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ABSTRACTS

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STATISTICAL CLASSIFICATION OF TILL INTO LITHOLOGIES IN THE SATTASVAARA KOMATIITE AREA, FINLAND

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An empirical discriminant analysis program was used for the classifications of the fine fraction (<0.06 mm) of 9966 till samples from the Sattasvaara area, northern Finland. Training areas, chosen on the basis of geochemical and lithological information, were expected to reflect the background of basalt, komatiitic basalt, basaltic komatiite, komatiite, felsic rock, quartzite, granite gneiss, graphitic slate, and mica schist. After careful study of the homogeneity and the representativity of the training sets, 13 elements (Fe, Mg, Ca, Na, K, Ti, V, Cr, Mn, Co, Ni, Cu, Zn) were selected as discriminating variables. The Bayes' classifier, which minimized the average loss over the classes, was used as the decision criterion and the apriori propabilities were assumed equal for each class. A successful discrimination depends on the smoothing parameter and this was determined by iteratively classifying test sets, until a satisfactory small rate of unclassified samples was reached within the sets.

Most of the unclassified samples, ca. 500 in all within the whole area, are due to mineralizations and anomalies. Thus, referring to lithological information, the outliers associated to komatiite proper depend on extreme Mg, Cr, and Ni content and those associated to the felsic rocks depend on increased Cu, Co, and Zn contents.

The produced classification map corresponds well to the geological interpretation and proves that the method can be used to assist geological mapping and exploration where outcrops are rare and the reconnaissance geochemical data is representative enough.

MINERAL RESOURCE APPRAISAL OF PART OF NIGERIA

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A stream-sediment geochemical survey of part of the new Federal Capital Territory of Nigeria was carried out along with the geological mapping mainly to determine the mineral potential of this largely unexposed area of the Nigeria basement complex.

Results indicate the absence of economic mineral deposits which makes the area free for immediate development. However, the mean, background and ranges of the trace element values largely reflect the low level of concentrations in the different rock types though there are significant differences between them. The distribution patterns of Cu, Zn, Ni, and Mn as well as of element associations reflect mainly lithologic and environmental features.

THE GEOCHEMISTRY OF HEAVY MINERAL CONCENTRATES FROM ROCKS ASSOCIATED WITH THE SOUTH BAY MASSIVE SULPHIDE DEPOSIT, ONTARIO, CANADA: AN EXPLORATION TECHNIQUE

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The geochemistry of the heavy mineral fraction of rocks was investigated to determine the potential of the composition of the medium as an exploration guide to massive sulphide deposits in the Archean greenstone belts of the Canadian Shield. Approximately 270 samples were selected from around the South Bay massive sulphide deposit, in the Uchi greenstone belt of the Superior Province. The rocks were crushed, ground to 74-500 μm, and separated using bromoform (S.G.=2.89). After removal of the magnetic fraction, the samples were pulverized, and analyzed by atomic absorption spectrophotometry for Cu, Pb, Zn, Ag, Fe, Mn, Co, and Ni.Corresponding pulverized whole rock samples were analyzed to provide a basis for comparison of the composition of the heavy mineral concentrates obtained from rocks.

Analysis of whole rock samples delineated halos of Pb and Ag extending 1.5 kilometers along strike, away from the South Bay Deposit, and a Zn halo extending 2.5 kilometers along strike, away from the deposit. Geochemistry of the whole rock samples was dominated by rock type. Either good geologic control in the sampled area, or the analysis for major elements, followed by the use of multivariate statistical technique is requiread to differentiate anomalous concentrations related to rock type from those related to mineral deposits.

Analysis of the corresponding heavy mineral fractions of rocks revealed strong and extensive halos of Cu, Pb, Zn and Ag surrounding the South Bay massive sulphide deposit. The Pb and Ag halos extended throughout the entire felsic volcanic unit sampled, persisting for at least 10 kilometers along strike, south of the deposit. Very highly anomalous Pb values delineated a 1.5 kilometer area around the deposit. Zinc and Cu halos extended 5 kilometers along strike, south of the deposit, a Mn halo 4 kilometers, and a very weak Fe halo 1.5 kilometers along strike, away from the South Bay Deposit. Geochemistry of the heavy mineral fractions was dominated by effects of the mineralization. Although rock type exerted some influence on composition of the heavy mineral fractions, geologic control is not a primary requirement for interpretation of the geochemical data.

Mineralogical observation of selected heavy mineral concentrates indicates that the trace metals occur predominantly in the sulphide minerals pyrite, chalcopyrite, and sphalerite. Location of the sulphide minerals in rocks of the area indicates that the geochemical signatures are caused by enrichment of trace metals in the felsic lava hosting the massive sulphide deposit, and by hydrothermal alteration related to the mineralizing event.

Elimination of the dilution effects of quartz and feldspar by use of the heavy fraction of the rock allowed enhancement of those trace metal concentrations occurring in sulphide minerals, and delineation of strong and extensive halos of Cu, Pb, Zn, Ag, and Mn around the South Bay massive sulphide deposit. The heavy mineral fraction obtained from rocks shows great potential as an exploration guide to similar massive sulphide deposits.

CONDENSING MULTI-ELEMENT GEOCHEMICAL RECONNAISSANCE DATA

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An empirical discrimination program has been used for classifying multi-variate data from geochemical reconnaissance samples, so that they were related to known geological units or characterised as outliers. Cluster analysis of the outliers revealed samples with element associations which were related to various types of mineralization, unmapped geological units and other geological features.

The data was obtained from a reconnaissance geochemical survey in South Greenland and consists of 2174 stream sediment samples analysed for 17 elements. An additional 3 variables were provided at each sample site by water samples analysed for conductivity, pH and uranium.

Training sets for the empirical discrimination were formed from samples taken over 14 different geological units. Each training set had previously been carefully screened so as to include only samples reflecting background conditions of the geological unit in question. The training sets included 515 samples in all.

Empirical discrimination forms density functions of the training sets by adding exponential functions over each sample. The shape (flatness) of the density functions is determined by a smoothing parameter, parallelling the variance of a normal distribution. The value of the smoothing parameter is chosen empirically to maximise the correct classification of the training sets.

It was possible to obtain a 100% correct classification of the 14 training sets with smoothing levels between 0.8 and 0.5. The condensed geochemical map resulting from the classification of all samples corresponds well to the geological map.

The number of outliers found could be varied by changing the smoothing level. With the levels 0.8, 0.7, 0.6 and 0.5, 16, 33, 110 and 289 outliers were found respectively. The smoothing level of 0.5 was empirically chosen so that enough outliers were obtained to reveal geographically grouped anomalies. The 289 outliers were classified into 30 groups with similar elemental characteristics using Q-mode cluster analysis. Most of these groups could be explained in terms of the different types of mineralization, or the mixing of sample material from different sources particularly from geological units which are too small to have been mapped. For example there were 6 clusters which were related to high uranium values each one characterising different uranium mineralization. Also clusters related to mineralization with niobium, zirconium and rare earth elements were found. Other clusters could be related to other types of mineralization, small geological units not included in the training sets or poor sample material.

NEW TIN-TUNGSTEN OCCURRENCES IN THE SURPRISE LAKE GRANITIC COMPLEX OF THE NORTHERN CANADIAN CORDILLERA: A GEOCHEMICAL EXPLORATION CASE HISTORY

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Analysis of regional stream sediment and stream water samples collected as part of the National Geochemical Reconnaissance Program first indicated that the Surprise Lake intrusion of the northern Canadian Cordillera is a "metallogenetically specialized granitoid". Computer-generated coloured maps of regional data pointed out the Mo-W-Zn-Sn-F elemental association and showed Sn-W and Sn-Zn anomalies.

Lithogeochemical investigations and detailed follow-up stream sediment studiesincluding heavy mineral and size fraction analysis led to the discovery of previously unknown Sn-W mineralization.

In terms of collision-type orogenic tectonic events, a model is presented to describe magma evolution and explain its geochemical characteristics. Markedly similar to Tischendorf's "specialized" tin granite classification, this "tin-fluorine" intrusion is an example of a highly evolved silicic magma enriched in fluorophile elements (U, Th, F, Sn, Rb, Nb, Y, Cs, REE, Be, etc.) and depleted in Sr, Ba, and Zr compared to average low-calcium granites. Boron is notably absent.

Related to late- and post-magmatic processes, the Sn-W and Sn-Zn mineralization is emplaced in greisens, greisen-bordered veins, and replacement veins. Its presence is critically dependent on the availability of magmatic-meteoric hydrothermal fluids circulating in convection cells related to deeply penetrating fractures produced during the rupturing of the outer crystallized granitic carapace.

POLYGENETIC CHARACTER OF ENDOGENIC HALOS ASSOCIATED WITH MASSIVE SULPHIDE DEPOSITS

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Endogenic geochemical halos (EGH) associated with massive sulphide deposits have been considered to be of a single stage character,formed simultaneously with the ore bodies because their zoning relationships are similar to the general zoning present in hydrothermal ore deposits. Likewise, the occurrence of the halos in overlying formations (rocks) has been considered to be an indication of the epigenetic character of the sulphide ores.

Recently numerous new data have demonstrated a long and complicated history of the formation of EGH. The polygenetic character of massive sulphide deposits has been shown to be much more developed in halos than in ore bodies, a feature caused evidently by a longer duration and wider range of conditions of formation of the halos.

As a rule halos of different genetic types coincide and envelope pyrite deposits. Halos of the hydrothermal-metasomatic deposits are more often single stage, but investigations of the chemical composition of the minerals in these halos indicate that the components that are syngenetic with metasomatism and with later ore formation can be distinguished. Typical multi stage (polygenetic) halos are formed around hydrothermal-sedimentary deposits. Features syngenetic and epigenetic with the ore bodies are normally distinguished in these halos. The former are represented by hydrothermal-metasomatic halos below the ore and by flanking hydrothermal-sedimentary halos. The epigenetic features are developed in the overlying formations as a result of the post-ore activity of hydrothermal ore-bearing solutions.

Post-ore dislocations as well as regional and local metamorphism produce some changes, including redeposition of ore minerals and their associated EGH. However, dislocations and regional metamorphism up to the amphibolitic stage do not cause notable changes in the morphology and zoning of EGH. Only changes of composition in the ore minerals reflect the local redistribution of the ore components in the EGH caused by metamorphism.

The EGH are also stable also during "dry" contact metamorphism. Only rarely have redistributions of the ore components and radical changes of the initial composition, morphology and zoning of EGH been observed as a result of the influence of thermal fluids. An example of "dry" contact halos is provided by "dyke" halos, formed as a result of the local redistribution of ore components along post-ore dykes cutting the ore bodies.

The polygenetic character of geochemical halos of pyrite deposits is determined by complex geologic and mineralogic-geochemical criteria. However, geochemical indications of different genetic types of halos have a subordinate significance.

The similarity of the zonal structure of polygenetic halos associated with pyrite deposits is explained first by unidirectional changes in space and time of the composition of halos. Halos of the latest stages of ore formation, as well as frontal zones of single stage halos, have an essentially polymetallic (Pb, Zn, Ag, Ba) composition. In addition, we assume that the distribution of indicator elements reflects the totality of the long activity of ore-bearing hydrothermal systems, the last stages of which may be represented most widely and clearly, and may mask the preceeding stages. Zonal structure is considerably complicated in contact-metamorphic halos and in the cases of superimposed non-pyrite mineralization.

The polygenetic character of halos must be taken into consideration in geochemical forcasts and in prospecting for blind massive sulphide ores. On the other hand, the occurrence of epigenetic halos in overlying rock formations permits geochemical prospecting for blind mineralizations up to depths of one hundred meters and more.

For the classification of geochemical halos it is necessary to determine their genetic type and their association with ore-forming processes or with processes of transformation metamorphism of ore deposits.

An evolutionary approach to the study of EGH is one of the ways to increase the effectiveness of geochemical methods for forcasting and for prospecting for blind mineralization

STREAM SEDIMENT SURVEY OF THE BOHEMIAN MASSIF

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About 40 000 samples of stream sediments were collected within the area of the Bohemian Massif. The sampling program covered for the first time the drainage system of the Epivariscan basement (42 000 km^2). The mean density of sampling was 0.95 samples per km^2. The -80 mesh fraction was analysed by atomic absorption spectrometry for Cu, Pb, Zn, Ni and Mn, and the -200 mesh fraction was analysed by emission spectrometry for Cu, Pb, Zn, Ni, Ag, As, Bi, Co, Mo, Sb, Sn, Li, B, Be, V and W. The analytical results and uniform geographical coordinates were processed by computer. The processing of atomic absorption data and emission spectrometry data was different because of the quantitative and semiquantitative nature, respectively, of these two analytical methods. The thresholds of anomalies were defined statistically for maps at a scale of 1:50 000 and they were arbitrarily estimated for maps at a scale of 1:200 000.

The high density of old mining works and intensive sources of pollution caused false anomalies which were recognized by observing the concentration relations within the anomalous areas. On each of the 15 maps at 1:200 000 about 5-8 new anomalous areas were detected. They are now under detailed study by a complex of geochemical prospecting methods including heavy mineral, hydrogeochemical, stream sediment and rock geochemical surveys. The results of the stream sediment survey also found use in an ecological study, as the water environment sensitively reflects the variations of the natural geochemical field caused by anthropogenic activities, especially by mining, processing of ore and agricultural, industrial and urban pollution.

FORMATION OF TIN ORES: A NEW APPROACH TO GEOCHEMICAL PROSPECTING

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The most productive types of tin deposits are quartz-cassiterite, quartz-sulphide and quartz-silicate veins. The tin-productive mineral association is characterized by quartz, cassiterite, wolframite and arsenopyrite and was formed by hydrothermal Na-K chloride-bicarbonate solutions at 300-400°C. Fluorine was the permanent component of the tin-bearing solutions.

The experimental determination of the solubility of quartz and cassiterite has shown that the solubility depends on the pH of the solution during the formation of tin deposits. Investigation of the differences in chemical composition of gas-liquid inclusions of the different generations of quartz, deposited during crystallization of the quartz-cassiterite association, has indicated that the crystallization of cassiterite was accompanied by an increase in pH. This was caused by interaction of the mineralizing solutions with the wall rocks.

Investigation of the geological, geochemical and mineralogical features of the tin deposits has permitted us to conclude that the interaction between the solution and the wall rocks occurred in automixing cells. These were formed during the formation of cracks in the wall rocks characterized by irregular permiability. The pH increased in the solution when it penetrated the wall rocks and the elements that could not be transported by the alkaline solution (e.g., Sn) precipitated. The alkali elements were redistributed along the cross-section of the mineralized zone. Tin precipitates in cracks into which solutions, after having penetrated wall rocks, return and mix with initial tin-bearing solutions.

The revealed mechanism of the deposition of cassiterite gave criteria which can be used to predict the size and localization of tin ores in quartz-cassiterite veins.

GEOCHEMISTRY IN THE NORDKALOTT PROJECT

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In 1980 the Nordic Council of Ministers initiated a project to assess the mineral potential of Nordkalotten (Fennoscandia north of 66°N), an area of some 300 000 km^2, using geological, geochemical, and geophysical mapping. The project is a co-operative survey carried out by the Geological Surveys of Finland, Norway, and Sweden. Geochemical samples will be collected from approximately 10 000 sites at a density of one site per 30 km^2.

Mineral stream sediments, stream humus, aquatic mosses (bryophytes), till, and humus (topsoil) are collected where available, and stream water is also being collected in Finland and Norway. The samples are being analyzed for 10-30 elements by X-ray fluorescence, inductively coupled argon plasma spectrometry (ICAP), atomic absorption spectrometry (AAS), neutron activation, and ion chromatography. For ICAP and AAS HNO_3-leach and total extraction are being employed. The heavy mineral fractions of till and inorganic stream sediments are also analyzed.

The geochemical data now available from the Nordkalott Project indicate large differences in metal content levels in different parts of the area. For example, the concentration of HNO_3 extractable Mo is frequently over 20 ppm in stream sediments in northern Sweden whereas values below 0.3 ppm are common elsewhere, and P exhibits a five-fold difference in content over the area. The moving weighted medians for Ni in till calculated for circular areas of radius 30 km, are below 20 ppm in large parts of Sweden and over 100 ppm in large parts of Finland and Norway.

In some cases distribution patterns of elements coincide with known geological structures whereas they seem to indicate the presence of unknown structures in other cases. The eastern large Karasjok greenstone belt in Norway is characterized by high contents of Cr and Ni in till, whereas the western Kautokeino greenstone belt shows more moderate concentrations of these elements. Large granite massifs can be sub-divided based on the surface geochemistry. A Mo province in Sweden, more than 10 000 km^2 in size, was discovered in the stream sediment and stream moss data. Some regions with high contents of Au in stream moss were detected.

Anomalies of limited areal extent were obtained near known deposits as well as elsewhere. Follow-up investigations of some of these anomalies (Au, Pb-Zn, and U) have indicated mineralized sources.

The regional distribution patterns of contents for a given element in different sample types may overlap, whereas in other cases each sample type contributes differently to the total picture.

REGIONAL GEOCHEMICAL EXPLORATION AND DETAILED GEOCHEMISTRY OF THE SHANGANI GREENSTONE BELT, ZIMBABWE, SOUTHERN AFRICA. A CASE STUDY OF NI-CU MINERALIZATION IN ARCHEAN LITHOSTRATIGRAPHIC SEQUENCES

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The Shangani Greenstone belt is located some 90 km northeast of Bulawayo within the Archean craton of Rhodesia, which contains numerous similar belts consisting of relatively well developed volcano-sedimentary sequences of greenstone signature.

During the late sixties and early seventies intensive prospecting was carried out over several belts to determine the Ni potential of the lowermost ultramafic komatiitic lithostratigraphic units of the Sebakwian Group. Although several interesting Ni-Cu sulphide occurrences were finally located, only one of them, the Shangani Nickel Deposit, was subsequently developed into a mine.

The Shangani Belt, which is only partially covered with soils, was initially investigated with a regional soil geochemical survey in which the samples were collected at 50 m intervals along traverse lines spaced 300 m apart. As a result of this survey numerous Ni and Cu anomalous areas were identified over some of the lithological units of the Sebakwian Group.

High Ni values ranging from 1000 to 6500 ppm were commonly found over serpentinitic rocks of two types, viz. ultramafic komatiites and basal duniteperidotite-harzburgite assemblages belonging to differentiated layered bodies. The Ni anomalies over the latter were particularly enhanced by an intensive surface alteration, with the development of limonitic material displaying abundant secondary opaline silica and minor magnetite veining.

The Cu anomalies, with values between 100 and 300 ppm, were lower and in general were restricted to basaltic units and sulphide (pyrite-pyrrhotite) facies-banded iron formations. A few of the copper anomalies, however, were found over ultramafic rocks which displayed also prominent Ni anomalies. Areas with superimposed Ni-Cu anomalies were subsequently investigated with detailed geochemical programmes in which soil samples were collected at 25 m intervals along 50 m spaced traverse lines. In addition, surface mapping and shallow drilling were carried out over these areas in order to investigate their nature and economic interest. As a result of this study, the existence of at least two different types of Ni-Cu anomalies became apparent. One type is associated with sulphide-bearing ultramafic komatiites. A second type appeared to be related to layered bodies, in which the high Cu values detected in soil samples from within the areas of influence of the ultramafic rocks belonging to the differentiated complexes were indicative of the presence of late-intrusive pegmatoid phases partially enriched in Cu.

A detailed rock geochemical programme over outcrops of potentially interesting horizons, in areas adjacent to ultramafic rocks, also helped to differentiate the Ni-Cu bearing gossans from the barren sulphide (pyrite-pyrrhotite) facies-banded iron formations. The latter were developed as stratigraphic units at the top of acid to intermediate aquagene tuffs, during quiescent periods between major volcanic cycles.

Numerous rock samples (particularly of mafic to ultramafic volcanic varieties) from different lithostratigraphic units were analysed for major and trace elements and these were compared with established classes of Archean volcanics.

GEOFIZ: THE INFORMATION CENTER FOR MINING — GEOSCIENCES - WATER MANAGEMENT

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GEOFIZ is one of twenty information centers planned to be set up in the Federal Republic of Germany. Some of these are already in operation.

These information centers have been started as part of the information and documentation program of the Federal Republic. The aim is to group the existing scientific and technical documentation centers into twenty information systems, to provide a complete documentation in all areas of science and technology through cooperation agreements and to make the literature and collections within the various fields available to a wide public. GEOFIZ is working at the Federal Institute for Geosciences and Natural Resources of Germany.

GEOLINE, the database implemented by GEOFIZ covers world-wide technical literature on geology and geophysics. It organizes and indexes papers from over 5000 serials and other publications such as books and book chapters, conference papers, government publications, theses, dissertations, reports, maps, and meeting papers. The subject coverage of the publications indexed includes the following major areas: geology; boglands, moorlands, and peat; economic geology; environmental geology; engineering geology; hydrology; isotope geochemistry; marine geology; mineralogy; extraterrestrial geology; geochemistry; geochronology; geomorphology; geophysics; mineral economics; paleontology; soil sciences; petrography; sedimentation; stratigraphy; tectonics.

For the geosciences about 50 000 publications are documented annually. An international association for documentation takes charge of the input. Members of this association are: American Geological Insitute (USA); Centre National de la Recherche Scientifique (F); Bureau de Recherches

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GEOLINE is the first data-base implemented by GEOFIZ at the Information System Karlsruhe (INKA) and it is accessible to users with their own on-line terminals via telephone lines, Euronet, or Datex-P. The INKA computer offers the possibility to switch to all of the 50 data bases, for example COAL, COMPENDEX, DECHEMA, DETHERM, ENEC, ENERGY, ENERGYLINE, INSPEC, PHYS.

For the Association of German Metal Producers and Mines (GDMB) and the Mining Research GmbH (BBF) two other data-bases are in preparation by GEOFIZ.

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Bibliography	Bibliography of literature on the Mediterranean region with author and keyword indexes appears biannually

DISPLAY OF REGIONAL GEOCHEMICAL DATA

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Under the Nordkalott Project geochemical maps are being produced for an area of some 300 000 km^2 in northern Finland, Norway, and Sweden (see Bergström et al., this volume). Ideally these maps should show various background areas, structures favourable for mineral deposits, and isolated anomalies. Experiments were carried out to show how the choice of symbols and content intervals to be represented would affect the anomaly pattern displayed on maps. Colour techniques were tested on filtered data. Ni in till was used to demonstrate the results.

The results show that an anomaly pattern is strongly influenced by the choice of symbols and especially by the way the symbols are related to the content range to be displayed. Dots, the diameters of which increase exponentially with exponentially increasing contents, were found to be satisfactory for display of geochemical patterns. Care should be taken, however, in the choice of relation between the symbol-size range and the content range because by this choice the variability of a specific part of the content interval may be accentuated. An unfortunate choice may show the variability in areas of low background, while anomalies in areas of high background will not visually stand out.

Colour maps prepared from filtered data show features that are not apparent in maps of data displayed by symbols. The disadvantages are the long computional times and the expensive colour map production and reproduction of copies.

BUILDING-UP OF SECONDARY HALOS OF BLIND ORE CLUSTERS AND THEIR GEOCHEMICAL EXPLORATION ON THE SURFACE

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Geochemical halos in near-surface media are formed by ascending streams of fluids caused by: a) static head of ground water; b) rock pressure either from non-consolidated rocks at the depths of hundreds of meters or from semihard ones in the first few thousands of meters; c) evapotranspiration; d) elasticity differences between vapours and underground air.

Except in the last case the capillary fringe should not be below the predominating vegetation root system. Under geochemical landscape conditions where buried lithological and hydrogeochemical paleohalos are missing the detection of blind ore clusters by use of near-surface media is impossible.

Secondary geochemical halos may be detected even when the orebody and also the associated primary halo are tens or hundreds of meters below the bedrock surface. However, geochemical anomalies in transported overburden, soil, weathering crust, vegetation, water, and air are often determined not by the primary halos, but by the redistribution of trace elements among interacting media containing the system of secondary geochemical halos.

Under little fluid inflow, considerable biomass growth rate, and small amount of vegetation fallout, the consumption of ore elements by plants is comparable with their total intake. In this case detailed biogeochemical maps fill out "gaps" within soil- and hydrogeochemical anomalies. In one ore province with 30-80 m deep alluvial overburden the dependence between ore element content in the grass ash (C_{gr}) and their content in the dry matter of alluvial water (C_w) is approximated by the relation:

$$C_{gr} = K/(C_w)^m, \text{ where } m = 1\text{-}2 \qquad (1)$$

At an increased element intake the inverse relation (1) changes to a direct one. Similar inverse relations have been observed between the ore element content in plants and soil, as well as between those in humic and illuvial soil horizons.

The chemical composition of hydro-, litho-, bio-, soil-, and air-geochemical anomalies is continuously changing. Sufficient approximation of the primary halo composition may be obtained only by simultaneous sampling of soil and predominating vegetation, or soil and ground water, or weathering crust and ground water, or the lower chemically active layers of the overburden and ground water.

Under complex geochemical landscape conditions it seems reasonable to normalize all trace elements characteristic of the zoning of ore deposition, as well as those of broad dispersion, against major elements (within the humic soil horizon also against humus content). Attention should be paid to anomalies and elements within various media which remain anomalous after re-calculation.

USE OF SEAWEED AND SLOPE SEDIMENTS IN FJORD PROSPECTING FOR LEAD AND ZINC

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Shoreline geochemical prospecting in fjords, done from a small boat, was found to be an easy and rapid way of detecting sulfide deposits in the cliffs above. Near Maarmorilik, West Greenland, anomalously high lead and zinc values were found below each of the three principal known deposits of high-grade massive galena-sphalerite-pyrite. All three deposits outcrop high on nearly inaccessible cliffs. The sampling was done on seaweed, which grows semicontinuously along the shoreline, and on slope sediments from the semicontinuous colluvial apron at the base of the fjord cliffs. The stream sediment samples were analyzed in the field by dithizone colorimetry, which measures the integrated cold-extractable amount of seven heavy metals: Zn, Pb, Cu, Co, Ni, Sn, and Ag. Of these, zinc usually constitutes the main registry. The seaweed samples were either deep-frozen immediately after collection or sun-dried in the field and sent to Copenhagen. Here all samples were ashed and analyzed by dithizone colorimetry and emission spectrography.

One of the sulfide deposits, the Black Angel at Maarmorilik, has been mined since 1973, and lead- and zinc-bearing tailings are dumped into the fjord. Since 1972, continuous systematic and detailed sampling has been done to monitor fjord pollution from the mill. Mean background lead values of fresh seaweed run less than 1 ppm, but 6 km away from the mine, after three years of mining, lead had increased to 8 ppm. Outside the Maarmorilik area, the whole fjord system sampled remains essentially unpolluted. The grade and tonnage of all three of the main lead-zinc deposits was established by surface and underground work and by diamond drilling. The Maarmorilik area therefore affords an exceptionally clear picture of the behaviour of heavy metals over a decade, as related to the lead-zinc deposits, both before and after significant pollution from mining. Sampling was done by several investigators using several types of samples and several methods of analysis. Corroboration of these investigations is attested by the general agreement of the results and by the recognition of the three known lead-zinc deposits.

PRINCIPLES AND METHODS OF GEOCHEMICAL DATA ANALYSIS FOR CONSTRUCTION OF INDICATOR ELEMENT MAPS

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A major problem in geochemical prospecting is in selecting an appropriate procedure for displaying patterns of associations of geochemical indicator elements; their position in space and their element composition in relation to the ore body (halo zoning). The indicator elements and associations of halos are determined by the processes of epigenetic geochemical dispersion, and are related to endogenous ore-genesis.

The processes of geochemical dispersion which accompany the formation of the rock complexes at the site of geochemical sampling govern the element composition, the ratios of element concentrations, and the spatical distribution of associations developed simultaneously with the formation of the complex.

Representing element concentrations as a composite of two geochemical dispersion fields (components) is a productive basis for the quantitative analysis of geochemical data, both for prospecting and for understanding the complex geochemistry of the bedrock. The two component model is complicated by random fluctuations representing sampling and analytical variability:

$$\Xi(x,y) = [C_A(x,y) + C_O(x,y)] \cdot \Psi \qquad (1)$$

where $\Xi(x,y)$ is the m-dimensional random field which is the model of element concentrations observed in the sampling site (x,y); $C_A(x,y)$ is the m-dimensional component which describes the variation of indicator element concentrations caused by halo-forming processes; $C_O(x,y)$ is the m-dimensional component which describes the variation of syngenetic concentrations, within the rock; Ψ is the m-dimensional random function which is independently and identically distributed with a unit vector of expectations.

The delineation and analysis of the component $C_A(x,y)$, which is stipulated by superimposed halo-forming processes, is realized by an automated system of data processing for geochemical exploration (ASOD-GEOPOLE). The principal basis of the system is the filtering of the random fluctuations with a problem-orientated band-pass filter. This method decreases the errors of analysis as well as differences in background concentrations of elements between different rock types. The next stage is construction of the maps of the associations of the indicator elements. The system of data analysis does not demand a prior knowledge of background parameters or of the number and types of ore complexes, the halos of which may be discovered within the area of geochemical sampling. The determination of the m-dimensional component $C_A(x,y)$ of the indicator elements has been realized using the correlation matrix based on the principal component method.

Using this model and procedure it is possible to construct geochemical association maps which reflect features of the geochemical dispersion processes which occurred during the formation of the rock complexes.

THE PROSPECT FOR GEOCHEMICAL EXPLORATION - PREDICTED ADVANCES AND NEW APPROACHES

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Areal (two dimensional) geochemical surveys, based mainly on secondary dispersion halos and trains in media such as surface waters, soils, and drainage sediments, have proven particularly successful in recent years and have greatly assisted in the discovery of a large number of varied mineral deposits. In the future we can expect refinements and greater use of clast (float) and light and heavy mineral surveys utilizing soils and stream and lake sediments as media. Such surveys will prove to be particularly useful in locating gold, tin, tungsten, and platinoid deposits. One can also predict that more sophisticated overburden drilling techniques for sampling will be employed in future exploration for all types of mineral deposits.

Three dimensional surveys based on primary halos and primary and secondary leakage halos have received relatively little attention to date. Such surveys offer many novel approaches for discovering blind mineral deposits deeply buried below overburden or within their host rocks. In this category we can expect increased use of various techniques utilizing analyses of surface rock samples and drill cores to define the type and distribution of enveloping and leakage halos associated with mineral deposits, particularly the application of various ratios (e.g., K/Na, Th/U, etc.) to estimate approach to ore, the determination of changes in lateral and vertical zonation of elements in mineral deposits for estimating possibilities of ore in depth or in areal extent, and the determination of changes in geothermometric, geobarometric, and thermoluminescent parameters to aid in assessing extensions of ore in depth or in areal distribution.

Ground waters generally have deep penetrative power in most mineral belts, in some belts up to 500 metres or more. Ground-water samples provide, therefore, an ideal media for analyses in geochemical surveys. We can expect that this media will find much greater use in detailed surveys, not only to locate mineral deposits of many types but also to aid in exploring extensions and subsidiaries of deposits already known.

