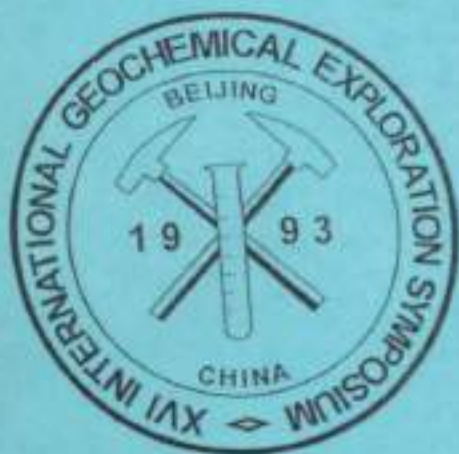


THE 16TH INTERNATIONAL GEOCHEMICAL EXPLORATION SYMPOSIUM  
THE 5TH CHINESE EXPLORATION GEOCHEMICAL SYMPOSIUM

# ABSTRACTS



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# **PART I**

*Abstracts from countries and districts outside China*

*List of authors from countries and districts outside China*

*Author's index*

## PROSPECTING FOR CASSITERITE IN SOUTHER FINLAND

AARIO, R.T., PEURANIEMI, V.J.

The heavy mineral geochemistry of till has been used successfully in the reconnaissance phase of ore exploration in Finland. The late Precambrian Viipuri rapakivi intrusion and its satellites in southern Finland are known as tin-critical areas. Heavy mineral analyses of till were employed as the main method when investigating possible mineralizations in this wide area, and subsequent low-density heavy mineral sampling revealed several tin anomalies, all in cover moraine and located within the central ice lobe just inside the Second Salpausselkä ice-marginal complex, an area heavily eroded during the deglaciation. Ice transport was usually short, not more than 8 km, and the anomalies were coherent.

In order to trace the characteristics of the source rocks of these anomalies, the mineralogical and chemical composition of the cassiterite in the anomalous samples was studied. That in one anomaly contained high Nb, Ta and Fe, suggesting that the source rocks may have been a complex pegmatite. When the source rocks was traced, it proved to be a large but subeconomic pegmatite body. In some other anomalies the cassiterite contained lower Nb, Ta and Fe, suggesting a greisen source. Two of these were later drilled and a greisen mineralization was found in both sites.

Heavy mineral till geochemistry was also used for prospecting W ores in the Proterozoic Hämeenlinna schist area in southern Finland. The area belongs to the Pyhäjärvi ice lobe in an area characterised by more pronounced deposition during the deglaciation. Here, too, ice transport was short and the anomalies coherent. In addition to W, 29 other elements were analyzed. Another unexpected result was the finding of Sn anomalies, some of which were also anomalous for Nb and Ta. This suggests that there may be a complex pegmatite province in the schist area. Some of the Sn anomalies occur inside the area of mafic volcanics, possibly referring to quartz-cassiterite or quartz-tourmaline-cassiterite veins.

Accordingly, one can conclude that the Hämeenlinna schist area, which has been considered one of the most important tungsten provinces in Finland, also has a potential for rare-metal pegmatites and Sn vein formations.



# WEATHERING CRUSTS IN FINNISH LAPLAND AND BANGLADESH-SIGNIFICANCE FOR GEOCHEMICAL EXPLORATION

AARIO, R.T., PEURANIEMI, V.J., ISLAM, MD.R.

The existence of a soft preglacial weathering crust in central Finnish Lapland has been known since the early days of the gold rush in the late 19th century. Systematic Quaternary geological and geochemical surveys have shown that almost the whole area of the former ice divide of central Lapland is underlain by this weathering crust. The main ore prospecting method in Finland has been till geochemistry, samples being taken with various types of percussion drill. Some of the samples from central Finnish Lapland were taken from the weathering crust and some from the till and this has created problems in interpreting the results.

In order to decipher the nature of the weathering and the dispersion of elements, a comparative survey was carried out in Finnish Lapland and Bangladesh. Finnish Lapland is situated in the temperate climate zone north of the Arctic Circle, so that the weathering crust there can be regarded as fossilized, while Bangladesh is situated in the subtropical and tropical climate zones and the weathering crust is recent.

TABLE 1. Chemical composition (wt %) of the representative samples from Finnish Lapland and Bangladesh. Compared to the typical sandstone analyses (7-8).

