenetically associated with the chamber of acid magma which produced the rhyolite-granite complex. The subalkaline leucogranites of the Pjostrinsky massif contain Ag, Sn and Pb and to a lesser extent W and Zn. The geochemical specialization is well recognized in biotites of granites. The biotites from coarse-grained leucogranites of the main massif facies are enriched in tin, silver, lead and zinc. Tungsten is present only in biotites of aplite-like granites. High concentrations of lead are common (Table).

Elements	F	Rb	Li	Cs	Be	Ba	Sr	B	Sn	W	Zn	Pb	Ag	Mo
Coarse-grained leucogranites	485	166	30	2	3,2	345	79	60	22	1,2	48	31,5	485	-
Fine-grained leucogranites	1150	197	28	1,5	4,4	160	64	61	3,35	1,2	42	29	185	-
Biotites from leucogranites	10000	280	512	20	2,1	250	51	14	75	6,3	520	150	150	2,1
Aplite-like granites	1600	114	75	5	1,5	466	310	2830	10,1	3,4	41,3	10,1	94	-
Biotites from aplite-like granites	34500	n.d	810	n.d	n.d.	n.d.	n.d.	n.d.	8,1	160	150	1000	130	5,1

By origin the endogenic GFC refer to magmatogenic and, like granitoids of the Pjostrinsky massif, they are specialized for silver, tin, lead and to a lesser degree for zinc and tungsten.

The prolonged and multi-staged processes of magmatogenic GFC formation within the framework of the studied ore-magmatic system contributed to the diversity of geochemical fields. Two types of geochemical fields have been distinguished: (i) pneumatolitic and (ii) hydrothermal.

The GFC of pneumatolitic stage are closely connected with formation of tin-rare-metal mineralization in greisens, scarns and stockwork zones.

This type of fields is well studied for stockwork zones. The main typomorphic elements are W, As, Bi and Sn. A well pronounced vertical zonation (Fig.1) is established in their distribution. The frontal parts contain lead and silver, whereas back parts contain copper. Further down, the highly contrasting contents of arsenik and bismuth are replaced by tungsten, molibdenum and tin. The lower ore horisons are characterized by low contrasting associations of these elements, small amounts of copper.

GFC formation of hydrothermal genesis mainly occured at three stages: early sulphide-polymetallic and later tin-silver and silver-polymetallic.

Sulphide-polymetallic GFC are characterized by multi-component composition, low contrasting contents, areal morphology. The poly-formational manner of development of ore mineralization is particularly common. The main typomorphic elements are As, Cu, Zn, Pb, Cd, Co. The high concentrations of silver, bismuth and manganese are likely to be associated with overlapping of later stages of ore mineralization: tin-silver and silver polymetallic.

Tin-silver GFC are also widely developed. The fields have linear morphology, diverse composition, high contrasting contents.The main typomorphic composition is As, Sn, Ag, and Bi (Fig.2). The near-surface zones widely display contrasting polyelement geochemical fields diverse in composition. The main elements are As, Sn, Ag, Bi, Pb, Zn, B. Further to the depth their contrasting contents decrease. The element associations mainly of polymetallic composition start to appear.

Silver-polymetallic GFC developed later relative to tin-silver geochemical fields. They show distinct linear morphology, simpler ore-element composition and clear zonal structure (Fig.3).

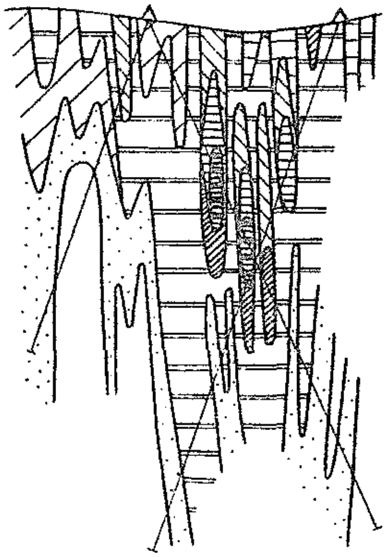
As compared to GFC of tin-silver stage the silver -polymetallic GFC have a local development, high intensity, occupy a somewhat different structural position unconformable with rupture dislocations which control the tin-silver mineralization. The highly contrasting haloes produce Ag and Pb, contrasting-Hg, mid-contrasting As, Mn, Sn, low-contrasting-Zn.

The vertical geochemical zonation is reflected in the distinct replacement at depth of Hg and As associations in super-ore intervals by highly-contrasting associations of Ag and Pb with appearing in the low-ore and below-ore horizons of maximal concentrations of Mn and Zn.

The exogenic geochemical fields in secondary settings are very important for study of GFC of ore-magmatic systems.

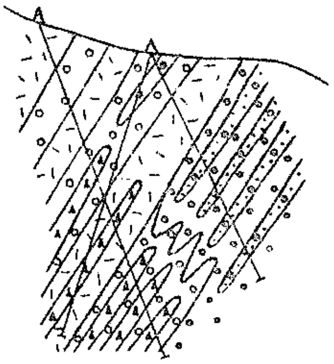
The surveys from secondary lithochemical haloes revealed tin- rare-metal, sulphide-polymetallic and silver-polymetallic GFC. The poly-element geochemical map provides the notion on the composition and structure of secondary haloes.The exogenic zonation found from secondary haloesis a reflection of endogenic zonation found from the primary haloes. This may be well exemplified by the ore zones of silver-polymetallic deposit (Fig.4). On the background of low-contrasting halo of the deposit ($\frac{Pb}{6} - \frac{Mn}{4} - \frac{Ag}{3}$) is well traced, along the strike of ore zones in the direction from the weakly eroded to deeply eroded zones there is a regular replacement of geochemical associations of elements: 1 ore zone - $\frac{Ag}{200}$ $\frac{Pb}{60}$ $\frac{As}{10}$ $\frac{Hg}{6}$ II- $\frac{Ag}{100}$ $\frac{Pb}{40}$ $\frac{Mn}{10}$ III-IV - $\frac{Ag}{80}$ $\frac{Pb}{30}$ $\frac{Mn}{20}$ $\frac{Zn}{5}$ V - $\frac{Zn}{45}$ $\frac{Pb}{30}$ $\frac{Ag}{30}$ $\frac{Mn}{20}$. The high concentrations of silver are replaced by low, the lead contents decrease, arsenik and mercury are replaced by manganese and zinc.

Comparison of secondary lithochemical haloes with endogenic (primary haloes) showed identity of their qualitative composition and regular decrease of contrasting fields in the direction: primary halo-secondary halo.



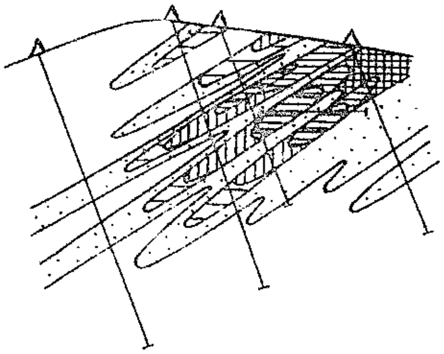
GFC	W	As	Bi	Sn	Cu	Pb	Mo	Ag	Geochemical associations of elements
≡	8000/4000	340/170	1.2/12	38/19	30/3	40/2	8/4	0.25/2.5	**W** **As** Bi Sn Mo
▨	1200/600	240/120	0.7/7	14/7	30/3	40/2	5/2.5	0.2/2	**W** **As** Bi Sn
☰	900/450	350/175	25/250	16/8	25/2.5	100/5	5/2.5	0.4/4	**As** **W** **Bi** Sn Pb Ag
▧	90/45	2000/1000	8/80	6/3	40/2	50/2.5	–	0.2/2	**As** **Bi** W
☰	180/90	440/220	2/20	10/5	30/3	40/2	–	–	As W Bi Sn
☰	30/15	700/350	5/50	10/5	30/3	40/2	–	–	As Bi W Sn
▨	24/12	440/220	1.6/16	9/4.5	35/3.5	–	–	–	As Bi W Sn
⁘	20/10	120/60	0.6/6	12/6	55/5.5	–	–	–	As W Sn Bi Cu
	16/8	60/30	0.6/6	7/3.5	25/2.5	–	–	–	As W Bi Sn

Fig.1. Tungsten deposit. Poly-element endogenic geochemical fields. In Tables (here and further) the numerator shows average element concentrations, denominator shows average values of contrast coefficients of elements.



GFC	Ag	As	Pb	Zn	Cu	Bi	Sn	B	Geochemical associations of elements
⁘	10/100	400/200	400/20	2000/20	80/8	6/60	300/150	250/25	**As** Sn **Ag** **Bi**(B,Pb,Zn,Cu)
●	5/50	300/150	300/15	2000/20	200/20	3/30	200/100	200/20	**As** **Sn** Ag Bi(Zn,Cu,B,Pb)
○	2/20	80/40	400/20	2500/25	200/20	3/30	100/50	150/15	Sn As Bi Zn Pb Cu Ag
▲	0.5/5	20/10	600/30	4000/40	400/40	1/10	20/10	50/5	Zn Cu Pb (As,Sn,Bi,Ag)
⁄	0.5/5	20/10	40/2	300/3	30/3	0.5/5	10/5	30/3	(As, Ag, Sn, Bi)

Fig.2. Tin-silver deposit. Poly-element endogenic geochemical fields.



GFC	Ag	Hg	As	Pb	Zn	Bi	Mn	Geochemical associations of elements
▦	0.6/6	0.3/30	120/60	100/5	–	0.5/5	–	**As** **Hg** (Ag)
☰	8/80	0.8/160	200/100	400/20	–	0.6/6	500/2	**Hg** **As** Ag Pb
≡	80/800	0.2/40	100/50	6000/300	400/4	0.6/6	2000/8	**Ag** **Pb** As Hg (Mn)
▥	3/30	0.04/8	30/15	600/30	1000/10	–	3750/15	Ag Pb Mn As Zn
☰	2/20	–	20/10	500/25	2000/20	0.3/3	2500/10	Pb Zn Ag (Mn,As)
⁘	0.6/6	–	–	80/4	200/2	–	500/2	(Ag, Pb, Mn)

Fig. 3. Silver-plymetallic deposit.Poly-element endogenic geochemical fields.

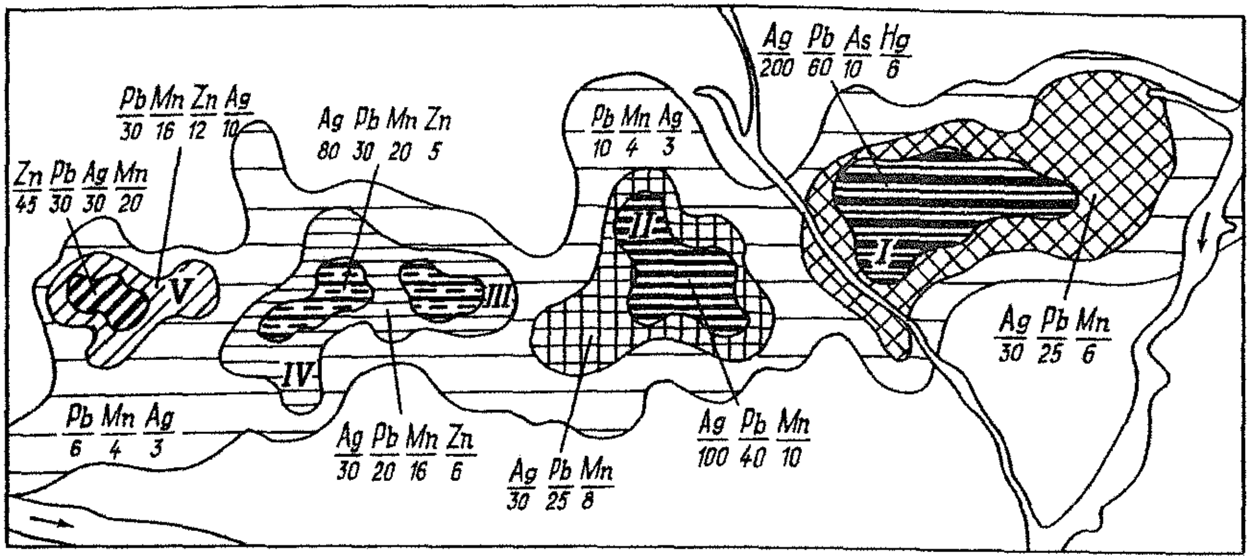


Fig.4. Survey area,(1:10 000 scale) from the secondary lithochemical haloes. Silver-polymetallic deposit. Poly-element exogenic geochemical fields. I-V - numbers of ore zones. Denominator shows average values of contrast coefficients of elements.

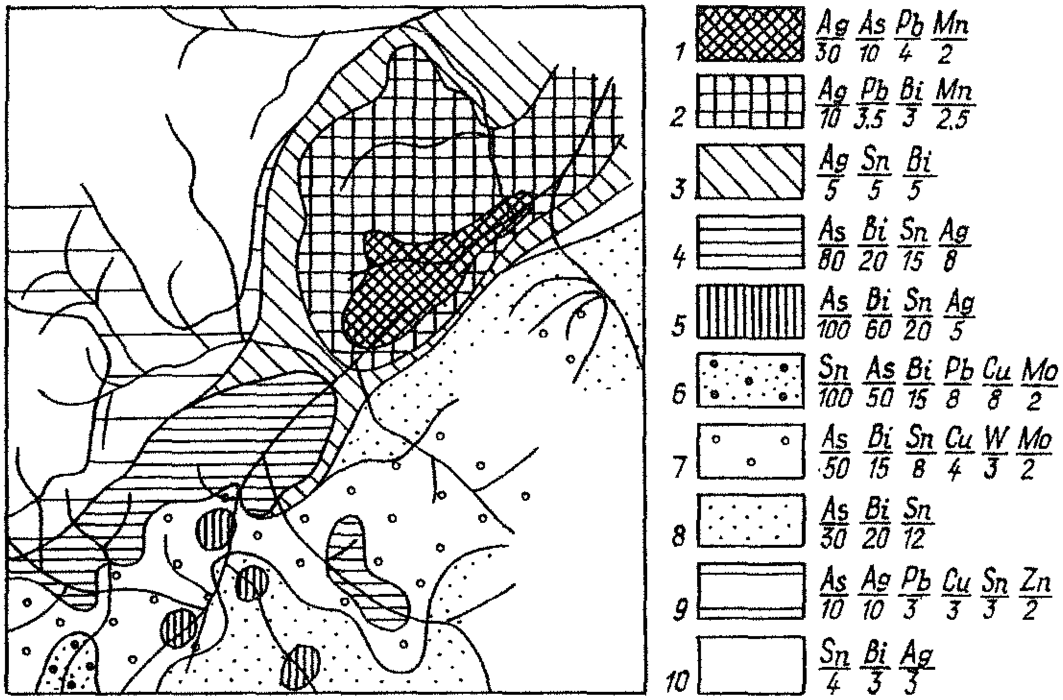


Fig. 5. Survey area (scale 1:50 000) from the lithochemical stream sediments. Poly-element exogenic geochemical fields (1-9): 1-2 - silver-polymetallic, 3-5 - tin-silver 6-8 - tin-rare-metal, 9-10 - zones of the dispersed sulphide mineralization.

The tin-silver mineralization from the lithochemical haloes is not observed, for its areas are mainly overlapped by the loose sediments. The thickness of eluvial-deluvial sequence are several metres. Low information of the secondary lithochemical haloes in case of the overlapped areas is one of weak points of this method. On the zones of cryolitegenesis the prospecting from the secondary lithochemical haloes is unsuccessful, even when the sequence of loose sediments is 0,4-0,5 m.

The four fractions (1-3, 1-0,25, $<$0,25 and $<$1(common)/ of the lithochemical stream sediments were studied. This study indicates, that all established types of mineralization are widely distributed on the investigated area of GFC. The study of 1-0,25 and $<$0,25 fractions provides the more realible data. The polymetals and manganese are mainly concentrated by the 1-0,25 fraction and other elements by the $<$0,25 fraction. The results are given as the multi-element geochemical map (Fig.5).

The low contrast coefficient, the common character of the development, disturbance of quantitative element relationships are the characteristc features of the lithochemical anomalies from the stream sediments. For instance, high silver concentrations are observed in zones with commercial silver-polymetallic mineralization and in zones of the dispersed sulphide-polymetallic mineralization. The same refers to tin. Tin concentration in the stream sediments is a little bit higher as compared to the secondary halo. At the same time simlicity, speed, the possibility to obtain information on ore-formational and metallogenic features of the region are the favourable aspects of the lithochemical survey from the stream sediments.The fractions should be used for the lithochemical survey from the stream sediments. The two fractions: 1-0,25 and 0,25 should be studied for the zone of cryolitegenesis with low and middle mountains.

The data of the complex geochemical investigations show that the composition and structure of the exogenic FGC are in good agreement with the composition of the eroded and drianed objects. The specific features of the zonal development of ore mineralization in most cases are reflected in the structure of exogenic geochemical fields.