Trees and shrubs draw metals from considerable depths in mineral belts. This is the basis of biogeochemical surveys utilizing analyses of plant ash. We can anticipate extensive refinements in the techniques of biogeochemical surveys, and can expect that areal biogeochemical and geobotanical surveys will be carried out in the future in a manner similar to those utilizing drainage sediments. The materials of bogs as sampling media will ultimately find greater regional use in a manner similar to that of lake sediment surveys.

The search for hydrocarbons (petroleum and natural gas) by geochemical methods is now just beginning in earnest. We can expect to see the development of many sophisticated techniques based on hydrocarbon halos in overburden and bedrocks to locate concentrations of oil and gas.

Research in pathfinder elements, including the mineralizers (e.g., B, CO_2, S, Cl, Br, I, and F) will undoubtedly receive much more emphasis and should result in finer tuning of rock, soil, drainage sediment, and biogeochemical surveys. The use of stable and radioactive isotope methods, a field hardly touched in geochemical prospecting, should see considerable activity in the coming years.

Likewise, gases as indicators, particularly radon, should find increased employment in mineral and hydrocarbon surveys. Mathematical interpretative procedures will undoubtedly be improved and utilized more intelligently in future geochemical surveys. And finally, we can expect many improvements in analytical techniques for the estimation of the content of the less abundant elements (e.g., Au, Pt, Bi, etc.) in geological materials.

GEOCHEMICAL CRITERIA IN SEARCH FOR SEDIMENTARY DEPOSITS

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The Institute of Mineralogy, Geochemistry and Crystallochemistry of Rare Elements initiated methodological geochemical investigations for discovery of sedimentary, mainly phosphorite, deposits based on the success of geochemical exploration methods in the search for hydro-thermal deposit (Yanishevskii and Grigorian, 1963; Ovchinnikov and Grigorian, 1967; Beus and Grigorian, 1967). Investigations of the distribution of elements in sedimentary formations of humid areas have shown the existance of zonal distributions in an "ideal" facies profile (Strakhov, 1968). A coherent series of ordered zonal distribution of elements was established:

$$(Mo_1\text{-}Ba_1\text{-}Cu_1) - (Pb\text{-}Cr) - (Mn\text{-}Cu_2\text{-}Zn)$$

$$(Co\text{-}V\text{-}Ni) - (Sr\text{-}Ba_2\text{-}Mo_2)$$

This pattern appears to be independent of conditions of facies formation, composition of parent rocks, source of the terrigene material and size of the sedimentary basin.

The distribution of chemical elements in the stratigraphic section of sedimentary rocks enclosing productive phosphorite-bearing series is characterized by consistent patterns which extend over large areas of the sedimentary series. Structural-facies zones favourable for the formation of phosphorites have distintive major and trace element signatures. These features are valuable for predicting areas containing phosphorites.

Data on special geochemical features of phosphorite deposits indicate that geochemical methods can be successfully and efficiently applied in the search for not only phosphorite occurrences, but also for other mineral resources of sedimentary origin.

SELECTIVE EXTRACTION TECHNIQUES IN EXPLORATION FOR VOLCANOGENIC SULPHIDE DEPOSITS: EASTERN BLACK SEA REGION, TURKEY

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Selective extraction techniques employing 0.05 M EDTA, 1M hydroxylamine hydrochloride in acetic acid, 0.157 M ammonium oxalate in oxalic acid, and a hot nitric acid solution were used to assess the mode of occurrence of trace elements in the various geochemical sample media and to increase the anomaly contrast over the concealed massive ore bodies.

In hematititzed pumice tuffs, an exhalate horizon overlying the Madenköy Massive sulphide ore body, trace elements such as As, Cu, Zn, Pb and Mo are partly associated with sulphides and partly occur in clays and in Fe- and Mn-oxides.

The extraction data for stream sediments indicate that hot nitric acid attack is the best digestion procedure for detecting mechanical dispersion trains in regional geochemical programmes. Comparison of the extractabilities of metals in soils from mineralized areas with those from the background Sirtköy soils by the different extraction procedures demonstrates that EDTA, and to a lesser extent hydroxylamine hydrochloride, are the best extractants for increasing the anomaly/background ratio. These two extraction procedures were also found to enhance Zn and Pb anomalies over the cover rocks of the Madenköy massive ore body relative to the largely exposed stockwork impregnation zones.

Of the EDTA, hydroxylamine hydrochloride and ammonium oxalate extractions, only the last one afforded considerable amounts of As from the soil samples. Vapour-phase analysis suggested that mercury occurs mainly in sulphide form, which is leachable only with ammonium oxalate solution, which also leaches the adsorbed mercury. The EDTA and the hydroxylamine hydrochloride solutions only extract adsorbed mercury. These three extractants have no effect on either mercuric oxide or mercuric sulphate.

ROLE OF GEOCHEMISTRY IN THE INTEGRATED SEARCH FOR DEEPLY BURIED DEPOSITS: THE ATHABASCA BASIN, SASKATCHEWAN

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The Athabasca uranium deposits occur near the unconformity between metamorphosed Archean-early Proterozoic basement and unmetamorphosed Athabasca sandstone of later Proterozoic age. The early discoveries were made near to the outcrop edge of the unconformity. In more recent years exploration has moved into the Athabasca Basin, with discoveries of small, but high grade, deposits being made beneath 200 m of sandstone cover. This challenging exploration environment calls for an integration of the best geological, geophysical, and geochemical methods of exploration.

The principal controls on mineralization are, firstly, favourable basement (footwall) lithologies and, secondly, fracture zones that are continuous from the basement through the overlying sandstone. Airborne and ground electromagnetic methods and airborne magnetic gradiometry are effective in locating favourable basement lithologies and also fracture zones.

At first sight the Basin is an unpromising environment for geochemical surveys. The Athabasca sandstone is silica-rich and has a very low background for most elements, including uranium. However, there has been major dispersion of ore and associated elements along the fracture zones that host the deposits. Such geochemical indicators have reached the present erosional surface of the sandstone directly above some deposits, but in other cases, not. Thus care must be taken in the interpretation of data.

This paper reports on the geochemical aspects of a comprehensive study of exploration methods within a portion of the Athabasca Basin that hosts a majority of the known deposits. The principal contributions of geochemistry to exploration in this and similar terrane are:

1. A regional biogeochemical mega-anomaly for uranium, that is not reflected in soils, sediments, or waters.
2. Drainage survey (lake sediments and waters) anomalies that identify the major, mineralized fracture zones.
3. Extensive alteration haloes in the sandstone around the deposits.
4. Overburden geochemical surveys, including radon, that identify where traces of mineralization have reached the present erosional surface along fracture zones.

ANOMALOUS STRONTIUM IN THE BEDROCK AND GROUNDWATERS OF WESTERN OHIO AND ITS RELATION TO GLACIALLY DISPERSED MINERALIZATION

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Celestite is associated with a belt of minor lead-zinc-fluorspar deposits in northwestern Ohio and parts of adjacent states. Recent work has shown that anomalous strontium in groundwaters can be used as an exploration tool within the region of mineralization. High concentrations of strontium in the groundwaters of west-central Ohio and eastern Indiana (Allen County, which lie outside the mineralized area in the direction of ice advance) have been known for many years. This anomalous strontium has been attributed variously to concealed celestite deposits, to celestite-bearing till, or to a combination of both.

To establish if concealed celestite deposits were likely to occur, the strontium content of the bedrock from western Ohio and eastern Indiana was investigated. Ratios of Sr/Ca x 1000 were compiled for more than 500 analyses of dolomite and limestone varying in age from Ordovician to Middle Devonian. A positive correlation between celestite mineralization and high ratios in the dolomite host rock was noted. Ratios ranged from less than 0.01 to more than 60, having a median value of 0.52. All ratios that were higher than 3.0 (six percent of the samples) are associated with celestite mineralization and occurred in the Lockport Dolomite and the Salina Group (Silurian). Trend surface maps of this ratio did not outline any previously unknown celestite deposits.

Strontium concentrations and ratios of Sr/Ca x 1000 were examined for more than 200 samples of groundwater across the region as a measure of glacial dispersion. The bedrock in northwestern Ohio is overlain by glacio-lacustrine sediments, but to the south and southwest a cover of hummocky clay-rich till is found. For wells in the region of celestite mineralization, median values for Sr and Sr/Ca x 1000 were 17 ppm and 170 ppm, respectively. Wells from bedrock adjacent to the mineralization in the Lake Erie drainage basin gave median values of 10 ppm and 70 ppm. Groundwaters from west-central Ohio yielded median values of 4 ppm and 45 ppm. In the latter region no significant difference in values could be noted between wells in moraine and those in till-covered bedrock. Although concentrations of strontium and ratios of Sr/Ca x 1000 both decreased as distance from the mineralized area increased, anomalous values could be detected at the glacial border in southwestern Ohio. South of the glacial boundary median values were 0.2 ppm and 3 ppm. The mode of occurrence of strontium in the till is not known and work on the geochemistry of the till is in progress.

CHARACTERISTICS OF PRIMARY ELEMENT DISPERSION PATTERNS IN THE RED MOUNTAIN PORPHYRY-COPPER DEPOSIT SYSTEM, SOUTHERN ARIZONA, USA

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The Red Mountain porphyry copper deposit is located about 80 kilometers southeast of Tucson, Arizona, within a major region of copper deposits that extends from northern Arizona to northern Sonora, Mexico. The deposit at Red Mountain is part of a major alteration-mineralization system that extends for several kilometers around the surface projection of the highest copper concentrations.

Previous geologic, mineralogic, alteration, and fluid-inclusion studies of surface material and drill-core samples indicate that the Red Mountain deposit is part of a complex mineral deposit system. The system includes several major overlapping periods of mineralization which are now represented by a younger, deeply buried, generally well delineated, chalcopyrite-rich mineral system and an older, essentially barren, pyrite-rich system.

Bulk samples for analysis were collected from a fence of seven holes that transects the center of the Red Mountain system. Samples were collected every 15 meters along the length of each drill hole. Each bulk sample was composited from a 3-meter run of core and analyzed for 34 elements by semiquantitative emission spectrographic methods and for as many as 12 elements by various wet-chemical and other analytical techniques. Plots were made of depth versus concentration for each element in each hole in order to determine the locations of anomalies. Three types of concentration curves can be distinguished. Type 1 curves exhibit a broad peak and a generally low anomaly contrast. These curves are mostly associated with major elements and can be used to separate differing lithologic units. Type 2 curves exhibit sharp peaks that may represent an interval of as much as several hundred meters in a drill hole. Type 2 curves show a high anomaly contrast and are mostly associated with those elements that form the element-enrichment zones around the deeply buried copper deposit. Type 3 curves also exhibit sharp peaks; these peaks usually represent an interval of less than 50 meters and also show a high anomaly contrast. Type 3 curves may indicate thin element-enrichment zones within the deposit system, but more likely indicate mineralization in late-stage veins that cut across the chemical zoning in the overall deposit system.

The element zoning, based primarily on type 2 curves, generally confirms the previously developed concept of an early, widespread period of mineralization and a later, more restricted and concentrated period. Most of the mineralization associated with the earlier period has been eroded; the remaining part can be identified geochemically, within the fence of holes studied, as a strong sulfur anomaly near the surface.

The later, deeply buried, chalcopyrite-rich deposit has been less affected by erosion and is distinctly zoned, although many of the zones overlap. A barren core is best defined by enrichments of Na, Ca, Ba, Sr, and possibly other elements. Surrounding this barren core is the main copper zone, which is enriched in Ag, Mo, and S, with less significant enrichments of Co, Te, Zn, and Cd. Four element-enrichment zones extending outward from the copper zone include, in order of increasing distance, the suites (1) Mn-K-Au, (2) Zn-Cd-Be, (3) As-Sb-Co, and (4) Ag-Au-Pb-Te-S. The elements enriched in zone 4 are present at least 1500 meters beyond the most enriched part of the main copper zone.

This geochemical study emphasizes that the relative placement and geometry of element-enrichment zones, taken in conjunction with lithologic, mineralogic, alteration, and other forms of geologic information, should be of significant value in identifying and delineating major, deeply buried, zoned mineral deposits.

THE IMPLEMENTATION OF AN AUTOMATED GEOCHEMICAL COLOUR MAPPING SYSTEM

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To extract maximum information from a set of reconnaissance exploration-geochemical data, the method of data presentation is an important consideration. A variety of maps has been used to present exploration-geochemical data, and some of these are (a) the point-source map, (b) the point-symbol map, and (c) the grey-scale map. The point-source and point-symbol maps do not allow the integration of concentration values or symbols into meaningful geochemical patterns. The grey-scale maps suffer from the drawback of the limited dynamic range that can be represented by the grey scales. It is also difficult to study the spatial correlation of multielement data when each element is plotted on a separate map. To obviate some of the problems mentioned, an automated geochemical colour mapping system was implemented.

The system generates a plot tape on a CYBER and displays the results on a DIPIX Image Analysis System. The AGRG mapping package with further development at the University of New South Wales was used to process the data, and to produce regional element distribution maps and filtered anomaly maps. The processing of very large data sets is made possible by the line-by-line operation of the mapping algorithm on the data. The mapping package generates a copy of grey-scale map on a lineprinter and writes a digitized copy onto a plot tape in a form readable by the DIPIX.

The DIPIX was originally designed for the analysis and display of LANDSAT data, and as such, the size of a geochemical data set is not a problem even with a large scale reconnaissance exploration-geochemical program. DIPIX provides a large number of functions and options that control the form and style of the output image on a high resolution colour monitor. The system is interactive, and the interactive sequence for the execution of the image display task is relatively simple and involves, in most cases, entering simple commands as they are prompted by the system. To display a map of 6000 cells takes approximately 2 minutes and this includes the time for entering the necessary commands. A Dunn camera connected to the system generates a high quality microfilm hardcopy of the map.

On the DIPIX, images may be displayed as single variable image or composite of multi-colour image when three separate images, each being a map of one element in one of the colours, red, green and blue are combined. The colour composite is found to be a very useful technique for showing simultaneous multielement concentration and ratio variations, and provides considerable insight into both regional and localized problems of geochemical data interpretation.

The utility of the automated geochemical colour mapping system is illustrated with various mapping options and display topologies using several elements including Cu, Pb, Zn, Sn, U, Th, Ce, and Y from a reconnaissance stream sediment survey. Interpretation of the data using single element maps and multielement colour composites are also discussed.

THE APPLICATION OF STATISTICAL MAP ANALYSIS TECHNIQUES TO RECONNAISSANCE STREAM SEDIMENT DATA FROM THE SEIGAL (N.T.) AND HEDLEYS CREEK (QLD.) AREAS, AUSTRALIA

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A reconnaissance stream sediment survey of the Seigal-Hedleys Creek area has been conducted by the Bureau of Mineral Resources, Canberra. The Seigal and Hedleys Creek lie either side of the Northern Territory/Queensland border. The area is approximately 6000 km^2, and from which 2508 samples were collected. The overall sample density achieved by the survey was 1 per 2 km^2 for the Seigal area and 1 per 3 km^2 for the Hedleys Creek area. The minus 0.18 mm fraction of the Seigal samples were analyzed for 25 elements by AAS (Be, Co, Cr, Cu, Fe, Li, Mn, Ni and Zn) and by XRF (As, Ba, Bi, Ce, F, Mo, Nb, Pb, Rb, S, Sn, Th, Ti, U, W and Y). Ba, F, S and Ti were omitted from the above list when the Hedleys Creek samples were analyzed.

The data were processed by a statistical map analysis technique to: (a) display the broad-scale regional distribution patterns of the elements using a cell-average gap-fill mapping technique, and (b) delineate anomalous areas using the picture frame filter (PFF) and the Kolmogorov-Smirnov filter (KSF). In the cell-average gap-fill procedure, a geochemical map is considered to be divided into a number of square cells of size 1.0 km x 1.0 km and the value for an occupied cell is represented by the mean of those values located within that cell. The small gaps in the data are smoothly filled in using an iterative gap-filling algorithm based on neighbourhood averaging. In the PFF the mean of the values in a 3 x 3 central block of cells is contrasted against the mean and standard deviation of the values in a square annulus at an effective radius r cells away from the current central cell. The central cell is considered to be anomalous if the central mean exceeds the annulus mean by two or more standard deviations of the annulus values. In the KSF, the distribution of the central block of values and that of the annulus values are subjected to a Kolmogorov-Smirnov two-sample test. The central cell is taken to be anomalous if the central distribution is stochastically higher than the annulus distribution at a level of significance less than or equal to 0.05.

The spatial distributions of Be, Bi, Ce, Nb, Rb, Sn, Th, U and Y clearly form a distinctive pattern coincident with the granites and the acid volcanic rocks. In addition U is also enriched in the conglomerates. High responses of Co, Cu, Cr, Fe, Mn, Ni, Ti and Zn occur in mafic igneous rocks. Anomaly filtering of the data has clearly identified the various known occurrences including uranium, tin, tungsten, copper, lead and zinc, and in addition has delineated several anomalies for detailed survey of the Seigal-Hedleys Creek area.

REGIONAL GEOCHEMICAL PROSPECTING IN CALABRIA (SOUTHERN ITALY)

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In 1974 the Italian Government initiated a regional program to assess the mineral potential in Calabria, the most favorably mineralized region in southern Italy. More detailed follow-up surveys were conducted in selected areas.

The Calabria area is geologically extremely complex. Penninic and Austroalpine nappes, comprised of ophiolites, metasedimentary rocks (phyllites, paragneiss, granulites, amphibolites), and granitic and granodiorite plutons, overthrust carbonate Apenninic nappes. Pre-Alpine stratabound and vein-type base metal sulfide mineralization predominates. This mineralization was tectonically redistributed during the Alpine orogeny. Mineralization in the follow-up area consists predominantly of molybdenite and chalcopyrite occurrences associated with granodiorite bodies intruded by microgranular granites.

The regional assessment of the 10 000 sq. km Calabria area was based on 5518 stream sediment samples. The dried minus 80 mesh fraction was analyzed by X-ray fluorescence and atomic absorption methods for Cu, Pb, Zn, Hg, Fe, Mn, As, Ba, W, Mo, Sn, and Be. The follow-up investigation of the 39 sq. km Ferdinandea-Bivongi area was based on 760 soil samples. The soils were analyzed for Fe, Mn, Zn, Cu, Pb, K, Mo, and Au. Simple and multivariate statistics (R-mode factor analysis) were employed to aid data interpretation.

The five-factor R-mode solution was selected as most appropriate for showing geological and mineralization features in the reconnaissance data. Factor 1 (Fe-Mn-Cu-Zn) reflects the surficial coprecipitation phenomena which largely controls Fe and Mn distribution in the stream sediments. Factors 2 (Be-Sn) reflects the presence of pegmatites within metamorphic and magmatic rocks of Calabria. Factor 5 (Mo), and, subordinately, Factor 4 (As-Pb-Zn-Hg-Cu) reflect mineralization. A number of new anomalous prospects were identified in the regional survey.

The three-factor R-mode solution was selected as most appropriate for the follow-up investigation. Factor 2 (Mo-K) clearly reflects Mo mineralization and associated hydrothermally altered areas. No additional target areas were defined.

THE MERCURY CUP: A SIMPLE INTEGRATIVE MERCURY SAMPLING TECHNIQUE FOR THE EXPLORATION FOR BLIND MINERALIZATION

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Mercury appears to be well suited to the search for gold deposits (especially Carlin-type disseminated gold deposits) and polymetallic sulfide deposits and has received much research and exploration attention in the recent past. The results have nevertheless been highly equivocal. Additional studies have shown that gas signals in general and the mercury gas signal in particular are highly influenced by atmospheric variations and soil geochemistry. Complicating atmospheric variations include both soil and air temperature, pressure, and humidity on both daily and seasonal scales. The composition of soils, especially their organic content, Fe-Mn oxide and hydroxide content, clay content, and moisture content also cause difficulties in the interpretation of the gas signal in traditional soil mercury gas-geochemical exploration programs. The mercury cup is a simple mercury gas integrative device particularly suited to geochemical exploration since it eliminates many of the complications in the interpretation of the mercury signal caused by these atmospheric and soil variations.

The technique involves the use of a precious metadetector mounted in a plastic cup that is buried in the ground and allowed to collect mercury by amalgamation for some appropriate period of time (usually 15-45 days). The device is later collected and analyzed for its mercury content.

The Cripple Creek and Victor mining districts in Colorado contain structurally controlled gold veins in an alkalic volcanic complex. Previous studies have demonstrated anomalous mercury in rock anomalies associated with anomalous gold in rock and economic gold mineralization. The mercury cup was compared with traditional mercury in soil techniques and found to be superior in identifying known mercury and gold in rock anomalies without producing spurious anomalies over barren areas.

GEOCHEMICAL REFERENCE STATIONS AT THE GEOLOGICAL SURVEY OF SWEDEN

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A network of geochemical reference stations is being established by the Geological Survey of Sweden. The reference stations are located to natural springs in non-mineralized areas within the national ground-water network of Sweden. This network consists of 75 areas with approximately 650 monitoring stations, representing various geological and climatological settings. The purpose of the stations is as follows:

1. To establish background values of chemical elements in various media within different geological, physiographical and climatological environments of the country.
2. To study the relationship between the chemical composition of samples from springs and from ground water.

3. To study long term and short term fluctuations in the chemical composition of various types of samples (organic and mineral sediments, biogeochemical samples, water).
4. To study the effect of airborne heavy-metal pollution and acid rainfall on the geochemical samples in various parts of the country.
5. To study the relationship between the geochemistry of the soil profile and
   A: the bedrock geology
   B: the ground-water geochemistry
   C: various samples from the drainage system.

GOLD IN DOUGLAS-FIR, A CLUE TO HIDDEN MINERALIZATION AT THE RED MOUNTAIN STOCKWORK, YELLOW PINE DISTRICT, IDAHO, USA

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Evidence from this study indicates the presence of exploration targets beyond the stockwork not only for concealed deposits of Au and Mo, but also for W and Sn. The targets are new and, to a considerable degree, unexpected from other surface evidence. The biogeochemical anomalies that help define the targets are extensive, and the deposits that might be sought are presumably of low grade.

Red Mountain, which lies on the western edge of the ring-fracture zone of the Eocene Quartz Creek cauldron, has been prospected for Au and Ag for at least 50 years. A biogeochemical study was conducted in 1980-82 in an attempt to better assess the mineral potential of the stockwork area. Bedrock contacts are concealed by colluvium, glacial deposits, and forest cover. Soil and plant samples were collected on 200-m centers over an area of 1100 m x 2500 m. The wood of douglas-fir *(Pseudotsuga menziesii)* and the leaves of beargrass *(Xerophyllum tenax)* were used because they concentrate Au and Mo, respectively. Results of the metal content in soil were trivial, although they did indicate a W anomaly south of the stockwork. Analysis of ashed wood by instrumental neutron activation yielded Au values of 0.07-14.2 ppm and revealed two distinct Au populations. More importantly, the highly anomalous samples ($>$4 ppm) are concentrated in the southern quarter of the grid in an area that has no anomalous Au in the sampled soils, has not been prospected, and lies within inclusion-bearing granodiorite, not stockwork. Beargrass samples, which typically contain 20 ppm Mo, contained $<$5 to $>$500 ppm. A belt of above-median values of Mo transects some part of every map unit except the quartz body at the summit. The great extent and the continuity of this belt require some comparably extensive bedrock source of the Mo. The location, shape, and Mo content of the bedrock source remain conjectural, but the source must be large. Subsequent geomagnetic traverses confirmed the belt configuration.

EXPLORATION GEOCHEMICAL MAP OF THE SIBERIAN PLATFORM FRAGMENT

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The method of geochemical prospecting by sampling in drainage systems at wide spacing is rather effective to accelerate detection of mineral resources within wide regions including platform territories marked by difficult prospecting conditions: boggy areas, poor outcropping, thick loose deposits, subhorizontal occurrences, etc. The method is especially efficient when combined with statistical techniques.

Depending upon the survey scale these maps allow establishment of general patterns of distribution and types of deposit, and also the discovery of new promising areas. By content these are predictive maps. Map scales used may be 1:50 000, 1:200 000, and 1:1 000 000 with sampling densities of 1-2 samples per km^2, one sample per 5-10 km^2, and one sample per 20-30 km^2 respectively. The map scale 1:200 000 shows some deposits and allows determination of their type. Maps at 1:500 000 and smaller are mainly used for regional exploration tasks: determination of spatial distribution of deposit as well as detection of large abnormal areas (regions, nodes, zones, etc.).

A region of 600 000 km^2, characterized by platform conditions, was geochemically mapped at a low sampling density to distinguish regional geochemical and mineralogical features. The geological structure of the region consists of subhorizontal sedimentary rocks of Cambrian and Ordovician periods, complicated by a set of anticline and syncline structures, by numerous systems of dislocations with a break in continuity, and by morphostructures of central type. Paleozoic structures are completely overlain by unconsolidated formations of various origins having a thickness up to 10 m and more.

Geochemical mapping in drainage systems is based on sampling of silty (fraction -1 mm) river sediments with a densities of one sample per 6 km^2 and one sample per 1 km^2.

In addition to monoelement maps, multielement maps are constructed based on data obtained using the method of multidimensional field. This map simultaneously represents concentrations of a large number of elements and is therefore named multidimensional. These maps of multidimensional geochemical classes (fields), reflect true element associations and bear most valuable information. When outlining geochemical classes, world clarks of the lithosphere are used for small-scale maps and regional background for intermediate-scale maps.

The maps reflect geochemical and mineralogical features of the territory. Jointed zones in the platform (transcontinental fractures of meridional direction, as well as a number of interesting sublatitudinal zones of deep fractures) are clearly indicated by abnormal geochemical classes. In addition, morphostructures of central type with diameters from 40 to 300 km are established. Some structures are confirmed by satellite imagery. The structures are characterized by a higher content of Ag, Mn, Ba, and some other elements.

Some geochemical classes containing P, Ni, Co, and V are controlled by particular stratigraphic and lithological units of the sedimentary cover of the platform. The most intense anomalies are connected spatially and genetically with structural-tectonic zones. For example, a polymetallic anomaly occurs in the northeastern part of the territory. It is related to a jointed platform zone and extends beyond its limits. Pb and Zn concentration in the anomaly exceeds the world clark by 10-20 times.

In addition to determination of abnormal fields, geochemical maps allow delineation of regional geochemical zonation that differs from metallogenic zonation mapped in previous stages.

The element associations are related to the largest zones of sublatitudinal and submeridional directions. Anomalies with the highest contrast are located at nodes of intersection between the latter and morphostructures of central type. In addition, morphostructures situated in the platform cover and in the basement are characterized by high-temperature element associations, related to basic and intermediate rocks at depth, and also by rare earth and rare-metal associations resulting from granitic rocks of the platform basement. The morphostructures of central type, formed in sedimentary platform cover, are often related to salt diapirism and they have their own geochemical specialization (Ba and others). Geochemical features of terrigenous sedimentational foredeep Ordovician formations are characterized by associations of phosphorus and related trace elements. In the central parts associations of Ni, Co, and V characterize the accumulation fields of sedimentary iron ores.

The investigation shows that intermediate- and small-scale maps of the geochemistry of drainage systems can serve as basis for the correct choice of areas for further exploration either within the platform or in regions with quite different prospecting conditions.

GEOCHEMICAL EXPLORATION IN THE MONTSENY MOUNTAINS, NE SPAIN

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A five-year program of systematic multi-element geochemical exploration of the Catalonian Coastal Ranges has been initiated by the Geological Survey of the Autonomic Government of Catalonia (Generalitat de Catalunya) and the Department of Geological and Geophysical Exploration, University of Barcelona. This paper reports the first-stage results of this regional survey, covering an area of 530 km^2 in the Montseny Mountains, NE of Barcelona, Spain.

The main geological units are: a) a basement of low to medium grade metamorphosed sediments of Paleozoic age (slates, limestones, greywackes and cherts) as well as gneisses and intrusions of granitic rocks, b) undeformed Triassic sandstones, limestones and red shales and c) Tertiary sandstones and shales. Mineralizations are skarns of magnetite - pyrrhotite or magnetite - sphalerite - scheelite (galena-chalcopyrite) and veins of F - Ba (Pb - Zn), Pb - Zn (Ba), Cu and Ba.

A total of 1069 stream sediment samples (sampling interval 400-500 m) and 790 stream water samples (sampling interval 600-700 m) were collected. The -80 mesh fraction of stream sediments was analysed after aqua regia attack for Pb, Zn, Cu, Ni, Co, Fe, Mn, Ag, Cd, As, Sb and Hg by flame and hydride AAS. The F content of waters was determined by specific ion electrode method.

Four different populations corresponding to the main lithologic types were differentiated for statistical purposes: slates and low grade schists, granitic rocks, Triassic sediments and detritic Tertiary. Four classes of samples were considered over each lithologic type: background ($\bar{x}$ to $\bar{x}+s$), possible anomaly ($\bar{x}+s$ to $\bar{x}+2s$), probable anomaly ($\bar{x}+2s$ to $\bar{x}+3s$) and sure anomaly (over $\bar{x}+3s$).

A correlation coefficient calculation and Principal Component Analysis were carried out over each lithology. The results indicate the following:

— only Pb and Zn have significant correlation over slates and low grade schists,
— Ag and Pb are not associated over any lithology,
— Hg shows no correlation with any element.

Four target areas for future survey were recognized:

1) A 40 °C zone of high values of Zn, Pb, Cu, Cd, Ni, Co, As, and Sb in the SW of the prospect. This geochemical association coincides with the first factor of the Principal Component Analysis, explaining 41 % of total variance.
2) A group of Pb - Zn (Ag) and Co, Ni, Sb and As anomalies over Triassic sediments at the NW of the Montseny (factors 1 and 2).
3) An anomaly of Zn, Cu, Pb and Co at the SE related to marbles and gneisses.
4) A strong anomaly of Hg at the SE without apparent relation to target areas 2 and 3.

There are several scattered anomalies of F in waters associated with F - Ba veins.

MERCURY DISTRIBUTION IN THE VICINITY OF CUPRIFEROUS SULFIDE DEPOSITS, TROODOS COMPLEX, CYPRUS

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A geochemical rock and soil sampling program has been carried out in the proximity of eight concealed 'Cyprus type' sulfide deposits, occurring in marginal mafic to intermediate pillow lava series of the Troodos Ophiolite.

The mineral paragenesis of massive and stockwork ore is characterized by the predominance of pyrite intergrown with less chalcopyrite and minor amounts of sphalerite.

To investigate the applicability of mercury as a geochemical pathfinder, the primary and secondary dispersion has been determined in soils, rocks, and selected ores, using flameless atomic absorption spectroscopy (SCINTREX HGG-3) in a field laboratory.

The mercury content (about 100 ppb) of the cupriferous pyrites is relatively low, due to the formation of these deposits by hydrothermal seawater circulation and the subsequent submarine weathering.