	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	61.43	68.64	37.91	58.85	45.50	70.91	95.40	86.10	87.36	80.56	83.88
Al <sub>2</sub> O <sub>3</sub>	19.86	15.42	21.87	15.97	20.10	12.23	1.10	5.45	6.40	8.55	7.64
MgO	2.93	2.15	6.29	3.63	3.10	0.17	0.10	0.61	0.15	0.22	0.18
CaO	0.37	1.56	1.85	2.00	1.12	1.04	1.60	0.98	0.14	0.03	0.15
Na <sub>2</sub> O	0.99	3.34	0.56	0.94	0.17	2.76	0.10	0.55	0.34	0.15	0.44
K <sub>2</sub> O	4.68	2.43	0.61	0.40	0.61	3.04	0.20	0.96	1.56	1.12	1.78
Fe <sub>2</sub> O <sub>3</sub>	7.03	4.03	21.61	11.35	18.03	6.29	0.60	2.61	2.28	4.43	2.78
TiO <sub>2</sub>	0.78	0.58	0.60	1.37	2.16	0.38	0.20	0.74	0.25	0.76	0.27
MnO	0.04	0.04	0.29	0.14	0.21	0.19	-	0.06	0.02	0.04	0.03
P <sub>2</sub> O <sub>5</sub>	0.03	0.08	0.07	0.12	0.14	0.08	-	0.14	0.04	0.07	0.04
LOI	1.28	1.54	3.85	4.39	7.24	1.90	0.30	1.37	1.45	3.12	1.83
Total	99.42	99.81	95.51	99.16	98.38	98.99	99.60	99.57	99.99	99.05	99.02
Cr ppm	127	n.d.	312	164	162	14	n.d.	n.d.	95	425	389
Co "	n.d.	n.d.	124	76	90	78	n.d.	n.d.	168	10	5
Ni "	71	n.d.	129	88	207	15	n.d.	n.d.	22	22	28
Cu "	n.d.	n.d.	149	81	84	30	n.d.	n.d.	9	15	12
Zn "	n.d.	n.d.	278	141	272	138	n.d.	n.d.	22	20	20
Pb "	n.d.	n.d.	43	34	30	22	n.d.	n.d.	16	9	24
Au ppb	n.d.	n.d.	3	6	n.d.	1	n.d.	n.d.	n.d.	n.d.	5

Fresh bedrock 1. Sillimanite-garnet granulite rock, Kuttura area (Hörmann et al. 1980).

2. Biotite gneiss, Inari area (Meriläinen, 1976).

7. Orthoquartzite (Pettijohn, 1963).

8. Sublithic arenite (Pettijohn, 1975).

Weathering crust: 3. Lauttaoja, 4. Ponukuru, 5. Tankavaara Gold Museum, 6. Vuotso air field.

(Crushed samples) (4-5 granulite, 6. granite gneiss, from Finnish Lapland).

9. Mainamoti-Garurhat, Comilla.

10. Gaurisankar, Jaintapur, Sylhet.

11. Shaloshahar, Chitagong (9-11 sandstones from Bangladesh).

n.d. = not determined

The bedrock in Finnish Lapland is composed of metamorphosed rock types of Precambrian age and that of Bangladesh of sedimentary rocks of Tertiary and Quaternary age. Table 1 shows the results of chemical analyses of some representative samples from both areas. As one can see, Si has been depleted and Al, Fe and trace elements enriched in the weathering process. Table 2 shows the behaviour of some

trace elements in the weathering of phyllite at one survey site in western Finnish

TABLE 2. Trace element values in unweathered bedrock and weathering crust in trench I at Mantovuoma.

	1		2		3	
	Unweathered bedrock	Weathering crust	Unweathered bedrock	Weathering crust	Unweathered bedrock	Weathering crust
Cu ppm	340	1022	77	3010	80	1231
Zn ppm	13	88	15	59	29	93
Ni ppm	34	55	26	73	44	125
Co ppm	8	39	12	57	20	79
Mo ppm	2	14	2	75	2	1

Lapland. Copper has been enriched most markedly, the enrichment coefficient being 40 in places, and Mo also shows pronounced enrichment in some samples.