Thus, the evident zonal pattern of ore mineralization development, and the associated GFC are observed within the rare-metal intrusive-domal ore-magmatic system. The silver-polymetallic mineralization occupies the upper position relative to sulphide-polymetallic and tin-silver mineralization. In the entire vertical section, the silver-polymetallic GFC are replaced with the depth by the tin-silver ones and then by sulphide-polymetallic GFC. Deep horizons (endo-and-exocontact granitoid zones) are characterized by tin-rare-metal mineralization of the pneumatolitic stage. Geochemical specific features of the granitoid magmas are revealed in ore element composition of GFC of the magmatic stage and is expressed by the markedly heightened concentration levels of Ag, Sn, Pb, to less extent W and is in good agreement with the metalogenic pecularities of the studied area.

The investigations indicated that the zonation is common not only for each deposit (ore type) and the associated GFC but for the entire ore-magmatic system. The zonation pattern of the formation of ore-magmatic system is more evident in connection with G.L. Pospelov's view on the "self-developed" hydrothermal systems. In these systems, the anomalous ore concentrations and therefore the associated geochemical fields are the consequences of the "phase isolation of the enriched jets" within the vast fluid system, which possess the evolution pattern of the development (4-7).

GFC of the ore-magmatic system show the summary pattern of the successively developed process and contain all necessary information on the specific features of trend and scale.

The local GFC of the ore deposits are developed on the backgorund of the integrated regional geochemical field of the ore-magmatic system and are the markers of the supply process and element redistribution. The above features and first of all the evolution-zonal development pattern of the ore mineralization and the associated geochemical fields within the ore-magmatic system, widen the ideas on the theoretical model of the multi-level geochemical field of the natural pbjects, contribute to the prospecting the hidden mineralization. They also permit to evaluate the genetic nature of the distinguished anomalies.

The proposed procedure of geochemical prospecting, based on the complex approach and which consider the conditions of formation of geochemical fields (composition, structure, scale) within the ore-magmatic system on the whole, affect the efficiency of the developing criteria of forecast, prospecting the useful minerals and their assessment to the depth.

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REGIONAL GEOCHEMICAL CLASSIFICATION OF ENDOGENIC GOLD DEPOSITS FROM THE MODE OF SULPHUR, SELENIUM AND TELLURIUM DISTRIBUTION

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Ag, Te and Se are closely associated with gold in the deposits. Further we consider the behaviour of Se, Te and S in volcanics and the associated gold deposits, which is exemplified by four provinces of Siberia. The present article conserns the geochemical specific features of the folded regions and the cratons. Se and Te are deterimined by E.F. Kalistratova /1/, S determination is done by N.V. Lutskaya.

The majority of gold in the world is mined from the deposits, situated in the ancient greenstone belts and among the younger basaltic and other sequences of the basic composition. It indicates that the above mentioned rocks were the source of gold in the deposits. The ratios (Se/Te $\leq$ 1 and Ag/Au $<$ 1) are typical of these deposits. One of the examples of such provinces is the Kuznetski Alatau with the Riphean and the Early-Cambrain tholeiitic volcanism. The gold deposits are located among these rocks. Quartz is predominant in the ore composition, sulphides are scarce and the minerals of tellurium and bismuth are available. Gold is removed from the tholeiites by the waters of different genesis. In the tholeiitic and the associated gold deposits the low Se/Te and Ag/Au ratios are typical (Table 1, Fig. 1,2)

Table

S, Se and Te contents and Te:Se:S in volcanics and ores of some regions, Siberia (S-ppm, Se and Te -ppb, n - sample numbers)

Volcanics	Basic				Intermediate				Acid				Ore
Regions	S	Se	Te	n	S	Se	Te	n	S	Se	Te	n	Te:Se:S
Kuznetski Alatau	137	98	3,4	6					57	82	3,0	7	1:0,72:29000
Eastern Kamchatka and Kuril islands	160	95	1,75	22	180	85	1,85	26	130	55	1,85	21	
The Sredinny ridge Kamchatka	155	74	2,1	16	113	67	2,1	23	115	82	2,3	15	1:20:28000
O.Ch.V.B.													
marginal-continental magmatism	221	89	1,35	10	127	67	2,15	12	47	101	1,2	14	1:41:22000
Island arc magmatism	50	77	1,15	2	120	117	2,0	2					
Siberian platform													
Norilsk region	122	117	1,9	6									1:11:116000

In the Kuril-Kamchatka island arc the average composition of volcanic rocks of the Miocene-Quaternary age is andesite-basaltic. The rocks of the tholeiitic, calc-alkaline and subalkaline volcanic series are available here. They possess the similar S, Se and Te concentrations. Ore occurrence of the gold and gold-silver mineralization are observed in the associations with different series. The heightened Se/Te ratio is typical for the intermediate-basic volcanics as well as for the ore mineralization, as compared to the Kuznetski Alatau.

The gold-bearing copper-nickel sulphide magmatic deposits of Norilsk and Talnahk are associated with the Triassic traps of the Siberian Platform. The ore is marked by high average value of Se/Te = 11/2/ and Ag/Au = 26. The similar ratios are common for the deposits of the Baltic Schield (Se/Te =8, Ag/Au =29), the Kanadian Schield (the Donaldson deposit: Se/Te = 102, Ag/Au =20). The Merenski reef in the Busheweld complex is enriched by Te and Au: Se/Te = 2,2, Ag/Au = 2,4 /13,14, 15/.High Se/Te ratios are observed in the traps of the Siberian Platform (Table 1).

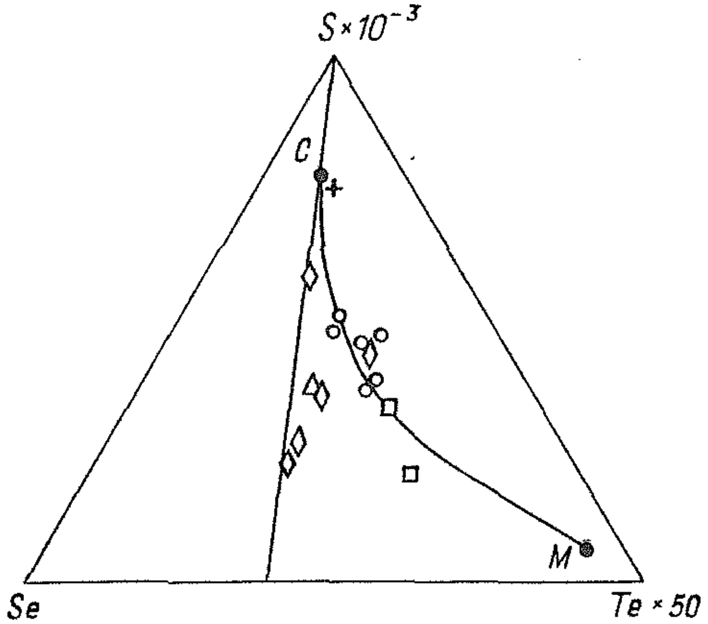

Fig. 1. S-Se-Te diagram of volcanic rock composition from the Kuznetski Alatau (squares), the Kamchatka (circles), Okhotsk-Chukotsk belt (rhombes) and the Norilsk region, the Siberian Platform (triangles). Black points - crust composition (C), and the undifferentiated mantle (M). Cross - the average composition of basalt glasses of the middle-oceanic ridges.

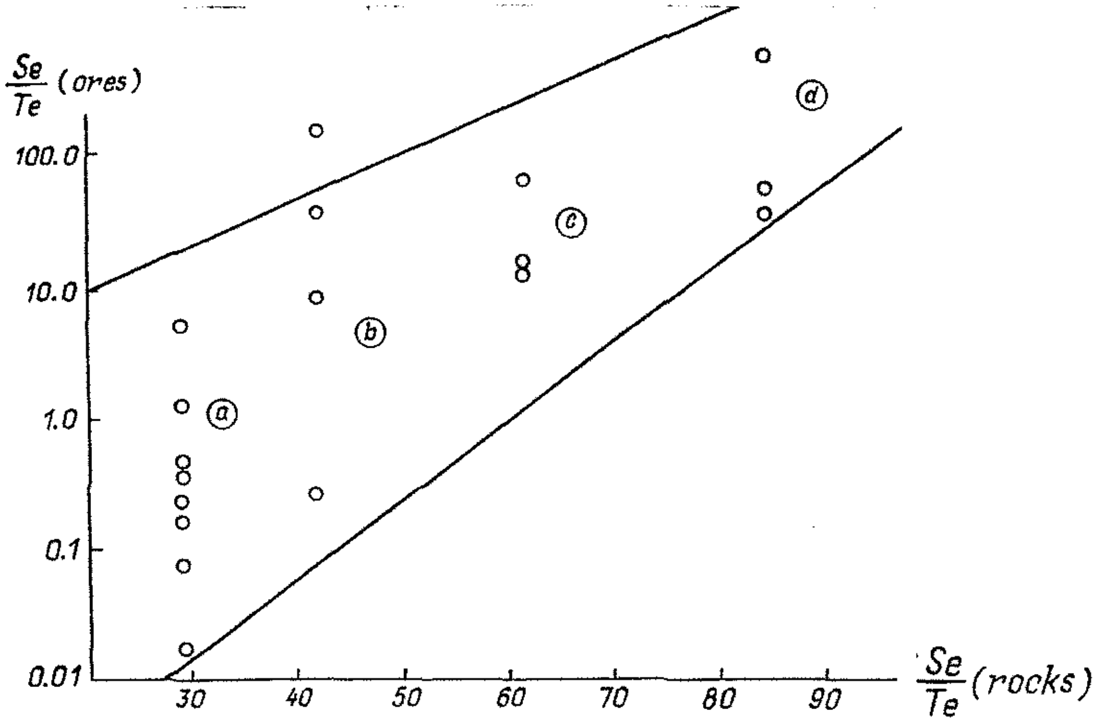

Fig. 2 Correlation of Se/Te values in the gold deposits and in the parent volcanic rocks from the Kuznetski Alatau (a), Kamchatka (b) Siberian platform (Norilsk region) (c) and Okhotsk-Chukotsk belt (d). Each point corresponds to one deposit. From 3 up to 70 samples of the similar ore were analyzed.

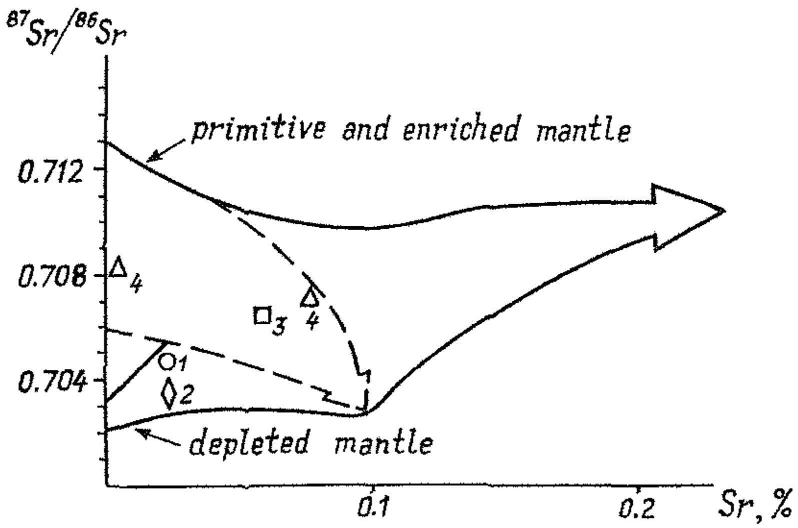

Fig.3. Formation of isotope composition of andesite-basalts in the mantle (according to G.S. Plyusnin et al., /10/

1 - Kuznetski Alatau, 2 - Kamchatka and the Kuril islands, 3 - Norilsk region 4 - Ohkotsk-Chukotsk belt

The gold-silver mineralization is predominant in the Okhotsk-Chukotsk Volcanic Belt (OChVB). In ores Se concentration is several times more as compared to Te concentration /3/.(The Okhotsk part of the belt is considered). This mineralization is usually located among the liparite sequences, which are similar in age, and assocoated with the evolution of the corresponding acid melts/4/. The Late-Cretaceous paleogenic volcanism posses the intermediate and acid composition. It is widely distributed in the Okhotsk-Chukotsk Volcanic Belt (OChVB). Further the high Se/Te ratio is typical of the basalts and andesite-basalts from the ancient Uda-Murgal island arc, which preceeded the Okhotsk-Chukotsk Volcanic belt. According to the data of M.M. Konstantinov /16/ the background Ag/Au ratio in the OChVB liparites changes from 300 up to 1000 and is higher than the clark concentration. It indicates the geochemical specific features of the volcanics and the mantle in this region. The rare gold-telluride mineralization is later and associated with the andesite magmatism /3/. It correlates with low Se/Te ratio in the OChVB volcanics of middle composition. Silver-gold deposits with the heightened Se/Te and Ag/Au ratios are widely distributed along the eastern continental margin of the Pacific Ocean.

Thus, the direct correlation between the values of Se/Te ratios in the gold-bearing ores and the parent volcanics is observed (Fig.2). The Se, Te, S volatility markedly decrease in the series from sulphur to tellurium. The sulphur volatility is singificantly higher as compared to Se and Te volatility /5/. Se and Te seperate in the endogenic processes.It correlates with Ag and Au seperation. Se/Te ratio in the carbonaceous chondrite C1 is 8,1 /6,7/, in the depleted mantle -0,63 /8/, in the undepleted mantle -0,68 /8/, in the earth crust -75 /8/. The Ag/Au ratio also changes. It is equal to 7,5 (meteorite C1) -5,6 (undepleted mantle)- 5,0 (depleted mantle)- 17,1 (earth crust).

On the S-Se-Te diagram (Fig.1) the composition of the above volcanics lies between the two boundaries. One boundary is formed by the curve, which reflect the change of S, Se and Te ratio in the course of forming the crust from the mantle substance according to the simple melting model or degasing. The greater melting degree or degasing, the closer compositions of the crust and the mantle. Another boundary is the line of Se/Te ratio in the earth crust. The displacement of volcanics composition toward the "selenium angle" may indicate their fusion from the undepleted mantle and the influence of the crust substance. It is confirmed by the data on the isotope composition of volcanics. The primary $^{87}Sr/^{86}Sr$ ratio in tholeiitic basalts of the Kuznetski Alatau is 0,7046 ± 0,0008 and in the basalts and andesites from the Kamchatka and the Kuril islands - 0,7033 (0,7029-0,7042) /9/ under the average concentrations of Sr 0,02-0,03%. It corresponds to the volcanic fusion from the substance of the depleted mantle (Fig.3) /10/. The same ratio in the traps from Norilsk is 0,70649 (0,704-0,710, Sr = 0,06%) /11/, in the OChVB basalts and andesites - 0,70654 (0,7052-0,7093, Sr = 0,078%), in the acid effusives of the OChVB -0.7081 ± 0,0003 /12/, Sr ≈0,002%. It indicates the mantle fusion from the substance of the enriched mantle (Fig.3). The change of Se/Te ratio in ores directly correlates with the change of this ratio in the basalts. Therefore, it may indicate that the enrichment of the gold deposits with silver, selenium and tellurium should be connected with geochemical specialization of the mantle sources. At the same time, it is known, that the gold-silver, selenium deposits are mainly epithermal and the gold and gold-telluride are usually mesothermal. It indicates the influence of ore-forming conditions on the ore composition.

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THE EFFECT OF WITHDRAWAL ON GROUNDWATER CHEMISTRY

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It is supposed that thic and highly permeable deep artesian aquifers might be endangered by overdevelopment indicated by decreasing pressure (Erdélyi, Gálfi, 1988). The effect of withdrawal on chemical water quality on the basis of long term variation in the composition of deep groundwater is the objective of this study.

Methods

This study is based on the analyses of drinking water wells during a 15-year period from 1975 to 1989. Groundwater samples from 80-600 m depth were collected, cooled and analysed within 24 hours. Water hardness, chemical oxygen demand (COD), electrical conductivity, alkalinity, iron, manganese, ammonium, nitrate, nitrite, chloride and sulphate ions were determined according to Hungarian Standard Methods. Original static water levels in drinking water wells (m below surface) (Urbancsek, 1963-1986), and static water level from 1975 to 1988 in a test well of 493 m depth were used to characterise withdrawal.

Long-term trends in the different chemical constituents were detected using concentration-time relationship. Linear trends were fitted to concentration-time data. Correlation between chemical components and static water level in the test well were also calculated. Regression analyses with two independent variables - depth and time - were used to evaluate withdrawal in the water flow systems. The statistic significance of all correlation coefficients was tested at the 95 % confidence level.

Location

Pleistocene groundwater from the southern part of the Great Hungarian Plain has been studied. The location of the study area is shown in Fig. 1.