Background values of mercury are in the range of 3-6 ppb for surface rocks and 8-12 ppb for soils. Anomaly/background ratios of 10:1 (soils) and 5:1 (rocks) have been found only very close to fault-related shallow-seated mineralizations. Under these specified conditions mercury shows significant correlations with copper, zinc and sometimes cobalt and barium.

In rock samples from boreholes no indication of primary dispersion halos could be detected neither for mercury nor for copper, zinc, and cobalt. Only barium shows in some cases a narrow aureole in the investigated hanging wall lavas.

Owing to the low mercury content of the ore but suitable migration channels formed by fault zones cutting the mineralization, a significant secondary mercury dispersion pattern has been developed only in exceptional cases. The use of mercury as indicator element for the investigated type of deposits is therefore restricted and the mineralizations are delineated more distinctly by copper, zinc and in some cases barium.

METALLOGENY OF FINLAND, NORWAY, AND SWEDEN

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Finland, Norway, and Sweden have a great number of metallic mineral deposits. At present 44 mines are active. Several metallogenic epochs and provinces can be discerned. The bulk of the deposits are confined to the Precambrian, most occurring in Early Proterozoic rocks 2.2-1.6 Ga old and only a few in Archean and Middle-Late Proterozoic rocks. The Caledonian mountain chain hosts a number of important occurrences.

The deposits are associated with metavolcanics and metasediments, or less commonly with plutonic rocks. The ores and mineralizations are mostly metamorphosed and their origin can in many cases only be inferred. Within the Precambrian three tectonic events can be distinguished: 1. the Pre-Svecokarelidic orogeny (over 2.6 Ga) affecting Archean basement rocks, 2. the Svecokarelidic orogeny with its peak around 1.9-1.8 Ga, and 3. the Sveconorwegian tectonothermal activity and plutonism 1.1-0.9 Ga ago affecting SW Sweden and S Norway. The Caledonian orogeny, comprising Palaeozoic and Precambrian rocks, culminated in Mid-Late Silurian and probably continued into Early Devonian.

In the Archean basement gneisses in eastern Finland and Norway there are greenstone belts about 3.0-2.8 Ga old which contain iron formations (Björnevann, Norway and Huhus, Finland) and Ni-Cu sulphide deposits associated with ultramafites (Arola, Finland). In Finland 2.8 Ga old gneiss granites host molybdenite occurrences (Mätäsvaara and Aittojärvi).

Between the Archean basement and the Proterozoic rocks there is in N Finland a long belt containing several intrusions of layered, differentiated ultramafic to mafic plutonic rocks 2.4 Ga old. The intrusions, which belong to a Pre-Svecokarelidic, probably intracratonic event, contain deposits with Ni-Cu sulphides (Porttivaara), vanadium-bearing magnetite (Mustavaara), and chromite (Kemi). The Koitelainen gabbro lying further north contains chromite and platinoides.

The great majority of the economically important ores are found in Early Proterozoic supracrustal formations 2.2-1.9 Ga old.

In Central Sweden acid to intermediate metavolcanics and intercalated limestones-dolomites, more than 1.9 Ga old, contain stratabound iron ores (Dannemora), manganese oxide-silicate ores (Långban), and Cu-Zn-Pb-(Ag) sulphide ores (Falun, Åmmeberg, and other), all of which are of volcano-sedimentary origin. In addition there occur apatite-bearing iron ores (Grängesberg) of magmatic origin. The Orijärvi area, SW Finland, and the Bamle area, S Norway, show certain metallogenetic similarities.

The Skellefte district in Sweden contains syngenetic, volcano-sedimentary Cu-Zn-Pb-(As) sulphide ores (Boliden, Långsele, and others) in acid to intermediate metavolcanics. The Pyhäsalmi and Vihanti ores, NW Finland, are in some respects similar. An island-arc environment of deposition has been suggested for these deposits.

The Enåsen Au-Cu mineralization in a sillimanite quartzite is the only economic deposit in a vast metasediment area between the Skellefte district and Central Sweden. The origin of the ore is uncertain, but it is possibly of hydrothermal nature.

In the Early Proterozoic metasediments in SE Finland there is a long sineuous strip of serpentinites and associated siliceous rocks, dolomites, skarn, and black schists which host deposits of Cu-Zn(-Co) sulphides (Outokumpu, Vuonos, and Luikonlahti). The ores are of volcano-exhalative origin.

In the northern part of Finland, Norway, and Sweden, basic metavolcanics and metasediments contain different types of stratabound, volcano-sedimentary iron ores. Manganosiderites (Porkonen-Pahtavaara, Finland) and manganese-bearing iron ores (Karasjokk, Norway) occur in basalts presumably older than 2.4 Ga. In younger basalts and metasediments (2.2-1.9 Ga old?) there are skarn- and iron sulphide-bearing magnetite ores (Rautuvaara, Finland and Kaunisvaara, Sweden) which in part are copper-bearing (Laurinoja, Finland). The basalt metasediment association contains occurrences of chalcopyrite as stratabound disseminations or breccias (Pahtavuoma, Finland, Bidjo vagge, Norway, and Viscaria, Sweden). At Aitik, Sweden, in metasedi ments probably younger than the greenstones, veins and disseminations of chalcopyrite with some gold occur. The mineralization is considered as syngenetic-metamorphic. In the same region, acid to intermediate metavolcanics, at minimum 1.875 Ga old, host apatite bearing iron ores (Kiirunavaara and Malmberget). The ore formation is assigned to both magmatic and exhalative-sedimentary processes.

Svecokarelian synkinematic, mafic to ultramafic plutonic rocks, about 2.0-1.9 Ga old, containing Ni-Cu sulphides are abundant in central Finland (Kotalahti, Hitura, and Vammala) and occur locally south of the Skellefte district (Lappvattnet). Mafic plutonites with Fe-Ti-V ores occur at Otanmäki, Finland and Kramsta-Gruvberget, Sweden. Around the vast "granitoid of central Finland" there are deposits of sulphide ores (Cu-Mo, Kopsa; Cu-W, Ylöjärvi; Cu-Au, Haveri; Cu, Virtasalmi). Magnetite occurrences possibly related to plutonic rocks of the same age are found at Misi, Finland. The ore is associated with albite gabbros and albitites and is considered as magmatic, formed from a hydromagma.

In connection with late-kinematic Svecokarelian granites, about 1.8-1.75 Ga old, there are in Sweden mineralizations of scheelite (Yxsjöberg and Storuman) and of molybdenite (Arjeplog area). In the latter area, in acid metavolcanics and plutonites, there are several 1.875-1.74 Ga old vein deposits that contain uranium (Pleutajokk). Some granite intrusions, which are 1.7-1.6 Ga old and post-kinematic in relation to the Svecokarelidic folding, contain tin mineralizations (Eurajoki, Finland).

Metallic mineral deposits in Middle and Late Proterozoic formations are rare and mostly without economic value. In Sweden Fe-Ti-V ores occur at Smålands Taberg in a hyperite about 1.6 Ga old and at Ulvön in an olivine dolerite 1.245 Ga old (Jotnian). Of uncertain age and origin are molybdenite occurrences (Knaben) in the 1.6 Ga (?) old supracrustals and granites in S Norway. A magmatic as well as a sedimentary origin is postulated for the molybdenite. The region has been intruded by 0.95-0.85 Ga old plutons of granite and anorthosite charnockite. Around Egersund there are in norites-anorthosites several deposits of magnetite-ilmenite (Tellnes).

In the Caledonides which are built up of thrust nappes transported from the west to the east onto the Precambrian basement there occur a great number of stratabound sulphide ores. Disseminated Pb-(Zn) mineralizations (Laisvall, Sweden) are found along the Caledonian front in autochthonous and lower allochthonous Late Precambrian and Cambrian sandstones and quartzites. The ore-bearing fluids were introduced prior to the thrusting tectonics in Silurian-Devonian. In the inner part of the Caledonides, within the metamorphic, tectonostratigraphically higher nappes, massive to disseminated Cu-Zn Pb sulphide ores (Lökken and several others in Norway and Stekenjokk, Sweden) occur in Silurian and Ordovician metasediments and acid or basic metavolcanics. These ores are considered as formed in a eugeosynclinal island-arc environment. Stratabound, most probably syngenetic, iron ore deposits occur in Norway in the Rana and Fosen districts. Included in the Caledonides are a variety of deposit types probably of Precambrian age, for example the Fe-Ti-V ore Ruotevare, Sweden, which lies in an anorthosite-gabbro complex.

In the unfolded Phanerozoic platform cover there are few metallic mineral deposits. The Cambrian alum shales Sweden are of economic interest for their content of kerogen, uranium, and trace elements such as vanadium and molybdenum.

In the Oslo graben where the tectonic and magmatic activity is related to rifting in Permian time, there are a variety of metallic mineral deposits, mainly sulphides with Cu, Zn, Pb, and Mo. They occur in the surrounding Precambrian rocks (Kongsberg with native silver), in the Palaezoic cover and in Permian plutonic and volcanic rocks.

OPTIMAL COMPOSITE SAMPLE SIZE SELECTION, APPLICATIONS IN GEOCHEMISTRY AND REMOTE SENSING

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Nearly all the data in exploration geochemistry and remote sensing are derived from composites, very rarely is a single mineral grain, or its equivalent in another sample media or system, analysed. However, composites may arise either implicitly or explicitly. Bearing in mind that a common exploration task is the classification of data as being above or below some predetermined threshold the size of the composite may be critical to the recognition of a relatively rare, anomalous event.

In several kinds of exploration geochemical sampling programs more physical sample material may be available than it is considered necessary, or possible due to financial constraints, to analyse. Examples could be drill core and till samples in an area of high access cost where a low incremental cost is incurred with collecting additional samples along a traverse. In both cases the question would be, how many 1 m sections, or till samples, could one explicitly composite and still be able to recognize that one member of the composite contained above the threshold values?

In remote sensing all data are composites, each value representing a finite area defined by the resolution of the sensor. Here the question is how areally extensive and how big a contrast does a feature have to be so that the presence of the feature may be recognized within the implict composite value representing the surface being sensed?

A model has been defined, based on composite or feature size, contrast of "anomalous" to "background" levels, and natural variability in the "background" data which allows the probability of recognition of the composite as being above a threshold to be estimated. The thresholds are defined in terms of the variability of the "background" data and may be selected on the basis of probability of missclassification. That is, how many false alarms, Type II statistical errors, one is willing to persue in order to detect as many truly "anomalous" situations as possible. Tables are presented for a range of the model parameters and control graphs may be prepared from these to facilitate interpolation for specific problems.

The utility of the tables has been evaluated for an explicit composite example from exploration geochemistry, and for an implicit composite example from remote sensing. The results are discussed and it is concluded that the tables are useful for assisting in geochemical composite sample size selection and evaluating system sensitivity for detecting small "anomalous" features in remote sensing.

EXPERIENCE WITH LIBO$_2$ FUSION AND ICPES ON LATERITIC SAMPLES

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Inductively Coupled Plasma Emission Spectrometry (ICPES) promises to provide both the high throughput and the high sensitivity required for analyses in geochemical research programs. However, the method has its own problems and is undergoing development and adaptation.

The introduction of ICPES, primarily used to analyse solutions, offers advantages:

(1) The sensitivity is good for most elements.
(2) There are few chemical or physical interferences and even the most refractory compounds are decomposed.
(3) The use of solutions ensures homogeneity of the subsamples.
(4) The ICPES does not require electrodes, eliminating a possible source of contamination.

The drawbacks are:

(1) Spectral interferences, characteristic of emission spectrometry, need to be corrected for by using sophisticated computerized correction programs.
(2) Sample dissolution is complex and time consuming compared with the preparation for arc source spectrometry or XRF.

ICPES systems are usually introduced progressively in stages, based on increasing expertise and experience gained with operation on real sample runs.

Stage 1: Major and minor elements that are held in refractory minerals. Fusion followed by acid dissolution.

Stage 2: Trace elements reachable without preconcentration step.

Stage 3: Acid extraction and preconcentration for low level trace elements.

Stage 4: Hydride technique for Sb, Bi, Sn, etc.

The first sample suite, for the ICPES laboratory, consisted of lateritic and mature gossan samples, some reaching near iron ore level of Fe content. In "stage 1" these samples were fused in $LiBO_2$ and the melt dissolved. Contradictory conditions have to be satisfied: the analytes must be dilute because of limited solubility in some cases and the tendency for concentrated solutions to clog the nebulizer. Generally 1% total solid, i.e., sample + flux, in the analyte is used. Hence significant dilution of the original solid sample occurs, reducing achievable detection limits. To limit dilution caused by the flux, 1 part sample + 4 parts flux by weight ratio was adopted. After premixing these, the hot melt was clear; however, the iron-rich samples on cooling produced insoluble iron oxides. Chilling the melt in the platinum crucible helped in most cases. The extreme iron concentrations require simultaneous chilling, in water on the outside, and blowing air from above. In this way the loss-on-ignition can be determined as well.

Instrumental analytical methods are usually operated on the basis of daily calibration. This approach presupposes stability of the system. Owing to the large number of elements and interferences between them, valid full daily calibration is impossible in ICPES. Usually a single point is used to adjust the calibration curves to the changed conditions. However, when unknown samples are being run the occurrence of changes is not always obvious. The signal levels may change significantly, often several fold, without any change showing in gas flows or power level. The drift generally is caused by the nebulization system, but the aging of the torch also contributes. Very infrequently one encounters sudden blockage of the sample introductory system. To overcome this problem "normalization" of recordings was introduced. This is achieved by running a special "norm" sample fairly frequently, say every 5th. After accumulating several days' readings the mean values for the norm-sample are established. The daily readings are then adjusted by establishing the deviations of the bracketing norms from the mean and assuming a linear change for the samples (or standards) in between. The scheme improves the comparability of readings.

The norm-sample is prepared the usual way by fusion and nitric acid dissolution. It has significant signal levels for the elements of interest to minimize instrument quantification errors. This requires spiking for some elements, but overall the sample can be considered to have fairly similar characteristics to unknown samples.

RECONNAISSANCE GEOCHEMICAL SURVEY IN NORTH GREENLAND

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During the regional mapping of North Greenland by the Geological Survey of Greenland, 1100 drainage samples were collected for reconnaissance geochemical exploration from an area of 50 000 km^2. The distribution of sample localities is rather irregular as sampling was more or less restricted to working areas of the field teams.

The bedrock geology comprises from south to north a Proterzoic platform sequence with sandstone and basalts, a Lower Palaeozoic carbonate platform and a Cambro-Silurian trough sequence with deep-water clastic sediments. In the northern part of the area the through sediments are included in the Lower Palaeozoic North Greenland fold belt, which comprises metamorphic rocks of the northernmost part.

Where possible, two types of samples were collected from first order streams, 200 g silt and ca. 1 l sand. The minus 0.75 mm fraction of the 656 silt samples was analysed for 20 elements by radioisotope-excited X-ray fluorescence. By leaching techniques (0.3M ammonium citrate + 2% hydroxylamin hydrochloride) Fe-Mn coatings of 440 sand samples were analysed for Cu and Zn by AAS, and the mineralogy of 590 polished sections from magnetic and non-magnetic fractions of heavy mineral concentrates of the sand samples was investigated under reflected light.

The average Cu, Pb, and Zn contents in the silt samples are 29, 6, and 69 ppm, with peak values 298, 79, and 320 ppm, respectively. The analyses of Fe-Mn oxide coatings show average contents of 1.9 ppm Cu and 3.2 ppm Zn, threshold values of 5 and 11 ppm (average + 2 x std. dev.), and peaks of 11 and 30 ppm, respectively. By the ore microscopic study the following sulphides were identified and the number of grains counted: pyrite, chalcopyrite (max. 71), galena (max. 20), sphalerite (max. 10), pyrrhotite, marcasite, bornite, chalcosite, digenite, and covellite. Preliminary results were reported in 1980.

Copper shows high background values in silt samples from the Proterozoic basalts and sandstone areas. The distribution of native copper occurring as inclusions in the silicate grains of the sands reflects the extension of the basalts, whereas the highest amount of chalcopyrite-rich samples and peak values are found in the fold belt. The copper distribution in the Fe-Mn coatings corresponds to that of silt samples. Copper anomalies in silt samples cluster in two areas with basalts and sandstones respectively.

Zinc shows high background values in silt samples from the fold belt, mainly concentrated in areas with mudstone bedrock. The Zn content in Fe-Mn coatings shows a similar distribution pattern. Sphalerite is identified in seven samples originating from the same area. Anomalous zinc values occur in silt samples from the carbonates near the transition fo flysch.

Lead in silt samples shows only a weak correlation with different types of bedrock. Galena was mainly identified in samples from the fold belt.

The occurrences of chalcopyrite and galena and to a minor extent sphalerite combined with the analytical results from the silt samples indicate an area enriched in base metals in the fold belt. An examination of rock samples from this area revealed a chalcocite-disseminated mudstone with 8.9% Cu and 0.5% Pb. Anomalous base metal values in two cases on a regional scale appear to follow lineaments. A number of isolated anomalies of Cu, Zn, and Pb are found in various types of bedrock geology.

The results of this regional investigation shows that the metal distribution patterns of Cu, Zn, and Pb found in the media applied are not strictly coincident, but are complementary to one another. It is therefore recommended to use both sand and silt samples in a reconnaissance programme in dry Arctic areas in order to delineate target areas or geological units which may contain mineral deposits.

RADON AS A GEOCHEMICAL EXPLORATION TOOL

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Radon is a unique element in the radioactive decay chain of uranium that has properties quite different from the other isotopes. It is an inert mobile gas, and because radon is radioactive it can be detected at extremely low concentrations. It thus provides the basis for a very sensitive geochemical method that is quite different from many ordinary solid or liquid geochemical methods. Radon has proven useful in exploring for not only uranium but for other elements that may be associated with uranium. It has also been used for exploring for geothermal sources, in earthquake prediction and in many other applications.

With wider use of radon as geochemical tool in recent times has come a better understanding of the factors influencing its release, movement and detection. Studies of radon emanation from a wide variety of uranium- and radium-containing minerals have shown the effects of water content and other chemical and physical factors on the emanation rates. A recent model of the way in which radon is released from water-covered particles has shown that the water actually enhances radon emanation rates by significant amounts. This has been confirmed by experiments that show dry materials releasing only about 10% of the generated radon while the same moist materials will release over 40%. These differences may explain some of the very large variations observed in measuring radon concentrations in soil gases. Published results from field research on radon movement and experience with radon as an exploration tool for uranium exploration have resulted in new data about the movement of radon and its precursors in typical field situations.

In radon measurements made during drilling operations, radon halos have been detected up to 70 meters above the uranium-mineralized zones and radon concentrations in soil gases have shown significant anomalies (10 to 20 times background) above uranium deposits at depths of 175 meters.

During the last twenty years several new techniques for making integrated radon measurements have been developed, and a few appear to have some distinct advantages over the older grab sampling detection methods. The newer methods, like the passive Track Etch detectors, have been found to be simple and easy to use in the field even by untrained people while at the same time eliminating measurement variations that are caused by the natural fluctuations in radon concentrations in the soil gases.

With the additional research already underway it is believed that radon will find a wider use as a geochemical tool in the future.

AN APPLICATION OF RANK-ORDER STATISTICS TO EXPLORATION GEOCHEMISTRY

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Geochemical data are frequently interpreted using parametric statistical methodology. Parametric statistics are those based on quantities, or parameters, that characterize the population density function. Non-parametric techniques are essentially distribution-free; that is, they make no assumptions about the precise form of the sampled population. We have found distribution-free estimators derived from rank orders to sometimes identify geochemically anomalous areas more clearly than do common multivariate parametric techniques, such as factor analysis.

A simple program (RANK) was written such that chemical data for every variable (element) of interest can be recorded into a vector of ascending order. The rank of any sample in this vector is its position in the order. Thus the smallest data value for each variable has a rank of '1', and the largest has a rank of 'n', where 'n' equals the total number of samples. When tied observations occur, they are assigned the mean of the ranks they would have had if they had been distinct. The ranks for each sample can be summed for a suite of elements believed to be related to a particular mineral deposit type. The net effect of this procedure is to transform any number of separate element distributions into a single unitless distribution that represents a total metal signature for the summed elements. The rank sums are easily divided into percentile classes to aid in the assessment of geochemical trends and anomalies.

R-mode factor analysis was applied to data for 2100 nonmagnetic, heavy-mineral concentrates of stream sediment and active morainal material from south-central Alaska. Lode gold mineralization within the Upper Cretaceous Valdez Group is characterized by varying amounts of galena, stibnite, and (or) arsenopyrite from different districts. Au, Ag, As, Pb, and Sb all had significant positive loadings onto one factor that was related to gold mineralization. Little distinction was possible between the various areas that showed contrasting metal associations. We have found this to be a rather common complication in the application of factor analysis to large, regional geochemical data bases; that is, genetically distinct types of mineral deposits that have some duplication in their geochemical signatures are often described by a single factor. RANK allowed us to rapidly identify and distinguish the different lode gold signatures, such as Au+Ag+As+Pb in contrast to Au+Ag+Sb.

Stream sediment data from the Wallace 1^0 x 2^0 quadrangle, Montana and Idaho, were evaluated using R-mode factor analysis in order to define localities with highest favorability for base- and precious-metal veins containing Pb, Zn, Cu, and Ag. Anomalous scores for our interpreted vein factor also partially described some stratabound copper-silver (Cu+Ag+Pb), stockwork porphyry molybdenum-tungsten (Pb+Cu+Zn), and Sullivan-type (Pb+Zn) occurrences. However, using RANK to sum Pb+Zn+Cu+Ag, we were able to distinguish most of the areas with favorable vein signatures from those most probably characterized by other deposit types.

RANK was applied to hydrogeochemical data from the upper Little Kern River watershed, southern Sierra Nevada, California. This area is characterized by minor base-metal and tungsten-bearing skarn deposits. RANK proved superior to various parametric techniques in allowing us to better approximate the dominant ore minerals underlying various portions of the drainage net.

EXPLORATION ROCK GEOCHEMISTRY FOR GOLD, PARKES, NEW SOUTH WALES, AUSTRALIA

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The London-Victoria lode-type gold deposit near Parkes, New South Wales, was discovered in 1862 and became the subject of modern exploration in 1980 after about 75 years of little or no activity. The deposit lies within Palaeozoic tuffaceous, andesitic rocks. Soil geochemistry was the main technique used to define drill targets, and the deposit is now at an advanced state of assessment for probable development.

Rock geochemistry is being investigated as an aid in drill core interpretation in the search for extensions to the London-Victoria deposit and other similar deposits in the district.

At an early stage of the rock geochemical work it became clear that base metal mineralization was also present in the hanging wall at between 30 and 70 metres from the lode gold deposit. The base metal mineralization is presumed at this stage to be syngenetic and stratiform. Interpretation of the geochemical signatures for both major elements (Ca, Mg, Na, K, Fe) and trace elements (Cu, Pb, Zn, Mn) is confused by an overlap and merging of responses from the two types of mineralization. The measurement of bromine-soluble Sb, As, Bi, and Te, together with the more conventional major and trace elements allows for the discrimination of geochemical halos due to the gold and the base metal mineralization.

The results demonstrate the use of rock geochemistry for gold exploration, its usefulness in drawing attention to geological features, and the utility of a analytical technique for bromine-soluble trace elements commonly associated with gold mineralization.

ELECTROGEOCHEMICAL TECHNIQUES IN DEEPLY WEATHERED TERRAIN IN AUSTRALIA

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Measurement of H^+ ion and conductance of aqueous soil slurries as an exploration technique was developed for detection of mineralization buried beneath thick till in Canada. The technique is conceptually attractive for use in exploration in Australia where large parts of the land surface are mantled by very thick leached weathering residuum. However, the common development of carbonate horizons and the generally alkaline nature of the soils raised doubts about its applicability.

Tests have been conducted over a number of Australian deposits. Most of the work has been done over a massive sulphide deposit at Elura (360 km from Sydney in New South Wales) where production is beginning and at a small massive sulphide deposit at Mt. Bulga (also in New South Wales, about 140 km from Sydney). At Elura weathering extends down to about 100 m and the soils are red earths, frequently calcareous; at Mt. Bulga the soils are skeletal podzols and the weathering is less intensive.

At both deposits characteristic "rabbit-ear" anomalies, with a central peak in some instances, are recorded for H^+ ion. Conductance anomalous patterns are either sympathetic or mirror images of the $H+$ ion pattern, depending upon local conditions. The "ears" of the anomaly generally correspond to the zone of maximum current density of self-potential anomalies.

Particular exploration problems at Elura would have been resolved by using electrogeochemical techiques; over part of the deposit there is no conventional geochemical response in the soils, and there is a very strong transported Pb anomaly for a distance of about 900 m west of the deposit. There are characteristic H+ ion and conductance responses over the entire orebody, but there is no H+ ion and conductance response over the transported Pb anomaly.

The results of the work at Elura and Mt. Bulga demonstrate the potential usefulness of electrogeochemical techniques under some Australian conditions. The limitations have yet to be determined.

ARIADNE: A NEW INTEGRATED SYSTEM FOR MINERAL EXPLORATION

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ARIADNE is a complete system, from sampling to localization of prospective mineralizations, specially designed for use in glaciated terrain. However, parts of the system can be used elsewhere and has even been used successfully in archaeology.

The system's greatest advantage is the small number of samples needed (about one per 3-5 km^2) to effectively localize a mineralization to within an area of 0.25 - 0.50 km^2. This is made possible by the sampling medium used as well as by the sophisticated computer methods involved. These include both fuzzy logic and mathematical morphology. The sampling medium presently used is magnetite from till the trace element patterns of which are compared with those from different types of bedrock. The fact that the system first has to "learn" how magnetites from different rocks appear in their trace element content, is perhaps a drawback, but such data can be used again in other areas together with new data until eventually fairly universal models are obtained. In constructing this learning process it soon became apparent that fuzzy algorithms were superior to ordinary "hard" ones as the magnetites differ both within a rock body and in different types of rocks and the transition often is gradual between two rock types. Fortunately, the only ore-related rock type presently included in the system, that of sulphide ores, is rather distinct — not so much in the absolute amounts of Cu, Zn, or Ni but in the more or less typical proportions of the whole trace element assemblage. When the learning process is established the magnetites from till are included in the model and, by fuzzy classification, the proportions of magnetites related to different rocks are estimated. When such values for example for sulphide-related magnetites are plotted, a map is obtained that roughly gives the location of the sources by displaying the dispersion fans in the till. The next step is to take advantage of differences in variances-covariances between the rock types and between all other rocks together, as well as of differences in mean values. Heuristically it has been found that when till is diluted during transport the similarity due to variance-covariance persists much farther than similarities due to the mean vectors. By using the membership values in relation to the background mean and target-rock variance-covariance, a very clear distance related map is obtained the inverse of which, when properly filtered, shows maxima at or very near the source.

In an area of 1000 km^2, in Central Sweden, ARIADNE managed to pinpoint all known ores and mineralizations plus some fifteen new prospects of which the majority are located in geologically favourable areas.

PRIMARY HALOS IN MINERAL PROSPECTING

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The development of a theoretical basis for geochemical prospecting based on detailed studies of primary geochemical halos around ore bodies has enabled sound exploration criteria for concealed economic metalliferous mineralization at depth to be identified. Multi-component primary geochemical halos accompany all endogenous ore deposits, the chemical elements concentrated in ores forming halos around them.

Primary geochemical halos are generally appreciably larger than their associated ore bodies, particularly vertically. For example, the supra-ore halos of several elements at the Nikolaev lead-zinc deposit (Primorye) and the Kuzaisk skarn-magnetite deposit (Ural) are of the order of 1 km.

Geochemical zonality is a distinctive feature of the primary halos of ore bodies. Various sulfide-bearing deposits (in which sulfide is a major component) are characterized, for example, by a qualitatively identical vertical zonality. In a generalized form this may be represented by a series of common indicator elements of endogeneous deposits as follows: W-Be-Sn-Mo-Co-Ni-Bi-Cu-Zn-Pb-Ag-Cd-As-Sb-Ba-Hg-I (listed in the direction of movement of solutions from sub-ore to supra-ore sections). The series is derived from a statistical generalization of data on the halos of more than 200 deposits, including skarn-scheelite, skarn-polymetallic, porphyry-copper, copper-pyrite and pyrite-polymetallic, copper-bismuth, veined polymetallic, sulfide-cassiterite, gold, antimony-mercury, mercury and other deposits. The zonality of primary halos can be used to distinguish supra-ore halos indicative of the potential for blind mineralization, from sub-ore halos.

The primary halos of certain types of ore bodies are of negligible size and intensity. Such halos may be "enhanced" employing a method of multiplication of element contents whereby for each sample the contents of a group of indicator elements are multiplied together, and the halos of the products delineated. The multiplicative halos are larger and more intense than monoelement halos and their zonal pattern also exhibits a better contrast between supra- and sub-ore elements and is more stable than that of monoelement halos. The zonality of multiplicative halos may be used not only to distinguish supra-ore halos (which are promising for blind mineralization) from sub-ore alteration, but also to assess the level of erosion with respect to the mineralization.

These techniques of prospecting for blind mineralization are being successfully incorporated into geological prospecting programs in the U.S.S.R and a great number of ore-bearing localities have been assessed using lithogeochemical sampling in different regions. More than 150 of these have been shown to have potential for blind mineralization. Approximately 107 localities have been investigated by mining and drilling operations and in 93 cases commercial ores have been detected at a depth down to 800 m. At the remaining localities small non-commercial ore bodies and zones of dispersed mineralization have been recorded.

In assessing the effectiveness of lithogeochemical prospecting for blind ore deposits, consideration must also be given to the reliability with which unpromising geochemical anomalies can be excluded (negative assessment). Experience in the U.S.S.R. confirms the reliability of the method as a basis for the rejection of unpromising geochemical anomalies, developed in the lower sections or below ore bodies or formed by numerous zones of dispersed mineralization. The reliability of such "negative" assessments, can be demonstrated using the results of geochemical prospecting in Middle Asia (U.S.S.R.) where a large number of localities were shown to be unpromising. Twenty-eight were tested by drilling and the results confirmed the correctness of the "negative" geochemical assessment. The practical significance of the application of primary halos as criteria for the rejection of unpromising geochemical anomalies is most apparent when the large number of such anomalies is considered.

LEAD ISOTOPES - AN AID IN ASSESSING MINERAL PROSPECTS

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The isotopic composition of lead in most base metal deposits is known to vary systematically depending on the age of the deposit and the nature of the host rocks. Research has also shown that the lead isotopic composition within base metal deposits tends to remain constant over large metallogenic provinces such as the Lachlan Fold Belt, the Mt. Read Volcanic Belt, the Mt. Isa-MacArthur River district in Australia and the Vihanti-Pyhäsalmi ore zone in Finland. In contrast, leads from rocks and other mineralization have variable isotopic compositions. It is thus possible to make a lead isotopic distinction between samples representing exploration targets of greater or lesser potential in a given area.