The main clay minerals found in the samples from Finnish Lapland are kaolinite, halloysite and vermiculite, whereas kaolinite, chlorite and gibbsite are the main clay minerals in the samples from Bangladesh.

When making comparisons between Finnish Lapland and Bangladesh one must remember that also the surficial parts of the weathering crust also exist in Bangladesh, whereas in Finnish Lapland the continental glaciation in the Quaternary swept away the soft surficial parts and only the roots have survived under the glacial cover.

Quantitative Statistical Interpretation of Regional  
Geochemical Exploration Data for Gold in the  
Ife-Ilesa Schist Belt of S. W. Nigeria

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(Extended Abstract)

Alluvial and primary gold deposits occur in the Ife-Ilesa Proterozoic Schist Belt with the former showing a strong spatial relation with the amphibolite complex.

Gold production from this area contributed significantly to the national output since mining started in 1942 with peaked production between 1943 and 1946. The Ife-Ilesa gold field has remained the only gold field where active mining activities continued though intermitently until present and with a steady declining production.

Regional geochemical exploration for gold dates back to 1965. Since then, both active stream sediment and soil surveys have been carried out. However, qualitative interpretations of the resulting geochemical data were inconclusive in delineating potential areas of gold mineralization.

Recently, quantitative statistical interpretational techniques (viz population sorting, multivariate statistics, factor analysis, data smoothing and trend surface analysis) were employed in the interpretation of multielement regional soil (450) and active stream sediment (350) geochemical data. The main objective is to evaluate the effectiveness of these techniques in delineating potential areas of gold mineralisation.

The results of cumulative probability plots reveal that it is a more objective and effective method of recognizing geochemical population and anomalies. Also, K-mode factor analysis identified four factors with similar and comparable metal association in the stream sediments and soils. These are Mn-Co-Fe, Zn-Pb-Cu, Mg-k and Cr in the stream sediments; Co-Mn-Cu, Ni-Cu and Zn-Pb in the soils. These metal associations and their factor scores distribution together show that lithology is the dominant factor controlling metal dispersion in this tropical surficial environment with subtle but notable contributions from both environmental and mineralization factors.

The smoothing mapping method produce "Smoother" and "Cleaner" geochemical maps compared to the manually drawn maps of the raw data.

Trend surface studies show that low order surface fittings prove to be a more effective tool in revealing the main regional trends in the soil data than the stream sediment data. In the later, only the first to fourth order Co, first and second order Fe and first order Mn trend surfaces are significantly different from random at 0.05 level. However, all the computed trends for soil except first to fourth order Zn; third order Cr, Pb, Cd and first to third order Ag are significantly different at 0.05 level. The resulting positive residuals from these surfaces representing "non-random" geochemical variations in the data, reveal significant anomalous trace element geochemical patterns which show strong spatial relationship with potential areas of gold mineralization and geology. The overall results demonstrate the effectiveness of these interpretational techniques as potential and essential tools particularly in areas such as this where anomaly/background contrasts are generally low.



## Chromium contamination of aquifers from natural sources

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Leon, a city in the state of Guanajuato, central Mexico, is one of the important urban centers of the country. Its economy depends mainly on the tanning and shoe-making industries. Most of the tanneries (about 85%) use chromium in their processes and dispose of their waste waters without treatment directly into the Leon river through the sewage system. This practice was thought to be the source of chromium in Leon aquifer.

In 1987 a research project was undertaken to evaluate the levels of chromium, the contaminant distribution in groundwater and the pollution sources in the Leon-Guanajuato valley.

Sampling was performed in 90 wells distributed throughout the valley. The water was analyzed for physico-chemical parameters, Cr(VI) and Cr<sub>total</sub>. The analysis of the data, together with the hydrogeological and geological framework, clarified the chromium contamination problem.

Chromium was detected above the detectable level (0.004 mg/l) in most of the sampled wells (around 90%). Nevertheless, the concentrations were below the potable water limit (0.05mg/l) except in one small area located to the southwest of the valley, where concentrations as great as 50 mg/l were determined.