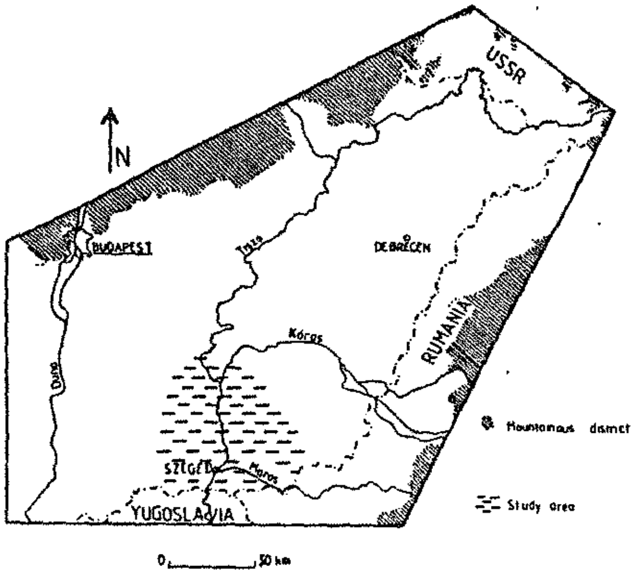

Fig.1. Location of the study area.

During the Quaternary period the River Duna (Danube) deposited material over the western part of the study area. The southeastern part of the study area is filled with the River Maros- the northeastern part with the River Körös deposits. The granulometry of the sediments deposited by the different rivers is different. The strata of the River Duna deposit consist of 50 % highly permeable sand with sand-flour, silt and clay. The sand percentage in the Rivers Maros and Körös deposits is only 30 % (Erdélyi, Gálfi, 1988).

Results

Over the study area there are two main types of chemically distinct groundwater. The two dominant water types are restricted to specific area and regional separation can be established. In the sediment of the higher sand content deposited by the River Duna there is a Ca-Mg bicarbonate type water and in the sediment with lower sand percentage deposited by the Rivers Maros and Körös a Na bicarbonate type water can be found. These two types of water correspond to two groundwater flow systems separated with the help of cluster and principal component analysis of chemical data (Varsányi, 1989). The sand percentage of the sediment (Erdélyi, Gálfi, 1988) and the direction of groundwater flow in the two flow systems is shown in Fig. 2.

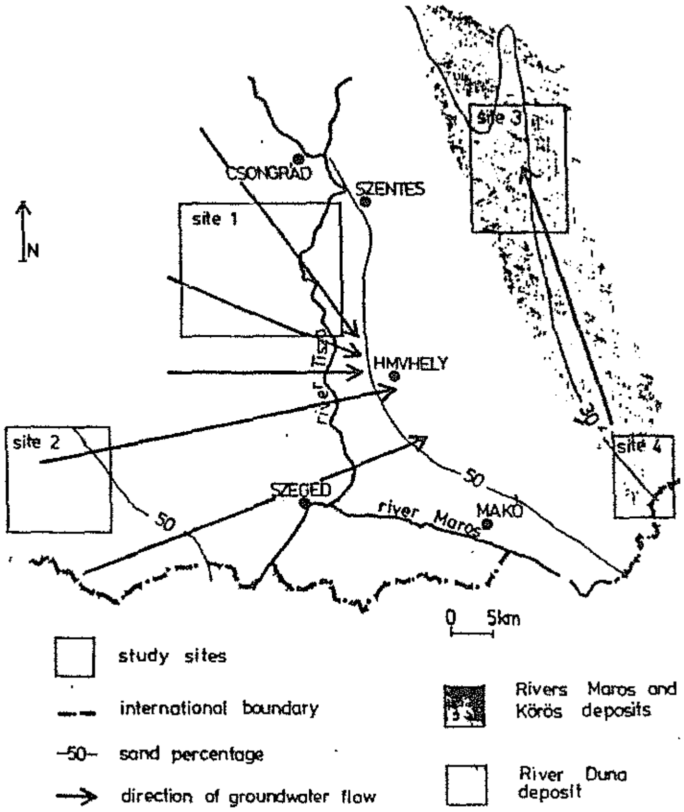

Fig.2. Groundwater flow systems in the River Duna and in the Rivers Maros and Körös deposits.

Study sites containing frequently sampled and closely spaced wells enclosed in boxes.
In the flow system of the River Duna deposit the groundwater chemistry is quite uniform. Only water hardness and sodium concentration changes towards the flow direction. Because the ion exchange hardness decreases and sodium contente increases. In the other flow system groundwater chemistry shows a greater variability. The sand percentage of this sediment is less and water movement is more restricted relating to the flow system in the River Duna deposit. In this zone of very slowly circulating groundwater the residence time is longer, water contains more dissolved material and local factors are reflected by greater variability in groundwater chemistry. The mean values and variances of the chemical components in the two groundwater flow systems are shown in Table 1.

Manganese, nitrate, nitrite and sulphate ions are under the detection limit.

Regression equations with two independent variables were calculated to establish the original static water level depending on time and depth in the two flow systems.

In the River Duna deposit: $Y=8.9-0.21X_1+0.025X_2$

In the Rivers Maros and Körös deposits: $Y=4.1-0.18X_1+0.021X_2$

Where Y is the original static water level (m below surface)

X_1 is the year of drilling

X_2 is the depth (m) of wells.

In the River Duna deposit: number of wells 100, depth of wells 150-600 m, year of drilling 1955-1986

In the Rivers Maros and Körös deposits: number of wells 18, depth of wells 80-450 m, year of drilling 1950-1984

The bivariate correlation coefficients are 0.58 and 0.74, respectively. The depletion of the original static water level is 21 cm/year in the River Duna deposit and 18 cm/year in the Rivers Maros and Körös deposits relating to the surface. The average specific capacity of wells in the two flow systems are 132 l/min/m and 92 l/min/m, respectively, corresponding to the 50 and 30 sand percentage. It is very interesting that, in spite of the different hydrogeological features of the two flow systems, withdrawal causes similar depletion of the original static water level.

Water flow system	Conductivity µs/cm		COD mg/l		Cl^- mg/l		NH_4^+ mg/l		Alkalinity mmol/l		Hardness CaOmg/l		Iron mg/l	
	X	S	X	S	X	S	X	S	X	S	X	S	X	S
River Duna	451	30	2.1	0.3	6	1	0.88	0.32	5.6	0.4	115	12	0.32	0.21
Rivers Maros and Körös	1162	141	7.3	2.6	27	8	1.64	1.30	14.1	1.3	41	16	0.20	0.14

X mean value, S standard deviation

Table 1. Water chemistry in the two groundwater flow systems-means and standard deviations

Two homogeneous groups of wells were chosen to study the temporal variation in chemistry in both groundwater flow systems. Homogenity of variables was tested by Bartlett-test. Water quality trends are shown in Fig. 3 by averaging changes in concentration over a one year period. Moving average technique allows one to compensate for the effect of "noise" produced by short-term variation. The average water quality in the four groups are in Table 2.

Site	N	Conductivity µS/cm	COD mg/l	Cl^- mg/l	NH_4^+ mg/l	Alkalinity mmol/l	Hardness CaOmg/l	Iron mg/l
1	261	453	2.0	6	0.65	5.5	123	0.25
2	107	467	2.0	6	0.55	5.5	121	0.43
3	110	1134	5.7	32	0.96	13.5	30	0.14
4	58	1220	10.3	31	1.56	14.3	56	0.07

N number of samples

Table 2. The average water quality at the four study sites

Regression analyses of data demonstrate the significant and similar increase in water hardness at each site. In the River Duna deposit there is a significant decrease in Cl^- concentration. At sites 2 and 4 COD, at site 4 alkalinity and at site 3 conductivity decreased during the period 1975-1989. Besides these long term trends there are temporal fluctuations in water chemistry.

Increase in water hardness is the only common significant long-term change at the four sites. Initial and final mean values of hardness were calculated from the equations obtained (Table 3).

Site	Water hardness CaOmg/l		Increase in water hardness/year
	1975	1989	
1	113	136	1.5
2	113	130	1.1
3	26	34	0.5
4	50	66	1.1

Table 3. Mean values of water hardness in 1975 and in 1989

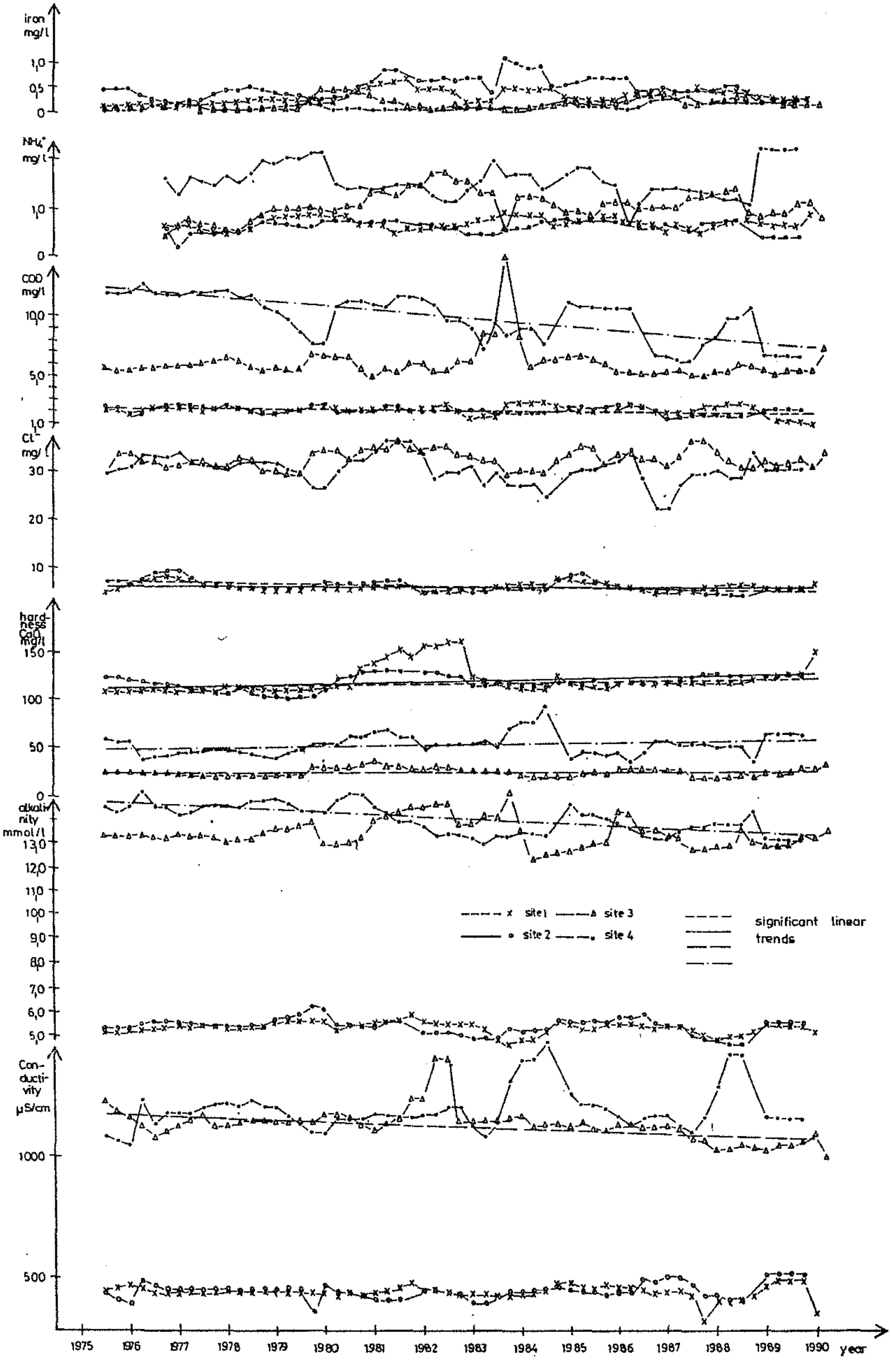

Fig.3. Changes in the chemical components during the period 1975-1989.

Depletion of the original static water level reflects a decrease in pressure in the aquifer. It can be established that there is a connection between pressure decrease and water hardness increase in the fluvial deposits. Further, quantitative evidence for the relationship between hardness and pressure is provided by significant correlation between hardness and static water level in the test well (R_1 -0.25, R_2 -0.58, R_3 -0.34, R_4 -0.60).

There is an evident relation between hardness, alkalinity and conductivity. Over the study area Ca and Mg bicarbonate constitute water hardness. The anions of weak inorganic acids (as bicarbonates) and/or of organic acids (as humates) determinate alkalinity. In the River Duna deposit water contains little organic matter COD 2.0 mg/l) and sodium concentration is 1.5-2.0 mmol/l. Neither the salts of organic acids nor Na bicarbonate play an important role in alkalinity. The average hardness is equivalent to 4.4 mmol/l alkalinity and it comes to 80 % of the total alkaliity. The 1.6 and 1.1 CaOmg/l increase in hardness would correspond to a 0.057 and 0.039 mmol/l increase in alkalinity if organic alkalinity and Na bicarbonate remained constant.

In the River Maros and Körös deposits because of the different hydrogeological features water chemistry represents another type of groundwater. Hardness comes only to 8 and 14 % of the total alkalinity at the sites 3 and 4. COD is 5.7 and 10.3 mg/l, respectively. Organic matter consists of humic substances. Alkalinity is mainly constituted by organic alkalinity and Na bicarbonate (Varsányi, 1985). The 0.5 and 1.1 CaOmg/l increase in hardness would correspond to 0.026 and 0.039 mmol/l increase in alkalinity. According to regression analysis there is no significant increse in alkalinity and in conductivity at the study sites. This suggest that with increasing hardness alkalinity caused by other constituents then Ca and Mg bicarbonate decreases. It is supposed that the primary control on long-term chemical changes is ion exchange. Ca^{2+} and Mg^{2+} are replaced by Na^+ while the concentration of bicarbonate anion, therefore alkalinity, remains unchanged. It is true that in general Ca^{2+} and Mg^{2+} will more easily replace Na^+ than Na^+ will replace Ca^{2+} and Mg^{2+} but there is no single universal replaceability. It depends on the experimental conditions and it is controlled by a considerable number of factors (Grim, 1953). For example if there are not enought free ions mobility is a more important factor than ion charge. The more mobile monovalent cations can be adsorbed in preference to the divalent cations (Hanshaw, 1964). The ions adsorbed on the surface of the clay minerals may affect the adsorbed water. According to Hendricks and co-workers (see in Grim, 1953) Na^+ is not hydrated but Ca^{2+} and Mg^{2+} are hydrated to 6 H_2O when adsorbed by the clay minerals.

This suggests that decreasing pressure promotes ion exchange reaction: the more hydrated Ca^{2+} and Mg^{2+} will be replaced by the less hydrated Na^+. This process - according to the Le Chatelier-Braun theory - acts against pressure depletion.

Conclusions

1. Withdrawal causes a pressure depletion in the aquifers in the southern part of the Great Hungarian Plain.
2. This depletion is similar - 21 cm/year and 18 cm/year - in the two study groundwater flow systems with different hydrogeological features.
3. Chemical components dissolved in groundwater show fluctuation during the period 1975-1989.
4. Water hardness shows a long-term increase at each study site from 1975 to 1989. It is supposed that this water hardness increase is in connection with pressure depletion caused by withdrawal.
5. Considering changes in alkalinity, conductivity and hardness ion exchange may cause the long-term increase in groundwater hardness.

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GETTING THE MOST FROM YOUR DUPLICATES, ESTIMATION OF BIAS AND PRECISION OF ROUTINE AND CONTROL LABORATORY

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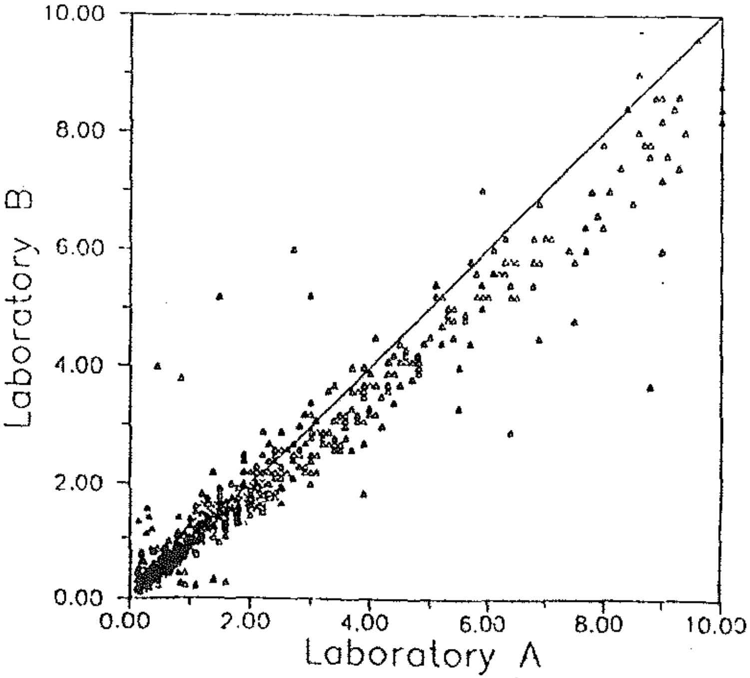
Introduction

Duplication of samples at various stages, like sampling, sample preparation, assaying, is commonly used in a geochemical exploration program to monitor precision and bias in the assays. However, the results of the duplicate assays are generally not fully utilized. This usually does not go further then plotting the duplicates in a scattergram (Figure 1). Quality control can take up to 10 % of the assay cost and the information contained in the duplicates should be fully utilized.
This poster describes a way to estimate the precission of both control and routine lab and the bias between them.
Assays normally cover a range of several orders of magnitude. To compensate for this the ratio of the duplicates was modelled. The model assumes an normal distribution of errors and constant relative bias and standard deviation over the assay range. Given a bias and relative standard deviations the resulting ratio distribution can be calculated and inversely the bias and relative standard deviations can be estimated from a given ratio distribution. This information can then be used to select laboratories for future exploration programs.
A computer program was developed which uses a simplex optimalisation to fit a ratio distribution. This has been applied to the duplicates from a feasibility study and the results show the presence of a large bias and a considerable difference in precision between the two laboratories.