Systematic research into the application of lead isotopic determinations to mineral exploration has been carried out at the CSIRO Division of Mineralogy during the past decade with particular emphasis on the assessment of suspected gossans in deeply weathered terrains. The investigation of more than a hundred case histories - fertile as well as barren - has demonstrated that the lead isotope method is effective in delineating attractive exploration targets in any given area and can assist in optimizing exploration expenditure. In relatively unweathered terrains massive stratabound mineralization can ususally be distinguished from vein mineralization even though they produce similar attractive surface geochemical anomalies. In recently glaciated areas, ore boulders found in glacial drift may be classified according to their lead isotopic composition. A more reliable evaluation is possible if "target isotopic ratios" have been established for the area under consideration by analyses of known ore deposits.

The lead isotope method is currently being routinely used by a number of major Australian exploration companies and further research is partly being funded by 15 companies through the Australian Mineral Industries Research Association (AMIRA).

PECULIARITIES OF PRIMARY HALO ZONING

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Primary near-ore halos are characterized by a zonal structure with a general element sequence shown by the Grigoryan-Ovchinnikov universal zoning order. However, there are plenty of examples where this rule is violated due to unusual compositions and thermodynamic conditions in some hydrothermal systems.

Data on zoning of primary halos are indicative of the depth of deposits of the same type. In Au-Ag deposits the upper and lower limits of halos vary when passing from the near-surface ores to deep-seated ones. The latter halos, containing elements of the "under-ore" group (Mo and W), are more intensive, and envelop the whole deposit, including the upper-ore intervals. In near-surface deposits these halos do not reach middle parts of the deposits. Halos of elements characteristic of the upper levels (Hg, Sb, As) are more intensive around near-surface deposits and extend down to the sub-ore sections. In deeper environments the elements disappear at middle and low sections of the ores. Hence, the As x Sb/Mo x W zoning coefficient which is useful for one deposit, may fail to assess deposits at other depths. The coefficient changes from 0.15 to 400 and from 0.01 to 5 for different depths.

The differences in coefficients are more evident for deposits of a multistage genesis. Thus, for near-surface gold deposits As, Pb, and Zn are accumulated in the sub-ore zone environments. At intermediate depths they accumulate in the ore zone, and in deep environments in upper ore zones.

The zoning coefficients are different for the different depths and stretch over ore sections of the adjacent horizons. At every depth horizon there is a relatively isolated and independent system with a specific evolution of chemical processes up-dip the mineralized zone. Thus it is obvious that mechanisms which control the migration and deposition of Au and associated trace-elements differ with depth.

Presently it is assumed that a large number of complex compounds are involved in the process of migration. This is a result of interaction between elements in zoning series of different formational types of deposit. For example, in the Au and Au-Ag deposits, Pb and Zn are mainly concentrated in supra- and sub-ore sections respectively. Tungsten is characteristic of the lower levels, but in Au-Sb deposits it reaches upper-supra-ore zones. In Mo deposits the position of W is mainly influenced by the level of F concentration in the system.

When the properties of geochemical elements are similar, their relative position in the halos depends upon their concentration in the initial solutions. The position of Ag is highly indicative in the halos of Au and Au-Ag deposits. The accumulation occurs in supra-ore zones in the former type. The distribution of Ag exhibits an undulatory character in the latter type because the initial concentration of Ag is higher than in Au deposits and, therefore, the limit of saturation of Ag is reached earlier.

A close interrelation between halo structure and zonation of near-ore alteration reflects physicochemical conditions of ore deposition and enables assessment of section levels of the deposits. Investigation of the distribution of elements like K, Na, Rb, Li, Cs, Ba, and Sr, which actively take part in reactions of metasomatic processes are important.

Elements with similar distributions, caused either by complexing or by coprecipitation, are highly informative. In particular, some Au deposits show a clear relation between the behaviour of Au and the variation of sulphides. Essentially the Au precipitation progresses with decreasing amount of sulphides in the syngenetic mineral paragenesis. The strong relation is in good agreement with the idea that Au probably migrates as hydrosulphide complexes.

COMPOSITION OF CASSITERITE AND ITS APPLICATION IN GEOCHEMICAL PROSPECTING

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In the 1550-1600 Ma old rapakivi granite stock of Eurajoki, SW Finland, cassiterite shows three different types of occurrence: 1) as an accessory mineral in the geochemically specialized topaz-bearing alkali feldspar granite (average tin content 80 ppm), 2) in pegmatite veins and pockets, and 3) in greisen veins. Electron microprobe analyses have shown that the composition of cassiterite varies systematically with the type of occurrence (Table 1.).

Table 1. Mean contents (%) of Nb_2O_5, Ta_2O_5, and FeO in cassiterite.

	Nb_2O_5	Ta_2O_5	FeO
Cassiterite in granite	3.5	2.5	1.8
Cassiterite in pegmatite	2.2	0.5	1.2
Cassiterite in greisen	0.3	0.0	0.1

The compositional differences indicate that the accessory cassiterite of the granite was not formed in association with the greisenization but is probably a primary constituent of the rock.

On the basis of these observations and data available in the literature it was concluded that the composition of detrital cassiterite grains in till of tin-anomalous areas may be used to estimate the genetic type of the source deposit. From the practical point of view it may be of great interest to know, for example, if the source rock is probably a granite with dispersed accessory cassiterite or a hydrothermal deposit. The method was tested in the Wiborg rapakivi area in SE Finland, where Rautaruukki Co. had found a large tin anomaly in till. Altogether 27 cassiterite grains from three localities of the anomalous area were analysed with electron microprobe. The analyses showed that 26 of the grains corresponded to the cassiterite crystals of greisen in Eurajoki and only one grain had higher Nb and Ta contents corresponding to cassiterite from pegmatite or granite. Later, diamond drillings unearthed a number of thin greisen veins and one larger, tin-bearing greisen body at the northern end of the till anomaly. Subsequently, the method was applied in several other tin-anomalous areas in southern Finland.

LASER ABLATION OF STREAM SEDIMENT PEBBLE COATINGS FOR SIMULTANEOUS MULTIELEMENT ANALYSIS IN GEOCHEMICAL EXPLORATION

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Laser ablation of the manganese and iron oxide coatings on stream sediments has been tested as a means of rapidly introducing this highly sorptive geochemical exploration medium into an inductively-coupled plasma emission spectrometer (ICP) for simultaneous multielement analysis.

Training data were obtained by selectively leaching coatings on about ten 1 cm diameter pebbles from 50 sites in the Allen drainage system, southwest England. The lead, zinc, iron and manganese concentrations of the resulting leachates were determined by atomic absorption spectrophotometry. This procedure is relatively rapid and economical, but the leachate is suitable only for the determination of a restricted range of elements (mainly heavy metals). The laser-microprobe testing data were obtained by vaporizing approximately 1 μg of coating from one pebble from each sample site with a single laser pulse, producing a crater in the coating 150 to 200 μm in diameter and 30 to 50 μm deep. The ablation was effected within a cell which the laser beam penetrates via a quartz window, and the vaporized material quickly condenses into an aerosol which is carried in a flow of argon passing through the cell to the ICP, for simultaneous determination of up to 36 elements.

Training and testing data for the elements determined were normalized by ratioing to iron or manganese following a preliminary statistical inspection of the data to ascertain predominant correlations. In the Allen drainage basin, where a narrow and impersistent galena vein with subordinate sphalerite occupies a north-south trending fracture, lead determinations on coatings correlate well with the iron content of coatings, while zinc correlates with manganese. The Pb/Fe dispersion patterns produced by the training and testing procedures are essentially similar, as are the Zn/Mn patterns from each of the procedures, demonstrating the potential of the novel laser microprobe technique.

Anomalous Pb/Fe and Zn/Mn ratios in pebble coatings occur in the vicinity of the mineralized fracture. These compare favourably in terms of anomaly contrast and length of dispersion trains (especially their extension beyond major confluences) with the lead and zinc anomalies detected by the more conventional analysis of the minus 200 μm fraction of the stream sediment. The low levels of potential pathfinder elements associated with mineralization do not lend themselves readily to determination in leachates derived from pebble coatings. Laser microprobe data, however, revealed a low-order but punctual As/Fe anomaly in a tributary, where this cuts the mineralized vein.

This research has substantiated the results demonstrated elsewhere that stream sediment pebble coatings provide high-contrast heavy-metal anomalies and long heavy-metal dispersion trains reflecting mineralization, and has introduced a rapid laser ablation ICP analytical technique that greatly extends the range of elements that can be (simultaneously) determined in coatings. An unusual feature of this technique is that the geochemistry of perhaps more than 1 km^2 of ground area is adequately represented by about 1 μg of pebble coating.

RARE EARTH ELEMENT ANALYSIS BY PLASMA/MASS SPECTROMETRY

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Recognition of rare earth elements as useful indicators of rock genesis has lead to the development of several analytical methods in recent years. Neutron activation, plasma emission spectrometry and a combination X-ray/chemical method have been used with varying degrees of success.

This paper concerns itself with utilisation of mass spectrometry through a newly developed plasma mass spectrometer manufactured by Sciex of Thornhill, Ontario, Canada. This instrument combines an inductively-coupled argon plasma, as ion source, with a quadrupole mass spectrometer by means of a unique interface which permits introduction of samples as solutions at atmospheric pressure. With this approach the sample throughput is comparable to that of ordinary plasma spectrometers. The spectrum is eminently simple (as compared to optical spectra), a significant point to anyone familiar with rare earth spectra. The possibility of employing isotope dilution for internal standardization and calibration exists which is also an important point if one considers the paucity of rare earth standards.

Data to be presented have been obtained on selected reference samples including BCR-1, SY2, SY3, Be-N and NBS 632A and on some typical samples representing Archean granites and volcanics, banded iron formation and metallic ore deposits in Ontario. Particular attention will be given to spectral resolution and sensitivity.

This project is partly funded by a grant from the Ontario Government BILD program; Exploration Technology Development Fund and by the Geological Survey of Canada.

A BEDROCK GEOCHEMICAL METHOD FOR GOLD PROSPECTING

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Bedrock geochemistry was used in Central Finnish Lapland for gold prospecting in Lower Proterozoic quartzites and associated conglomerates. The occurrence of gold-bearing layers within these formations was not known previously.

The whole procedure was based on rapid and inexpensive analyses of thousands of samples per year. Samples were treated with aqua regia solvent and analysed with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with an HGA-500 graphite furnace, autosampler AS-40 and deuterium background corrector using argon as purge gas. Reference analyses by the fire assay procedure proved the method used adequate in gold prospecting.

The samples were taken along lines over outcrops with a percussion drill. The rock powder in each sample amounted to about 20-30 cm^3 in volume.

During a number of years different sample intervals were used in the Kaarestunturi test-area. The first mineralizations were located with sample intervals between 1 and 10 metres along the lines.

In further studies an interval of 15 cm was used, and later as little as 2-3 cm. This was found to give far too many samples for judicious prospecting purposes. Through experience a compromise method was created. With an interval over one metre one could lose mineralizations which often occur as thin beds. An interval of approximately 10-20 cm was therefore chosen. From two consecutive samples half a gram of rock powder was taken from each and mixed. Without further milling it was analysed as one sample. Thus the number of analysed samples was 50 % of the number of samples taken. It was possible to cover relatively thick stratigraphic units with lines consisting of some hundreds of samples each.

The method was used on several locations within the prospecting area. The targets were chosen on a geological basis from outcrops having the stratigraphic sequence exposed by vertical faults. An example is the Kumputunturi quartzite formation, where conglomeratic layers with anomalous gold contents were located on several sample lines.

The method was found to be inexpensive and exact enough for prospecting. It should be suitable for prospecting. It should be suitable for prospecting of other elements having in certain geologic units the same mode of occurrence as gold has in quartzites.

RESULTS OF A GEOCHEMICAL ORIENTATION STUDY IN THE CHICHAGOF-YAKOBI WILDERNESS AREA, SOUTHERN ALASKA, USING HIERARCHICAL ANALYSIS-OF-VARIANCE

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A geochemical orientation study of an 1800 km^2 area in the vicinity of western Chichagof Islands and Yakobi Island, southeastern Alaska, was conducted to ascertain the applicability of hierarchical sampling scheme to more intensive sampling to be conducted during subsequent field seasons. The study included minus 80-mesh fractions from stream sediment samples and heavy-mineral concentrates of stream sediment samples from 29 stream beds that cut through all major lithologic units in the area, so that variations in the chemistry of the samples, both between and within these units, could be examined.

The sampling hierarchy consisted of four levels. In descending order, they were (1) streams, (2) two locations about 100 meters apart on each stream, (3) two sites about 10 meters apart at each location, and (4) one sample of each type from each site, each analyzed twice.

Using hierarchical analysis-of-variance computer program from the U.S. Geological Survey's STATPAC library, we estimated the variance components for each of the 18 metals in the data at each hierarchical level, and calculated F-values, which were used to estimate the significance of differences between the mean concentrations of the metals at each level of the design.

A common misconception concerning the results of hierarchical analysis-of-variance deals with the relationship of field-level (or natural) variance components to analytical variance components. If natural variation is a small percentage of the total variance of a particular metal, analytical variation will constitute a relatively large percentage. Hence, when natural variation is small, a more precise analytical method may be required. Ideally, within-stream variance (which includes analytical variance) would be zero; then all variance would be between streams, and one sample per stream would be perfectly efficient for estimation of the distribution of the metals. High within-stream variance relative to between-stream variance requires more intensive within-stream sampling. High analytical variance relative to field-level (natural) variance requires a more precise analytical method.

The hierarchical analysis-of-variance showed that the stream sediment samples, for most of the 18 metals, yielded larger variance components between streams than between locations or between sites. A large variance component at the stream level indicates minimal sampling is required within streams. Few stream sediment samples, possibly just one or two per stream, seem sufficient to distinguish geochemical differences between streams for Ba, Cu, Pb, and Zn in the study area. A similar situation exists for B, Ba, Cr, and Sr in the heavy-mineral concentrates. Analytical and site variance for Ti in both media, and for V in the heavy-mineral concentrates, sum to more than 90% of total variance, indicating that both more intensive sampling and more precise analytical techniques are needed for definition of the distribution and abundance of these two metals. The remaining metals in the study area have analytical variance components that fall between the two aforementioned extremes, and therefore require an intermediate degree of sampling intensity and analytical percision. Analytical replication confirmed that grinding of the heavy-mineral concentrates to an almost wax-like consistency (minus 300-mesh) was necessary to minimize otherwise unacceptably large analytical variance components.

STATISTICAL APPLICATIONS IN GEOCHEMICAL PROSPECTING: A SURVEY OF RECENT DEVELOPMENTS

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The paper addresses recent developments in the treatment of multi-element geochemical data, with particular reference to the analysis of correlation and regression. Problems are posed by the presence of inherent correlations, particularly between major element data as a result of reporting of composition in terms of percentages. This not only affects the interpretation of inter-element correlation matrices, including apparent trends in the data which are difficult to allow for, but also strongly influences the interpretation of any regression performed on the basis of supposedly "independent" predictors.

Possible ways of dealing with such problems are discussed in the light of recent developments in data transformation, and the application of ridge regression techniques. The recent interest among statisticians in methods for the identification of (multivariate) outliers, often relevent as "anomalous" samples of interest to the exploration geochemist, is also emphasised.

THE USE OF ELEMENT RATIOS IN MINERAL EXPLORATION

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Element ratios based on K, Rb, Tl, Sr, and Ba have been used in the past to identify rocks associated with various types of mineral deposits. Low K/Rb and Ba/Rb and high Rb/Sr ratios have been suggested as guides to mineralization by several workers (Armbrust, et. al., 1977; Tauson and Kozolov, 1973; Plimer and Elliott, 1979). Recently Ikramuddin et al. (1982; 1983) and Ikramuddin (1982) suggested the use of K/Tl and Tl/Sr ratios, as well as Tl, as potential guides to mineralization.

A review of the published literature indicates that most of the element ratios mentioned above are generally useful in delineating mineralized areas but in certain situations a given ratio may be misleading. For example, it has been found that high Rb/Sr and Tl/Sr ratios are generated in unmineralized rocks due to the greater mobility of Sr, as compared to Rb and Tl. In several cases this

author has found an overlap of K/Rb ratios in mineralized and unmineralized rocks. K/Tl ratios seem to work better than the other ratios but they have not been very useful in delineating the mineralized rocks which have been altered by high temperature hydrothermal fluids, as Rb and K are partitioned more into solid phases than Tl.

In order to evaluate the possibility of finding an element ratio that would be most useful as a guide in mineral exploration, about 600 rocks associated with various types of mineral deposits from the western United States have been analyzed for K, Rb, Tl, Sr, and Ba. In addition, Au, Ag, Cu, Mo, and U have been analyzed in selected samples. The samples were collected from 10 different localities in Washington, Montana, Idaho, Nevada, and Colorado. Gold and silver deposits examined in this study are associated with volcanic and alkaline rocks as well as limestones and shales. The uranium and molybdenum deposits are associated with granitic rocks, whereas copper-molybdenum mineralization occurs in granodiorite.

The concentrations of K, Rb, and Tl in altered rocks associated with the various types of mineral deposits mentioned above, are significantly higher than those in unaltered rocks. Tl is more concentrated than Rb and K, while Ba and Sr are depleted in mineralized rocks, as compared to unmineralized rocks. Examination of the data suggests that the concentration of Tl and the element ratios based on Tl can prove to be useful guides in locating mineral deposits of hydrothermal origin. The K/Tl ratio seems to be a better guide to hydrothermal alteration than K/Rb, Rb/Sr, and Tl/Sr, but in certain cases K/Tl values also overlap.

The results have provided ample evidence to suggest that the Ba/Tl ratio is probably the most useful ratio in separating mineralized rocks from unmineralized rocks. The Ba/Tl ratios in altered rocks associated with mineral deposits are distinctly lower than those in unaltered rocks and overlap of these ratios is not observed. Extremely low Ba/Tl ratios in altered rocks are probably generated as a result of enrichment of Tl and depletion of Ba in hydrothermal fluids, as Ba is preferentially incorporated into early K-bearing minerals. Ba/Tl ratios are also more useful than Rb/Sr or Tl/Sr ratios as Ba is not as mobile as Sr in a supergene environment.

It is concluded that the Ba/Tl ratio is probably the best ratio to delineate mineral deposits of hydrothermal origin. The sinificance of the K/Tl ratio in locating gold-silver deposits should not be overlooked, however.

A UNIQUE FLUORESCENCE TECHNIQUE FOR GEOCHEMICAL EXPLORATION

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Fluorescence spectroscopy has had wide application in characterizing hydrocarbon mixtures, especially in geochemical exploration. Fixed wavelength and synchronous scanning fluorescence suffers from non-selectivity and are generally ineffective in structural elucidation of mixtures. Despite the ability to select both the excitation and emission wavelengths, conventional fluorescence methods have limited applicability and produce results that are often difficult to interpret. In an attempt to overcome these problems, a methodology for total scanning fluorescence was developed. A total scanning fluorescence system has several advantages over simpler scanning methods: (1) the acquisition of multiple fluorescence spectra is faster; (2) the amount of fluorescence data per sample is greatly increased; (3) the stored data can be extensively manipulated by computer; and (4) individual excitation spectrum can be retrieved from the total fluorescence spectrum. A total fluorescence spectrum is a powerful and useful "fingerprinting" tool.

The total scanning fluorescence technique has been applied to correlation (oil/oil and oil/source rock) and surface geochemical prospecting studies. The fluorescence system acquires a total fluorescence spectrum of emission, excitation, and intensity for wavelengths between 200 and 800 nm with 2 to 10 nm resolution using a computer controlled UV-Spectrofluorometer (Perkin-Elmer 650-40). The resulting matrix of intensity values, can be presented in a three-dimensional, contour and/or tabular presentation. Similarity indices calculated on a point-to-point basis are used to compare spectra in correlation studies.

Fluorescence analyses of a suite of North Slope of Alaska oils demonstrated the presence of two oil types, i.e., Prudhoe Bay and Simpson-Umiat. Six other oils analyzed were determined to be mixtures of these two end members with one condensate being unique from the other oils. Fluorescence source rock/oil correlations in this study suggested that the Prudhoe Bay oils were primarily sourced in the Kingak Shale with contributions from the Shublik formation and that Simpson-Umiat Oils were primarily sourced in the Pebble Shale Unit. Shales of differing thermal maturities (as determined by R_0), within a single stratigraphic unit had very similar fluorescence fingerprints. Total fluorescence spectra appear to type organic facies and are not simply differentiating on the basis of maturity. A study of pelagic tars showed that fluorescence fingertips are also only marginally effected by degradation and water washing. Environmental tars from the South Atlantic Ocean were easily grouped using fluorescence patterns, despite varying degrees of biodegradation. The method has also been used as a regional evaluation tool in conjunction with surface geochemical prospecting programs. Shallow surficial ($>$2 meters) sediments collected over oil, condensate, and gas provinces have been shown to exhibit distinct fluorescence signatures representative of deeper reservoired hydrocarbon accumulations.

In conclusion, total scanning fluorescence is a useful correlation technique for grouping oils and evaluating oil/source rock relationships. It, no doubt, has to be used in conjunction with other correlation tools. However, it appears to be an inexpensive, fast, and effective correlation tool. The technique can be used in surface geochemical prospecting to differentiate oil and gas prone offshore areas.

FORMS OF ORE ELEMENTS IN FLUVIAL SILTS: APPLICATION IN GEOCHEMICAL PROSPECTING

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Effective prospecting for ore deposits by sampling of drainage sediments and interpretation of resulting geochemical anomalies, as well as understanding the drainage system environments which influence the formation of anomalies, require investigation of the forms of ore elements in fluvial silts. Knowledge of chemical and mineralogical composition of the silt is also important. This investigation is based on typical fluvial silt samples from eastern Transbaikalia. The samples were subdivided into a large number of granulometric and mineral fractions, each of which was analyzed in order to identify metals typical for deposits of the region (Pb, Zn, As, Mo, Au).

The highest concentrations of ore elements were observed in the heavy nonmagnetic and ferromagnetic silt fractions which contain primary and oxidized ore minerals as well as residual limonite and iron hydroxide precipitated in the surface environment. Elevated concentrations of ore elements are characteristic of organic matter and the finest grades of silt. The primary and oxidized ore minerals and limonite carry a minor content of ore elements. The major concentration of the trace elements are contained in organic material mostly associated with fulvic acids and in precipitated iron hydroxides. Mo was found in humic acids and partly in bitumens. Gold was found only in bitumens. Clay minerals, which play an important role as adsorbents, were not found to markedly concentrate ore elements.

The content of ore elements in the ferruginous and organic fraction of silt increases and forms clear geochemical anomalies in drainage systems near deposits. The formation of anomalies not associated with deposits is possible on margins of bogs and in the seepage areas.

As a rule, the composition of anomalies unrelated to ore is simpler than that of ore-related anomalies. This can be used to identify anomalies worthy of follow-up. Highly increased concentrations of ore elements in the heavy nonmagnetic and electromagnetic fractions, unrelated to re-sedimented ferruginous sediments and organic remains, confirms the ore-related nature of the anomalies.

Exploration success may be increased by analyzing ferruginous sediments and organic remains in drainage systems for their element composition.

APPLIED ASPECTS OF REGIONAL BEDROCK GEOCHEMISTRY

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Regional bedrock geochemical investigations have two main empirical tasks: (1) to determinate the geochemical characters of defined regions, (2) to study the internal geochemical structure of these regions and its relations to geological structure and to ore distribution. These problems are usually solved at different stages (scales) of the geochemical/geological survey.

The approach, based on regional investigation of magmatic rocks in Central Asia, is geochemical rock classification and comparative analysis of regional magmatic associations. The geochemical rock type is a group of rocks formed in a specific crustal environment and which have a similarity of composition. This follows the genetic classification of L. Tauson.

A regional magmatic association is defined as a group of geochemical rock types formed at a certain epoch, forming a distinctive association.

Regional geochemical investigation of Mesozoic magmatism in the western part of the Mongol-Okhotsky mobile zone has outlined the following:

1. Regional geochemical profiles and definition of metallogenic provinces and ore belts.
2. Geochemical rock cassification for geological mapping, especially useful for distinguishing rocks of similar petrochemical and mineralogical composition.
3. Geochemical zonation models, corresponding to the geological structure of large regions, to provide a basis for metallogenic analysis and regional prospecting.
4. Prediction models for missing ore-bearing members whithin characteristic regional associations.
5. Methods of estimating probable types and sizes of ore deposits associated with varieties of geochemical rock types.
6. The use of regional geochemical information in compiling special maps (tectonic, formational, metallogenic, ore distribution, ecological).
7. The method of petrographic-geochemical bedrock mapping of the most promising areas by low-density sampling (1:100 000 to 1:50 000), for production of single element and element association maps.

BIOGEOCHEMICAL FACTORS OF ORE INDICATOR ELEMENT DISPERSION

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Four biogeochemical factors affecting the distribution of ore indicator elements are discussed: 1) accumulation by roots, 2) excretion with transpired water from plants into the atmosphere, 3) excretion as gaseous compounds from plants into the atmosphere, 4) leaching from the shoots by the atmospheric precipitation.

1. The two most important factors affecting the accumulation of ore elements in roots are: a) the presence of physiological-biochemical concentration barriers and b) the mode of occurrence of indicator elements in the rooting soil zone. Under barrier-type accumulation the intensity of the biogeochemical cycling of ore elements decreases significantly in most plants above the ore deposits as compared to the intensity beyond the deposits.

2. The excretion with transpirated water from plants into the atmosphere was established for over 40 elements. It is important to note that the intensity of the excretion is controlled by factors other than the volatility of the elements. For example less iodine and mercury are excreted than iron and manganese.

3. The excretion of volatile gaseous compounds from living plants into the atmosphere is the least investigated process. It undoubtly occurs for nitrogen, mercury, selenium, iodine, bromine and radon which are significantly volatilized during storage of plant samples. It may be stated that some chemical elements that are considered to be non-volatile, are contained in terpenes and other volatile compounds excreted from plants.

4. The leaching of many chemical elements from plant shoots by the atmospheric precipitation is a factor that increases biogeochemical cycling. Precipitation may cause a 3-30 times higher cycling of elements than does the falling of leaves.

It is advisable to study the four discussed factors in programmes of further biogeochemical investigations in various geochemical landscapes and geological conditions of the Earth.

NONBARRIER BIOGEOCHEMICAL PROSPECTING FOR ORES IN THE SOUTH TRANSBAIKAL

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The biogeochemical methods are divided into three groups by their exploration informativity: 1) the nonbarrier, quantitatively informative; 2) the barrier, qualitatively informative; 3) the pseudobiogeochemical prospecting - the backgroundbarrier, noninformative investigations (Kovalevskii, 1973-1981).

Nonbarrier biogeochemical prospecting is based on the study of the most informative nonbarrier biological objects which accumulate the indicator elements in linear proportion to the concentrations in the soil. Nonbarrier bioobjects may be chosen from published tables (Kovalevskii, 1973-1983; Kovalevskii and Kovalevskaya, 1976-1982 - in Russian; Kovalevskii, 1974-1979).

Biogeochemical prospecting in the Transbaikal is mainly based on four bioobjects: bark of *Pinus silvestris*,*Larix dahurica*, and *Betula platyphylla*, as well as shoots of *Artemisiacea*. In 1974-1982 approximately 180 000 samples from an area of about 6000 km^2 were investigated in a region of wide-spread eolian cover. The main scale of prospecting was 1:50 000 and the sampling grid was 500x50 m. Detailed investigation of promising anomalies was conducted at the scales 1:20 000 - 1:5000 with sampling from a 200-50 m x 20-10 m grid. As a result of this prospecting by use of bark, over 100 high-contrast anomalies of Pb, Zn, Cu, Cd, As, Sb, Bi, W, Mo, F, Cr, Ni, Co, Sr, Ba, and Hg, exceeding the local background by 30-3000 times, were contoured. Most of the anomalies were complex containing from 5 to 42 elements. Trenching and drilling by the Industrial Geological Organization "Buryatgeologiya" at some 20 anomalous localities have led to the discovery of several occurrences, and new ore bodies in a known ore field as well as two new deposits (Ignatovich, 1980; Radchenko, 1979,1982).

The data from detailed litho-biogeochemical and geophysical work over the Zharchikhinskoe molybdenum deposit, covered to some 80 % by 0.5-30 m thick eolian deposits, will be discussed.

EXPERIENCES WITH A TUBE-EXCITED ENERGY DISPERSIVE X-RAY FLUORESCENCE SYSTEM IN FIELD LABORATORIES

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A radionuclide-excited energy dispersive X-ray fluorescence (EDXRF) system has been used in our mobile laboratory for several years for multielement prospecting (Kramar & Puchelt, 1981; Kramar, 1982). With the increasing concern about all types of radioactive sources, including nuclear power plants, the use of radionuclides for analytical purposes is being increasingly restricted and is diminishing. The administrative effort necessary to obtain permission for transportation and use of radionuclides has increased in recent years. In some countries it is now almost impossible to import even sealed radioactive isotopes for use in field laboratories.

The application of tube-excited EDXRF systems for multielement analysis in mobile laboratories was difficult in the past due to weight, size, high power requirements and the need for coolant water. Today small X-ray tubes are available that require only low power and are cooled by natural convection of air. Such an instrument, equipped with a 50 kV/1mA Rh tube, a Si(Li)-detector and a changer for 20 samples (TRACTOR SPECTRACE) was adapted to our mobile EDXRF laboratory (installed in a Land Rover 109). The instrument is compact and needs only 500 W of additional power requirements. With this system different conditions for the excitation of the characteristic lines of trace elements were tested. The widest range of application was obtained for a tube voltage of 35 kV with Rh filter between tube and sample. The arrangement tube-filter-sample increases the peak/background ratio drastically for energies below Rh-K-radiation.

The qualities of the tube-excited and the radionuclide-excited system were compared. As of now the tube-excited system has been tested for the simultaneous determination of up to 18 elements in the course of one measurement (K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, W, Pb and Th). For several elements a clear improvement of the detection limits was achieved with the tube-excited system in comparison with the radionuclide-excited system (Table 1).

Table 1. Detection limits of trace elements in rock samples for mobile tube-excited EDXRF and radionuclide-excited EDXRF

	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nh	Ph	Th
Tube EDXRF	5	5	5	5	5	5	5	5	5	5	5	10 ppm
Radionuclide EDXRF	100	50	30	30	10	10	10	10	10	10	20	50 ppm

These detection limits are valid for a measuring time of 500 s (10 min) and bulk powder samples. With this measuring time a sample output of ca. 50 samples/day, i.e. up to 900 single element determinations, is possible. Data evaluation is performed by computer. These detection limits are above background values in rocks for most of the elements. Shorter measuring times can be used if a slight fall off in the detection limits can be accepted (100 samples/day or more). It is also possible to measure liquid samples. Elements of high atomic number (Ag, Sn, Sb, Cs, Ba, La, Ce) can be determined by K-lines using higher tube voltages and other filters. For Cs, Ba and the rare earth elements the detection limit of radionuclide-excited EDXRF is much better than for tube-excited systems, due to the upper limit for the tube voltage (50 kV) of air-cooled systems.