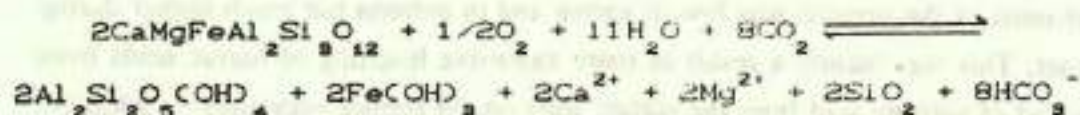
The wells to the east and south of the valley showed chromium concentrations with a maximum value of 0.04mg/l. The presence of chromium in this area may be associated with two sources: one anthropogenic and one natural.

In this region there are many small brick factories which use leather residues as a combustible. The combustion of leather may oxidate the Cr(III) used for tanning to Cr(VI). The residual ashes considered as fertilizer, are dispersed over the surrounding lands. Finally the action of rain and irrigation makes chromium

leaching possible and consequently provokes aquifer contamination.

To the east of the valley there is an outcrop of ultramafic rocks, pyroxenites, with a high chromium content (1525 ppm). A chemical characteristic of these types of rocks is their high concentration of magnesium (26.4% for samples of Leon pyroxenites). The alteration of these rocks has produced their serpentinization. Soils derived from serpentines are the highest in chromium, with an average concentration of 2000-3500ppm.

In view of the fact that pyroxenites give chromium and magnesium as weathering products, a correlation between these species in the groundwaters of the area near the outcrop was expected. The correlation index between these elements and also between saturation indices of minerals containing magnesium (dolomite and magnesite), as indicators of high magnesium levels and chromium concentration was determined for the wells located to the east of the valley near the outcrop and also for a number of wells located far from it. A correlation index of 0.93 was obtained between chromium and dolomite and of 0.82 between chromium and magnesite for wells located near the outcrop having high magnesium levels (>30mg/l) and of 0.19 for chromium and dolomite and -0.14 for chromium and magnesite for all the other wells. Those correlations may be considered an indication of the origin of chromium in this area, since the weathering of pyroxenites produces magnesium, calcium and bicarbonate as products through the following reaction:



These results allow us to infer that the presence of chromium in this area is associated with the ultramafic rocks. We also take into account the fact that during weathering chromium tends to oxidize easily. This together with the fact that there are no anthropogenic sources nearby, and the groundwater in this zone flows down from the mountains, where the pyroxenites are located, to the valley leads us to this conclusion.

The higher chromium values obtained from the wells located to the southwest of the valley about 13.5km from Leon are associated with the operation of a chromate factory.

## THE IMPACT OF OVERBURDEN TYPES AND OF SOIL GEOCHEMISTRY ON THE SURFACE WATER QUALITY IN WESTERN FINLAND

ÅSTRÖM, M., BJÖRKLUND, A.

In the coastal regions of western Finland extensive and deep ditching of till, peat and sulfide sediments has increased the soil depth of many areas. This has resulted in enlarged leaching of metals and of hydrogen ions which has deteriorated the water quality of many streams. The chemical components are most effectively leached out during the autumn rains and after the snow melt period in spring and, therefore, the water of many streams has a low pH (<4.5) and a high electrical conductivity (>300 mS/m) on these occasions. The affect of acid rains on the stream water quality is probably of minor importance in this part of Finland.

Ten streams with catchments ranging from 12 km<sup>2</sup> to 100 km<sup>2</sup> were studied. At three occasions; during the autumn rains, after the snow had melted in spring and during the dry period in the summer, pH and electrical conductivity were measured at several sites in each of the streams and in many of the feeder streams. In the autumn, in addition to the measurements, water samples were collected in the streams and in the feeder streams and later analyzed for 28 metals by ICP-MS at the chemical laboratory of the Geological Survey of Finland. The two largest streams were studied in more detail. In addition to the above mentioned measurements and analyses, the waters of these were analysed for total organic C contents. In the catchments of the two streams, till samples and clay/silt sediments were also collected and later analysed for the contents of 30 elements. The main purpose of the investigation was to study the impact of overburden and of soil geochemistry on the stream water quality.

The pH of most of the streams was low in spring and in autumn but much higher during the dry summer. This was mainly a result of more extensive leaching of humic acids from the peatlands and of sulfuric acid from the sulfate soils on the former occasions. In addition, in autumn and in spring the waters were cold (5-10°C) which inhibited buffering by organic activity.