Figure 1: Scattergram Duplicates Au 0 – 10 g/t



The theoretical distribution of the ratio of duplicated samples

The ratio is defined as: $\text{Ratio} = \dfrac{\text{Laboratory A}}{\text{Laboratory B}}$

If two laboratories have the same relative standard deviation then the ratio has a lognormal distribution. The standard deviation of the ratio distribution is √2 relative standard deviation of the laboratories. This result is in concordance with the Gaussian law on the propagation of errors.

If the precision of laboratory B becomes better the ln(ratio) distribution becomes convex and approaches a normal distribution as the precision of laboratory B approaches 0 %(Figure 2). Inversely the ln(ratio) distribution becomes concave as the precision of Laboratory A improves (Figure 3).

A difference in Bias only results in a shift of the curve parallel to the y-axis and does not change the shape of the curve.

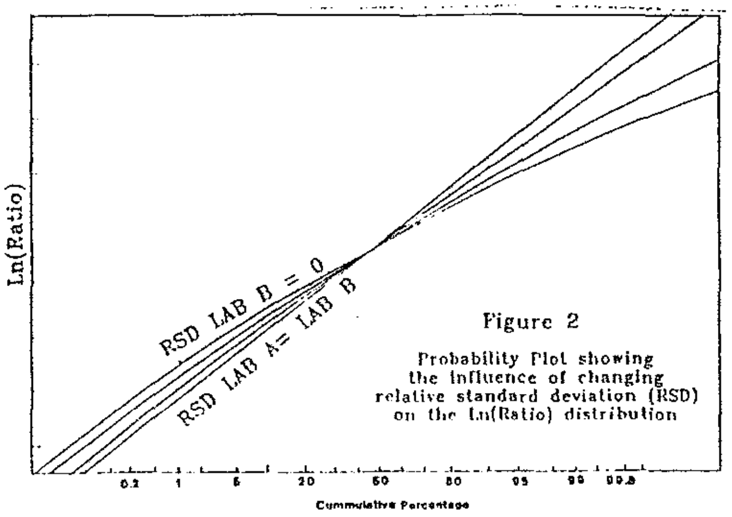


Figure 2

Probability Plot showing the influence of changing relative standard deviation (RSD) on the Ln(Ratio) distribution

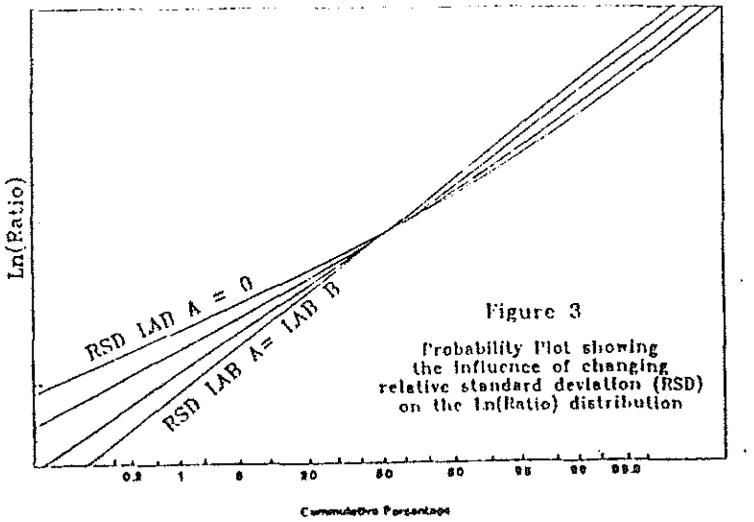


Figure 3

Probability Plot showing the influence of changing relative standard deviation (RSD) on the Ln(Ratio) distribution

Practical Application

During a feasibility study a bias was discovered in the Au assay. More then 400 samples over 1 g/t Au were reassayed (Figure 1).

The ratios distribution was modelled with a computer program. This clearly shows that laboratory B has a better precision then laboratory A (13.8 vs. 4.2 %). Also there is a large bias present, with laboratory A being 10 % higher then Laboratory B. Since laboratory B was the routine lab used during the feasibility study this gave a conservative margin to the calculated grades.

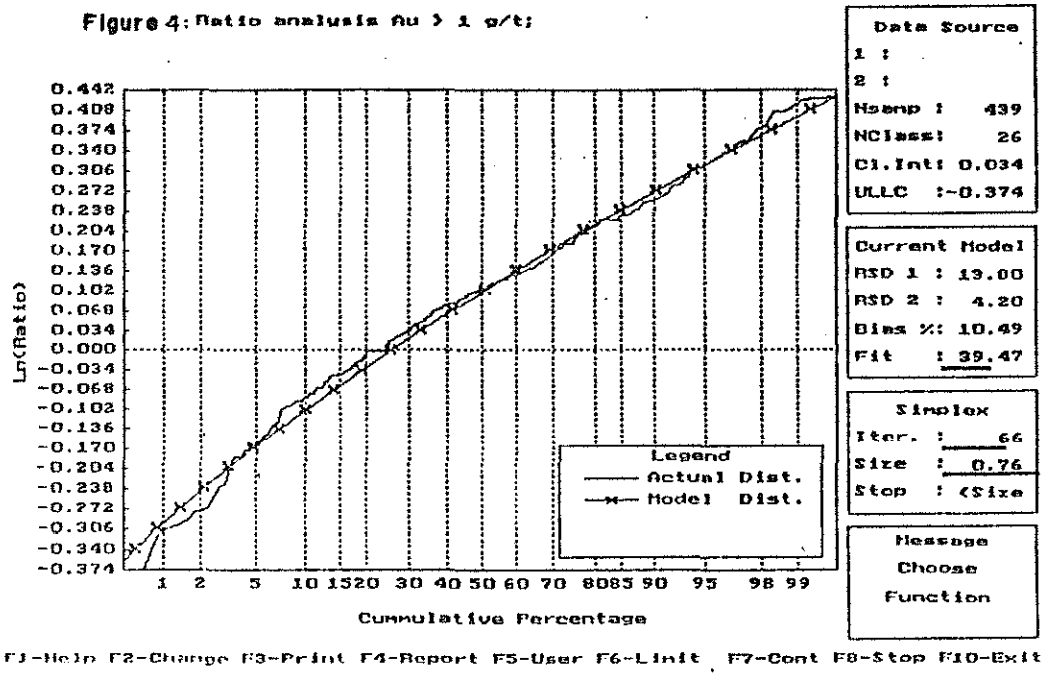


Figure 4: Ratio analysis Au > 1 g/t;

```
Data Source
1 :
2 :
Nsmp :    439
NClass:    26
Cl.Int: 0.034
ULLC  :-0.374

Current Model
RSD 1 : 13.00
RSD 2 :  4.20
Bias %: 10.49
Fit   : 39.47

Simplex
Iter.  :    66
Size   :  0.76
Stop   : <Size

Message
Choose
Function

F1-Help F2-Change F3-Print F4-Report F5-User F6-Limit  F7-Cont F8-Stop F10-Exit
```

Computer Program

A computer program was written in Pascal to facilitate the modelling of the ratio distribution. This program uses a simplex optimization to find the best possible estimates for the relative standard deviation and bias.

The optimizing parameter chosen is similar to a chi^2 statititistic used for testing distributions for normalities:

$$\text{Fit} = \sum_{i=1}^{i=N^{class}} \frac{(model-actual)^2}{model}$$

Conclusions

It is possible to estimate the quality of a laboratory or assay method without sending duplicates to the laboratory.

The developped model makes it possible to calculate the RSD of each laboratory (method) and the bias between the two laboratories.

Computer modeling of mercury ore-forming process.

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The development of geochemical researching shows that eloborating of genetic models of different types of ore-forming process is the base of systematic metallogenetic analyse and forecasting of ore deposit. The model way to the reavealing of combined factors of the formation of the ore deposit allows to put investigation on more elevated level.

The thermodynamic model of rock alteration, mercury transport and metal deposition is suggested. In the study we test the hypothesis that the intensive interaction wall rock-fluid may be a cause for the precipitation of native mercury and cinnabar in different zones of alteration envelope. The model may be described as irreversible thermodynamic system with using the local equilibrium assumption. To test the process of alteration and ore-forming at Terlig-Xaya deposit mass transfer calculations were performed the GIBBS computer programs were used. The method of reaction progress (ξ) presented by Helgeson have been used both for modeling rock alteration and ore precipitation. The hydrothermal model of mercury deposit may be described as H-O-K-Na-Ca-Mg-Al-Si-Fe-C-Cl-S-Hg system at temperature 150°C. The initial composition of hydrothermal fluid have been determined by method which combines, on the one hand, the data of researching of fluid inclusions in minerals, and on the other hand, the reaction progress (ξ) between silicates of wall rock and hydrothermal fluid.

The calculated composition for every stage of evolution of hydrothermal system and physicochemical conditions are given at Tables 1,2. Fig.1 explains the speciation of Hg-complexes, changing type of fluid for quarts+kaolinite paragenesis and forquarts+hydrosilica association accordingly.

1. Pre-ore-forming stage. The formation of quarts+kaolinite paragenesis in inward part of altered volcanic rocks. mH_2S 10^{-6}-10^{-4}; mHg 10^{-5}-10^{-7} mole. Mercury is most likely transported as Hg-Cl complexes in sulfide poor fluids (mH_2S 10^{-5}). Fig.2 explains well why primary mercury is precipitation accordingly to the equation
$2FeCl^{+}+HgCl_4^{2-}+3H_2O \rightarrow Fe_2O_3+ Hg^{\circ}_{(liq)} +6H^{+} +6Cl^{-}$

Transformation Hg(I)→Hg(o) connects with transformation Fe(II) →Fe(III) at the same time. The equilmolal transformation exsists between mercury species and ferreous species. Precipitation of liquid Hg from the saturated by $Hg^{\circ}_{(aq)}$ species fluid occured in responce to oxidation which suggested the presence of hematite.

2. Ore-forming stage. The formation of quarts+hydrosilica phase in inward zones of the alteration envelope, that reflects a second stage of evolution of hydrothermal system. It is characterized by increasing of total sulfur, value of activity of K^{+}ions, pH values and decreasing of mercury content in acid solution. m H_2S 10^{-2}-10^{-1}; mHg 10^{-7}-10^{-6} mole. Precipitation of cinnabar is coupled with the destabilization of mercury complexes and could be written for example, as $Fe_2O_3 + 2Hg(HS)^{\circ}_{2(aq)} + OH^{-} +2H_2S^{\circ} \rightarrow 2FeS_2+ HgS +HSO_4^{-} +2H^{\circ} +2Hg^{\circ}$
Precipitation at Terlig-Xaya in the outward zones occured in responce to oxidation of sulfur connects with reducing of ferreous. The modification of redox state expected as a result of interaction between andesite and acid fluid with due regarding for data of simulations.

Table 1. Calculated fluid composition of ore environment

Formation of metasomatic rocks composition	NaCl	CO_2	$CaCl_2$	KCl	HCl	H_2S	Hg
quarts+kaolinite	2 0	0 1	0 5	0 1	$10^{-4}-10^{-2}$	$10^{-5}-10^{-2}$	$10^{-7}-10^{-4}$
quarts+hydrosilica	2 0	0 1	0 5	0 5	-	$10^{-2}-10^{-1}$	$10^{-7}-10^{-6}$

Table 2. Fluid composition and condition of ore deposition

Temperature range	180°-85°C
Depth range	0- 450 m
Salinity	1 -22 0 eq.NaCl
pH	2,3 -5,6
Σ m H_2S	$10^{-5}-10^{-1}$ mole/kg
Σ m CO_2	0.1 mole/kg

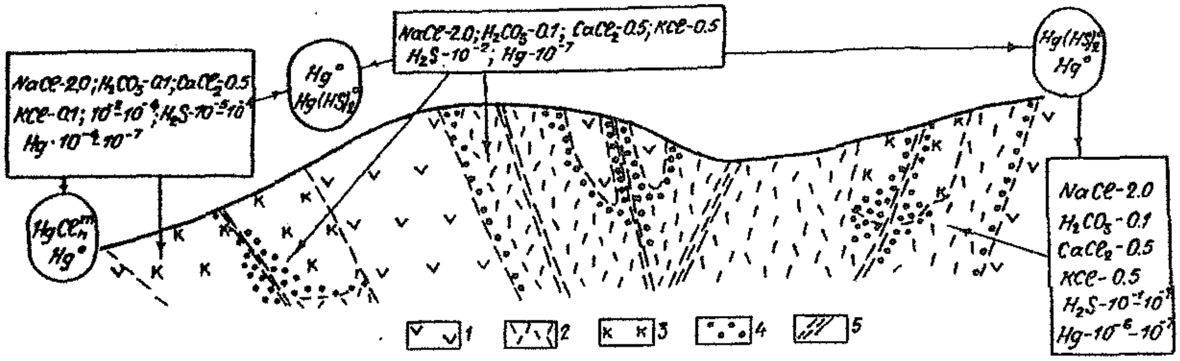


Fig.1. Speciation of Hg-Cl complexes involving in mineral reactions accompaned argillization.

1.- andesite; 2.- quartz-kaolinite; 3.- quartz+hydrosilica; 4.- cinnabar; 5.- tectonic fractures.

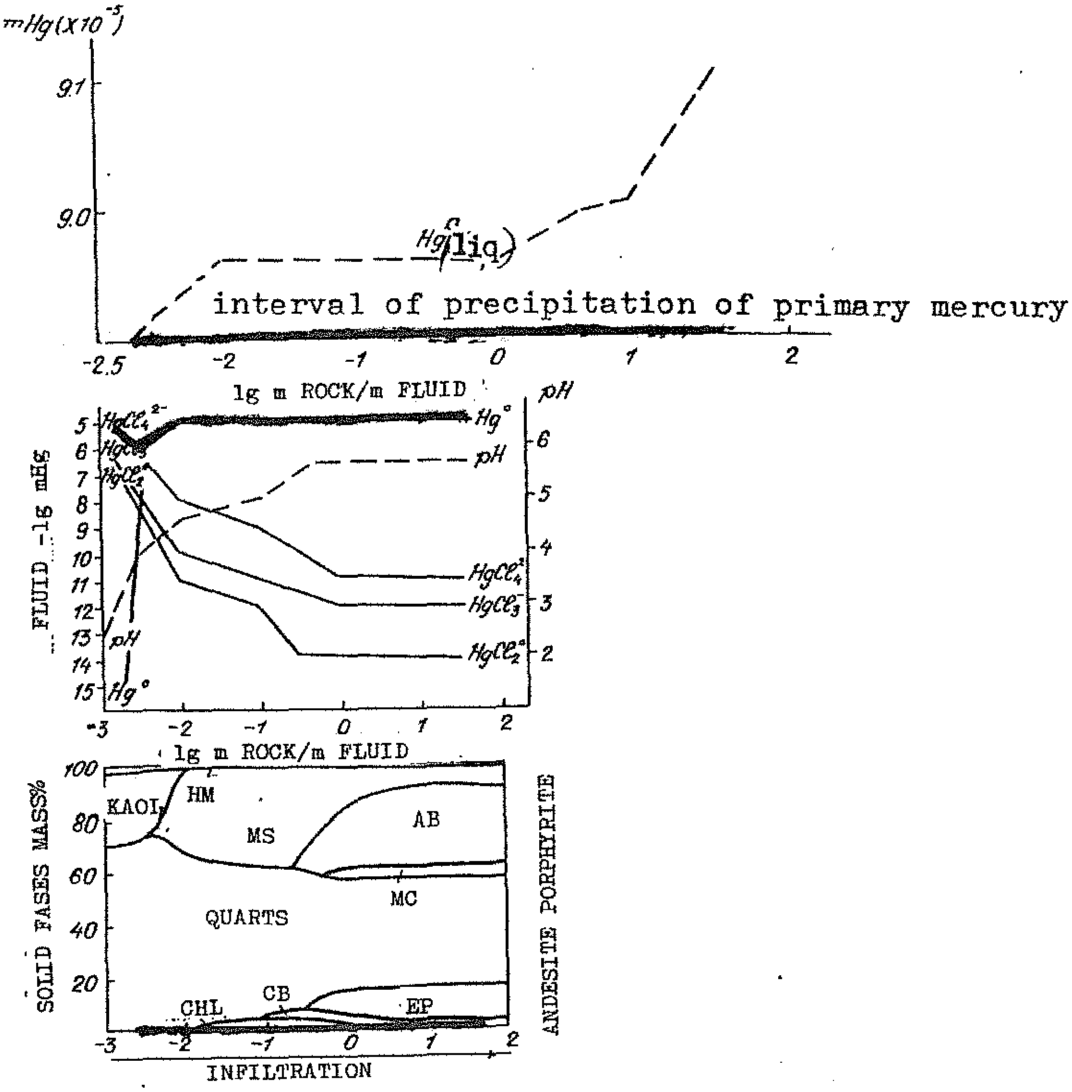


FIG. 2. Mass abundance results of the mass transfer calculation involving the reaction of andesite with acid chloride fluid

Abbreviations: KAOL-kaolinite; HM-hematite; MS-muscovite; AB-albite; MC-microklin; CHL-chlorite; EP-epidote

JOANNEUM RESEARCH

INSTITUT
FÜR UMWELT-INFORMATIK

LEITER
UNIV.-PROF. DR. MONT. JÜRGEN WOLFBAUER

DISCRIMINATION OF NATURAL AND MAN-MADE HEAVY METAL ANOMALIES IN SOILS BY ROBUST PRINCIPLE COMPONENTS ANALYSIS

O.Weinzierl

The present study was undertaken to investigate the distribution of heavy metal anomalies and to discriminate between natural and anthropogenic anomalies in the detail soil survey area using multivariate statistical methods. Of the methods used, robust Principle Component Analysis proved to be best suited for the task. Other methods attempted included robust Canonical Correlation, Cluster Analysis and robust Correspondence Analysis.