The tube-excited X-ray system for use in mobile laboratories is now in test stage for field applications. Examples of reconnaissance surveys will be reported.

GEOCHEMICAL INDICES FOR PROGNOSTICATING MASSIVE COPPER-PYRITIC DEPOSITS OF THE ELSHITZA TYPE

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The geochemical prognostication of the Elshitza type massive sulphide copper and pyritic deposits of Central Srednogorie is based on the following regularities in the composition and structure of their primary geochemical aureoles:

1. Morphology and geologic position of the primary geochemical aureoles. They have an elongated or lenticular form and are parallel and subparallel to the contacts of the ore-bearing Upper-Cretaceous layered pyroclastic and volcanic rocks and concordant faults. This determines the appurtenance of these deposits to the stratabound type, information that guides the choice of methods for exploration and evaluation of new mineralizations of this type.

2. Geochemical differences between pyritic and copper ores. As heterogenic deposits formed in the pyritic stage and the copper-polymetallic stage, they generally contain two types of ore, pyritic ore and copper ore, normally situated in one integral zonal column, with the pyritic ore in the rear part and the copper ore in the frontal part. Knowledge of the geochemistry of these types of ores provides a basis for classification of associated geochemical anomalies by using multiplicative geochemical coefficients of the type:

$v_1 = Zn \times Pb \times Cu / S^2 \times Fe$ or
$v_2 = Zn \times Pb \times Cu / Co \times Ag \times Bi$

3. Axial ("vertical") zoning of the primary geochemical aureoles. The determined consecutive position of the maximum concentration of indicator elements (from top to bottom) - Zn, Pb-Au, Cu, Ba-Mo, Co, Bi - provides a possibility for estimation of the depth at which geochemical anomalies occur. From this the position of possible ore bodies may be evaluated according to coefficients of zoning:

$Kz_1 = Pb \times Zn / Bi \times Co$ or
$Kz_2 = Pb \times Zn / Mo \times Co$

4. The intensity of manifestation of the ore forming geochemical processes is a geochemical index for the possibility of finding economic ore bodies. As a criterion for quantitative evaluation of the intensity of these processes, coefficients of intensity are derived as a ratio of contents of ore elements and leached elements:

$K_i = Bi \times Cu \times As / Sr \times Mn \times Ga$ or
$K_i = Cu \times Pb \times Zn / Ti \times K \times V$

CHARACTERISTICS OF THE GEOCHEMICAL ORE ZONATION IN THE ARCHEAN VOLCANIC STRUCTURES OF THE SOUTH-EASTERN MARGIN OF THE BALTIC SHIELD

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1. The geological structure of the Archean Sumozero-Kenozero greenstone belt was analysed (Kulikov, Kulikova, 1979) using the geophysical material collected by PGO "Sevzapgeologia" and the drilling data obtained by "Sevzapgeologia" and "Archangelskgeologia". This enables us to outline some Archean centres of volcanism. These presumably represented the central type of volcanoes formed at the final developmental stage of greenstone belts (Kulikova, 1981).

2. Fields of granodiorite and diorite composition, which form irregular ovals in the plan, are distinguished in the modern erosion section in the central part of the hypothetical volcanic structures. The amount of the igneous rocks preserved is observed to increase from the centre towards the periphery. In the latter case the sedimentary-volcanogenic sequences are the thickest reaching 3 km and more. Their geological structure reflects the developmental history of the structures. Products of tholeiite-komatiite volcanism are characteristic of the lower parts of the sequence, whereas in the upper portion acid volcanites are observed. Acid volcanism seems to be closely related to the intrusion of sodic and potash-sodic granitoids spatially conjugated with subvolcanic rhyodacite and rhyolite bodies, respectively.

3. The ore-bearing formations known in the region show both lateral and vertical zonation in the distribution of metals. The following deposits are observed from the centre of the volcanic structure towards its periphery: 1) ore occurrences with Cu content of up to 0.4 % throughout the rock; 2) thin stratiform deposits of chalcopyrite showing polymetallic (copper-zinc) specialization were stripped 3-5 km away by PGO "Archangelskgeologia" and "Sevzapgeologia".

The vertical zonation is due to the transition from polymetallic to iron ore (magnetite quartzites) and stratiform pyrite (lead-zinc) ore manifestations.

4. Volcanic structures are substantially altered by subsequent folding, and granitization, ore metasomatosis and recrystallization. At the same time the Archean pegmatites of the muscovite-rare metal formation, possibly genetically related to subalkaline granites, are confined to the peripheral parts of the volcanic structures. In these structures circular and arched faults, which mark the basement of the stratovolcano, are most common.

5. Relics of volcanic structures revealed in Archean greenstone belts and considered with due regard for some regularities of volcanogenic ore formation (Ovchinnikov, 1981) enable us to assess in a new manner the Precambrian areas which are still poorly studied.

FACTOR ANALYSIS IN HYDROGEOCHEMICAL EXPLORATION

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The study area (36 sq. km), the Bazois basement basin on the western border of the Morvan massif (France) consists of volcanites to the North, granites in the center and volcanosedimentary rocks to the South. The bedrock is covered by 10 to 100 meters of Triassic (a silicified karst) and Liassic (claysand carbonates) rocks.

Uranium deposits are known in outcropping granitic and volcanic basement. The purpose of the survey carried out by Cogema at the French Atomic Energy Commission's request was to find uranium occurrences in the basement, under the sedimentary cover, especially by means of hydrogeochemistry.

The main acquifer is confined and located at the interface between the basement and the sedimentary cover, in the silicified karst. Due to its large horizontal extent and its location close to the basement, it is supposed to give a good image of the basement geochemistry. The direction of water flow is roughly to the South; its velocity was measured by means of hydraulic gradients, colouring, and ^{14}C dating. Upstream, one finds $Ca\text{-}HCO_3$ waters with a large amount of recent waters (presence of ^{3}H) and a velocity of 100 cm/day. Downstream Cl-Na waters with a ^{14}C age of 3000 to 18 000 years, and a velocity of 0.1 cm/day occurr. Some occurrences of $CaSO_4$ waters also exist.

Below the studied aquifer, in the joints and fractures of the basement there is another aquifer above the Liassic carbonates.

Water samples were taken in 43 boreholes. Hydrogeological data, pH, temperature and conductivity, and contents of major elements, U, Rn, and He were measured.

For each sample of the main aquifer, factor analysis gives the amount of water coming from the sedimentary cover (characterized by a factor involving SO^{2-} and Ca^{2+}) and from the basement (characterized by a factor involving Cl^-, Na^+, and He). North of a piezometric frontier, where the flow runs from the sedimentary cover to the basement no basement waters enters the main aquifer. Only on the southern side of this frontier, where the water flows into the sedimentary cover, carrying basement waters upwards into the main aquifer, the conditions are favourable for detection of uranium occurrences.

The factor model also enables computation of the regional variations of He concentrations related to the same factor as the Cl-Na concentrations. Substraction from the observed concentrations gives a "residual He" the anomalies of which are correlated with those of U, Rn, and F. This indicates that residual He, U, Rn, and F may have a common origin, possibly uranium occurrences.

ASSOCIATION OF METALS WITH DIFFERENT PHASES OF STREAM SEDIMENTS

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Stream sediments play a major role in geochemical exploration programs of the Geological Survey of Norway (NGU). In the present work the association of 29 elements with different phases of stream sediments was studied by means of a sequential extraction technique. The results are compared with those obtained using the NGU standard extraction procedure for geochemical exploration work, which involves treatment with 7M HNO_3 for 3 hours at 110°C.

The sequential extraction separates the sediment into an exchangeable, an oxidizable, a reducible, and a residual fraction. The scheme consists of the following five extraction steps:

1. Exchangeable ions at the surface of particles: 0.05M $CaCl_2$, pH 7, 18 h
2. Easily reducible oxides of Mn and Fe: 0.1M $NH_2OH \cdot HCl$, pH 2, 30 min
3. Organic material: H_2O_2, 30% HNO_3, pH 2, 2.5 h + NH_4Ac, pH 2, 3 h
4. Moderately reducible oxides of Mn and Fe: 1M $NH_2OH \cdot HCl$, pH 1.3, 4 h
5. Residual fraction: HF/HNO_3 1:4 + H_2SO_4.

The material selected for this study was the -0.18 mm fraction of 21 stream sediments from Finnmark, N. Norway, representing areas with varying bedrock geology. The extracted fractions were analyzed in duplicate by ICP emission spectrometry for the major elements Si, Al, Fe, Ti, Mg, Ca, Na, K, Mn, and the trace elements Li, Be, B, P, Sc, V, Cr, Co, Ni, Cu, Zn, Sr, Zr, Mo, Ag, Cd, Ba, La, Ce, Pb. The reproducibility of the sequential extraction procedure was satisfactory in most cases.

In order to see whether steps 1-4 would result in any attack of silicate minerals in the stream sediments, the sequential extraction procedure was also applied to pure mineral fractions of the major minerals identified in the sediments by X-ray diffraction.

The percentages of Fe and Mn extracted in the first four steps correlate, but are not directly proportional to the content of organic matter as determined by loss on ignition.

The amount of Mn extracted in steps 2 and 4 is higher than in steps 1 and 3 but is less than 40% of the HNO_3-extractable fraction. Some of the trace metals like Cu, Ni, Zn, and Co are released predominantly from fraction 3.

The amount of trace metals extracted in steps 1-4 seems to be independent of the mineral composition of the sediment. The largest release of elements from silicate minerals takes place in steps 3 and 4.

MODE OF OCCURRENCE OF ELEMENTS IN THE SECONDARY ENVIRONMENT

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V.I. Vernadsky (1921,1934) was the first to introduce the idea of "mode of occurrence of chemical elements". He distinguished four types: 1) in molecules and their combinations in minerals, rocks, liquids and gaseous masses; 2) present in living orgaisms; 3) occurring in silica-alumina magma; and 4) dispersed. His investigations formed the starting-point for further development of this problem which has scientific and practical applications. The great variety of geological, hydrogeological, physical, and chemical conditions is typical of the zone of hypergenesis, a feature that yields a diversity of modes of occurrence of the elements. In the secondary environment, chemical elements occur mainly: dissolved in water, adsorbed, incorporated in organic matter and Fe-Mn oxides, in secondary minerals (sulphides, sulphates, carbonates, phosphates, etc.), in clay minerals, as isomorphous mixtures in resistant silicates, and so on.

Prospecting, based on the geochemistry of dispersed elements and mineral and organic matter, is a rapidly developing science for which different analytical techniques are now employed.

For some years we have been developing artificial sorbents for prospecting purposes (V.K.Lukashev, K.I. Lukashev, 1978). These successfully combine hydrogeochemical methods based on adsorbing materials. The methods involve the fixation of mobile forms of many elements, the estimation of their contents more confidently by using ion-exchange resins of both cationic and anionic character, and the selection of sorbents with highly selective properties. Synthetic ion exchange resins, as well as other sorbents, have been used (cellulose-polyphosphate or cellulose ethylenediamine tetraacetate-borate). These sorbents have been employed in different ways, being planted for a period of time in soil at a depth of about 1 metre, on lines 50-200 m apart in regions subjected to prospecting. This report considers some case histories from different environments where the use of artificial sorbents has been compared with other prospecting methods.

The Adangheian ore field in the mountainous region of Abkhazia was chosen as an example of a polymetallic ore deposit. Two ore bodies outcrop at the erosional surface and are buried by 4 to 5 m and 20 to 25 m of colluvium respectively. One ore body is associated with well-defined secondary aureoles of zinc, copper, and other trace elements. The displacement of the mechanically transported aureoles down the mountain slope is 70 to 80 m for zinc and copper and 40 to 50 m for silver. The cellulose-polyphosphate sorbents fixed undisplaced haloes of these metals immediately above the orebody. The second orebody (overlain by 20-25 m of colluvium) could not be traced at the surface by conventional methods. However, the use of sorbents enabled detection of halos of zinc, copper, and silver without displacement. Concentrations of copper on the sorbents above the orebody were 5 to 6 times background. Analyses of the mode of occurrence of the different memtals, utilizing the technique of sequential extraction, indicated that in the overburden over the first orebody 95.8 % of the copper and 93.1 % of the zinc were tightly bound in the lattice of minerals and were not leached out. About 4.7 % of the copper and 13.7 % of the zinc were bound by ferric oxides. The bulk of the easily leached (mobile) lead also occurred in ferric oxides. The contents of metals in all extractions were higher in samples above the orebody. Almost all of the cadmium was associated with organic matter or easily leached materials.

Another experiment was carried out in a swampy area covered by fluvio-glacial and alluvial sediments 17-30 m deep. The target of the investigation was halos associated with metasomatic bodies containing beryllium and rare-earth mineralization. Zinc and lead were used as pathfinder elements. The conventional methods of soil sapling of different horizons were unsuccessful. It also proved impossible to indicate the orebody by means of HCl extraction techniques. However, marked anomalies of zinc, lead, and some other elements above the ore body were obtained by analysing metallo-organic (peat) complexes. In regional surveys this method gave a number of false anomalies which warranted further investigation. An analysis of the mode of occurrence of metals by sequential extractions indicated that the metals were bound mainly in organic complexes (almost 100 % for lead and cadmium; also most of the zinc) in peat layers of this region. For this anomaly we used ion-exchange resins and also cellulose-phosphate sorbents. The latter were the more effective.

Finally, experiments were carried out under extreme prospecting conditions in a region of the Byelorussian crystalline shield covered with 150-170 m of sediments (chalk and till). A preliminary survey revealed some geophysical aomalies, and a test borehole encountered sulphide mineralization in Precambrian rocks. Sorbents were left in the ground along profiles over the geophysical anomalies for one year. The content of zinc on the sorbent above the mineralization was 0.15 mg/g. Along the same profile there were stations with higher contents of zinc (up to 0.33 mg/g) and copper (up to 0.05 mg/g) over other geophysical aomalies not tested by drilling. At background statitons the contents of metals on the sorbents were very low (generally only traces). This did not prove the absence of these elements in the overburden, but rather indicated that they do not occur as cations (the sorbent used was a cation exchanger).

Although the mechanism of migration of metals through the thick cover of sediments is not yet completely known, it is suggested that the following factors are involved: deep weathering, activity of microbes in pore solutions, movement of metals in water films, and electrochemical processes. Thorough studies of these processes will provide a basis for the wider use of different modes of occurrence of elements, and hence an improvement in exploration techniques.

EVIDENCE FOR FAST MIGRATION OF METALS THROUGH THE BEDROCK: A POTENTIAL NEW EXPLORATION TECHNIQUE

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Our studies on the distribution of radon in the ground indicate that the transportation mechanism for radon is dominated by a flow component capable of carrying radon considerable distances within its lifetime. The model predicts that radon atoms can be trapped energetically at the gas-water interface of bubbles in a stream of ascending gas.

Probably this transportation mechanism is not restricted to radon. We think that also a number of stable elements can be trapped and transported towards the ground surface by this mechanism. This implies the existence of a one-way upward transport mechanism capable of transporting matter in a state of single atoms or aggregates of atoms through the bedrock to the surface.

Since the process is an ongoing active one it might be exploited as a source of new techniques in exploration. To test this model three independent techniques have been used over different types of known targets. A brief review of the work done and the results achieved will be presented.

DEFINITION OF ORE-BEARING STRUCTURES AND GEOCHEMICAL SPECIALIZATION OF ROCKS BY GEOCHEMICAL MAPPING

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The results are presented of medium- and large-scale geochemical mapping in the search for mineral deposits over Precambrian and Paleozoic granitized and hydrothermally altered cherts, sandstones and shales.

These results indicate:

1. The Precambrian and Paleozoic rocks could be grouped on the basis of the abundance and variance of elements.
    (a) rocks characterized by low element variance and varying concentrations of gold,
    (b) rocks with high element variance and high contents of gold.
2. Geochemical specialization of rocks: flysch: Zn, Cu, V; carbonaceous rocks: Cr, Ni; volcanics: As, Ag, Mo; terrigenous rocks: Ag, As, Mo; chert: Mo, V.
3. Potential ore-bearing structures, represented by anomalies for Au, Sb, As, Ag, and W.
4. Geochemical anomalies for Au, As, Ag, Sb, and W associated with magnetically distinctive intrusive structures and hydrothermal alteration.

THE RELATION BETWEEN Tl, Rb, AND K IN GOLD-SILVER VEINS AND ASSOCIATED VOLCANIC ROCKS

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In an attempt to use the ternary relationship between Tl, Rb, and K as a guide for gold-silver mineralization and to understand the behavior of these elements during hydrothermal processes, approximately 250 rock samples from two mining districts have been analyzed for Au, Ag, Tl, Rb, and K. The samples analyzed include fresh hornblende- and quartz-hornblende-pyroxene andesites, hydrothermally altered volcanic rocks, and quartz and carbonate veins. The samples of volcanic rocks and associated veins were collected from the Republic mining district of northeastern Washington and the Como mining district of western Nevada.

The contents of Au, Ag, Tl, Rb, and K in altered volcanic rocks from both areas are significantly higher than those in unaltered andesites; Au and Ag are comparatively more enriched than Tl, Rb, and K. A comparison of the abundances of lithophile elements in altered and unaltered volcanics indicates that Tl in altered rocks is more enriched than Rb which, in turn, is more enriched than K. The behavior of Tl, Rb, and K, which exhibit different degrees of enrichment in altered rocks, is consistent with the geochemical characteristics of these elements, as Tl is known to concentrate more in hydrothermal fluids.

Abundances of Au and Ag consistently increase in order from fresh volcanics to least altered volcanics, highly altered volcanics, and gold-silver bearing veins. The abundances of Tl, Rb, and K, on the other hand, do not exhibit similar patterns in their distribution. Tl, Rb, and K show a consistent increase in their concentrations from fresh to altered volcanics but the abundances of these elements decrease drastically in gold-silver bearing quartz and carbonate veins. It is interesting to note, however, that K/Tl ratios show a consistent and systematic decrease in order from fresh volcanics to least altered volcanics, highly altered volcanics, and finally gold-silver veins. The K/Tl ratios in highly altered volcanics and veins, which contain anomalous Au and Ag, are significantly low; $K/Tl \times 10^4$ values of about 1 or less are quite common. Quartz veins from several other areas (work in progress) contain similarly low K/Tl ratios. The plots of Tl, Rb, and K values of 250 rocks on a ternary diagram show a clear and distinct separation of gold-silver veins and mineralized rocks from unmineralized rocks, the former plotting very close to the Tl apex.

Based on the data obtained in this study it is suggested that high concentrations of Tl in volcanic rocks and/or low K/Tl ratios in volcanic rocks and quartz and carbonate veins can be used successfully to locate gold and/or gold-silver deposits associated with volcanic rocks.

THE APPLICATION OF CORRESPONDENCE ANALYSIS TO THE STUDY OF LITHOGEOCHEMICAL DATA: GENERAL STRATEGY AND THE USEFULNESS OF VARIOUS DATA CODING SCHEMES

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Descriptive factor analysis methods are useful tools for the study of lithogeochemical data, because they are designed to extract non-redundant variation patterns from large data tables (e.g., several hundreds of samples analyzed for 15 or more elements). Correspondence analysis is used because it treats samples (rows) and variables (columns) in a symmetrical manner, and offers much flexibility in data coding.

The strategy used in the study of lithogeochemical data is based on the recognition that the behavior of major elements ("framework" elements) and trace elements ("substitution" elements) is determined by different parameters. Major element behavior is directly related to mineral stability, whereas trace element behavior is dependent upon the interaction between the trace elements and existing host-minerals. Such a strategy allows a natural interpretation of the data in terms of the mineralogy and petrography of the samples, and of the geological processes that affected the chemical composition of the samples.

The lithogeochemical data are studied in several ways. Firstly, variation patterns for major and trace elements are determined. The factors obtained for major elements are interpreted in terms of the mineralogy and petrography of the samples. The factors obtained for trace elements are correlated to the major element factor space and trace element behavior interpreted in this framework. The correlations and discrepancies (non-correlations) between major and trace elements are thus evaluated more objectively than if all elements were treated together; discrepancies in particular, provide information that is unique to trace elements. Secondly, several coding schemes are applied to the data in order to enhance underlying variation patterns in different ways. The use of rank coding (ordinal, reduced coding) follows the study of the raw analytical data; it increases the robustness of the factors and the homogeneity of the variation patterns, particularly for trace elements, and is also an intermediate step before the use of disjunctive coding. Disjunctive coding (binary coding) gives access to another level of information by permitting the study of non-linear patterns of element behavior.

In this paper, the usefulness of such an approach is illustrated using lithogeochemical data from two different geological environments: an Archean metavolcanic complex in northwestern Quebec (host to volcanogenic massive sulfide deposits), and the Helikian Athabasca Basin of Saskatchewan (host to unconformity-type uranium deposits).

HYDROTHERMAL ALTERATION HALOS OF AS, SB, AND NA SURROUNDING ORE BODIES

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According to Grigorian (1976) As and Sb dispersion halos are typical for polymetallic ore deposits. Both elements are common constituents of hydrothermal orebearing solutions. Some of the As and Sb are captured by sulfide minerals but considerable amounts are dispersed in the country rocks, forming broad halos. The extension of these halos depends on the porosity of the country rocks.

Twenty-four elements were followed along two orthogonal profiles across the volcanic-sedimentary sequence of the Woodlawn Syncline, New South Wales, Australia.

Contents of the elements K, Na, Fe, As, Ba, Ce, Co, Cr, Cs, Eu, Hg, La, Lu, Nd, Rb, Sb, Se, Sm, Ta, Tb, Th, U, W, and Yb were determined by neutron activation analysis.

The results may be summarized as follows:

- only Na, As, and Sb vary more than one order of magnitude in concentration
- Na decreases are associated with increases of As and Sb
- although Na varies by 2 orders of magnitude K, Rb, and Cs stay constant
- REE, Co, Th, Ta, Hf, and Sc show low variations

The ratios As/Na and Sb/Na seem to be suitable geochemical indicators for definition of the alteration halos. These ratios vary within 5 orders of magnitude. The areal extension of the halos as determined by these ratios is in good agreement with that of Hg anomalies as observed by v.d. Boom and Pöppelbaum (1980). The highest anomalies are found along the axis of the syncline and not surrounding the Woodlawn Cu-Pb-Zn deposit. This deposit, however, is well within the anomalous area, the latter being about 2 km in diameter perpendicular to the axis of the syncline.

The ratios As/Na and Sb/Na are suggested as a useful tool in defining hydrothermal alteration halos in country rocks.

MOBILITY OF ELEMENTS IN SECONDARY DISPERSION HALOS AND ASSESSMENT OF THE EROSION LEVEL OF ANOMALIES IN BEDROCK

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Secondary dispersion halos are results of physical and chemical weathering combined with redistribution of elements through a number of transformations caused by various geochemical factors. The final result of the influence of these factors is either depletion or selective concentration of elements in weathering products.

Different mobility of elements in the hypergene zone results in change of the ratio between elements or groups of elements, the numerical value of which is the major geochemical criterion for determination of the erosion level of anomalies in the bedrock. It is clear that the change is minimal for secondary mechanical disperison halos, formed as a result of physical disintegration of ore-bearing rocks, but it increases sharply, when the formation of halos is related to chemical and biochemical redistribution of the material in different sections of the weathering crust and in overburden.

The above statements indicate the necessity of taking different approaches in establishing selection criteria for interpretation of secondary lithochemical (geochemistry of inorganic sediments) anomalies in different landscape - geochemical situations, as well as the importance of the assessment the intensity of hypergene element redistribution, that determines the degree of changes in quantitative characteristics of secondary halos relative to their endogene analogues.

It is convenient to assess the hypergene migration intensity of indicator elements in different deposits by comparing the ratios between average concentrations or element productivity in halos of the overburden and of the source rocks. The numerical values of these migration coefficients (ratios), arranged in increasing order of magnitude, characterize mobility of each element in comparison with other elements of a specific geochemical system. The range of the migration coefficients (difference between the migration coefficient of the most mobile and the least mobile element) also allows evaluation of the magnitude of change of indicator element ratios for secondary halos under the specific landscape-geochemical conditions.

The range of migration coefficients indicates the level of difference between the parameters of the primary and secondary halos for a specific landscape-geochemical situation. In Arctic areas these differences are small but in humid areas they are large. In the first case, the factors of hypergene influence can be neglected in definition of hypergene anomalies. In other cases it is necessary to correct for the "changes" conditioned by the hypergene processes. A method of compensation for distorting influences of hypergenesis is proposed. It is based on the appropriate selection of elements of the numerator and the denominator of indicator element ratios. The selection is based on the migration properties in oxidation processes, and on the position of the element in the series of endogene geochemical zonality of the primary halos.

FLUORIDES AS INDICATORS IN HYDROGEOCHEMICAL PROSPECTING IN THE EAST AFRICAN RIFT VALLEY

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A hydrogeochemical survey carried out on streams, rivers, and lakes in the Mt. Meru area, northern Tanzania, revealed the presence of abnormally high fluoride concentrations, genetically related to the East African Rift Valley volcanism. Maximum contents occur in sodium rich volcanic rocks, (e.g., in nephelinites 0.25-0.28 %), while rocks with low alkali contents have small amounts (e.g., in olivine basalts 0.09 %). Carbonatites exhibit the highest contents (Oldoinyo Lengai carbonatite: ca. 2.0 %). In areas draining rift volcanics of the Mt. Meru area, F concentrations were found to be 10 to 100 times higher in Majiyachai and Engarenanyuki streams (5-20 ppm) and 100 to 1000 times higher in some ponds and Momella lakes (50-600 ppm) as compared with the F contents of natural waters elsewhere considered normally to be 0.1-0.5 ppm.

In the absence of Ca, fluoride is mobile and a good indicator of F-rich mineralizations (e.g., fluorite, apatite) and carbonatites. In the studied watersheds Jekumia warm mineral springs discharge highly fluoridic water into the Engarenanyuki river (36 ppm). Fluorides are mainly leached from sub-surface sodic volcanics of Mt. Meru formed by recent volcanic activity (The last reported eruption was in 1877). The mobility pattern in surface water bodies is complicated by phenomena such as F adsorption in clayey weathering products of sodic volcanics, the different rate of leaching from river beds (mainly lahar), and dilution and concentration during wet and dry seasons.

Rift Valley volcanism is considered to have given rise to fluorite deposits (e.g., the Kerio Valley deposit, Kenya). A stream sediment survey for fluorite (Williamsons Diamond Ltd.) revealed F contents of 0.05 % in basement areas, 0.12 % in areas of alkali volcanics, and 0.25 % in areas close to carbonatites, but no appreciable mineralizations were found. Neither has the present hydrogeochemical survey so far led to the discovery of any economic fluorite or apatite deposits in northern Tanzania.

In the study area (especially the Majiyachai drainage area) people suffer from fluorosis as the result of drinking fluoridic water and using "magadi" (trona: $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), which is rich in fluorine, as salt in their diet.

MODE OF OCCURRENCE OF COPPER AND ZINC IN TILL OVER MINERALIZED BEDROCK

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The mode of occurrence of copper and zinc in the minus 2 mm fraction of till was studied in basal till of Talvivaara, Outokumpu, and Maaselkä in Finland. The bedrock of the Talvivaara and Outokumpu areas is mineralized by copper and zinc sulphides, the bedrock of the Maaselkä area by copper sulphide only. Maaselkä differs from the other two target areas in having a cover of 2-25 m thick pre-glacial regolith over the fresh bedrock.

The variation of copper and zinc contents with grain size was studied in selected samples by analyzing the contents of these elements in the grain-size fractions: 2000-500 μm, 500-64 μm, 64-2 μm, and minus 2 μm. The fixation of copper and zinc to different minerals was investigated in the 500-64 μm and the minus 64 μm fractions by using heavy liquid separation (d 2.89 g/cm^3), microscope, microprobe, electron microscope, and X-ray diffraction.

The results demonstrate that the distribution of copper and zinc between the four grain size fractions is very similar in all target areas. The only clear exception is the distribution of zinc in Maaselkä. The copper and zinc contents tend to be highest in the minus 2 μm fraction and to decrease with increasing grain size until, after reaching a minimum in the 500-64 μm fraction (in Talvivaara in the 64-2 μm fraction for copper), they increase in the coarsest material. This feature is assumed to be typical for till over Cu-Zn-mineralized bedrock. In Maaselkä the zinc contents in the coarsest fraction are as low or a little lower than in the 500-64 μm fraction. The reason for this exception is assumed to be the low background level of zinc contents in this area.

The anomalous part of copper in the till of Talvivaara is mainly fixed to chalcopyrite and that of zinc to sphalerite, which indicates that the till was mainly formed from fresh bedrock and that post-glacial alterations are slight. In the till of Outokumpu and Maaselkä sulphides are rare. In Outokumpu the probable reason for this is the post-glacial weathering of sulphides and in Maaselkä the reason may be abundant mixing of highly weathered, sulphide-poor, pre-glacial regolith with the till material. In both target areas copper seems to fix to limonite and, particularly in Maaselkä, to clay minerals in till. Zinc seems mainly to be hosted by limonite in Outokumpu. In Maaselkä it is enriched in the heavy fraction but the exact mode of fixation is not known.

MINERALOGICAL-GEOCHEMICAL ZONING OF ORES AND PRIMARY GEOCHEMICAL AUREOLES IN THE FILIZCHAI DEPOSIT

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The sheet-like ore body of the Filizchai pyrite-polymetallic deposit (in the metallogenic province of the Alpine terrigenous geosyncline of the Greater Caucasus) occurs in the sandy-argillaceous formations of non-segmented Plinsbach-Toar. The orebody is the result of a combination of various stages of mineralization, and is the most complex orebody among the pyrite deposits of the eastern Caucasus. Different ores, including stratified-striated pyrite-polymetallic, massive pyrite-polymetallic, pyrite and copper-pyrrhotite, mottled brecciated and streaked impregnated types, constitute this deposit. The major ore components are copper, lead, and zinc, the average weight ratio of which is 1:2 and 3:6 respectively.

The ore body of the Filizchai deposit is conventionally classified into three depth levels: upper (absolute elevation 1300-1000 m), middle (1000-700 m) and deep (below 700 m). The vertical mineralogical and geochemical zoning of the deposit is expressed downward by an increased content of chalcopyrite-enriched ores and a decrease of galena-sphalerite ores. This is especially pronounced for sphalerite and galena. In the upper, middle and deep stratal levels the average zinc content is 1.62, 1.49 and 1.00 and the average lead content 1.73, 1.29 and 1.00 respectively. Corresponding Zn/Pb ratios are 2.33, 2.87 and 2.48. In the horizons about 700 m, increased amounts of sphalerite are present. Relatively high amounts of galena are typical for the highest horizons (1300-1000 m). An increased copper content is characteristic of the upper part of the deep horizons (hypsometric level 700-600 m).