The total organic C content (TOC) of the waters was very high in the upper parts of the two streams studied, >30 mg/l and >50 mg/l, respectively. Downstreams the TOC contents decreased and at the outlet there was <10 mg/l and <20 mg/l of total organic C, respectively, in the two streams. In the upper parts of the catchments large areas are covered with peat. From these areas high amounts of humic- and fulvic acids are leached which resulted in the observed dark colour and the high organic C content of the waters. In the lower parts of the catchments acid sulfate soils, which have developed on sulfide-bearing sediments, becomes more important. From these soils acidic waters with high contents of cations are discharged

which results in a decrease of pH and in a rise of the conductivity of the stream waters but also in flocculation of the humic material. The decrease in TOC contents downstream was mainly a result of this flocculation.

The metal contents were very high in most of the streams studied. For example in Riddardiket, which is mainly draining acid sulfate soils, the contents of Al, Cd and Zn were 95 mg/l, 5.4 µg/l and 1950 µg/l, respectively.

The high contents in the stream waters of several of the elements studied (Zn, Al, Ni, Co, Cd, Mn, Ca and Mg) seemed mainly to be a result of extensive leaching from the acid sulfate soils while other elements (Fe, Pb and As) were leached in approximately equal amounts from the acid soils and from the soils developed on till. Only one element, V, was enriched in the waters from till and peat compared to the streams in acid sulfate soils. There are also indications that the element contents of the stream waters are not only related to the overburden types in the catchments but also to the geochemistry of the overburden and of the soils.

GEOCHEMICAL AND MINERALOGICAL STUDIES ON SOME WEATHERED  
GRANITIC ROCKS, UMM TAGHIR AREA, EASTERN DESERT, EGYPT

BY

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ABSTRACT: During weathering there are many mineralogical and chemical changes which lead finally to complete change even in the chemical percentages of different elements. The mineralogical end - product suggests humid climatic conditions as in Egypt. The main weathering products of the granitic rocks are kaolinite, illite, chlorite and gibbsite. Through weathering processes, elements as Na and K are leached, others as Ca and Mg are concentrated. From this study, we can differentiate between two distinct and different processes; exit of elements from the structure of the mineral which acts the destruction and weathering of that mineral; and the concentration and leaching of an element which depends on its geochemical behaviour and have no relation with the weathering of minerals included.

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## Mineral Exploration Procedures and Geochemical Exploration in Australia

**M. Aubrey and J.J. Xie**

*In general, an exploration project involves following stages*

- 1) Literature search
- 2) Exploration Licence (EL) application
- 3) Reconnaissance field work
- 4) Follow-up, and
- 5) Evaluation of exploration data

Of course, a particular project may not include all the above stages and can be terminated at any time. Geochemical exploration methods are used at every stage of an exploration project. During reconnaissance stage, stream sediment sampling, satellite imagery interpretation, airborne geophysics are the most popular tools for quick covering of a large area. While on a prospect scale, soil, rock chip and ground geophysics are often used. Based on the results of surface work, it will be decided if a drilling programme will be carried out.

Statistics on the exploration projects carried out in Australia will reveal the trends of Australian exploration since 1950's. This will cover following aspects of mineral exploration.

- 1) Geochemical methods used
- 2) Targeted mineral deposit types
- 3) Deposit ages
- 4) Geographical distribution over Australia
- 5) Hosting lithologies, and
- 6) Structure controls.

ECOLOGICAL-GEOCHEMICAL MAPPING IN THE LANDSCAPES OF THE SOUTH  
SIBERIA (IRKUTSK-SHELEKHOV REGION)

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Geochemical mapping is one of the most reliable approaches, aimed at pollution assessment and monitoring of the environment. The survey from dispersion flows is particularly significant under study of large areas, though some methodological aspects of this approach should be developed.

Geochemical survey has been accomplished from dispersion flows in Irkutsk and its surroundings with the aim to select the express ecological-geochemical mapping approach (3.500 sq. km, 1 sampling point per 16 km<sup>2</sup>). The bottom (0.25, 0.25-1, 1-3 mm fractions), overbank (0.25, 0.25-1mm) sediments, surface waters and plants (birch, willow, moss) were sampled.

The most part of the region is composed of the Jurassic terrigenous sequences from the southern margin of the Siberian Platform. The small part of the mapped area is occupied by the Precambrian magmatic and metamorphic complexes. The predominant relief is the moderately dissected hilly plain of denudation.