INTRODUCTION

A detailed soil and rock sampling campaign of the Walchen mineralization near Öblarn in the Styrian province of Austria was undertaken because results of an earlier regional stream sediment survey were not sensitive enough to distinguish known mineralizations. In the detailed sampling campaign, soil samples of the B-horizon and rock samples were taken at 773 locations in alpine pastures and woods.

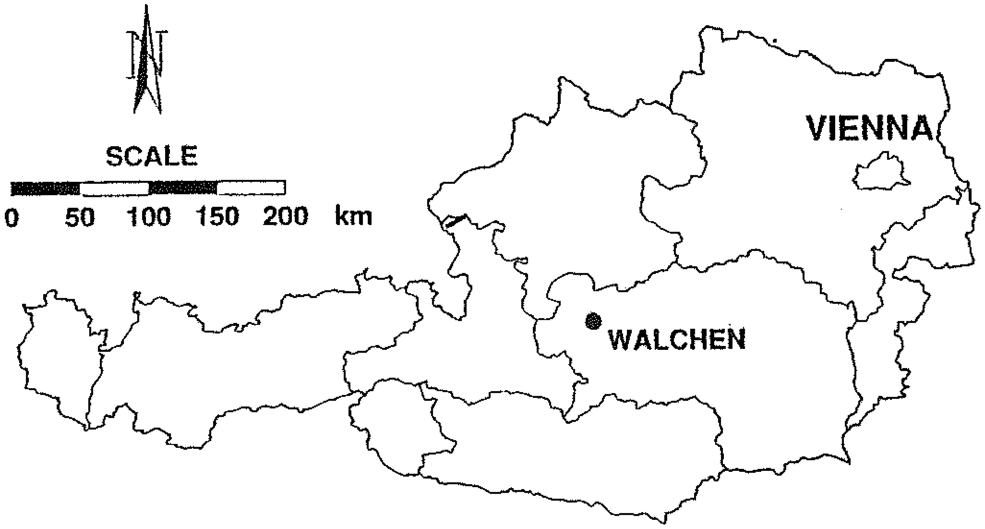


Fig.1 Location of the study area in Austria.

This initial investigation implicated a possible anthropogenic origin for increased heavy metal values in the anomalous area, as univariate mapping of soils in the area showed increased heavy metal concentrations where no previously known mineralizations existed.

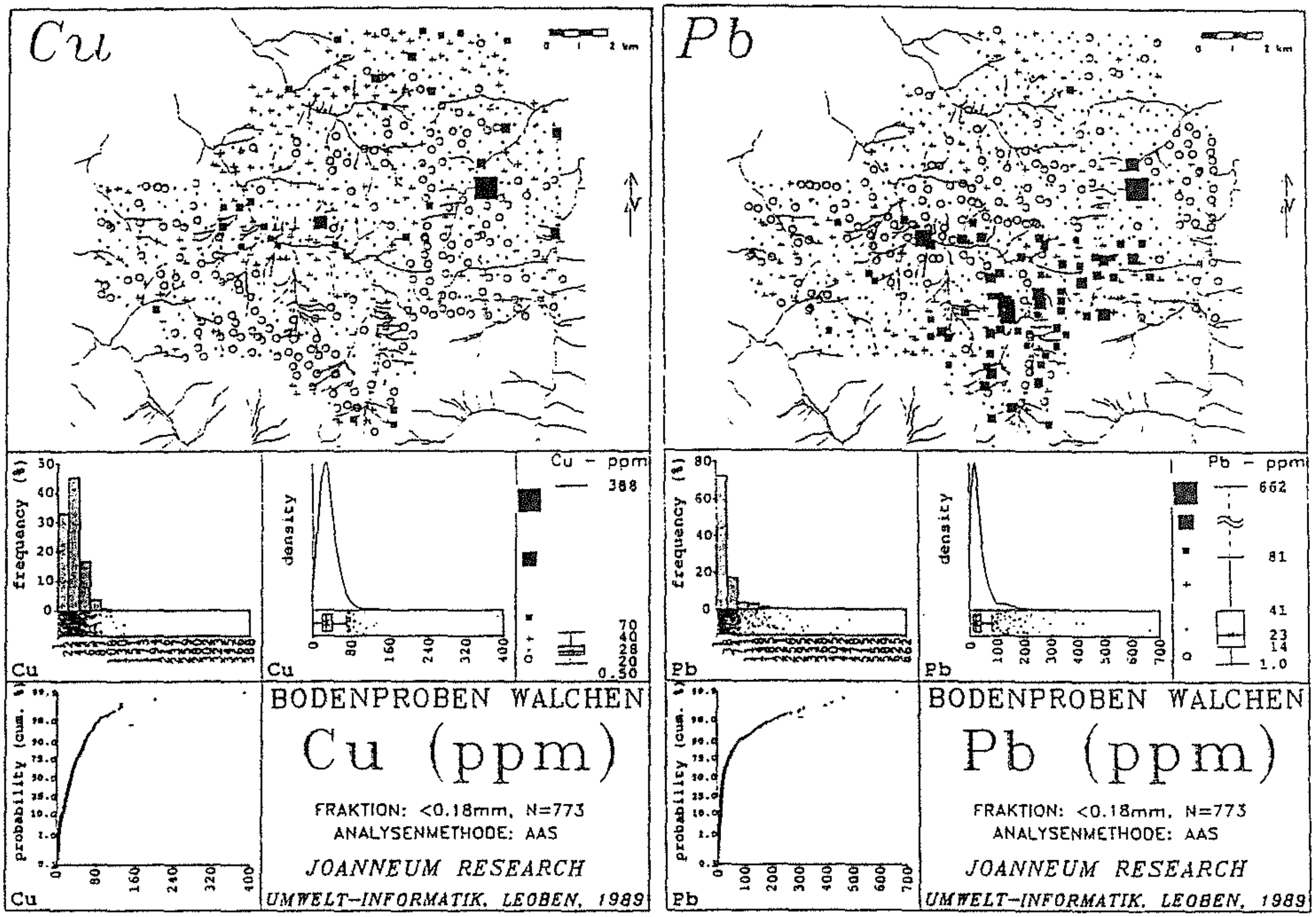


Fig.2 Univariate maps showing Cu and Pb distribution in the soils of the study area.

Additionally, the suite of metals in the anomaly (As, Sb, Pb) was significantly different from the areas of known mineralizations (Co, Cr, Cu, Mn, Ni and Zn).

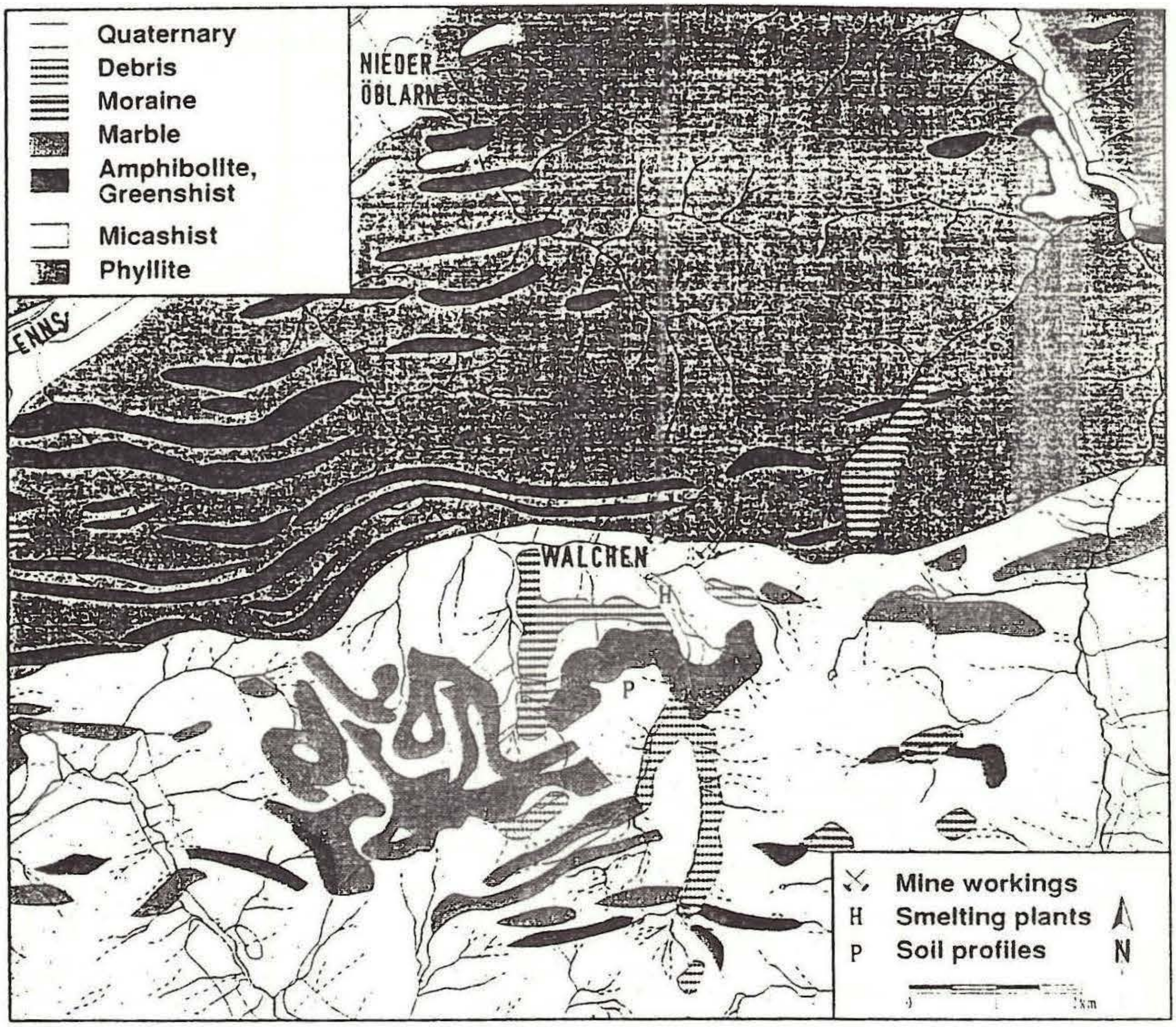


Fig.3 Lithologic map of the study area.

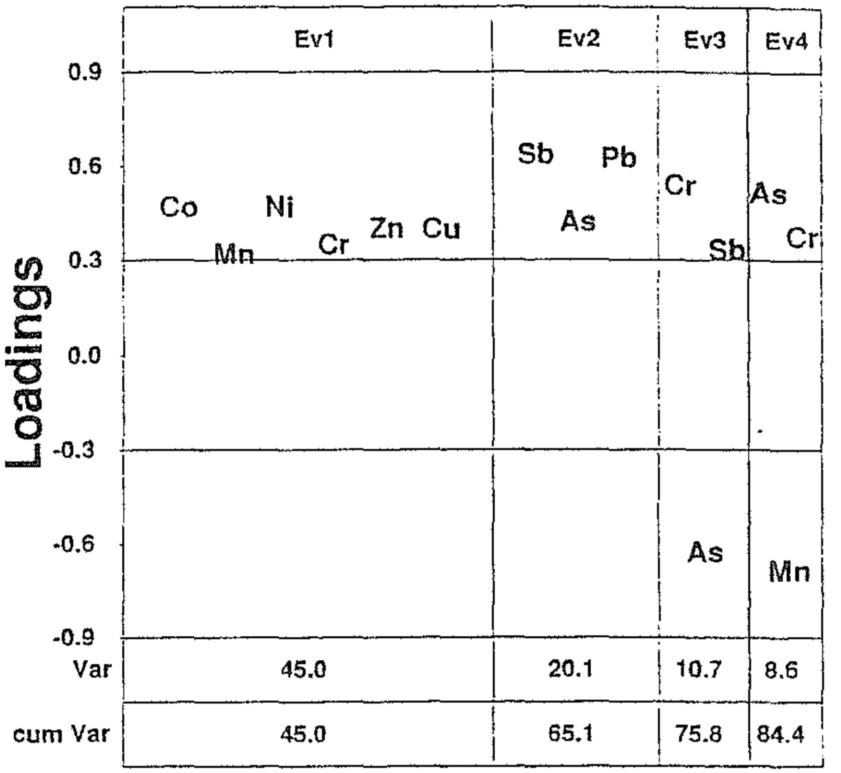
The anomalies in the vicinity of the known mineralizations were related to known host rocks which include greenshists and amphibolites and are trend- related occurences associated with Co, Cr, Cu, Mn, Ni and Zn anomalies.

The anomalous area of no known mineralizations in the southern part of the study area is in a completely different geologic setting including mainly mica schists and marbles. Also the observed As, Sb, Pb anomaly cross-cuts the geology.

Records about mining and smelting activities in this region for centuries mention frequent complaints of farmers about the smoke of the smelting plant, that would ruin their woods and pastures. This hints toward a human influence on the heavy metal contents in the soils of the area. In addition, the local climate and morphology both support a hypothesis of a partial atmospheric input of heavy metal in the area south of the Walchen mineralization.

RESULTS

To check this hypothesis, a robust Principal Components Analysis (rPCA) was applied. Of the first two eigenvectors, two dominate element groupings were found.



Eigenvectors and Eigenvalues

Loadings

	1. Ev.	2. Ev.
Cr	0.339	0.017
Ni	0.469	- 0.047
As	0.020	0.419
Sb	0.081	0.637
Cu	0.400	0.106
Zn	0.403	- 0.014
Pb	- 0.142	0.627
Mn	0.318	0.098
Co	0.464	- 0.050

	Eigenvalues	rel. %	cum. %
1. Ev.	4.048	44.98	44.98
2. Ev.	1.811	20.12	65.10
3. Ev.	0.965	10.73	75.83
4. Ev.	0.769	8.55	84.38
5. Ev.	0.540	6.00	90.38
6. Ev.	0.327	3.63	94.01
7. Ev.	0.269	2.99	97.00
8. Ev.	0.196	2.18	99.18
9. Ev.	0.074	0.82	100.0

Fig.4 Loadings of the rPCA Eigenvectors.

The first eigenvector stressed the elements Co,Cr,Cu,Mn,Ni and Zn thus represents an element grouping indicating the known mineralizations. The second eigenvector is dominated by the elements As,Sb and Pb corresponding with the probable man-made anomaly in the south. Mapping the PC–Scores shows the two types of anomalies with PC1 showing a distinct local connection to the mineralizations and the corresponding lithology while PC2 shows a mere local restriction south of the old mining area.