The vertical geochemical zoning of trace elements is generally characterized by the following features: the contents of bismuth, cadmium, indium, gallium, antimony and arsenic decrease with depth, whereas the cobalt content tends to increase; the content of selenium, mercury, thallium and expecially manganese is highest in the middle horizons; the amount of tellurium and germanium is low and nearly equal for all horizons. The Zn/Cd and S/Se ratios increase with depth. The zoning index (Zn x Pb/Cu x Co) falls from 600 to 390 between the 1300 m and 900 m horizons.

Maximum contents of lead and zinc coincide and occupy almost the whole western portion of the orebody. Increased copper concentrations form local areas on both the eastern and the southern flank of the body. The areas of the highest zinc and copper (lead and copper) concentrations are separated; concentration maxima of one element coincide with the minima of the other.

The contents of zinc, lead, bismuth, cadmium, indium, thallium, gallium, antimony, arsenic, mercury and manganese tend to decrease whereas the copper, cobalt and selenium contents tend to increase along the strike of the body from west to east. A decrease in the same direction for the Zn/Cd and S/Se ratios and an increase for the Se/Te ratio are observed. Zoning indices for the western flank, central part, and eastern flank are 3310-750, 870-110 and 250-70 respectively.

No distinct zoning is observed along the pitch of the orebody. Across the orebody differences in elemental concentrations are distinctly pronounced between individual ore types: zinc, lead and thallium concentrations increase from the hanging to the foot wall, whereas the cobalt and selenium concentrations tend to decrease. Sulphide minerals, especially pyrite and chalcopyrite, from the hanging and the foot wall can be clearly differentiated by measuring the concentrations of their trace elements.

Vertical zoning, as expressed by the enrichment of zinc, lead and thallium in the supra-ore strata of the orebody and of copper, cobalt and tin in the sub-ore strata are typical for the primary aureoles of the deposit.

LITHOGEOCHEMICAL EXPLORATION FOR PORPHYRY-TYPE MO-CU-AU DEPOSITS IN THE PROTEROZOIC RAUTIO BATHOLITH, WESTERN FINLAND: COMPARISON WITH TILL AND STREAM-SEDIMENT RESULTS

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The margins of the multiple 25 km x 15 km Rautio batholith are composed of diorites and quartz monzodiorites and the core, which accounts for 80 % of the batholith, is composed of granodiorite. The Mo-Cu-Au mineralization at Susineva is associated with a granodiorite porphyry. There is a systematic change in contents of several elements from diorite to granodiorite. The variation of Cu and As in granodiorite is distinctly higher than in the other phases which is considered to indicate mineralization. The variation of the differentiation index (D.I.) and of the contents of Ti, Sc and Ba in granodiorite is slight, but systematic and indicates that the crystallization proceeded from the margins towards the core. Large Rb/Sr and K anomalies are located northeast of the most extremely fractionated granodiorite, a feature that has been attributed to regional postmagmatic alteration. In the area of the Susineva mineralization Cu and As form a large anomaly. At a regional scale this anomaly is not spatially related to the differentiation or postmagmatic alteration. The anomalously high Cu and As values reflect primary aureoles of mineralized fine-grained stocks and indicate the ore potential of the central portion of the batholith. Mo values are low and do not exhibit well-defined anomalies.

The Mo and Cu anomalies of a regional till survey are incoherent. The highest Mo values are within and the highest Cu values outside the area of granodiorite. The mineralization at Susineva is indicated by restricted Mo and Cu anomalies. Most of the other anomalies are restricted. Mo values are high in organic sediments of practically every stream in the granodiorite area. The Susineva mineralization is revealed by a weak Mo anomaly, but not by Cu.

Granodiorite porphyry differs geochemically from the coarse-grained type by higher D.I. and K values and lower Ti values. The Mo, As and Sb anomalies occur in the fine-grained body. High Cu and Au occur around the Mo anomalies. In the coarse-grained granodiorite they are associated with anomalies of Rb/Sr and may indicate previously unknown blind mineralization.

The Mo and Cu anomalies in till in the Susineva area roughly reflect anomalies in the bedrock. The Mo values in the fine fraction of till are substantially higher and Cu values are lower than in the bedrock. This feature is attributed to the mode of occurrence of metals in the bedrock.

The study showed that lithogeochemistry is a useful and inexpensive method for exploration for porphyry-type deposits. The history of crystallization of the batholiths can be delineated, and the potential phases with their mineralized zoned can be identified. Till geochemistry is useful in exploration for elements such as Mo, the primary aureoles of which are small. The geochemistry of organic stream sediments may be useful in identifying ore-potential batholiths.

MULTIVARIATE SCREENING OF TRAINING SETS FOR CLASSIFICATION AND THE DEFINITION OF GEOCHEMICAL BACKGROUND

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The definition of geochemical background has previously been based on univariate statistics using cumulative frequency curves and histograms. During the course of screening training sets for use in discriminant analysis we realised that, where the data are available, a multivariate approach might be a more powerful tool than univariate methods for defining background populations.

The multivariate screening technique used was based on R-mode factor analysis of groups of samples from streams believed to be draining only one geological unit. Samples, which were incorrectly included in these groups, were identified and screened out either because they gave rise to factors which were incompatible with the geochemistry of the geological unit or because they had a high residual value of the chosen factor model for that particular geological unit. The advantage of this screening technique over univariate methods lies in its ability to reveal unusual element combinations in addition to single element outliers.

The data on which this study was made was derived from 2500 reconnaissance drainage-sample sites from 14 000 km^2 of South Greenland. These were divided into 14 populations on the basis of the geological unit mapped in the upstream catchment area. These populations were then screened using both the R-mode factor analysis models and the univariate method. The factor analysis method revealed 67 % of all the screened outliers, while the univariate method revealed the rest. Closer examination of the screened outliers indicate that most of them are either due to geological miscoding or the influence of unmapped geological features within the catchment area.

The conclusion is that this method could be used for defining background populations more effectively than using univariate statistics alone. The best results, in terms of the confidence that could be put in the background character of the screened data set, were obtained by combining factor model residual screening, factor score screening on factors not related to background conditions and univariate screening.

DISTRIBUTION OF URANIUM AND THORIUM IN THE BASEMENT COMPLEX OF NIGERIA

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The uranium and thorium contents of migmatic gneiss, metasediments (schists and quartzites), granite gneiss, granites and pegmatites of the Precambrian Basement Complex of Nigeria were determined by delayed neutron measurement. Average uranium and thorium contents of the rocks are:

	U ppm	Th ppm	Th/U
Migmatic gneiss	4.7	25.3	5.38
Schist	0.3	2.0	6.67
Quartzite	1.1	5.0	4.55
Granite gneiss	2.1	49.7	23.67
Fine porphyritic granite	1.9	27.0	14.21
Coarse porphyritic granite	29.0	29.5	1.02
Pegmatite	3.6	14.0	3.89

The uranium contents of the gneisses (migmatic gneiss and granite gneiss) compare favorably to some published data on uranium of granitic rocks and indicate that the gneisses are derived from igneous rocks. The relatively high concentration of thorium in the granite gneiss may be due to metasomatism. The concentrations of the radioactive elements in the metsediments are generally low and similar to those in normal non-uraniferous sediments. A strong positive correlation between U and Zr in the metasediments suggests that the radioactive elements are hosted by zircon. The average concentration of uranium in the coarse porphyritic granite — a late phase in the granite cycle of the Basement Complex of Nigeria — is more than 10 times the average contents of uranium in the other granitic rocks. This uranium enrichment in the coarse porphyritic granite can not be explained by magmatic differentiation. Geochemical features, such as, low Th/U ratios and low Zr contents (Zr = 87 ppm) rather suggest that uranium was concentrated by anatexis of pre-existing crustal rocks of moderate levels of uranium into melts from which the coarse porphyritic granites formed.

OXIDATE ACCUMULATION IN STREAM SEDIMENTS

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Stream sediment data from Norway indicate that the northern part of the Oslo graben is highly increased for Cd, Co, Fe, Mn, Mo, and Zn contents.

Stream sediments contain oxides and hydroxides of iron and manganese (oxidates). Few studies are available on the regional distribution of these oxidates. During geochemical mapping of 100 000 km^2 of southern Norway poorly crystalline oxidates were not found in the sediments of every stream, but their occurrences showed a regional distribution pattern. Grains from streams draining the silicic rocks of the northern part of the Permian Oslo graben, for example, have thick Fe-Mn crusts and nodules are very common. Stream sediments are here to a large extent composed of oxidates, although Fe-Mn crusts and nodules locally may be absent. In areas of Precambrian silicic rocks surrounding the Oslo graben, oxidates are only locally developed. Stream sediments are here composed of rock-forming minerals.

Oxidates and rock-forming minerals have quite different chemical composition and properties. Stream sediments from the two studied areas are therefore not comparable. To investigate contents unrelated to oxidates in stream sediments, concentration ratios metal/Fe, metal/Mn or metal/Fe+Mn are commonly used. The ratios show the northern part of the Oslo graben to be enriched in several metals.

To test the significance of the Oslo graben as a geochemical province, comparable samples of nodules (oxidates) were taken. These nodules are composed of amorphous Fe, Mn, and of organic substances mixed with small amounts of silicate grains. Microprobe, neutron activation, atomic absorption spectrometry, and optical emission spectroscopy were used for analysis. Microprobe and microscopic investigations show that parts rich in Fe or in Mn are distributed at random and that the Mn/Fe ratio varies considerably within a single nodule. Except for one anomaly of 1.0 % Zn and 0.1 % Co, the contents of Cd, Co, Fe, Mn, and Zn are similar within and outside the Oslo graben. However, the Mo contents are more than a thousand times enriched in stream nodules from the Oslo graben compared with the surrounding areas. This indicates that the northern part of the Oslo graben is a Mo province.

The composition of stream sediments must be considered when interpreting geochemical maps. Ratios do not satisfactorily compensate for the oxidate effect. Oxidates may successfully be used in geochemical prospecting owing to the high concentration of several elements. In the present study As, Au, B, Ba, Br, Cd, Co, Fe, La, Lu, Mn, Mo, Sb, Sm, Sn, Ta, Th, U, W, Y, and Zn were found to be higher in nodules than in ordinary stream sediments. Some of these elements have the same concentration in the nodules of both areas, while others show differences.

GEOCHEMICAL METHODS IN THE SEARCH FOR HIDDEN MINERALIZATION

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As easily identified orebodies found by geological and geochemical prospecting become exhausted, exploration geochemistry is increasingly directed towards the development of methods for the discovery of hidden mineralization. This includes two main categories:

- — blind orebodies; in which the ore-bearing rocks occur beneath the erosion surface which cuts the supra-ore alteration zone,
- — buried orebodies; in which the ore body is overlain by thick deposits of young sediments including allochthonous material.

Detailed local sampling (at a scale of 1:10 000) is of value in the search for hidden mineralization generally. In the search for blind mineralization, the identification of primary geochemical halos is of value but where mineralized bedrock is overlain by thin autochthonous sedimentary overburden, prospecting is carried out with the help of secondary lithogeochemical halos. Special features of the composition of primary halos (the source of secondary halos) are used in the interpretation of secondary halos.

Various methods aimed at the detection of superimposed dispersion halos (indicators of mineralization) as well as primary halos are applied in the search for both buried and blind buried mineralization. Two types of superimposed halos are of particular importance. These are firstly lithogeochemical and secondly gaseous geochemical halos. In recent years several modifications to methods for the identification of superimposed halos have been developed. Initially, in prospecting for the buried (blind buried) mineralization, the superimposed halos are identified at the surface (or near-surface atmosphere, in the case of atmo-geochemical prospecting). This is followed by a second stage involving the drilling and mapping of the bedrock down to a few metres, to evaluate the primary halos.

Maps of landscape geochemical features are an essential prerequisite for the successful planning and execution of geochemical prospecting for blind mineralization generally.

GRAIN-COUNTING: A NEW APPROACH TO TUNGSTEN EXPLORATION IN GLACIATED TERRAIN

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Geochemical exploration for tungsten in glaciated terrain usually relies on the dispersion of scheelite grains in the drift. The detection limit for the analytical procedure should be in the range 1-10 ppm. Extraction of a heavy concentrate is a very expensive technique and neutron activation of the fine fraction means long feedback times.

To make tungsten exploration more efficient a scheelite-grain counting system has been developed. The sample is dried and sieved to a fraction of 0.2-0.4 mm. The number of scheelite grains is counted in a sample of the order of one million grains in a 5-minute run. The number of grains can be reproduced better than to within 2 to 5 grains depending on the number of grains and the fraction used. The detection limit can be lowered by running larger samples.

The procedure permits a rapid and inexpensive estimate of the scheelite content in till samples. It can be used for reconnaissance as well as follow-up work. An example showing its application in follow-up work is given.

TILL AND BEDROCK GEOCHEMISTRY IN TIN EXPLORATION

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The youngest intrusive phases of the rapakivi granites in Finland are known as tin granites. The endocontact and exocontact zones of the Viipuri rapakivi massif and its satellites have been considered on theoretical grounds as critical areas for tin deposits. The area between the Viipuri rapakivi massif and its satellite, the Ahvenisto massif, was considered to be tin-critical and was selected for prospecting.

Heavy mineral geochemistry was the method used in the reconnaissance phase. Till samples (10 l) were taken from the surficial part of the till deposits. A wide-spaced sampling grid was used. The samples were concentrated with a heavy liquid after panning. The non-magnetic heavy fraction was analyzed by XRF. Quite a large and coherent glaciogenic tin anomaly was found, the head of which terminated in the southern part of the Ahvenisto rapakivi massif.

The source of the anomaly was sought by taking basal till and bedrock samples with a tractor-mounted percussion drill. The fine fraction of till was analyzed by AAS and the bedrock samples by XRF and AAS. Mainly on the basis of tin and copper anomalies in basal till and bedrock 10 holes were diamond drilled into bedrock. Several topaz-bearing greisen bodies with uneconomic tin content were penetrated. The results demonstrate the soundness of the theory and the methods used.

GEOCHEMICAL DISPERSION OF COBALT-BEARING PYRITE IN TILL: PATTASOJA, NORTHEASTERN FINLAND

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The effect of glacial dispersion on geochemical anomaly patterns has been investigated near a massive cobalt-bearing pyrite mineralization in northeastern Finland. The bedrock of the area belongs to the Kuusamo schist area - a part of the Karelidic schist belt. The mineralization is associated with a narrow albitite seam in contact with quartzite and mica schist. The width of the sub-outcrop of the mineralization is 20 m and the length is 40 m. The overburden consists mainly of till.

Till sampling during the prospecting phase was made with a tractor-mounted auger drill and with a petroloperated light-weight percussion drill. The till samples from the auger drilling were wet-sieved on a 2.0 mm sieve and the pyrite content was counted semi-quantitatively from the fraction >2.0 mm. The fine fraction of the till (<0.149 mm) was analyzed by AAS (Co, Cu, Ni, Zn).

A clear pyrite and cobalt anomaly occurs in the basal till. The anomaly is strongest just above the mineralization. The maximum cobalt content in till is 2200 ppm.

Dispersion was also studied by digging 10 exploration pits with a tractor excavator. Two pits were dug just above the mineralization and the others in on morainic hummock east of it. The stratigraphy, fabric, petrography, texture, heavy minerals and geochemistry of till in the pits were studied. In the surface parts of the hummock the anomaly is very weak. The mineralization is weakly indicated by geochemistry and mineralogy in the immediate vicinity of the sub-outcrop. The number of pyrite grains is low in all the pits (maximum content 25 grains in a 2 kg sample of till) and the sulphur content of the fine fraction (maximum 0.20 % Si) does not differ markedly from the background values. The pH-values do not indicate more acid conditions in till near the sub-outcrop than elsewhere.

The results establish that the glacially dispersed anomaly is confined to the proximity of the sub-outcrop. Deposition has been the prevailing mechanism and erosion has been minor owing to the glaciodynamic and topographical conditions.

TRACE ELEMENT GEOCHEMISTRY OF BEDROCK AS A GUIDE TO MINERAL DEPOSITS IN PRECAMBRIAN GRANITES OF NORTHERN FINLAND

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Ten samples of granites from various parts of northern Finland representing both the Archean granites (ca. 2.6-2.7 Ga) of the Presvecokarelian basement gneiss complex and the Proterozoic granites (ca. 1.8 Ga) of the Central Lapland granite batholith and of the Oulu region were analyzed by instrumental epithermal neutron activation and X-ray fluorescence. The reference rock, apparently barren, against which the rest of the samples, are compared, is a Proterozoic granite from Tepasto, Kittilä. This granite, which belongs to the Nattanen type in the classification of E. Mikkola, is 1800 ± 30 Ma in age and is known to be associated with molybdenite mineralizations. Preliminary results suggest that high Rb, U, Nb and Lu, and low Ba, Zr and Sr contents, and low K/Rb, Ba/Rb and TiO_2/Ta and high Rb/Sr ratios can be used as criteria for an assessment of the geochemical specialization and the ore-bearing potential. Geochemical specialization, or an anomalous nature of the ore-bearing granites, is also evident when contents of trace elements are plotted on a Rb-Ba-Sr ternary diagram, where the specialized ore-bearing granites fall nearest the Rb apex. The specialization is also clear on a Rb/Sr-Rb diagram and on a Th-K-U ternary plot where the ore-bearing granites fall near an apex (the U apex). On the other hand, the SiO_2 - CaO+Mgo+FeO -$Na_2O+K_2O+Al_2O_3$, K - Na - Ca and Fe - Na+K - Mg ternary diagrams do not discriminate between normal ("barren") and specialized or productive granites. In these diagrams part of the barren and the ore-bearing granites fall within the fields demarcated for specialized granites.

GEOCHEMICAL EXPLORATION IN COVERED AREAS OF THE ARCTIC ZONE

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Permafrost occurs over an area accounting for about 23 percent of the land surface of the globe. The arctic zone has been even more extensive. In the resent past arctic conditions prevailed in the periglacial zone of the North American and European continental glaciation. In these wast areas, where numerous traces of cryogenic processes (buried mudboils, frost cracks, etc.) can be found, secondary aureoles of arctic type were formed. Many metalliferous zones, controlling the distribution of ore deposits in high-relief areas, extend under adjacent thick cover of loam and other allochthonous (transported) deposits. Thus these covered areas are considered to have a good ore potential.

Mechanisms of formation for secondary aureoles around buried deposits are: mechanical redistribution of sediments in frost cracks directly at the contacts of ice bodies; their pseudomorphs and forms of the arctic microrelief; mechanical and hydromorphic upward displacement of elements during the freezing of artesian water; winter upward migration of dissolved elements in water towards the cooling front; and biogenic precipitation within specific horizons of the soil profile.

Recently studies have mainly concentrated on buried placers in Northeast Soviet Union where producing horizons are at depths of 40 to 110 m. All bodies of the hypergene zone were sampled. Secondary aureoles were only recognized after data multiplication. Anomalies in the inorganic overburden (lithochemical anomalies) are restricted to the area superjacent to the ore deposits and have a good spatial correlation with biogeochemical aureoles. Anomalies obtained in hydrochemical sampling provide a picture of a more regional nature.

A set of geochemical methods useful in delineating ore-potential were tested, viz. sampling of inorganic stream sediments, and water from lakes and streams, and profile sampling of inorganic overburden along valley slopes. A number of combined hydro- and lithochemical anomalies which were confined to various geophysical anomaly fields were detected. These coincident areas of geophysical and geochemical anomalies correspond to placer and ore targets. The paper presents some examples of results obtained in such comprehensive studies.

In the interpretation of data, from which natural and analytical noise has been filtered out, the following types of anomalies are considered:

- anomalies of "ore nature", generated by cryogenic processes above buried ore and placer sources, as well as instances of inherited characteristics of drainage systems (ancient and recent) as reflected by local accumulations of the heavy minerals in the section,
- anomalies of a "non-ore nature", associated with other buried geological bodies, or caused by local peculiarities in the geochemical landscape, or anomalies in the accumulation of heavy minerals in recent non-placer bearing drainage systems, etc.

GEOCHEMICAL METHODS IN STUDYING THE REGULARITIES OF DISTRIBUTION OF MINERALIZATION

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The practical value of geochemical prospecting methods is based on their ability to detect anomalies associated with mineral deposits. Determination of regularities in the regional distribution of mineral deposits is also an important aspect of geochemical prospecting. These regularities provide a basis for identifying the genesis of the deposits, factors governing their distribution, and for identifying areas with a high potential for the discovery of mineral deposits.

In this paper the detection of the regularity of the regional distribution of deposits is examplified.

The method of multidimensional fields (MF) was developed specificallyto process geochemical data and to construct geochemical maps. The general principle of this method involves the classification of the data on the basis of chemical element covariance in the samples. Then, the spatial distribution of the classes based on geochemical associations of elements is plotted. This allows identifaction of the anomalous associations and the levels of erosion as well as the prediction of mineralization at depth based on geochemical zoning. The mode of data presentation simultaneously represents concentrations of a large group of chemical elements each of which is of a definite dimension (concentration); that is why the field obtained is called multidimensional. In addition to the map of MF (multielement) single element maps are also provided.

In some respects the MF method is similar to that of factor analysis which also represents geochemical associations but differs from it as preliminary and intermediate hypotheses are not required. It is also important to note that the information can be represented in one map, not in several as is the case with factor analysis.

Examples illustrate that application of the MF method allows detection of regularities of the spatial distribution of deposits and of zonal distribution of mineralization more efficiently than geological data alone. The method facilitates the recognition of mineralized, rocks and linear tectonic faults, and ring structures controlling the anomalies as well as predominantly large deposits within the intersection of structural lineaments when applied to data of regional geochemical drainage surveys.

Regularities and zoning of the distribution of mineral deposits indicated through geochemical associations are reflected on the detailed geochemical maps and in geochemical profiles.

CASE STUDY OF A GEOCHEMICAL ANOMALY IN A KOMATIITE AREA IN NORTHERN FINLAND

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Regional geochemical mapping in the Sattanen area indicated some interesting targets for exploration. High priority was given to investigations around the Sattasvaara komatiite complex where anomalously high Cu, Ni, and Co contents in till were found.

The northern part of the anomalous area is well exposed and hilly. The overburden is mostly 1-3 m thick. The southern part is covered with peat and the overburden is 5-20 m thick. The samples have been taken from the bedrock-till interface with a hydraulic percussion drill.

From north to south the rocks are komatiitic basalt with basaltic komatiite interlayers, sulfide-bearing graphitic slate containing intercalations of komatiite proper, and albitized rock and tuff associated with felsic metavolcanic rocks. The felsic rocks are older than the komatiites.

The detailed investigation revealed the Cu-Ni-Co anomalies to be accompanied by Au anomalies in many places and to lie in albitized rocks, which cover extensive areas around the komatiite complex.

TRANSVERSE DISTRIBUTIONS OF PHOSPHORUS, SULPHUR, AND SULPHUR ISOTOPES IN A STRATA-BOUND BASE METAL MINERALIZATION, KANGASJÄRVI, FINLAND

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The Kangasjärvi strata-bound massive base metal mineralization is located in the Vihanti-Pyhäsalmi-Pielavesi Zn-Cu ore province which forms the northwestern part of the Main Sulphide Ore Belt and which lies in the boundary zone between the Archean basement complex and Proterozoic Svecokarelian schists and associated plutonic rocks. The Kangasjärvi mineralization is hosted by a sequence of volcanogenic gneisses and their altered derivatives. The alteration is largely attributed to submarine hydrothermal activity and is at present characterized by minerals such as sillimanite, anthophyllite, and sericite. In addition to pyrite and sphalerite also chalcopyrite and pyrrhotite are present as disseminations and veins. Rarity of galena is characteristic of the Kangasjärvi mineralization. The mineralization can be considered to associate with calc-alkaline, mainly intermediary, and acid volcanogenic rocks proximal to the volcanic centre.

The sampling was done by the chip-channel method, and 322 samples were analyzed from a vertical core profile for phosphorus and sulphur by X-ray fluorescence. The isotope determinations of pyrite sulphur were made with a Varian GD 150 mass spectrometer from 55 samples of disseminations, veins, and massive modes of pyrite.

Phosphorus is mainly contained in euhedral metamorphic apatite. It shows a pronounced negative halo around the mineralization. The content of phosphorus in volcanogenic gneisses averages 0.3 %. When sulphur is enriched in the rocks phosphorus decreases to less than 0.05 %. This is in agreement with the known increased solubility of phosphate in acid aqueous systems. The pulsative behaviour of phosphorus content in the sedimentary sequence may well be due to active stages of volcanism accompanied by weak and restricted alteration.

The massive pyrite has a $\delta^{34}S$ maximum value of +8.4 per mil. Stratigraphically immediately above the massive sulphides in a core penetrating the mineralization the $\delta^{34}S$ values show marked temporary lightening to a minimum of -13.7 per mil. The lightening is considered to reflect primordial change in the isotope composition and hence also a change in the depositional conditions.

The results are compared with a case at Vihanti, where high contents of phosphorus, uranium, and iron characterize the metasediments forming the stratigraphic bottom unit of an ore hosting a sequence of volcanogenic gneisses, dolomites, and skarns.

SPECIALIZED LARGE-SCALE GEOCHEMICAL PROGNOSTIC MAPS BASED ON GEOCHEMICAL HALOS

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New achievements in the theory and practice of geochemical exploration become increasingly important in forecasting the probability of mineral deposits in both areas of operating mines and areas of promising mineral resources. Application of geochemical information in the resource evaluation stage in areas, measuring hundreds and thousands of square kilometres (scale 1:50 000) has recently increased considerably as a result of success in investigation of primary halos and their correlation with halos developed in the hypergene (secondary) zone. Practical application of these halos studies results in definition of volumetrical features having higher mineral potential. Specific features of blind, concealed and blind-concealed mineralization can reliably be defined to depths of several hundred metres and even to more than a kilometre, thus providing predictive capability in the depth dimension.

Areas of endogene mineral deposits can be defined by geochemical investigations because of extensive complex geochemical anomalies of indicator elements caused by dispersed mineralization. Within the area of the mineralized rocks, halos around concentrated mineralization (individual ore bodies and occurrences) are locally formed. Thus, dispersion around an ore body can be considered as a limited portion of the total volume affected by the mineralizing event. For example, the total area affected may occupy tens of square kilometers whereas the halos reflecting an individual deposit may only occupy a few square kilometres. This allows reliable detection and mapping of favorable environments at the scale 1:50 000. The geochemical special prognostic maps, at the scale 1:50 000, define the geochemical space affected by ore processes. Orebodies are localized at the stage of detailed investigation (1:10 000) by mapping associated halos, developed within the space of the general halo.

Large-scale prognostic geochemical maps of quantitative geochemical data demonstrate:

(1) Contours of ore-related geochemical anomalies, including the ore fields and mineralized rocks defined by the multiplicative anomaly index.

(2) Halo contours of individual occurrences within the general mineralized area, indicated by zonally developed anomalies and halos of the main ore elements.

(3) Composition (commercial type) of the predicted blind mineralizations based on the geochemical zonality of the identified halos (the established sequence of indicator elements).

(4) The erosion level of the mineralizations under investigation based on the tabulated values of the multiplicative coefficient of zonality, specific for each commercial type with distinct supra-ore, and sub-ore halo sections.

(5) Predicted ore resources for every mineralized halo, by use of the productivity of the main ore element (elements) with regard to the erosion surface level. Recognition of halos of large, average and small mineralizations.

The last three features are used to identify areas for further exploration.

SIMPLE FIELD CHARACTERS IN MINERAL EXPLORATION PROGRAMMES: AN EXAMPLE OF GEOBOTANICAL PROSPECTING IN INDIA

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The concept and use of plants as indicators of the geochemistry of an area have long been known. Up to now, reconnaissance surveys for mineral prospecting have been carried out with procedures that are expensive. Economically backward and especially developing countries have, to a large extent, been unable to map the geochemistry of their territory. Such countries need, therefore, to establish simple field characters for plants which can be observed by school children and other laymen for preliminary selection of sites for detailed prospecting. Such a step would reduce the cost of exploration, and, with a little incentive, it could generate a massive public involvement in such a national cause.

In pursuing the urgent need for such data, especially with reference to India, investigations were initiated in and around the Khetri Copper Belt, a region of producing copper mines in the semiarid zone of Western India. Several populations of two plant species, *Vernonia cinerea* and *Asphodelus tenuifolius*, from undisturbed and disturbed habitats from the region were selected and analysed for heavy metals such as cobalt, copper, nickel, manganese, and zinc, along with the soils from their root zones. The data revealed that pink-flowered plants of *V. cinerea* had higher concentrations of Co, Cu, Zn, and Ni than both purple- and mauve-flowered plants. Also, the pink forms accumulated much higher concentrations of these metals than those found in soils.

The concentrations of all metals but cobalt were higher in the white-flowered plants of *A. tenuifolius* than in the pink form. The white-flowered form contained much higher concentrations of Zn than the soils.

The investigations established a relatioship between flower colour, geochemistry of the plants, and geochemistry of soils. Flower colour is a simple character which can be observed by anybody and if this relationship can be coupled either with frequency or with density of occurrence of differently-coloured forms, a very simple but effective means of exploration will be provided for future use.

ZONING OF FORMS OF GOLD IN THE SURFICIAL ENVIRONMENT AS A CRITERION FOR BURIED GOLD DEPOSITS

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Gold deposits under allochthonous (transported) sediments more than 10 m thick give very weak geochemical anomalies in the soils. The concentration of gold rarely exceeds 4 ppb in soil above deposits and the anomaly coefficient (proportion of anomalous to background samples) is only 0.2 - 0.3. Information on the mode of occurrence of gold in overlying soils and sediments is valuable for interpretation of weak anomalies. The different forms of gold in the overburden are zonally distributed around the subcropping deposits.

Lateral hypergene zoning in the overlying sediments and soils can appear as increasing contents of native gold particles, and as increasing amounts of soluble gold complexes in ground water when approaching the deposit.

In background soils, allochthonous sediments, and weathering crust, gold is predominantly accumulated in the insoluble mineral residue (22-61 %) and in fulvic acids (17-43 %). To some extent it is also contained in humin (9-26 %) and humic acids (5-20 %). Only 4.6-7.2 % of the gold occurs as free native particles. Gold has not been detected in pore solutions, or in extracts of water or of potassium iodide solutions in background unconsolidated sediments (the detection limit of the gold determination was 1 ppb), indicating the essential absence of soluble forms of gold.

In unconsolidated sediments of gold-bearing areas of hundreds of sq. km, three forms of gold predominate: native gold, gold in insoluble residue, and gold in fulvic complexes. These make up almost 2/3 of the total content. Gold is sporadically contained in pore solutions and in extracts of potassium iodide and water.

High concentration of native gold particles (51-89 %) in combination with soluble complexes, determined in pore solutions, and in extracts of potassium iodide solution and water, are extremely significant indicators of proximity of buried gold deposits in ore fields.