The considered experiment can be divided into 3 stages: 1) sampling, express semiquantitative (partly quantitative) OES analysis (Ag, Pb, Zn, Cu, As, Ni, Cr, Co, V, Ti, Mo, Li, Ga, Ge, Sn, Mn, P, B, F, V, Hg) of the samples, combined by compiling the set of geochemical maps; 2) analysis of the samples by the quantitative methods and compilation of different geochemical maps; 3) sampling of soil profiles (50 km) and sections of the overflowed sediments (15 sites).

The "Multi-dimensional field" computer programme was used for data processing. It provides the statistical parameters, the singleelement maps, determination of geochemical classes (associations of elements) and geochemical(multielement) classes maps. The pattern of the latter significantly depends on the chosen background.

By the content of the majority of trace elements the average compositions of waters and alluvial sediments correlate with those for other regions of the world. The overbank sediments, particularly their fine fraction) are enriched in the majority of trace elements, though the compositions of different fractions of the same alluvial facies are similar. The anomalies in the fine fraction of the overbank sediments are mainly vast and contrast. They well coincide with the hydrogeochemical and biogeochemical anomalies. The pollution anomalies correlate with industrial and economic activity: industrial-settled zone of Irkutsk (Ag, Cu, Zn, Pb, Hg, Ni, Cr); zone around Shelekhov with aluminium plant (F, V, Cu, Mo, Pb, Cr, Ni); agricultural zone (Ni, Co, Ti, V, P, F, U, Mn, Hg).

The different horizons (A<sub>0</sub>, A<sub>1</sub>, B) leaves and branches of birches and moss are sampled at the base stations. In case, the correlation between geochemical anomalies of the horizon (A<sub>0</sub>-A<sub>1</sub>) and B one, possessing lower contents of the associated elements (Be, Hg, Pb, Cd, F etc.), is not available, the anomalous concentrations in the soils result from the man-made affects. It is confirmed by the correlation of such anomalies with certain pollution sources.

The intensive accumulation ( up to 2-3 times) of heavy metals ( Hg, Cd, Pb, Ag, Au) are observed in the upper part (0-10 to 20-30 cm) of the overflow sediments within the zone of man-made anomalies. The significantly increased concentrations (up to 2-3 times) are evident deeper than 70 cm, which is, possibly, due to secondary contamination of the terrace sediments by the ground waters.

The analysis of the obtained data indicate that the geochemical mapping from fine dispersion flows, based on cheap and express semi-quantitative analysis, which is preferable than the mapping from the overbank sediments, can be widely applied for express geochemical assessment of pollution by metals, planning of territory use and more detailed ecological works.

The assessment of anthropogenic influence intensity may be given using (1) change of natural chemical element associations; (2) comparative study of different geochemical media, facies and fractions; (3) comparative analysis of geochemical maps with the maps of zoning and industrial use; (4) traditional approach i.e. application of geochemical indicators of change and state of the environment.



## POSSIBLE EFFECTS OF IRON COATING IN THE RECOVERY OF GOLD IN A DRAINAGE SURVEY

K. BHEEMALINGESWARA

13 stream sediment samples about 5 kg each, of minus 20 mesh size were collected, as part of a drainage survey, from an area of known Precambrian multi-metal deposit (Cu, Au, W etc.) located in Central India. The aim of the survey was to standardise the geochemical exploration methodology for gold.

The samples were dried and sieved to obtain -30+50, -50+80, -80+120, -120+200 and -200 mesh size fractions. Since the quantity of the finer fractions (from -50 mesh onwards) was not sufficient to make required number of aliquots, only the -30+50 mesh size fraction was considered in the present study. One half of the fraction was processed for heavy mineral concentrate using bromoform and run in Isodynamic separator (I.S) at different ampere ranges of 0.4, 0.8 & 1.2. Other half was directly run in I.S at similar settings. All the magnetic (collected at 0.4, 0.8 & 1.2A) and non-magnetic (at 1.2A) fractions of both mineral concentrate and bulk sample were analysed for Au using AAS. Contrary to expectation much higher values ranging from 0.3 to 1 ppm were recorded in magnetic and negligible values, from 0.1 to 0.3ppm, in non-magnetic fractions in both the cases. To confirm the data, all the fractions were scanned under stereo-zoom microscope. The mineral identification in the case of magnetic fraction was difficult due to the presence of heavy iron coating. The non-magnetic fraction, on the other hand, was weakly coated and contained mainly quartz, mica, feldspar etc.