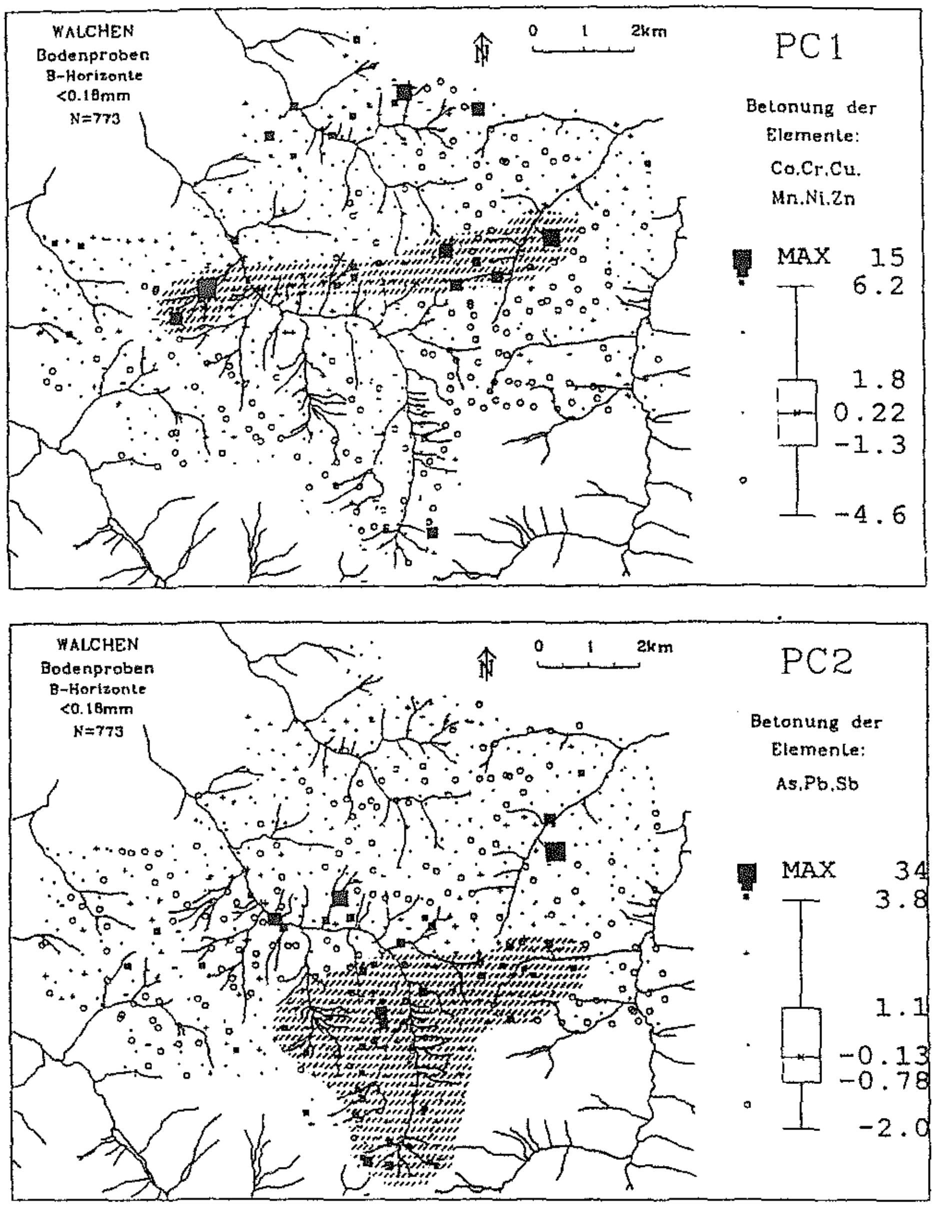


Fig.5 Maps of the first two rPCA–scores.

Additionally, a plot of the first and second eigenvector was used to group the soil samples according to their position in the diagram.

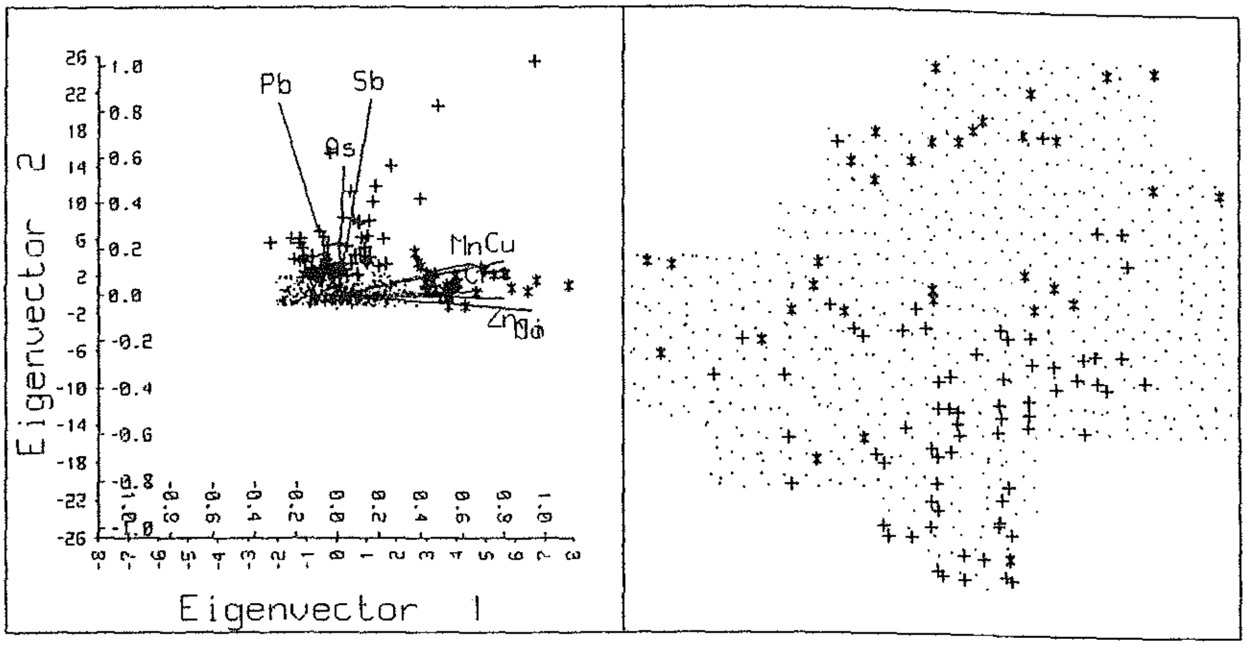


Fig.6 Results of interactive grouping of the first two rPCA Eigenvectors.

This grouping was mapped and demonstrates that the samples dominated by the first eigenvector are again indicating mineralizations and that samples dominated by the second eigenvector are mainly restricted to the area of the southern anomaly. This grouping was also checked with robust Correspondece Analysis and proved to be reliable.

CONCLUSION

Based on the results of the rPCA and the information about local geology, climate, morphology, mining history and other historical reports, the anomaly south of the known mineralizations is therefore interpreted as indicating atmospheric input of the old smelting plants of the local mines.

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MINERALOGICAL-GEOCHEMICAL MAPPING OF RARE-METAL AND MIAROLITIC PEGMATITE FIELDS AIMED AT PROSPECTING

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The use of geochemical features of minerals in mapping of geological objects is a promising trend in prospecting geochemistry. This problem is considered referring to pegmatites.

Li, Be, Cs, Ta, Nb, Sn deposits as well as the deposits of piezooptic and gemstone raw materials are associated with rare-metal and miarolitic pegmatites. Several evolutional geochemical (mineragenetic) pegmatite groups are distinguished. Each group unites genetically and spatially connected assemblages of pegmatite bodies of the same specialization, but distinguished in the productivity degree with the major commercial mineral or element. Commercially, the tantalum-beryllium, lithium and complex (Li-Be-Ta-Cs) evolutional groups are the most important among the rare-metal pegmatites /1/, while the crystal-bearing, topaz-beryl, tourmaline and spodumene (kunzite, hiddenite) groups /2/ have the largest significance among miarolitic pegmatites. Each evolutional group is terminated with a certain commercial pegmatite type. But only minority of pegmatite bodies within the fields and the vein series is of commercial type. The prospecting and evaluation of the pegmatites with gemstones and piezo raw material are especially difficult since the useful mineralization in them is limited and uneven.

The efficiency of prospecting and evaluation works in fields of rare-metal and miarolitic pegmatites significantly increases when we use mapping of geochemical features of different pegmatite minerals, especially feldspars and micas /3,4/. Feldspars and micas are enriched in Li, Rb, Cs, Tl and depleted in Ba and Sr, simultaneously K/Rb, Rb/Cs,Ba/Rb are decreased as pegmatites productivity for rare metals and crystal raw materials increases. The same regularities are established along transition from early to late generations of micas and feldspars.

Because of different conditions of formation each geochemical (mineragenetic) pegmatite group is characterized by a certain set of mineralogical-geochemical indicators of the commercial mineralization. The most informative element for the lithium pegmatite evolutional group is Li, while Rb is for Ta-bearing pegmatites. The Cs-bearing pegmatites are distinguished with highest Cs contents, relatively significant Rb contents and low Rb/Cs ratios in minerals. Besides, the quantitative characteristics of each indicator are distinctive for specialized different pegmatite fields. As Table shows the commercial types of three most important rare-metal pegmatite evolutional groups are distinguished one from another with the levels of Li, Rb, Cs and Tl average contents in feldspars and micas. Moreover, distinctions of these pegmatite groups are established even in non-productive pegmatite bodies. For example, the average Li contents in K-feldspars from Mesozoic non-productive pegmatites of lithium, tantalum-beryllium and complex groups in Trans-Baikal area are equal to 50, 24 and 3 ppm accordingly. It may be used for a rapid determination of pegmatite fields specialization.

It seems surprasing that K-feldspars from non-productive pegmatites of the complex evolutional group contain smaller amounts of Li as compared to the K-feldspars from the tantalum-beryllium pegmatites evolutional group. This is obviously due to different contribution of fractional and emanational differentiation factors at formation of different pegmatite evolutional groups. In cases when the pegmatite system is poor in F just as lithium and tantalum-beryllium evolutional groups, the Li presence in K-feldspars is limited with its bulk concentration in pegmatite melts. If the the system is more rich in F, like the complex pegmatite group, Li is mostly bonded with F at early stages of pegmatite crystallization and concentrates in later (relative to K-feldspars) micas and another lithium alumosilicates. But as Li contents increase extremely in final differentiates of complex pegmatite evolutional group, the concentrational factor of Li entry in K-feldspars inevitably starts operating as well.

Diverse special forecast-evaluation diagrams based on the contents of two or three most informative elements and their ratios in feldspars and micas are elaborated for the main groups of rare-metal and miarolitic pegmatites. These diagrams consist of parts corresponding to non-productive, weakly-productive and commercially productive pegmatites, considering their specialization (see, for example, Fig.1,3). The correspondence of each sample to an appropriate part of the diagrams is reflected on maps through special simbols (Fig.4) which may be united in the appropriate fields with stable geochemical features of micas and feldspars (Fig.2).

Table

Average Li, Rb, Cs and Tl contents (ppm) in K-feldspars (1) and light micas (2) from Mesozoic commercial pegmatites of main geochemical groups.

Geochemical pegmatite group	Li		Rb		Cs		Tl	
	1	2	1	2	1	2	1	2
Lithium	460	2970	3100	4110	95	130	31	9,0
Tantalum-Beryllium	93	590	3300	3790	180	215	14	4,3
Complex	24	12100	5700	7550	600	3790	49	33

The stability of geochemical features of these minerals within the areas, sufficient to be plotted on maps, is far more distinctive for fields and vein series of rare-metal pegmatites as compared to miarolitic ones.

The mineral samples weighing 1-2 gr are collected both from the outcrops and the aluvium-diluvium pegmatites piles. This is especially important for sorting of areas with poor outcropping.The mineralogical-geochemical mapping of different scales (from 1:25000 to 1:2000) of some rare-metal and miarolitic pegmatite fields of the USSR has been performed.The mineralogical-geochemical mapping permits to recognize the specific features of zonation of pegmatite fields, difficult to be established via other methods, to determine specialization and the potentials of fields, their seperate domains and individual pegmatite bodies, including the forecast of "hidden" zones productive for rare metals and gem-stones. Some examples are illustrated in Fig.1-4.

Figure 2 shows the map of geochemical specific features of K-feldspars for one of lithium pegmatite field in Siberia and Fig.1 shows "key"-diagram used for construction of this map. Li and Rb are the most informative elements for that sort of pegmatite fields. The two trends on Li versus Rb plot appear to describe the evolution of geochemical features of K-feldspar (Fig.1). One of them is close to the lithium axis and is terminated with widely distributed commercial spodumene pegmatites within region 1 (see Fig.2). Another trend is situated along the rubidium axis, that as was cited, is usual for pegmatites with prevailing Ta-mineralization. Different pegmatites, including spodumene-bearing ones, within region 2 (see Fig. 2) are related to this trend. Similar geochemical distinctions are typical for pegmatite micas from regions 1 and 2 as well. Thus, the results of mineralogical-geochemical mapping show region 2 as not promising in respect of commercial Li-mineralization. This fact was confirmed by data of mining and drilling.

The efficiency of mineralogical-geochemical mapping is higher within the pegmatite fields of complex and lithium evolutional groups in comparison with tantalum-beryllium ones. As to miarolitic pegmatites, the mineralogical-geochemical prospecting and forecast method is far more effective in reference to tourmaline and spodumene groups than

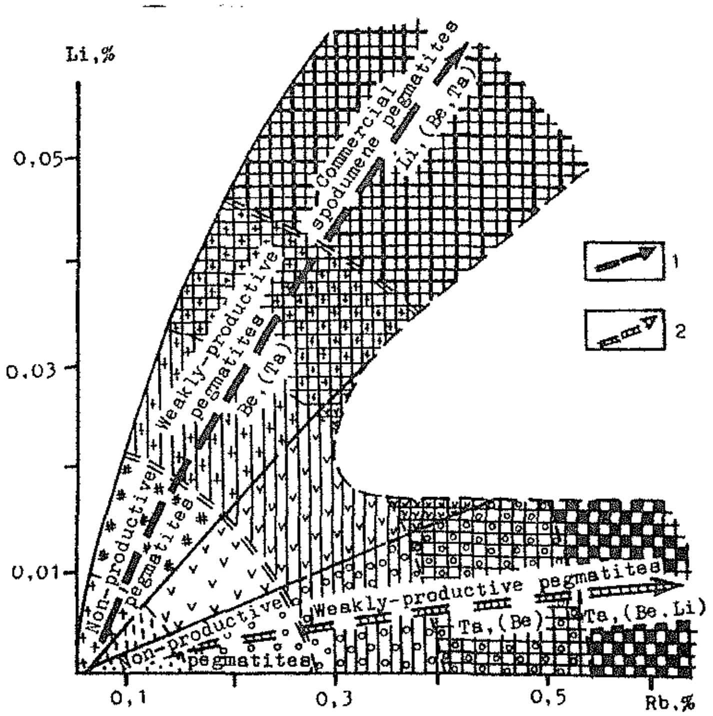

Fig.1. Li versus Rb diagram for K-feldspars from the pegmatite field of the lithium evolutional group, Trans-Baikal area. It is "key"-diagram for constructing the mineralogical-geochemical map shown in Fig.2.

1- the evolutional trend of Li-Rb-correlation for vein series with commercial spodumene pegmatites; 2 - the same for spodumene-bearing pegmatite vein series without commercial Li-mineralization (with prevailing Ta-mineralization).

Chemical indexes show the type of rare-metal mineralization:main (beyond brackets) and secondary (within brackets).

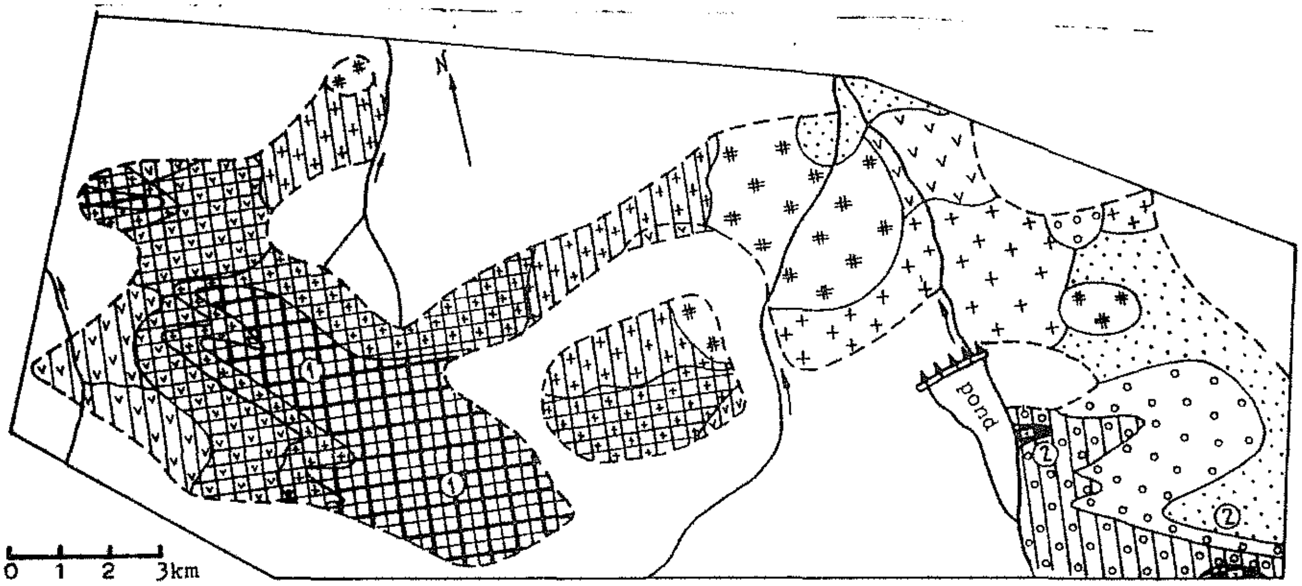

Fig.2. The map of Li-Rb-correlation in K-feldspars for the pegmatite field of the lithium evolutional group, Trans-Baikal area. The"key"-diagram (Fig.1) is used for constructing this map. See explanations in the text.