Based on calculations using recent thermodynamic data and results of pH and Eh measurements and on fractionating by exchange resins and major ligand concentrations in real solutions, it has been shown that an increase of sulphate and decrease of gold in complex forms occur in oxidizing environments when moving away from buried deposits, toward neutral and alkaline conditions. The outlined sequence is:

$$AuX_2^- - AuY^- - Au(OH)_2^- - Au(OH)_4^-$$

where: $X = Cl, Br, I$;

Y = combinations of pairs with Cl, Br, I, and OH according to the increase of stability of their complexes with gold.

The sequence of change of form of the disolved gold upward in the hypergene zone is controlled by change of conditions from reducing to oxidizing. In acid environments (zones of cementation and oxidation) this may theoretically be presented by the sequence:

$$Au(H_2S,HS)^0 - AuI_2^- - AuBr_2^- - AuCl_2^- - AuCl(OH)^-$$

In near neutral and alkaline environments (cover of unconsolidated sediments) the sequence is:

$$Au(HS)_2^- - AuS^- - AuI_2^- - AuI(OH)^- - AuBr(OH)^- - Au(OH)_2^- - Au(OH)_4^-$$

Metastable thiosulphate and sulphide complexes of gold may be found in soils immediately over buried oxidized deposits.

NUMERICAL MODELING EXPERIMENTS IN VAPOUR GEOCHEMISTRY: IMPLICATIONS FOR MINERAL EXPLORATION

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This study examines the development of vapour anomalies in one-layer and two-layer media with different diffusion coefficients, over a number of gas and vapour sources having different time-dependent stabilities. Theoretical concentration patterns are computed using two-dimensional finite-difference numerical solutions of the diffusion equations. The calculated diffusion patterns are compared with *in vitro* experimental data, and their general features are shown to be comparable. Results are discussed in terms of possible applications to vapour-geochemical exploration, with particular reference to the detection at the surface of buried gas and vapour sources.

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GEOHYDROLOGIC EXPLORATION USING EQUILIBRIUM MODELING: A CRITICAL ANALYSIS OF EH AND PE

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A number of computer programs (WATEQ, GEOCHEM, PHREEQE, etc.) have been developed to aid in the interpretation of the chemistry of natural aqueous systems. In theory, at least, a ground water that has been in contact with a hidden ore deposit should carry a different chemical signature than water that has passed through barren wallrock. The problem lies in properly interpreting the chemistry of the mineralized water in order to reveal the presence of the hidden ore deposit. Most of the computer programs require some estimate of the equilibrium redox state of the system, such as Eh or pE.

We continue to develop a family of computer programs to aid in the interpretation of the chemistry of natural waters, with the hope of applying these programs to hydrogeochemical exploration for hidden mineral deposits. Our present package of programs is called SEARCH. The central program in the package is the equilibrium water model WATEQFC. We have previously published a description of the potential uses of WATEQFC in exploration for uranium (Runnells and Lindberg, 1981).

The first section of SEARCH reads analyses from a magnetic tape and formats the analyses for input to WATEQFC. WATEQFC then computes the equilibrium distribution of aqueous species and the saturation indices of solid minerals and compounds. Another program, SELECT, searches the output from WATEQFC and prepares the values for mathematical transformation, statistical analysis, or machine plotting.

We have used our programs to read a magnetic tape of ground-water analyses obtained from the U.S. National Water Data Exchange (NAWDEX). This search yielded 681 complete ground water analyses for which field Eh, pH, and at least one aqueous redox couple (such as ferrous ion/ferric ion) were reported.

Results of our work reveal that the observed Eh, as measured with a platinum electrode, does not correspond to the theoretical Eh as computed from any one of the analyzed redox couples reported in various samples of the 681 analyzed ground waters. Use of Eh as an equilibrium master input variable in water equilibria models is therefore not justified. Although similar suggestions have been made previously in the geochemical literature, to the best of our knowledge our work is the first to fully document this problem on the basis of a large number of high-quality analyses.

Observed Eh values in 681 ground waters from the U.S. range from about (-)565 mV to approximately (+) 745 mV. Values of pH range from about 2.8 to approximately 9.5. Plots of log (molality Fe) and log (molality Mn) reveal no systematic relationship whatever to Eh. Maps of the saturation index (SI) for magnetite over an area of approximately 260 square kilometers in the state of Indiana (U.S.A.) show rapid and large changes from supersaturation to undersaturation. However, based on our observations of non-equilibrium with regard to redox in natural ground waters, we reluctantly conclude that such maps are probably meaningless.

We conclude that equilibrium modeling of the redox chemistry of natural aqueous systems is not realistic as computed from Eh or pE as a "master" redox variable. A lack of internal equilibrium eliminates the possibility of specifying a single redox state for the water, and measured values of Eh do not correspond to any particular redox couple in solution. Equilibrium modeling should therefore be restricted to non-redox (metathetical) systems. If redox chemistry is to be considered, investigators must analyze the waters for the specific valence states of the elements of interest, such as As(III)/As(V).

ANOMALOUS METAL CONTENTS OF AQUATIC BRYOPHYTES AT TVERRFJELLET AND SNERTINGDAL, CENTRAL NORWAY

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Aquatic bryophytes (stream mosses) represent a potential sampling medium in regional geochemical exploration for minerals and in geochemical mapping for environmental control.

Sampling and multielemental analysis of 168 moss samples was undertaken in two areas with known anomalies at five different times during the summers of 1977 and 1979. One area is north of the Tverrfjellet massive sulphide deposit, which contains more than 1.0 % Cu, 1.5 % Zn, 0.3 % Pb, and 35 % S. The other area is at Snertingdal where the rocks contain some 1 % Pb as galena dissiminated in quartzite.

A total of 168 moss samples were collected. The mosses were ashed overnight at 430 °C, dissolved in concentrated nitric acid, and analysed for 29 elements with an inductively coupled plasma emission spectrometer. The mean content of several subsamples was used for each site.

Contents in dry matter of stream mosses were compared with the values obtained in a comparable extraction and analysis of the <0.18 mm fraction of stream sediments.

The results suggest that the variation in the metal content as a function of sampling time is smaller than the sampling error and variation between sampling stations.

The average values from each site were treated by R-mode factor analysis in variable space. The principal axis factor loadings were used in a Q-mode factor analysis in sample space followed by a paired hierarchical cluster analysis to divide the data into a background and an anomalous population. A correlation analysis based on metal contents, the frequency distributions of which were transformed to symmetrical distributions, formed the basis for assignment of trace metals in the stream mosses to a siliciclastic, organic, or Fe-Mn-oxide phase.

At Tverrfjellet the concentrations of Ni and to a certain extent of Cd in stream mosses correlate with elements of the siliciclastic component (i.e., Ti, Al, Cr, and Li). Cu, Mo, Ag, and partly Pb seem to correlate with Fe. The concentration of Zn appears to be governed by the concentration of both Fe and Mn in the background population. Ni and Cr correlate with Mn in both populations. At Snertingdal Pb accompanies a non-siliciclastic phase.

The anomaly in stream mosses is wider than in stream sediments, especially for elements like Mo and Cd which are below the detection limit for many of the stream sediment samples. However, the contrast between anomaly and background is not higher for stream mosses than for stream sediments.

UPTAKE OF LEAD IN SPRUCE AND BIRCH BARK OVER A BURIED GALENA DEPOSIT AT SNERTINGDAL, CENTRAL NORWAY

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The concentrations of Pb and 24 other elements in ash of bark of spruce (*Picea abies*) and birch (*Betula pubescens*) were measured by inductively coupled plasma emission spectrometry after dissolution in hot (110°C) 7N HNO_3.

The concentration of Pb in the spruce bark is proportional to the concentration in the A_0- and C-horizons, and reaches over 10 000 and 1000 ppm, respectively. The concentration of Pb in the birch bark does not exhibit a distinct pattern and seems to be independent of the concentration of Pb in the soil. No correlation between the concentration of Pb and other elements in the spruce and birch bark was found.

It is concluded that spruce bark is a nonbarrier, and is favourable with respect to the uptake of Pb. Birch bark has a high barrier, and it does not accumulate Pb in relation to the concentrations measured in the soil.

RAPID GEOCHEMICAL PROSPECTING IN COVERED AREAS

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Areas where ore-bearing bedrock is overlain by young allochthonous (transported) sequences are promising targets for new mineralizations,even within ore districts. Such areas are large (in the U.S.S.R. some 2.4 M km^2) and are typical in steppe, desert, and tundra-marshland landscapes.

Buried and blind-buried mineralization is typically accompanied by epigenetic secondary dispersion halos of many elements (copper, lead, zinc, arsenic, nickel, cobalt, mercury, silver). Halos are developed through the entire thickness of the overburden (profiles up to 150 m deep were investigated) and are clearly reflected in the humus soil horizon. These halos are formed by capillary-film transportation of ions (electrodiffusion) towards the surface, combined with the infiltration transport of elements by underground waters. There are two varieties of epigenetic halos; superjacent halos, developed exactly over the primary halos and ores and; displaced halos, restricted to the exposure of ground waters.

The mode of occurrence of trace elements in epigenetic halos is determined by the chemical properties of the elements (iron, manganese, calcium, sulphur, aluminum, silicon). Therefore, the investigation of the modes of occurrence and the development of techniques for the selective extraction of various forms of the elements are a basis for the detection and investigation of epigenetic halos.

It has been established that the halos with the highest contrast are connected with sorptive-saline and organo-mineral modes of occurrence. Field methods for rapid detection of trace elements in these forms were developed.

The rapid technique of prospecting consists of 1) sampling of the humus soil horizon, 2) extraction of separate phases of chemical elements, 3) determination of the sum of heavy metals by modified methods, 4) mapping of geochemical anomalies in the field and landscape-geochemical interpretation, 5) detailed sampling in any anomalous area for checking and localization of high-concentration centres, 6) drilling, and 7) rapid analysis of drill samples in the field and interpretation of the data in terms of indicator associations of elements in different types of the weathering crust.

Commercial use of rapid methods in covered areas has shown that it is possible to carry out the whole cycle of prospecting from reconnaissance to the evaluation of mineralized zones during one field season. The method is characterized by high interpretation and economic efficiency.

SELECTIVE SEQUENTIAL DISSOLUTION OF ORGANIC-RICH STREAM SEDIMENTS FROM TALVIVAARA, FINLAND

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Organic-rich stream sediments, which are a widely used material in geochemical prospecting in Finland, were investigated by analyzing six heavy metals after a series of selective extractions chosen from the literature.

The investigation was carried out in the Kainuu schist area at Talvivaara, eastern Finland. The region is characterized by sulphide- and graphite-rich black schists. A Ni-Cu-Zn mineralization is known in one of these. The main ore minerals are pyrite, pyrrhotite, sphalerite, pentlandite, and chalcopyrite. Mean contents of Co, Ni, Cu and Zn are 0.02, 0.26, 0.14, and 0.53 % respectively. Forty-six organic-rich stream-sediment samples were collected in areas over mineralization and background.

Loss on ignition (500 °C) of the samples was 20-95 %. The pH of the samples, measured in the laboratory before drying, was 3.4-6.2, with a mean of 4.2. The Eh of stream water was +240 to +300 mV. Samples dried at 70 °C were ground and sieved through a 0.5 mm screen.

The <0.5 mm fraction was subjected to a sequential extraction as follows: NH_4-acetate for exchangeable cations - cold $NH_2OH \cdot HCl$ for dissolution of hydrous Mn oxides - H_2O_2 for destruction of organic material - hot $NH_2OH \cdot HCl$ for dissolution of Fe oxides - $HF/HClO_4$/aqua regia for dissolving the residue. Mn, Fe, Co, Ni, Cu, and Zn were analyzed by flame-AAS from each extraction. The sum of the concentrations of an individual element from the extractions was considered to be the total concentration. The concentrations of the elements in different extractants are presented as percentage portions of the total. Correlation analysis was carried out on the data.

Co correlated well with Mn. Mn and Co were enriched in the acetate leach and in the residue. Thirty-seven % of Mn and 21 % of Co were NH -acetate-soluble and 44 % of Mn and 48 % of Co were $HF/HClO_4$/aqua regia-soluble. Co exhibited little affinity to Fe oxides; only 1.1 % of Co was dissolved in hot $NH_2OH \cdot HCl$. Unlike Mn, a large part of Fe (43 %) was H_2O_2-soluble. The portions of Fe in exchangeable form and in the residue were smaller than those of Mn. The significant portion of Mn, Co, and Fe in the residue cannot be explained only by silicate material eroded from the bedrock. More plausibly there were some Fe oxides insoluble in the $NH_2OH \cdot HCL$-extraction. Cu was enriched in the organic component, as 67 % of the total Cu was H_2O_2-soluble. Only 6.4 % of Cu was in exchangeable form. These two findings indicate a strong complexing ability of Cu with organic material. Cu favoured Fe oxides rather than Mn oxides. In spite of the evident affinity of Cu to organic material, there was no correlation between loss on ignition and Cu concentration, indicating the excess of complexing sites of the organic component. The behaviour of Ni was much like that of Cu, but exhibited a more exhangeable character and more affinity to Mn oxides than did Cu. Twenty % of Ni was NH-acetate-soluble. Zn was more evenly distributed between different extractions than the other elements. Extractable Ni and Zn tended to increase with increasing total concentration.

GEOCHEMICAL RESPONSE IN TILL OVER KOMATIITIC ROCKS

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The lithology of bedrock was correlated with regional till geochemistry in an area where komatiites prevail. At Sattasvaara and Kummitsoiva in the volcanic belt of central Lapland komatiites appear as well-exposed hilly areas. The overburden, mostly till, is only a few meters thick and is mainly of local origin. Large amounts of preglacial weathering products are present because the ice divide lies only some forty kilometers north.

For geochemical mapping a total of 13 000 till samples were collected from an area of 1200 km^2. Chemical analyses were carried out on the fine fraction of till (-0.06 mm) and the trace element contents were analyzed with a direct-reading optical emission spectrometer (OES). Maps were prepared using weighted moving medians based on at least three points within a circle of 0.5 km radius, with weight from five to one depending on the distance from the central point.

The geological and geochemical maps are supportive of each other and rock boundaries can be detected even in geochemical maps. The analyses done with OES, an instrument considered to be only semiquantitative, are quite satisfactory because the chemical composition of the metavolcanic rocks differs markedly from the composition of the surrounding slates and schists.

Through regional geochemical mapping, komatiites and associated metavolcanic rocks can be distinguished even in poorly exposed areas. Rocks promising for exploration can probably also be recognized. For examples, the nickel content, as generalized, is higher in certain rocks of the Sattasvaara and Kummitsoiva komatiite complexes, than in other rocks. Different types of metavolcanic rocks can also be distinguished on the basis of their trace element contents. The chemical composition of till differs over komatiite proper (Mg, Ni), basaltic komatiite (Mg, Ni, Cr, Co, Ti, Ca), komatiitic basalt (Ca, Mg, Ni, Cr, Co), basalt (Ca, Cu, Ti, Mn, V), and felsic metavolcanic rock (Cu, Co). Such differences should assist exploration of economic mineralizations in these rocks.

BEDROCK GEOCHEMISTRY AT THE GEOLOGICAL SURVEY OF SWEDEN

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Mineral alteration zones in host rocks surrounding mineral deposits have long been used as indicators of ores and recent interest has stressed the importance of the distribution patterns or halos of elements . The halos can be more extensive, since the mineralogical variation and the lattice substitution in the minerals are reflected in the chemical composition.

One of the outstanding problems is the possible presence of several populations of contents in the samples. Only some of these populations are related to the halos while others disguise them. Several mining areas in Sweden have been investigated, and the results are presented here.

The Stollberg ore field, Central Sweden, is located within Precambrian volcanic rocks. Several stratiform Zn-Pb and Fe ores are situated in a 6 km long part of a stratigraphic horizon. Drifts are extended to a depth of 575 metres. Approximately 3000 rock samples have been sampled from outcrops, drill-cores and drifts.

The contents of elements are difficult to use owing to the presence of several populations. After reducing the skewness, factor analysis was used which generally indicated distinct multielement zonations. After interpretation of these, factor scores were used as input in discriminant analysis. In this manner chemical halos were obtained which have an extension of more than one kilometre in all directions around the various ore types in the area. Some new promising prospects were discovered which will be drilled.

There are obviously two types of halos present in the Stollberg area. One type, obtained from the discriminant analysis of metal contents of the hanging wall and footwall, was probably formed by submarine volcanic processes. There are, however, no pipes present. The zonation of these halos, which occurs with distinct borders around all known ores, is also observed in the new anomalies discovered. The other type of halos exhibits a symmetrical pattern both E and W of all the ore types. A mobilization of the elements has probably occurred in connection with metamorphism. These halos have an extension of more than 1 km.

A clear pattern of zoning is obtained after using discriminant analysis, and it is even possible to interpret the distances to the known ores by using the discriminant scores.

The use of factor analysis to obtain the relevant associations and the use of discriminant analysis of factor scores to obtain a gradation of the value of the factors, was shown to be efficient.

It was possible to locate all the known ores at a regional and a detailed scale. Even vertical zonations was detected, which means that it should be possible to detect deep-seated blind ores.

INDUSTRIAL MINERALS AND ROCKS IN FINLAND, NORWAY, AND SWEDEN

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Though the industrial mineral sector is the lesser known branch of mineral exploitation, the value of global production of industrial minerals (including minerals used for ballast and also precious stones) exceeds that of global production of metals. Consumption of industrial minerals is also increasing at a higher rate than metal consumption. Industrial minerals and rocks have a wide diversity of uses in the modern industrial community. They are used as basic raw materials for building and construction work, as auxiliary components in various industrial processes, as carriers of the life-sustaining nutritive substances phosphorus and potassium, as the principal raw materials in the production of glass, china, refractories, mineral wool, etc., and as filling agents and pigments in paper, paint, rubber, and plastics.

In this paper the emphasis is on the following issues:

- geological conditions for mining of industrial minerals and rocks in Finland, Norway, and Sweden,
- present production,
- consumption rate,
- development potential in a long perspective.

TILL GEOCHEMISTRY IN EUROPE AND NORTH AMERICA

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The glacial boundary in North America and Europe divides two significantly different terrains with respect to exploration geochemistry. South of the boundary, the non-glacial soils have been formed largely *in situ* by chemical decomposition of underlying bedrock, and sediments derived from them contain components from within easily identifiable drainage basins. North of the glacial boundary, glacial sediments and soils (and sediments derived from them) have been formed largely by the physical processes of glacial abrasion and crushing of fresh bedrock, chemical processes generally playing only a minor role in the development of the relatively weak post-glacial solum. Furthermore, components of the unconsolidated mantle of glacial sediment have been transported over topographic barriers along relatively straight lines across one or many drainage basins, except in areas of alpine glaciation. For these fundamental reasons, many of the classical methods of exploration geochemistry, developed in areas outside the glaciated higher latitudes, are ineffective or, at best, inefficient in these environments.

It is only in the past 20 years that a growing awareness of the fundamental contrasts between glaciated and unglaciated terrain has sparked an increasing interest in combining the principles of glacial geology with those of exploration geochemisry so that more effective ways of mineral exploration might be found.

The way in which these disciplines have been combined however, has differed between North America and Northern Europe, largely for demographic and economic reasons. In Canada, for instance, with its vast, largely unexplored, lightly populated areas, geochemical research has focused on developing methods to be applied at a regional scale, with the objective of covering large areas and producing diffuse targets to which other more traditional methods of exploration can be applied. In Fennoscandia, Ireland, and the United Kingdom geochemical reconnaissance is carried out at a much smaller scale, because of the more detailed geological information available and because of lower costs resulting from the more evenly distributed populations. Drift geochemical exploration is also more important in Europe than in North America because there are no longer any "easy-to-find" ore bodies in Europe, and serious research into the obscuring effects of the glacial cover had to be undertaken decades ago. In contrast, drift prospecting is just beginning to gain some acceptance in North America and is still looked on with suspicion by many exploration companies.

Although the theory of continental glaciation has been accepted for over eighty years, the popular conceptions of the history and configuration of both the Fennoscandian and North American ice sheets have recently undergone major revisions that have direct bearing on mineral exploration in glaciated terrain. Studies of the glacial history of the Canadian arctic, for example, have shown that the Laurentide Ice Sheet, which covered most of that portion of the Canadian Shield with high potential for mineralization, was a much more complex and dynamic body of ice than had previously been supposed. Rather than consisting of a monolithic mass of ice centred on Hudson Bay during each of four major glaciations, it was found to comprise several independent, confluent centres of outflow toward which ice fronts may have shrunk one or more times during each major glacial stage. The history and configuration of centres of outflow has considerable bearing on interpretation of geochemical dispersal patterns, even at a local scale.

Similarly, in Fennoscandia, stratigraphic work carried out in conjunction with mineral exploration programs has shown that deposits of multiple glacial events with divergent directions of ice flow complicate interpretation of glacial geochemical dispersal, particularly in Finland. This recent discovery of major flaws in our concepts of the basic glacial geological framework of North America and Northern Europe suggests that the science of glacial geology is still at a rudimentary stage. It is, then, no surprise that the sophisticated analytical and statistical techniques of exploration geochemistry are often unsuccessful when applied to terrain where both glacial sediments and glacial history are poorly understood.

Along with the changing ideas about the North American and Fennoscandian ice sheets, a revolution in understanding of glacial sedimentation has been taking place. In the past 15 years glacial sedimentologists, led principally by Boulton of Britain and by Shaw of Canada, have presented models of glacial and near-glacial sedimentation, based largely on observations and experiments made around modern glaciers. As a result of this work, the genesis of glacial and associated sediments is much easier to understand now, and better sample control is possible when doing drift geochemical sampling. Nevertheless, several aspects of glacial processes and deposits, listed below, are in need of further study and explanation:

1) Rogen or ribbed moraine, for example, is a common landform around former centres of ice dispersal in Finland, Sweden, Newfoundland, Quebec-Labrador, and District of Keewatin. These short, sinuous, transversely-oriented ridges occur over many areas of potential mineralization and are sometimes intimately associated with mineralized boulder trains, particularly in Canada. An understanding of its genesis is essential in interpreting and planning geochemical surveys in areas where Rogen moraine occurs. Presently there is no concensus about whether these features are proglcial or subglacial although the author and several others feel that they are most likely the products of shearing of the glacial bed with subsequent stacking of the plates of debris during ablation of a largely stagnant ice mass.

2) Processes of esker sedimentation are also imperfectly known, and the relationships of esker composition to the composition of the basal load of an ice sheet, which forms till adjacent to the subglacial channel, must be clarified. The author and others have observed that eskers often follow zones of structural discontinuity in the bedrock, such as faults, an observation that may indicate that eskers can be preferentially located over sites with high potential for mineralization.

3) The relationship of ice movement history to directions of effective glacial transport is not well established. In many places striae or till fabric may indicate several directions of ice flow during a single glaciation, particularly near ice divides or isolated late-glacial ice caps. In many cases, however, dispersal apparently occurred along only one of the azimuths of flow. Although the reasons for this are not clear, the phenomenon is probably related to flow directions prevailing just after the first passage of an ice front across an area, as the glacier is growing. Thus, striation and till fabric orientation, although reliable indicators of dispersal direction in many instances, do not necessarily bear direct relationship to direction of debris transport.

4) There are also a number of geochemical aspects of till that are poorly known or described. DiLabio and the author in Canada and Evenson in the U.S. have studied the trace element distribution of debris entrained in Alpine-type glaciers. On Bylot Island, off the north tip of Baffin Island, debris bands in glaciers draining Precambrian metasediments show strong vertical variations in trace-element chemistry. The geochemical nature of the till that will eventually be formed by these bands will depend on whether the till is formed by basal meltout, preserving the integrity of the vertical variations, or by supraglacial meltout or basal lodgment, homogenizing the debris bands into a till that varies little geochemically from bottom to top.

5) Postglacial weathering can have a radical effect on the geochemistry of drift to considerable depths, depending on the configuration of the local ground-water or permafrost table. Furthermore, the effects of weathering on the geochemistry of relatively impermeable till are quite different than those on some of its more permeable derivatives, such as esker or other ice-contact gravels. In an oxidizing environment, i.e. on well-drained slopes, labile minerals such as sulphides and carbonates are generally destroyed above the water or permafrost table, their chemical constitutents being carried away in solution or scavenged locally by clay-sized detritus and secondary oxides/hydroxides, depending on the element and the local geochemical environment. In poorly-drained sites, where the water table is at or close to the surface and/or the surface is covered with an organic mat, very little destruction of primary labile minerals occurs. In permeable glacial sediments, particularly well-sorted sands and gravels, destruction of labile components also takes place, but weathering of some of the more labile silicates produces a fine debris of mixed layer or other clays, oxides, etc. which can be physically translocated from the surface downward through the deposit. This is especially important in esker or similar deposits that stand largely above the ground-water table. The enhanced scavenging ability of these fine secondary materials gives the fine fractions of glaciofluvial and similar deposits elevated background concentrations of trace elements relative to the same size fractions of nearby till, the fine fractions of till being produced largely by physical crushing of primary minerals with much lower exchange capacity. Thus, chemistry of clastic fragments above the water table will not usually reflect the presence of some of the more common (i.e. sulphide) economic minerals.

For reasons cited above, weathering restricts the use of heavy mineral or other coarse-grained fractions of till and derived sediments except in cases where ore minerals are resistant (tin, gold, chromite, etc.). The contrast between the mineralogy and chemistry of fine fractions of till and sorted sediments makes the requirement for sophisticated sample control absolutely essential to interpreting exploration geochemistry results in glaciated terrain.

One might conclude from the brief discussion above that geochemical exploration using till or derived sediments is a formidable task. On the contrary, I believe that the recent exponential increase in reliable models of glacial history and sedimentation augur well for the successful application of geochemical techniques to exploration in glaciated terrain. The very processes of glacial erosion and transportation produce glacial geochemical dispersal trains that are much larger than the original source, if only we can apply the appropriate glacial geological and exploration geochemical techniques to recognize them. To this end we will have to integrate the disciplines of glacial geology and exploration geochemistry more closely and will have to encourage universities to provide academic programs that provide the depth of training necessary to meet this requirement, particularly in North America.

ASPECTS OF ORGANIC AND INORGANIC COMPLEXES OF THE PLATINUM GROUP ELEMENTS IN NATURAL WATERS

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The stabilities of complexes of the platinum group elements have been evaluated from available thermodynamic data. Chloride complexes are important only for Ru and Ir, but there are few thermodynamic data available for other complexes of these elements. The aqueous hydroxide of Pd is predominant species in typical freshwaters and in seawater but the glycinate complex is also important in peat bog waters. Although there are no thermodynamic data for the Pt-glycinate complex, it is expected to be important on the basis of the similarities of the chemistry of Pd and Pt. The Pt-ammonia complexes dominate over Pt-chloride complexes in typical freshwaters and in peat bog waters.

The speciation of each platinum group element is substantially different and generalizations cannot be made concerning their dissolved state. Rhodium, for example, exists as the Rh^+ ion in "normal" soil waters, whereas the oxyanions of Os are dominant in these environments. In the past almost all discussions of secondary metal dispersion have focused on inorganic complexes. The data presently available clearly show that this approach is inadequate in that biologically-derived molecules may be important sequestering agents. Additional thermodynamic data for both organic and inorganic aqueous complexes are required if the behaviour of these metals is to be better understood.

GEOCHEMICAL PROSPECTING WITH MINERAL SUSPENSATES AND BOTTOM SEDIMENTS IN THE APPALACHIAN PIEDMONT PROVINCE, LOUISA COUNTY, VIRGINIA

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The mineral fraction of suspended stream sediments has been extensively tested as a geochemical prospecting sample for the first time. One hundred and eighteen samples were collected *in situ* using the mechanical vacuum-filtering unit described by Siegel (1982). Bottom sediments were taken for comparative study. The area investigated is southwest of Mineral, Virginia, where stratiform massive sulfide deposits have been found. It encloses known Au mineralization (thin veins with native Au, gold-bearing pyrite, and minor chalcopyrite, with local sphalerite and galena) and has potential for containing hidden mineralization beneath a thick cover of residual soil. Sampling was in the drainage basin of Northeast Creek, Pendleton Quadrangle, Louisa County, Virginia and the streams sampled approximated a Y pattern with northeast and northwest sub-basins. The study zone is underlain by two dominant lithologies: Upper Precambrian-Lower Cambrian metasediments and metavolcanic rocks. The mineral suspensate, a total dissolution of the -100 mesh size fraction of the bottom sediment, and cold acid leaches (with 1.5 % HCl and 3 % HNO_3) of this fraction were analysed for Zn, Cu, Pn, Fe, and Mn with flame atomic absorption against standards prepared with matching matrices.

In the northwest sub-basin, a cluster of one strong ($>\bar{x}+2s$) and four weak (between $\bar{x}+1.1s$ and $\bar{x}+2s$) anomalies were found in the mineral suspensates. Subsequently, we found out that this correlated with a large Zn-Cu anomaly in soil and a large EM-16 anomaly found by Texas Gulf

Sulphur (unpublished data) and that sulfide lenses were revealed by drilling (two holes). Total dissolution gave a high-low anomaly couple that corresponded with the high anomaly for Zn in the mineral suspensates. Both acid leach groups showed three strong Zn anomalies each (at the same sites) that correlated with the mineral suspensate Zn anomaly cluster. Au mineralization in the northeast sub-basin was not satisfactorily targeted by the elements analysed in the mineral suspensates although one high Cu anomaly was found bordering the mineralization. A second set of mineral suspensate samples is being prepared by low-temperature ashing to determine if the pathfinder elements Hg, As, and/or Sb will indicate the Au veins. Total dissolution was not useful in the area of Au mineralization, but Pb in both leachate suites was an indicator of the Au mineralization and was found along the run of a stream bordering it for about one kilometer. In the cold 1.5 % HCl extracts, there were two low Pb anomalies at the Au occurrence, followed immediately by five strong and then four weak anomalies.

The mineral suspensate seems to have excellent potential as a geochemical prospecting sample but requires further testing at different types of mineral deposits, in different climatological-topographic environments, and with a broader suite of chemical elements, to define its future utility.

GEOCHEMICAL EXPLORATION WITH STREAM SEDIMENTS IN LAS VILLAS PROVINCE, CUBA

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The San Fernando Mine, Las Villas Province, Cuba is located at N22°12′, W80°04′. The major commodities mined there are Cu and Pb; Zn is recovered as a minor commodity. Manifestations of chalcopyrite and cinnabar were found in a drainage system about one kilometer to the west of the San Fernando Mine and malachite and sphalerite were identified in the drainage system 1.5 to 2 kilometers east of the mine. The study area covers about 16 km^2 and contains andesitic lava, rhyolitic porphyry, dacitic rhyolite, granodiorite, and quartz diorite porphyry; major structural lineaments in the area are well-defined. A gossan cover may be present. Norms for stream-sediment geochemical exploration in the area were established from a pilot study in the drainage system from the San Fernando mineralization (from 1 km upstream to 3 km downstream of the mineralization) and were used to evaluate the zone 1.5 to 2 kilometers to the east. For the San Fernando mineralization, the geochemistry of the — 100-mesh size fraction of stream sediments, both from a total sample dissolution and from a 1.5% HCl cold acid leach established the location of the mineralization using Zn, Cu, and Pb; Ag was found at one sample site (that with the strongest multielement anomaly). The same approach in the unexplored area to the east showed lower concentrations but two anomalies for Cu and Zn were found. Follow-up exploration with stream sediment and panned concentrate ("jagua") geochemistry further defined the anomaly field. Detailed geochemical studies now in progress are confirming the existence of a prospect zone (p.c. JH). The correlation between the geochemistry of the total dissolution samples and the cold acid leach samples was good for both areas investigated. For the San Fernando system, the correlation between Cu-total and cold extractable Cu was +0.527; in the area to the east, the correlations (n=40) were +0.738 for the Cu-couple and +0.886 for the Zn-couple. For cost effectiveness and rapid turn around time for results, Cuban geochemists working in the area (or geochemists working in climatologically — geologically similar areas) can use the weak cold acid leach for analysis and establish the existence of anomalies that may reveal economic mineralization.