All the magnetic fractions of heavy concentrate & bulk sample were combined (to avoid repetition), treated with 10-20% HCl to remove the coating and were re-run in the I.S at similar ampere ranges. More than 50% of the material was found to be non-magnetic at 1.2A. The grains were clear and were again scanned under stereo-zoom microscope. Expectedly, two gold nuggets each (largest being 700  $\mu$ m) were found in the non-magnetic fractions from both the bulk sample and heavy mineral concentrate. Chemical analysis of these fractions confirmed the above observation. Gold values upto 1.5 ppm were recorded in the non-magnetic and <0.1ppm in the magnetic fractions.

The higher gold concentrations recorded in the magnetic fractions were thus due to the presence of heavy iron coating. The secondary iron coating has influenced part of the non-magnetic material including gold nuggets (while running in I.S) to move towards the magnetic fraction, thereby diluting gold values, expected to be higher in non-magnetic fractions. The results obtained in the study prove that there is a need for modification in the sample processing procedure for the panned concentrates when the non-magnetic fraction is used for chemical analysis.

A scheme is suggested for sample preparation in situations where presence of iron coating is conspicuous. This method not only enhances Au concentration in the fraction to be analysed but also helps in the maximum recovery of gold present in the sample.

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# DISPERSION OF GOLD AND ASSOCIATED ELEMENTS IN THE LATERITIC REGOLITH, MT. PERCY, KALGOORLIE, WESTERN AUSTRALIA

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## ABSTRACT

The dispersion of gold and over 40 other elements in the lateritic regolith has been studied at the Mt. Percy gold mine, near Kalgoorlie, Western Australia. Primary Au mineralization in the Mystery Zone at Mt. Percy occurs in fuchsite-carbonate alteration zones at the contact with porphyries intruding chloritic talc carbonate ultramafic rocks. The mineralized sequence has been deeply weathered and is concealed beneath an almost complete lateritic regolith over 60 m thick. The regolith consists of saprolite (50 m), which is clay-rich in the top 10 m, plasmic and mottled clays, and surficial horizons of lateritic gravels, lateritic duricrusts and pisolitic soils. The surficial horizons contain pedogenic carbonates and alunite is present in the upper saprolite. Samples from two sections across the Mystery Zone were collected at 1 or 2 m intervals at each 2.5 m level throughout the regolith as mining progressed. Samples of fresh rocks were obtained from diamond drill core. A selection of these samples, including a complete section through the primary mineralization, was analysed to illustrate element distributions in the fresh and weathered rocks. The elements associated with primary Au mineralization appear to be S, Ag, W, As, Sb, Te and, possibly, Ba, K and Pb, but except for Ag and Te, none has a very direct correlation with Au.

The Au distribution in the regolith is typical for the region, with minor enrichment and wide lateral dispersion in surficial gravels and duricrust (in part associated with pedogenic carbonates), leaching and depletion in the underlying clay-rich horizons, and some secondary concentration and minor dispersion in the saprolite. Examination of panned concentrates indicates that Au occurs as electrum and Au tellurides in the primary mineralization, whereas in the regolith most of the Au appears to be secondary, consisting of grains and crystals of pure Au with very low Ag contents (<0.5% Ag). Tellurium and Ag contents in primary mineralization are both in the range 0.25-19 ppm, with the ratio Ag/Te=1; these abundances are maintained in the lower saprolite, below about 40 m, but both elements are strongly leached above this depth. The occurrence of substantial secondary remobilization is marked by the presence of complex mixed grains of Au, Ag and/or Te, both elemental and as chlorides and bromides. Primary and saprolitic Au mineralization is indicated by a broad superjacent Au anomaly (100-5000 ppb) in the soils and lateritic horizons, and by high concentrations of W (5-60 ppm), Sb (7-25 ppm) and As (10-400 ppm). High K contents, corresponding to resistant muscovite, give surface expression to the alteration zone. Although Au contents are <100 ppb in the underlying clay-rich horizons, Sb, W and, to a lesser extent, As remain anomalous; high Ba, and K contents indicate the porphyries and alteration zones, respectively.