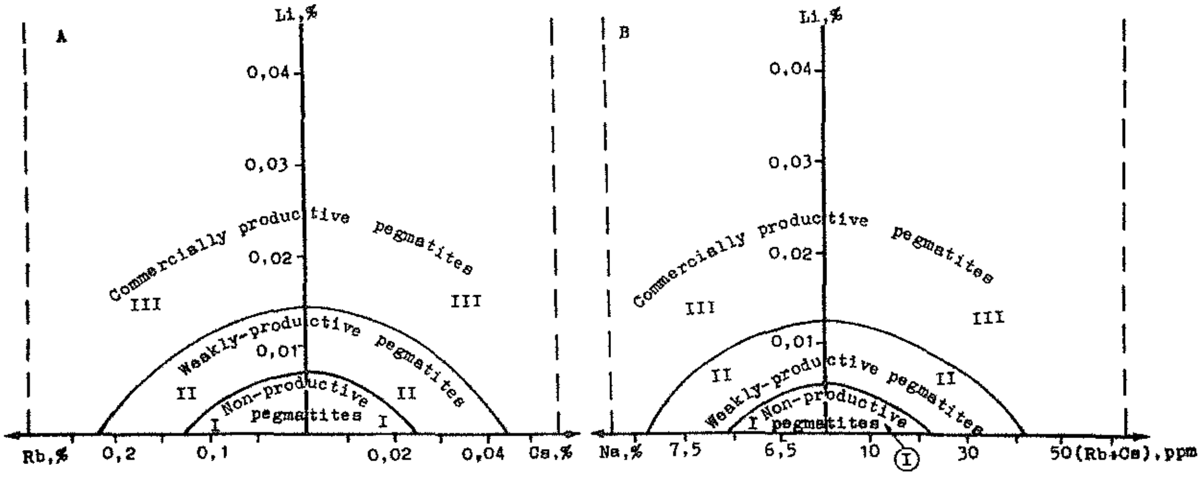

Fig. 3. Diagrams for evaluating productivity of coloured tourmaline-bearing pegmatites from geochemical specific features of K-feldspars (A) and Ca-Na-feldspars (B), the Malkhan pegmatite field, Trans-Baikal area.

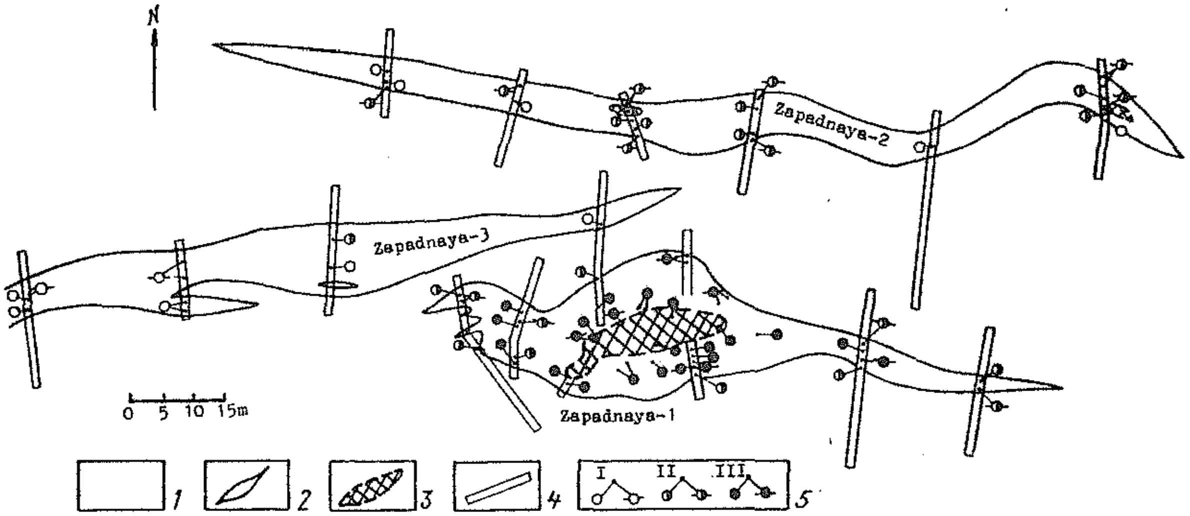

Fig.4. Results of mineralogical-geochemical sampling of some miarolitic coloured tourmaline-bearing pegmatites (Malkhan pegmatite field, Trans-Baikal area) with special "feldspars" forecast-evaluation diagrams (Fig.3).

1 - wall rocks; 2 - pegmatite bodies; 3 - coloured tourmaline-bearing zones; 4 - mining (trenchs); 5 - location of feldspar samples and their position on the forecast-evaluation diagrams. I, II and III correspond to plots with different productivity pegmatites in forecast-evaluation diagrams (see Fig.3): I - non-productive, II - weakly productive, III - commercially productive. Circles without lines - for K-feldspars; circles with lines - for Ca-Na-feldspars. See explanations in the text.

topaz-beryl and especially to crystal-bearing ones.

Specifically, very good results were achieved by mineralogical-geochemical mapping of the Malkhan tourmaline-bearing pegmatite field, Trans-Baikal area, where outcropping is poor /5/. At first, the perspective regions for subsequent detail prospecting of the productive pegmatite bodies were localized using sampling of eluvium-deluvium pegmatite piles (scale 1:25000 and 1:10000) and special "feldspars" forecast-evaluation diagrams (Fig.3). Then the potential productivity of discovered pegmatite bodies for coloured* tourmaline was evaluated after additional working and more detail mineralogical-geochemical sampling in these regions.

As Figure 4 shows, it is not difficult to interpret the mineralogical-geochemical data using "feldspars" diagrams (Fig.3). So, the evaluation of three pegmatite bodies productivity may be interpreted only like this: Zapadnaya-1 is commercially productive body, Zapadnaya-2 - weakly productive body and Zapadnaya-3 - non-productive one. This conclusion completely corresponds to real situation.

Commercial coloured tourmaline-bearing pegmatites in the Malkhan field provide reliable mineralogical-geochemical anomalies. Several feldspar samples only are normally enough for their sure forecasting. Being an extremely good example of succesful forecast, the pagmatite vein Irkutyanka was recognized as the high-productive coloured tourmaline-bearing deposit. It was enough to use only one K-feldspar sample, which has been collected from the natural outcrop, where any visual indicators of useful mineralization was absent.

The geochemical specific features of minerals in miarolitic pegmatites increase the "prospecting target" significantly in comparison with traditionally used visual mineralogical signs. Moreover, it turned out that the mineralogical-geochemical forecast evaluation of tourmaline-bearing pegmatites is more effective than any mineralogical indicator including appearance of coloured tourmaline itself. First of all, it is caused with the very stable direct correlation between the levels of Li contents in feldspars and quantity of differently coloured elbaites, that is to say lithium tourmaline variety, in every pegmatite body.

The available data on the fields studied may be used as "standards" for the evaluation of new pegmatite fields. But the age of pegmatites and provincial geochemical features of different territories affect the levels of element-indicators in the minerals from pegmatites/3/. Therefore, it is necessary to correct the forecast-evaluation diagrams for every pegmatite belt or field.The reliability of the local forecast increases as the mineralogical-geochemical data are accumulated for each pegmatite field.

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* Here and in further text any colours apart of black one are named as "coloured".

THE USE OF BACTERIAL CONCENTRATION BARRIERS INCREASES CONSIDERABLY THE DEPTH OF PENETRATION IN GEOCHEMICAL PROSPECTING

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New geochemical barrier types have been distinguished that are characterized by a very high ability to accumulate the matter brought in the course od remote salt migration of mobile chemical elements from deep ore sources. Such barriers, referred to as "bacterial", represent one of the constituents of natural biocoenosis existing in the upper layers of soil and fluvial formations. Various bacteria in the identified biological communities selectively absorbing chemical elements brought upwards play a protective role for vegetation composing a part of biocoenosis by protecting it from high concentrations of the whole number of chemical elements. In its turn, interaction between bacteria and these elements serves as an evolutionary established mechanism of their biological life.

The prospecting techniques using bacterial-geochemical concentration barriers is characterized by high rapidness provided by simplicity of sampling and by the possibility of identifying the determined totality of indicator elements in the course of field work. However, its main advantage consists in a very high resolution of prospecting together with the reliability of the obtained data. Fig. 1 shows an example of highly contrast bacterial-geochemical anomalies disentangled over gold lode buried beneath allochtonous deposits 20-25 m thick. Fig.2 illustrates a more interesting case showing an orebody distinguished from similar anomalies that occurs under volcanic rocks at about 3 km depth. New methods can be effectively applied in the regions with moderate and cold humid climate (USSR, USA, Canada, Alaska, Scandinavia).

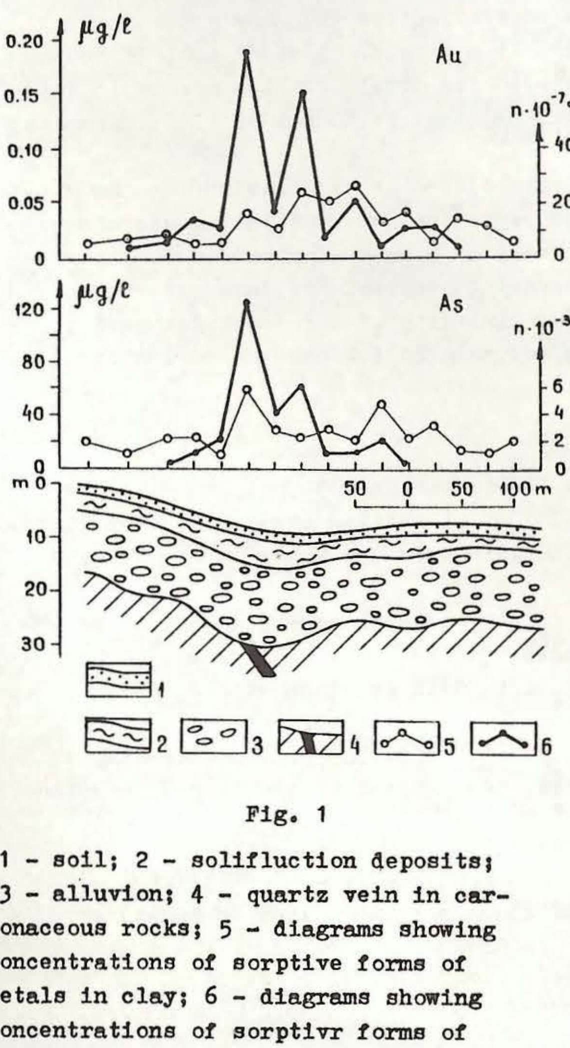

Fig. 1

1 - soil; 2 - solifluction deposits; 3 - alluvion; 4 - quartz vein in carbonaceous rocks; 5 - diagrams showing concentrations of sorptive forms of metals in clay; 6 - diagrams showing concentrations of sorptivr forms of metals in "bacterial" media

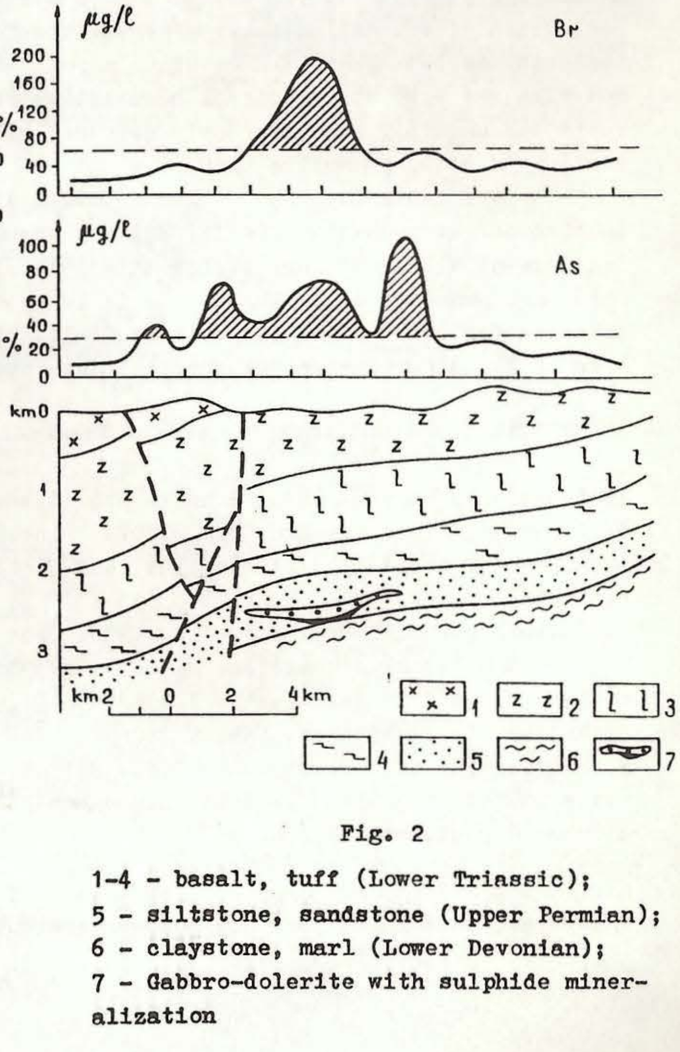

Fig. 2

1-4 - basalt, tuff (Lower Triassic);
5 - siltstone, sandstone (Upper Permian);
6 - claystone, marl (Lower Devonian);
7 - Gabbro-dolerite with sulphide mineralization

PATTERNS OF ELEMENT DISTRIBUTION IN POST-MAGMATIC FORMATIONS OF THE DARASUN ORE-MAGMATIC SYSTEM

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The Darasun ore-magmatic system unites the deposits of gold-sulphide formation. The structure of deposits includes gabbroids (Pz_1), granitoids (Pz_2 and Pz_3-Mz_1), subvolcanic intrusions and dykes (J_{2-3}) of porphyry rocks of middle and acid compositions with heightened potassium concentration (dioritic and quartz-dioritic) porphyrites, granodiorite and granite-porphyries, plagioporphyries and plagiogranite-porphyries, felsites and felsite-porphyries, volcanic glasses), ijection-explosive breccias (J_2 and J_3-K_1). Mineralization is associated with the complex of porphyry rocks and consists of four stages: tourmalinic (tourmaline, pyrite), pyritaceous (pyrite, arsenopyrites, pyrrhotite, chalcopyrite), polymetallic (pyrite, galenite, sphalerite), sulphosalt (chalcopyrite, sulphosalt Ag, Cu, Bi, As, Sb, Pb, etc.), post-ore chalcedony-carbonate. Quartz and carbonate are available in different quantatives everywhere. Quartz-sulphide veins (frequently with tourmaline), the mineralized fraction zones in tectonic dislocations (ore zones) and streaky zones in granites along the ore body continuation, represented by veins in gabbro are the case. There are four groups of main rupture dislocations on the deposit: north-east (main ore-containing structures), north-west and sublatitudinal direction (contain less extensive veins and the mineralized fraction zones with sulphide mineralization); barren submeridional, which contain the late chalcedony-carbonate veins.

The Darasun ore system was formed over three stages: pre-ore, ore and post-ore. The gabbroids, predominantly containing horn-blende-pyroxene and hornblende, are intruded by granites (Pz_2 and Pz_3-Mz_1) granitized and feldspathized on the pre-ore stage. The variagated hybride rock varities are formed: weakly granitized and feldspathized gabbroids, diorite, syenite-monzonite-like rocks, metasomatic granites and syenites. The granitization is terminated by the events of autometasomatic epidotization. From the viewpoint of physical chemistry the granitization process is characterized by K, Na and SiO_2 supply, Fe, Mg, Ca removal and high activity of H_2O, CO_2 and other volatiles (3).