A COLOURED GEOCHEMICAL MAP OF THE FEDERAL REPUBLIC OF GERMANY

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In six years, beginning in 1977, 80 000 water and 70 000 stream sediment samples were taken over an area of more than 210 000 km^2. The overall density was about one sample per 3 km^2, but varied according to the importance of the investigated region.

The sampling sites at small streams, sometimes wells and ponds, were chosen on the basis of 1:25 000 topographic maps, with environmental contaminations avoided as far as possible.

A mobile field laboratory for water analysis was moved between the sampling centres at a rate of about 100 km every three weeks during the sampling season, i.e. May to October.

The water samples were analysed for pH, conductivity, and F with electrodes. After enrichment in organic solutions, Pb, Zn, Cd, Cu, Ni, and Co were analysed by atomic absorption spectrophotometry (AAS), and U by fluorimetry. The characteristics of the streams were also recorded.

The stream sediment samples were dried at 100°C, sieved to -0.18 mm (about 80 mesh) and analysed in the central laboratories in Hannover for Pb, Zn, Cd, Cu, Ni, Co, and Li with AAS, for Ag, B, Ba, Co, Cr, Mn, Mo, Sn, Sr, V, Y, Ga, and Ge with optical emission (OE) technique and for U, F, and W with other techniques.

A data base of more than two million analytical values has been installed in a SIEMENS host computer. Colour raster software from ESC, Copenhagen, was used to produce coloured geochemical maps of the area under investigation at any required scale with the help of an inkjet plotter.

The poster presentation will show two- and three-dimensional coloured grid maps for different elemental distributions, the data of which have been classified into six statistical units. Single anomalous values within a chosen spatial unit of varying size can still be recognized, as well as the mean of values within an area.

PLASMA/MASS SPECTROMETRY: AN APPLICATION TO TYPE GOLD AND BASE METAL OCCURRENCES

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Application of a recently developed mass spectrometer, of novel design, to the determination of isotope abundance and element concentrations in rocks and ores associated with gold and base metal occurrences in Ontario will be discussed.

The instrument used in this study is the newly developed ELAN 250 inductively coupled plasma mass spectrometer (ICP/MS) manufactured by SCIEX of Thornhill, Ontario, Canada. This instrument combines an inductively coupled argon plasma, as ion source, with a quadrupole mass spectrometer by means of a unique interfacing arrangement. This combination of two well established technologies provides a reliable, medium precision (0.1 - 0.5 %), mass spectrometer capable of determining isotopic concentrations at rates many times faster than is possible with conventional mass spectrometers. The unit cost of such determinations is thereby substantially reduced making wider use of stable isotopic data a practical reality.

The speed with which spectral data are acquired by this instrument provides it with virtually multi-element capability. It therefore becomes economically feasible to collect elemental concentration data on a wide range of elements concurrently with the collection of isotopic data. Further, as collected data are stored permanently in computer memory the possibility for later search and comparative studies exists.

Other benefits derived from employing a mass spectrometer for elemental analysis are; a simple well-resolved spectrum, high sensitivity (0.1 - 10 ng/ml), wide dynamic range (4 - 5 orders of magnitude), and the possibility of employing isotope dilution routinely both as an internal standardization/calibration technique and for the production of highest quality elemental analyses in a routine way.

Application of this instrumentation to exploration geochemistry in general will be considered with particular attention given to the possibility of typing gold and base metal occurrences. Data on lead and sulphur isotope abundances for the various occurrences studied will be presented along with elemental concentration data for a suite of associated trace elements including Ni, Cu, Zn, Ag, Au, As, Sb, Te, Se, Sn, and W.

Results will be presented for isotopic abundances obtained on NBS lead and uranium standards together with similar data for lead obtained on a suite of galena and other sulphide-mineral separates kindly loaned to this project by Dr. J.M. Franklin of the Geological Survey of Canada.

This project is partly funded by a grant from the Ontario Government BILD program, Exploration Technology Development Fund.

MULTIELEMENT GEOCHEMICAL SURVEY IN STREAM SEDIMENTS OF THE PALAEOZOIC OF BELGIUM

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As a continuation of a stream sediment reconnaissance for uranium in the Palaeozoic of the Belgian Ardennes, a multielement survey is now being carried out in the same region.

The mean density is one sample per km^2 and the area covered is 12 000 km^2. Observations on drainage, colour and texture of the sample, possible contamination, lithological environment, etc. are recorded on field data forms. Dried samples are crushed and sieved and the minus 80-mesh fraction is retained for analysis. After a hot acid digestion, samples are analysed for twenty elements by direct current plasma emission spectrometry. Organic matter content and pH of samples are also determined. In selected anomalous areas, selective chemical extractions are carried out on an equal number of background and anomalous samples. The aim of this study is to better understand the control of anomalies and to enlarge them.

Data are reported on topographic maps, at a scale of 1:100 000. Special attention is paid to lithological influence when thresholds are determined. The maps indicate sample locations and metal contents. Anomalies are also presented based on regression and factor analysis of the data. Each report includes a description of geological and drainage conditions as well as known mineralisations.

IMPORTANCE OF AQUA REGIA LEACHING OF CLAY IN STREAM SEDIMENTS

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The purpose of this study was to compare the results of an aqua regia acid treatment of stream sediment samples with a subsequent hydrofluoric-nitric acid treatment of the same sediments. The 46 stream sediment samples utilized in this study were collected in the vicinity of the Magnet Cove and Potash Sulfur Springs igneous complexes, Arkansas, USA. These igneous complexes have intruded shale, chert (novaculite), and sandstone. Magnet Cove and Potash Sulfur Springs have been mined for associated vanadium, and Magnet Cove also has rutile and molybdenite mineralization. The sediments consisted predominantly of shale(clay), chert, and quartz; however, a few samples also contained some magnetite, rutile, and pyrite. The -40 to +95 mesh fraction of each sample was first treated with aqua regia and then treated with HF. Both acid solutions were then analyzed for Ag, Al, Fe, Mn, Co, Ni, Cu, Zn, V, Ti, Pb, Na, K, and Ba by atomic absorption spectrometry.

Plots of the aqua regia versus HF extractable concentrations for Fe, Ni, Zn, Mn, and Co reveal that these concentrations increase uniformly in both acid solutions forming a single trend. Furthermore, when the sum of the aqua regia plus HF extractable content of K or Na is plotted against similar Al or Fe content, a continuation of the same line occurs. These observations indicate that some of the material dissolved by the aqua regia is also dissolved by the HF treatment. Thus, the aqua regia leaches not only the Fe oxide coatings of sediment grains, but also attacks the clay itself. Silica in the alumino silicate structure of the clays is not dissolved by the aqua regia, and as soon as a layer of Al is removed from the surface, the remaining silica forms a barrier to further aqua regia leaching. The data also indicate that the aqua regia leach of the oxide coatings is not complete.

Thus, this study indicates that leaching of clays by aqua regia occurs and should be taken into account in interpreting stream sediment geochemical anomalies. Heavy metals leached from the clay could obscure some weak anomalies and/or produce false anomalies.

HYDROGEOCHEMICAL PROSPECTING OF GOLD IN THE ALPINE BALD MOUNTAIN ZONE

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The investigations were conducted within highly- and moderately-separated highlands and high plateaus where glaciers, stone streams, solifluction, and glacial and fluvio-glacial deposits are widely developed. A capping of Miocene basalts remains in the divides over the gold ore deposits and their oxidation zones. Young water-filled fractures traverse the ore-bearing structures and control the direction of the glacial and river valleys, as well as the location of the lakes, springs, and icings.

Gold occurs in small- to average-sized sulphide-gold-quartz veins and in a sulphidized black shale series of Precambrian and Paleozoic age. Both mechanical and hydromorphic dispersion of gold are exhibited clearly in the highlands. The latter is due to the processes of modern oxidation of the gold-bearing sulphide minerals. The anomalies of gold in streams and small lakes are related to supra- and sub-ice waters. In water of streams gold is present in three forms. Gold in colloid form comprises the most ample and contrasty anomalies. The truly dissolved gold is more local and manifests itself close to the source of the stream. Gold sorbed on suspended matter is evident because of a significant removal from the source into the solution. Migration of gold and formation of long (up to 2.5 km) and contrasty dispersions in waters of low dissolved solids is favoured by the absence of the organic matter and argillaceous and ferruginous suspensions as well as other sorbents.

In the isolated highland the anomalies of gold in water either coincide with anomalies in stream sediments over mineralized zones or indicate new mineralized areas not reflected in stream sediments. Of particular interest are the local high-contrast anomalies (CC[1] 10 - 100 and more) in the small channels, the slopes and bottoms of which are covered with stone streams and glacial and mudflow deposits. Many of these anomalies of gold are connected with the outflows of supra-glacier waters at the foot of massive taluses, stone stream slopes, and stone rivers and are brought to the surface by hydromorph dispersion of gold. The anomalies of gold associated with outflows of the sub-glacier waters are reflected in the ascending springs, icings, and lakes. In repeated sampling during 2-3 years the anomalies of gold were consistently reproduced. Biogeochemical anomalies are closely connected with those in water. The content of gold (0.0n - 0.n g/t) in lichen, moss, shrubs, bark of larch, and peats distinctly reflects the outflows of underground waters with high content of gold. The results of the hydrogeochemical prospecting of gold allowed considerable enlargement of the area favourable for detection of new zones of the gold mineralization. The complex anomalies of Au, Ag, I, F, and S_2O_3 in the glacial valleys located on the ore-bearing structures as well as in districts of known deposits deserve special attention. Many anomalies of gold coincide with geophysical anomalies and anomalies in stream sediments.

[1] CC is the average of anomalous values / the average background.

THE GEOCHEMISTRY OF PRECAMBRIAN TERRAINS

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(1) Modern geology has as its task two major interrelated problems solvable by geophysics and geochemistry: Formulation of a uniform scientific concept of the Earth's evolution and creating new technologies for exploring for deep-seated deposits of useful materials.

In the immediate future special attention should be paid to the tectonophysical, petrological, geochemical, and metallogenic characteristics of the primitive stages of the Earth's evolution as well as to the regularities of the geological development, magmatism, geochemistry, and metallogeny of mobile zones of the Earth for resolution of the first problem.

(2) The geochemical investigation of the cited problems should be carried out by a systematic analysis of the geochemical history of the elements, based on the theory of geochemical fields and geochemical typification of geological materials.

A geochemical field is defined as a geologically uniform area with similar parageneses and concentration levels of chemical elements in mineral associations formed in a similar manner and under the same conditions. A geochemical type of rocks is defined as a group of rocks formed under similar conditions, as reflected in the similarity of their mineral and major- and trace-element composition and also in their confinement to definite geodynamical environments.

Presently seven geochemical types of basic rocks and ten types of granitoids are distinguished:

(3) Based on the available geological, geochemical, and geophysical data three principal stages can be distinguished in the history of the Earth's evolution:

(a) the protoplanet stage (4.5-3.8 Ma ago);

(b) formation of the continental crust, hydrosphere, and atmosphere (3.8-1.6 Ma ago); and

(c) the active interaction of lithospheric plates (operative during the last 1.6 Ma).

These differ in the details of their development of geological processes of magmatism and metallogeny.

The protoplanet (lunar) stage is characterized by the formation of lava 'basins' on the surface of the earth as a result of collision with large heavenly bodies. The possibility of such an origin for these basins has been indicated by recent investigations in the Canadian Shield.

Based on the present conception of the crystal chemistry of crystallizing magma, one can infer the formation of lava basins on the surface of the anorthositic protocrust overlain in faulted areas by younger effusive peridotites and basaltic komatiites.

The formation of the continental crust, hydrosphere, and atmosphere was apparently characterized by an extensive selective melting of parts of the upper mantle to form silicate melts accompanied by intensive degassing of the upper mantle.

The selective melting process led to the formation of magmas with peridotitic and basaltic komatiitic, tholeiite basaltic and andesitic composition saturated with volatiles; also formed were acidic differentiates including plagiogranites of the tholeiite series and granitoids of the enderbite-charnockite series (andesite series).

The intensive degassing of the upper mantle promoted deep metasomatic alteration of the early magmatic and sedimentary rocks and led to the formation of the hydrosphere and atmosphere.

Depending on the scale of the metasomatic processes and the composition of the volatiles, the following intratelluric emanations were formed as a result of metasomatic alteration:

(a) geochemically distinctive magmatic complexes (among them the so-called "grey gneisses");
(b) ultrametamorphic granites;
(c) rapakivi granites; and
(d) complexes of metasomatites near faults.

The character of the geochemical types of magmatic and metasomatic rocks formed was apparently largely determined by the relative abundance of intratelluric emanations of water, fluorine, chlorine, and carbon dioxide.

Intensive metasomatic alteration of strata of basic composition, leading finally to their granitization, is considered to be the fundamental process of formation of the continental crust. The maximal activity of this process took place during the Middle Proterozoic (2.2-1.9 Ma) and is observed mainly in the near-polar parts of the northern and southern hemisphere (Laurasia and Gondwana).

The extensive loss of the readily melting silicate part and the degassing of the upper mantle produced a layer of depleted mantle with a thickness of 150-200 km.

The last stage of the geological evolution of the Earth, distinguished by a high mobility of ancient continental and young oceanic lithospheric plates, is characterized by a combination of varied geodynamic horizontal and vertical movements, by the generation of basaltic magma within the depleted mantle (tholeiite basalts, alkaline olivine basalts) as well as within the deep zones of the undepleted mantle (andesitic and shoshonite-latite series). Palingenetic processes, especially within intercontinental mobile zones also characterized this stage. The hydrosphere and atmosphere approached their modern composition.

(4) The characteristics of the Precambrian magmatites and metasomatites and the shift from a reducing to an oxidizing atmosphere determined the development of specific ore-bearing formations in the Precambrian such as large concentrations of nickel, copper, and gold related to intrusives of komatiitic and tholeiitic composition, and confined mainly to ancient greenstone belts; commercial concentrations of Nb, Ta, Zr, etc. in metasomatites near faults; and large metamorphic-sedimentary deposits of iron (jaspilites) and copper (copper shales and sandstones).

GOLD CONTENT IN BARITE AS A GEOCHEMICAL INDICATOR FOR GOLD-BEARING MINERALIZATIONS

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Barite is a wide-spread mineral in the Earth's crust. It occurs in endogenic and exogenic accumulations of ores of almost any genetic and compositional type, including gold-bearing deposits. A systematic study on the distribution of gold in barite has been carried out with the aim of finding indications of gold in known barite-bearing mineralizations.

The investigation included ores with and without gold mineralization in Bulgaria. The gold content in barite was determined by activation analysis (sensitivity 0.1 ppb; precision ±25 %). The results are shown in Table 1.

The gold content in barite is generally low and comparatively evenly distributed within each of the deposits. The mineralizations studied were divided into two groups; Group A represents gold-bearing deposits with high gold content in barite and Group B represents deposits without gold and with low content of gold in barite. The two groups of mineral deposits can be distinguished by the gold content in barite, and this can be applied as a criterion for definition of the gold potential of barite-bearing mineralizations.

The few published data on the gold content in barites do not contradict this finding. Therefore, we believe that the results are not fortuitous, but contribute to the problem of prospecting for gold-bearing mineralization.

Table 1. Au contents of barite from ore deposits with gold (Group A) and without gold (Group B). N is the number of samples.

Type of mineralization	Ore deposit	N	Content of Au (ppb):	
			Range	Mean
GROUP A				
1. Copper-pyritic	Celopec	3	38.6 - 39.6	39.0
gold ores	Baryta	5	24.2 - 288.8	113.5
2. Polymetallic gold ores	Madzarovo	3	135.0 - 139.5	137.7
3. Quartz-gold ores	Govezda	1	28.6	
GROUP B				
1. Baritic	Martinovo	1	9.1	
	Zlata	1	6.2	
2. Fluorite and	Mihalkovo	1	8.0	
fluorite-baritic	Trn	1	3.0	
3. Fluorite-barite-polymetallic	Jugovo	3	1.0 - 5.2	2.5
	Ustrem-Baryta	3	3.0 - 5.0	4.0
	Ciprovci	1	3.2	
4. Polymetallic,	Sedmocislenici	3	1.0 - 9.2	6.0
stratiform	Kremikovci	7	1.0 - 6.0	3.1
primary barite	Kremikovci	2	1.5 - 6.1	3.9
secondary barite				

DISPERSION OF TUNGSTEN IN GLACIAL OVERBURDEN IN BERGSLAGEN, SOUTHERN CENTRAL SWEDEN

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Prospecting for tungsten in the Western World has since the latter part of the 19th century been based mainly on mechanical concentration of heavy minerals in sediments (panning) followed by visual and chemical analyses of the heavy-mineral fraction. Since the early 1970's tungsten prospecting in Sweden has been based on the use of heavy minerals of till.

Recently, in New Zealand and the U.S., seeding of tungsten (New Zealand) and milled scheelite (U.S.) and later harvesting have indicated an accumulation of tungsten in trees, which was most pronounced in the roots. This shows that scheelite can be considered as a partly non-resistant mineral and that tungsten is adsorbed by plants. Thus, plants and humus can be used in prospecting for tungsten. In the U.S.S.R. and New Zealand tests have been made with organic samples and the fine fraction of till in prospecting for tungsten, with sampling carried out in traverses across mineralizations.

In tests performed in a scheelite-mineralized area in the Bergslagen area of central Sweden, samples from the A- and C-horizons of the podzolic profiles have been collected along grid lines across the ore as well as down-ice from the ore in the latest direction of glacial transport. The purpose of the study was to test which sample types should be used in geochemical prospecting for tungsten in the region.

The results show that all sample types studied can be used in geochemical prospecting for tungsten in southern central Sweden. The heavy-mineral concentrate of till is primarily recommended at a regional and local scale. Humus is given the lowest priority among sample types studied because of the low analytical reproducibility for some samples with high values of tungsten.

USE OF IRON-MANGANESE PRECIPITATES IN MINERAL EXPLORATION

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This study is part of a research project aimed at clarifying the origin, geochemistry, and regional distribution of different types of iron-manganese precipitates common in Scandinavia. The mode of occurrence of trace elements in these precipitates is described and the way in which these results can assist geochemical exploration is discussed.

Poorly crystallized mixtures of hydrous iron and manganese oxides, containing various amounts of silica, organic matter, and other colloids, show strong scavenging ability for many elements and content of trace elements varies within wide limits. Mixed with till, stream sediments, etc. they cause misleading geochemical anomalies.

A total of 170 samples of freshly precipitated (mostly ferrihydrite) and aged (mostly goethite and lepidocrocite) hydrous iron oxides and fresh and aged manganese (IV)oxides (mostly birnessite) were collected from various parts of Finland.

Clastic material was separated from the samples through decantation. To study the mode of occurrence of elements in these precipitates they were subjected to sequential selective extraction; with 1M sodium or ammonium acetate solution (NaAc or NH Ac) to dissolve loosely bound elements, e.g., hydroxycomplexes of Fe and adsorbed or labile organically bound elements; with 1M hydroxyl ammonium chloride solution (HXl) to dissolve oxidized forms of Mn and to leave hydrous iron oxides mostly unattacked; with a mixture of 1M HXl and 4M acetic acid (HXl-HAc) to dissolve poorly crystallized Fe oxides, and; with acid oxalate solution in light (Tamm) or with hydrochloric acid to dissolve crystalline iron oxides. The dissolution kinetics was studied using NaAc and HXl-HAc extraction with different time intervals.

In general the results indicate that especially the elements with high valence and those that form colloidal hydroxides (Sn, Nb, Ta, Zr, U, Th, REE, etc.) in the natural waters are co-precipitated with Fe and Mn and are strongly enriched. Therefore, Fe-Mn-precipitates can advantageously be used in exploration for tin and carbonatites.

The content of sulfide-forming elements (Cu, Zn, etc.) is dependent on the composition and state of crystallization of the precipitates and on the chemical processes leading to their formation. For instance, silica competes with organic matter for adsorption on the precipitates. As a consequence, the electrokinetic properties of the precipitate will change and when the electrical charge changes also the contents of bound elements are changed. Precipitates can not easily be used for exploration purposes. However, in areas where contents of Cu, Zn, Ni, Co, etc. are increased these elements bound by hydrous Fe and Mn oxides are predominantly in loosely bound form. Through selective extraction with NaAc, HXl, and HXl-HAc, anomalous concentrations of sulfide-forming elements can be recognized.

In regional geochemical exploration coatings of Fe-Mn precipitates on rocks in streams, stream sediments mixed with these precipitates as well as freshly precipitated hydrous Fe-Mn precipitates commonly found in ditches, bogs, small streams, and ponds may successfully be used as supplementary material. The selective extraction procedure can be considered as especially valuable in detailed studies of hydromorphous anomalies. The method is probably useful for studies of regolithic preglacial sediments found in Lapland and for geochemical exploration by use of lateritic soils common in tropical and temperate climates.

BACILLUS CEREUS, A METAL-INDICATOR MICROORGANISM: POSSIBLE APPLICATIONS IN PROSPECTING

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One aerobic spore-forming organism, *Bacillus cereus*, numerically dominates among the *Bacillus* species (spp.) in metal-stressed soils we have studied. We think this happens in the following way. Metal tolerant, penicillin-producing molds occur in large numbers in metalliferous soils partly because penicillin readily hydrolyzes to a powerful metal-chelating agent, penicillamine, which helps to protect them from toxic metals and gives them a special advantage over non-penicillin-producing molds. Most common soil *Bacillus* spp. are sensitive to heavy metals and are particularly sensitive to penicillin. *Bacillus cereus*, however, is the most metal-tolerant as well as the most penicillin-tolerant of the *Bacillus* group and prevails over other normally faster-growing species in metal-stressed soils. Whether the metals or the penicillin or both are directly selecting for *B. cereus* we cannot say, but the dominance of this organism in metalliferous soils is clear.

The conclusions result in part from a recent study of soils over two undisturbed copper deposits in Lewis and Clark County, Montana. Over both deposits, the percent of soil Bacillus organisms able to form colonies in penicillin-amended agar correlates significantly ($p=.001$) with soil copper and a number of other heavy metals. Yet higher correlations were found between *B. cereus* counts and the various soil metals. Close agreement between *B. cereus* counts and penicillin-resistant *Bacillus* spp. ($r=.99$) leads us to believe that the penicillin-resistant fraction of *Bacillus* organisms in these soils consists largely of *B. cereus*. We also tentatively conclude that the penicillin-resistance trait is a significant factor in the selective advantage of *B. cereus* in these soils.

In a study of 130 stream sediment samples from a 200 square mile (520 km^2) area of the Gunnison National Forest in Colorado, the distribution of *B. cereus* coincide with most of the known mineralized areas. These consist of gold-bearing quartz veins and Leadville-type sulfide replacement deposits in carbonate rock. *B. cereus* counts correlate significantly ($p=.001$) with hydromorphically deposited bismuth and arsenic on stream sediment oxide coatings, which are, respectively, the best local geochemical indicators of gold and silver mineralization.

Bacterial spores are much lighter and smaller than most mineral grains. Their density is about 1.4 g/cm^3, and their diameter about 1 micrometer. Their low density and small size may contribute to their usefulness in reconnaissance programs, because they are likely to travel much farther from their source than heavy mineral grains.

WATER AND STREAM SEDIMENT COMPOSITIONS NEAR ZN-PB-AU DEPOSITS AT MONTAUBAN, QUEBEC

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Drainage waters, sediments, soils, and tailings were sampled near Zn-Pb-Au deposits at Montauban, Quebec to determine their interaction in drainage systems and consequent implications for geochemical prospecting. Ninety-one water samples were analysed for Zn and $-SO_4$. About half of these were also analysed for major dissolved constituents. Conductivities and pH were measured in the field. Thirty-five sediment, tailings, and soil samples were analysed for Zn and Pb and, of them, twenty-two were analysed for major elements plus Rb, Sr, and Zr. Bedrock compositions were known from previous work.

Most of the anomalous concentration of metals in the stream sediments and waters can be attributed to the influence of tailings dumps rather than discharges from anomalous natural groundwaters or surface waters.

Stream sediments, where not influenced by tailings, gave major element compositions which correspond to glacial lake clays and silts in the area and differ from local bedrock (mostly quartzofeldspathic gneisses) and till compositions. These stream sediments are not likely, therefore, to contain detrital components from mineralized overburden or bedrock. This does not preclude the presence of hydromorphic anomalies in the sediments.

Tailings dumps in separate locations in the area have different compositions which resemble those of the host rocks to the ore (calc-silicate and cordierite-antophyllite gneisses). Tailings contribute high concentrations of up to two orders of magnitude of Zn and S to the local drainage in both detrital and solution forms. One dump contributed appreciable S but not much Zn contamination, whereas another provided Zn but not so much S. In a downstream direction from a tailings source, Zn and $-SO_4$ decrease in solution and increase in concentration in sediments. Major and trace element compositions of these sediments indicate a mixture of clay and tailings.

Groundwater flowing from a drill hole which cut mineralization is anomalous in Zn and $-SO_4$. Compositionally it could no be distinguished from tailings-contaminated waters. Although local topographic relief (20 to 50 m) suggested the possibility of significant ground-water contribution to the drainage systems, we did not find any indication of such discharge, and most of the local drainage appears to be due to surface runoff and shallow interflow.

FORMATION OF GEOCHEMICAL FIELDS OF CONCENTRATION IN THERMAL GRADIENT FIELDS OF INTRUSIVE BODIES: AN ANALYSIS

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Successive redistribution of metals in various geological processes and the long-term development of geochemical fields of concentration are (according to L.V. Tauson) the necessary preconditions for the formation of ore deposits. For mineralization of the granite association to occur it is necessary that metal migration takes place in a thermal gradient with accumulation in zones of isothermic and stationary-gradient regimes. These have been modelled using computer simulation of temperature and crystallization-front movements.

Analysis of the conditions under which geochemical fields and ore deposits form should be based on reliable geological data and regularities in the spatial distribution of intrusive activity should be considered. Geochemical maps are essential to such studies. In addition the following aspects should be studied.

1. The dynamics of melt - rock boundary movement and establishment of long-term magma chambers
2. The development of intensive fracturing associated with zones of increased permeability as a result of thermal stresses
3. The establishment of zones of constant temperature which favour ore deposition
4. The estimation of heat flow parameters for particular periods of time and also integrated over particular periods of time
5. The calculation of energy overfall values between model blocks which provide metal concentration in local sites of thermal gradients fields
6. The quantitative comparison of geochemical data on metal removal and concentration with thermodynamic parameters, considering time and dimension factors.

A two-dimensional model of one of numerous intersections between dykes and apatite bodies in limestones, based on the redistribution of REE, Pb, Sr, and other elements, is used as an example. The model area is 26 m x 15 m and the grid unit is 1 m x 1 m. Such a model enables a detailed study of metal behaviour in intrusive - host rock system unmodified by later processess, to be made.

Analysis of crystallization and temperature front movement shows that despite the complicated contact between the dyke and the apatite body the main thermal influence was from the line of intersection along the apatite body. A sharp decrease in REE generally and the total removal of the heavy REE in the zone of reworking and redeposition of ore, and remobilized metal concentration in primary ores was identified in the apatite body.

The zone of metal removal suffered a 740-520°C heating during the crystallization period (t_{cr}); 700 HFU heat flow value at the beginning ($0.1\ t_{cr}$) decreased to 8.8 HFU by the end of the period calculated ($5\ t_{cr}$). Maximum energy overfalls between blocks reached $23\text{x}10^7$J for this period, while energy in the 2.2 m thick removal zone was $9.9\text{x}10^9$J. Metal accumulation in primary ores (concentration coefficients 6.6-22.2 for REE) is related to a constant 530-490°C temperature (isothermic) regime at the boundary of two zones which existed throughout the period of time studied, and in other parts of the area it is relate to zones which suffered 460-480°C during a shorter period. The position of the area corresponds to the back slopes (with intensity 99-48 % of the peak) of heat flow and energy overfall curves which explains the zonation in metal distribution. The energy in the 4.5 m thick concentrations zone reached $15.9\text{x}10^9$J. Calculated diffusion coefficients for REE are $3.4\text{x}10^{-4}$ to $2\text{x}10^{-5}$ cm^2s^{-1}.

Application of such data to the problem of concentration of the metals near granite batholiths allows the dimensions of metal migrations in thermal fields to be calculated.

GEOCHEMICAL INDICATIONS OF DEPOSITS IN DOME-SHAPED STRUCTURES

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Dome-shaped structures characterized by magmatism and mineralization may be considered as ore-magmatic systems. Cluster analysis of geochemical data is used for the classification of deposits of one such system.

R-mode cluster analysis identifies several distinctive zones of mineralization as follows; rare-metal, tourmaline, pyrite, polymetallic, sulfosalt, mercury-antimonite, and barite. Q-mode analysis identifies similarities and inherited features of some types of mineralization which occur in all of the deposits and ore pipes.

All ore bodies localized in volcanics are characterized by a pre-ore zone in which the host rocks are transformed into listvenite-beresite. The mineral assemblage ranges from quartz, carbonate, sericite, chlorite, and serpentine to pyrite. The formation of the zones of hydrothermal alteration is accompanied by the addition of Fe, CO_2, and H_2O and by a slight loss of Na, Ca, and Mg. The rare elements (Pb, Zn, Au, B, As, Cu, Rb, Ba, Sr, V, Cr) are characterized by a low anomaly contrast coefficient[1] (2-10).

Geochemical anomalies associated with tourmalinization reflect quartz-tourmaline segregations in the enclosing listvenite-beresite and include mainly geochemical anomalies for B and Au which have contrast coefficients of up to a few hundred and a few tens respectively. The areas of tourmalinization occur in the core of the dome-shaped structure.

The pyrite zone which contains pyrite and quartz, often with chalcopyrite and arsenopyrite occurs at the eastern edges of the deposits in the central part of the dome-shaped structures. The principal elements are Au, Bi, As, and Cu. For Au the contrast coefficients reach a few thousand, for Bi and Ag a few hundred.

[1)] The contrast coefficient is the average of anomalous values/the average background.