During the pre-ore stage all host rocks: gabbroids, granitoids of different genesis, porphyry rocks were propylitized. According to rubidium-strontium dating propylites are 149 ± 8 Ma (1). Propylitization covers all the area of ore fields. The amount of new formations in the area of weak alterations is insignificant. On the average 10-15% of secondary minerals are carbonate, sericite, chlorite, biotite, development of actinolite, epidote, albite along the acid rocks (minerals, common for inner zones of local metasomatic columns) is sporadic.

The zones of mostly intensive rock transformation are located along the way of solution circulation. These are rupture dislocations of all directions, contact surfaces and the areas of gabbroid granitozation. The mineralized fraction zones and submeridional tectonic dislocations, the similar local metasomatic columns of propylitized rocks are observed in the vicinity of ore veins. In these columns towards the feeder channel the two facies of the propylitized rocks are distinguished: actinolite-epidote (on the average 0,4-1 m from the contacts of ore veins, ore zones and tectonic dislocations, as well as on the contacts of heteregenous rocks and in the regions of gabbroid granitization) and chlorite-epidote (on the average in 0,1-04 m from the contacts of ore veins, in ore zones, tectonic dislocations and granitization regions). Biotite and albite occurrence in the propylitized rocks indicate the heightened alkalinity of hydrothermal solutions (2). The inner zones of metasomatic columns in tectonic dislocations and ore zones host breccias and melonites of chlorite-epidote-quartz composition. Inner zones are often not evident, because of the overlapping of ore veins with syn-ore listvenite-berisite rimming and post-ore chalcedony-carbonate veins.

The propylitization regularities are well displayed in the rocks of mafic and middle composition, which are altered to a larger degree as compared to the rocks of acid composition. Table 1 represents the summary metasomatic column of the propylitized hornblende-pyroxene gabbro. A number of zones are distinguished in the propylitized gabbroids of actinolite-epidote facies in the direction to the feeder channel. The number of the secondary minerals in these zones increases by one unit, the secondary minerals amount from 20 to 85%. In the mostly altered rocks, they are albite,actinolite, epidote, carbonate, chlorite, sericite, quartz, biotite, clay minerals. Albite, actinolite and epidote are predominant. In the propylitized gabbroids of chlorite-epidote facies there are some zones, where on the contrary the number of the secondary minerals decrease by a unit, the quantity of the secondary minerals varies from 70 up to 100%, actinolite is absent, the partial or complete albite and epidote replacement by carbonate, sericite and chlorite takes place. This is observed in all zones of metasomatic columns. The epidote + quartz + pyrite association in the contacts with ore veins (with synore listvenite-berisite rims) - sericite+ quartz + pyrite is stable in ore zones and tectonic dislocations.

In granites of different genesis, plagiogranite- and felsite-porphyries the similar changes occur with sericite abundance and epidote presence. The replacement pattern of the primary minerals and the new formations quantity are different in these zones(Table2). The ore deposition according to Rb-Sr dating covers the period from 145 to 111 Ma(1). The ore veins are as a rule confined to the rock regions which are intensively reworked by the propylitization process, in gabbroids - preliminarily granitized. The ore veins (and streaky zones in granites) are accompanied by the formation of synore listvenite along the propylitized gabbroids and berisite along the propylitized granitoids. In the mineralized fraction zones the sporadic development of listvenite-berisite is observed only in individual regions with productive mineralization.

The listvenites-berisites (144 ± 10 Ma (1)) are narrow light zones 0,1-0,15 m thick in gabbroids and 0,05 m in granitoids near the vein contacts. They as if "complete" the propylites columns and also occur in inner parts of veins. The composition varies between the carbonate, quartz, sericite and chlorite (Table 3). In case of close proximity on the same area a great number of the branching veinlets as well as near the veins with a great thickness and higher content of ore components, the thickness of listvenite zones increases up to 0,8-1 m, berisites up to 0,3 m. In the mineralization regions of tourmaline, pyritaceuos, infrequently polymetallic stages in gabbroids quartz-chlorite metasomatites are widely developed in inner vein parts. In the mineralization regions of sulphosalt and frequently polymetallic stages sericite-carbonate metasomatites appear. Berisites have sericite-quartz composition with muscovite, ankerite and chlorite impurities.

In the vicinity of ore veins with high contents of ore components the rocks are more reworked towards the vein, the successive change of zones of weakly propylitized rock by the propylites of actinolite-epidote and chlorite-epidote facies, then by the listvenite-berisite. The thickness of intensively changed rocks of the sloping veins from the hanging side is more. Fine veinlets poor in ore components with listvenite-berisites in inner parts contact with the propylitized rocks of actinolite-epidote facies. Metasomatites of the chlorite-epidote facies are absent. The vertical zonation with the marked change of structures of metasomatic columns is not found.

In the granitized gabbroids, propylitized rocks, listvenites, berisites, ore veins, ore zones and non-mineralized tectonic dislocations the distribution of several element groups was studied: alkaline (K, Na, Li, Rb, Cs), rare alkaline earth (Ba, Sr), Fe family (Co, Ni, Ti, V, Cr, Mn) and forming ore bodies (Au, Ag, Bi, Cu, As, Sb, Pb, Zn, Hg, B). The levels of element concentrations are normalized after background and are expressed by contrast coefficients (CC). This permitted the geochemical fields of concentration (GFC), removal (GFR) and fields of dispersion (GFD) to be classified.

The following trends should be indicated. Potassium in the process of pre-ore and synore alteration of the host rocks tends to accumulation and formation of GFC. It is removed from the zones of maximum sulphide deposition (ore veins) and concentrated together with gold in listvenite-berisites. Relationships between Au and K in near vein zones and correlation of halos productivity indicate that alkaline metasomatism acts as the powerful mechanism of ore formation. Sodium on the contrary is characterized by the stable removal, which is observed from the propylitization process. Rare alkalies and Ba, as well as K, tend to accumulation. Along with it, in some metasomatic zones of granitized gabbroids, propylitized rocks and berisites, alkalies and Ba remain at the background level. Strontium and the elements of Fe group form GFR, which are connected with GFC of ore and alkaline elements. GFD of Co, Ti, Mn, Ni and V may occur only in the propylitized granitoids and berisites.

Such ore elements as Au, Ag, Bi, Pb start accumulating in the process of propylitization. Their contrast being low (CC up to 10). The spectrum of elements is extended in listvenites and berisites and corresponds to that of ore veins (Au, Ag, Pb, Zn, Cu, As, Bi, Sb, Hg, B), the contrast increasing up to 100. It is maximum (CC 100) in the ore veins, from which all petrogenic and associated rare "non-ore" elements are removed. The ore zones are characterized by average and high contrast GFC of ore elements, which are associated with K, Li, Rb, Cs, Ba, Mn and connected with GFR of other elements studied. Geochemical field of concentration of Li and low-contrast geochemical fields of concentration of ore elements, associated in some cases with GFC of K, Rb, Cs, Ba, Mn, Co, Ni, Ti, V are the markers of tectonic dislocations.

Gold in low concentrations occurs in propylites at the distance 5-10 m from ore veins and zones. Gold correlates with Ag, Bi, infrequently with Pb, Zn, Cu, As. Across the strike of ore veins, the spasmodic distribution of ore elements is observed. The heightened concentrations are observed in 0-0,1 m from the contacts with the vein in listvenite-berisites. This zone is used for their extraction. In 0,2-0,4 m from the contacts usually in propylites of the chlorite-epidote facies, the concentrations markedly decrease and at the distance 0,6 m again increase. Near the sloping veins from the hanging side Au and other element concentrations decrease at a large distance from the vein contact, as compared to the lying side. The distribution curves are asymmetrical.

The analysis of GFC, GFR, GFD of the Darasun ore-magmatic system indicates the juvenile supply of ore elements, B, K as well as displacement of Na and Fe group elements and redistribution and possible juvenile supply of Ba and rare alkalies. Specific features of mineral and chemical composition of hydrothermolites observed in the veins, ore zones and barren tectonic dislocations, specific migration features of elements at the post-magmatic stage, connection of GFR and GFC are proposed to be applied in prospecting, forecast and use of the deposits of gold-sulphide formation, located in magmatic rocks of basic and acid composition.

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Table 1. Generalized metasomatic column of propylitized hornblende-pyroxene gabbro

№№ Zone	Zone	Mineral composition	Amount of secondary minerals, %	Thickness, m	Reaction of replacement
1	Poorly-propylitized gabbro	(Pl)+(ClP)+(Amph)+Carb+ +Ser+Chl+Bt+rarely Ep+Act	5-15 (to 55)	Area development	Pl → Ser, Carb; ClP → Bt+ +Carb+Mt; Amph → Act+ +Chl, Act+Carb
		Actinolite-epidote facies			
2	Actinolite-biotite	(Pl)+(ClP)+(Amph)+Bt+Act+ +Carb+Ser+Chl+Ab	40-65	0,6	Pl → Ab+Ser+Carb; ClP → Bt+Act+Mt
3	Biotite-epidote-albite-actinolite	(Pl)+(ChP)+(Amph)+(Act)+ +Ab+Ep+(Bt)+Carb+ +Ser+Chl+Pe+Py	20-65	0,4	Pl → Ab+Ser+Carb+Ep+ +Pe; ClP → Act+Ep+Carb+ +Bt+Mt; Amph → Act+Carb+ +Chl+Ep+Mt
4	Epidote-albite-actinolite	(Pl)+(ClP)+(Amph)+(Act)+ +(Ab)+Ep+Q+Carb+ +Ser+Bt+Chl+Pe+Py	60-70	0,3	Pl → Ab+Ser+Carb+Ep+ +Pe; ClP → Act+Ep+Carb+Bt+ +Mt; Ab → Ser+Carb; Act → Chl+Carb
5	Actinolite-albite	(Pl)+(Ab)+(Act)+(Bt)+ +Chl+Carb+Ser+Q+Py	60-70	0,3	Pl → Ser+Carb+Chl+Ab Ab → Ser+Carb; Act → Carb+ +Chl; Bt → Chl+Mt
		Chlorite-epidote facies			
6	Chlorite-epidote-carbonate-albite	(Pl)+(Ab)+Carb+Ep+ +(Chl)+Ser+Bt+Py	80-95	0,2	Pl → Ab+Ser+Carb+Ep+ +Chl; Ab → Carb+Chl+Ser Chl → Ser+Carb
7	Chlorite-albite-carbonate	(Pl)+Carb+(Ab)+(Chl)+ +Bt+Ser+Ep+Q+Py	80-95	0,15-0,45	Pl → Ab+Ser+Carb+Ep+ +Chl; Chl → Ser; Bt → Ser
8	Chlorite-albite	(Ab)+(Chl)+Q+(Bt)+Ep+ +Ser+Carb+Py	100	0,1	Chl → Carb+Mt; Ab → Ser +Carb; Bt → Chl+Ep
9	Epidote-carbonate-quartz-sericite-chlorite	(Chl)+Ser+Q+Carb+ +Ep+Py	100	0,1	Chl → Carb+Ser
10	Epidote-quartz-chlorite	Chl+Q+Ep+Py	100	0,1	

Notes: Zone number according to the degree of icrease of the intensity process; zone 5 and 8 - transition to listvenites, zone 9 and 10 - mainly in tectonic dislocations and in ore zones. The secondary minerals in all Tables are given in decrease order, the secondary minerals with the content more than 10% are underlined, in brackets are relect minerals. Magnetite, apatite, tourmaline chalcopyrite may occur in all zones. Abbreviations are given in Table 2.

Table 2. Metasomatic column of propylitized granite*

№№ Zone	Zone	Mineral composition	Qantity of secondary minerals, %	Thickness, m	Reaction of replacement
1	Poorly-propylitized granite	Pl + KFsp + Q + Bt + +Ab + Ser + Carb + +Chl + Ep + Pe	5 - 15	Area development	Pl → Ab + Ser + Carb; KFsp → Ser
2	Average-propylitized granite	Pl + KFsp + Q + Bt + +Ab + Ser + Chl + +Carb + Ep + Pe + Py	40 - 50	0,4 - 1	Pl → Ser + Carb + Ab + Chl Ep + Pe + Hm; KFsp → Se Bt → Chl + Ep + Mt
3	Jntensely-propylitized granite	KFsb + Q + Ser + Carb + +Ab + Chl + Q + Ms + +Ep + Pe + Py	50 - 55	0,3 - 0,45	KFsp → Carb + Ser + Pe; Ab → Chl + Ser + Carb + Pe Chl → Ser, Ms, Carb

Notes: Relict minerals are underlined, magnetite and apatite occur in all zones. The abbreviations are: Ab - albite, Act - actinolite, Bt - biotite, Carb - carbonate, Q - quartz, KFsp - K-feldspar, Ms - muscovite, Mt - magnetite, Py - pyrite, Pl-plagioclase, ClP - clinopyroxene, Amph - common hornblende, Ser - sericite, Chl - chlorite, Ep - epidote, Hm - hematite, Pe - pelite

Table 3. Metasomatite varieties of listvenite - beresite composition*

№	Metasomatiites	Mineral composition quantity, %	Thickness m
1	a. Sericite-quartz-carbonate-chlorite	Chl (40-75), Carb (15-40), Q (5-20), Ser (5-15), Py (1-3)	0,1 - 0,7
	b. Carbonate-quartz-chlorite	Chl (20-90), Q (5-60), Carb (5-30), Py (1-3)	0,1 - 0,7
2	Carbonate-quartz-sericite-chlorite	Chl (20-70), Ser (10-45), Q (5-55), Carb (5-20), Py (no more than 15)	0,1 - 0,4
3	Sericite-chlorite-carbonate	Carb (15-50), Chl (15-40), Ser (15-20), Q (0-10), Py (5-10)	0,1 - 0,6
4	Sericite-carbonate	a. Carb (20-60), Ser (15-60), Q (3-15), Chl (5), Py (1-3)	0,1
		b. The same, with relics Pl (10-15)	0,1
5	Quartz-clorite	Chl (30-80), Q (15-20), Carb (5-10), Ser (5), Py (no more than 15)	0,1
6	Sericite-quartz	Q (50-55), Ser + Ms (30-35), Carb (10-15), Chl (5), Py (1-10)	0,05 - 0,3

Notes: 4-6 - in ore lodes and in contacts, chalcopyrite, tourmaline, magnetite, apatite are also present.

Table 4. Characteristics of geochemical fields of concentration (GFC), dispersion (GFD) and removal (GFR) of elements in post-magmatic formations of the Darasun ore-magmatic system

Object of research	GFC (concentration)	GFD (background)	GFR (removal)
Granitized gabbro	K, Rb, Cs; Ba	Na, Li; Sr	Co. Ni, Mn, Ti, V, Cr
Propylitized gabbro	K, Ba, Sr; low-contrast (CC up to 10) Bi, Ag, Au, Pb, B; in removal from lodes Na; by tectonic dislocations Rb, Cs, Li	K, Na, Li, Pb, Cs, Sr	Co, Ni, Mn, Ti, V, Cr near lodes Na
Propylitized granite	K, Cs; low-contrast Au, Ag, Bi, Pb, Bi; by tectonic dislocations Li	K, Na, Rb; Ba; Co, Ti, Ni, sometimes Mn	V, Cr, sometimes Mn, Ni; Li; Sr; near lodes Na
Propylitized porphyric rocks	low-contrast Au, Ag, Bi, Pb, B	K, Li, Rb, Cs; Co, Ti, Ni, Mn, V	Na, Rb; Ba, Sr; Mn,
Listvenites	K, Rb, Cs, sometimes Li; average-contrast (CC up to 100) Au, Ag, Pb, Zn, Cu, As, Bi, Sb, B	sometimes Li	Na; Ba, Sr; Co, Ni, Mn, Ti, V, Cr
Beresites	K, Cs; average-contrast Au, Ag, Pb, Zn, Cu, As, Bi, Sb, B	Rb; Ba; Co, Ti, Ni, Mn	Na, Li; Sr; V, Cr
Ore lodes	high-contrast (CC ≫ 100) Au, Ag, Pb, Zn, Cu, As, Hg, Sb, B; sometimes Mn, Co		K, Na, Li, Rb, Cs; B Sr; Ni, Ti, V, Cr, sometimes Ba, Ti, M
Ore zones	average and high-contrast Au, Ag, Bi, Pb, Zn, Cu, As, Hg, Sb, B; sometimes K, Li, Rb, Cs; Ba, Mn, Ti		Na; Sr; Co, Ni, V, C sometimes Ba, Ti,
Unmineralized tectonic dislocations	Li; rarely K, Rb, Cs; Ba: Mn; sometimes Co, Ni, Ti, V; B; low-contrast Au, Ag, Bi, Zn, Cu, As		Na; Sr; Co, Ni, Mn, V, Cr; rarely Ba

Note. CC - coefficient of contrast, standardized after background

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