The porphyries and ultramafic rocks can be discriminated throughout much of the regolith by relative abundances and ratios of Ti, Zr, Ba and K. However, the lateritic horizons over the ultramafic rocks have abnormal geochemical signatures. They have low Cr contents (<1000 ppm), because primary Cr is present in weatherable chlorite rather than resistant chromite, but are enriched in "immobile" elements derived from the porphyries. The distribution patterns of the elements are the result of the regolith developing and evolving under changing conditions. The lateritic regolith formed during an early warm humid period of strong leaching, and has been modified in more recent arid phases, during which the water-table declined, groundwaters have become saline and minerals such as calcite and alunite have precipitated in upper horizons of the profile. Physical erosion has resulted in minor topographic inversion.

## Acknowledgements

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## GEOCHEMISTRY AND GEOSTATISTICS USED AS AN EXPLORATION TOOL FOR VOLCANOGENIC MASSIVE SULPHIDES DEPOSITS: THE CASE OF THE MILLENBACH DEPOSIT, ROUYN-NORANDA, QUEBEC, CANADA

CARIGNAN, J.

The study of the global geochemical environment and more precisely of the systematic spatial variations in and around alteration pipes with geostatistical techniques has led to the development of a geochemical exploration technique useful in the search for volcanogenic ore deposits. The area studied is the immediate and proximal environment of the Millenbach mine near Noranda, Quebec. The ore deposit is part of the Abitibi volcanic belt and more precisely of the Dufault calc-alkaline unit. It is a classical example of a volcanogenic Cu-Zn massive sulphides deposit.

The results obtained are based on 368 samples analyzed for major elements and 24 minor elements. Variograms were used to determine the best sampling interval for drill holes of the studied environment, that is 25 meters. Migration of elements can be noted further than visible alteration, like dalmatianite, following the available plumbing such as porosity or degree of brecciation of the host rock.

The data treatment is done on a molecular base and nearly all elements are mobile. Correspondence analysis and classical profiles show close to deposit an increase of Fe, Mg, K, H<sub>2</sub>O and a decrease of Si, Ca, Na for major elements, an enrichment of Cu, Zn, Ag, Cd, Pb, Au, As and a depletion of Mn, Li, Ba for minor elements.

The best anomalies are at the "Amulet rhyolite"-QFP contact even though the deposit is at the higher QFP-andesite contact. These anomalies are shown by the use of an alteration index ( $QAl_2O_3 + QFeO + QMgO + QH_2O - QNa_2O - QSiO_2/Q_{total}$ ) and a mineralization index ( $\ln Cu + \ln Zn + \ln Cd + \ln Ag - \ln Mn - \ln Li - \ln Ba$ ). These indices are based on a correlation study and are normalized for each type of rock. Variations extend mostly between 100 and 275 m from the mineralized pipe but some traces were found up to 500 m.

All these conclusions are compatible with the fumarolic origin of volcanogenic massive sulphides deposits in agreement with the results obtained from the microthermometric study of fluid inclusions. The minimum temperature of the mineralizing fluid is around 150 °C and the salinity is from 15 to 20 % eq. NaCl.

All these observations have led us to establish a logical scheme for an exploration program.

## GEOCHEMICAL MODIFICATIONS OF AN AQUIFER RELATED TO WATER PUMPING: THE NIOBEC MINE, QUEBEC, CANADA

CARIGNAN, J., MARTIN, A.

The Niobec mine (a niobium deposit in carbonatite) is a good example of a brine in a carbonated environment. The interactions at the surface of the cone of depression between the surficial recharge and the upflow of deep brines induced by pumping can be quantified by a geochemical characterization of the aquifer with a proper modeling of the rock-water interactions.

The salinity (TDS = 2 g/l to 80 g/l) implies some corrections to estimate the carbonates saturation. The activity coefficients must be estimated; the salinity correction must be applied to the pH and the two acidity constants of CO<sub>2</sub>; all the chemical equilibrium constants must be corrected for all temperature differences and finally the ionic complexes contents can be calculated. It is seen that ionic complexes can increase the solubility of carbonates by a factor of 1 to 20.

Surficial recharge waters in the cone of depression are under-saturated in calcite and dolomite. In the deep aquifer (300 meters or more), calcite is saturated, even over-saturated because of the pressure effect. The pressure has been calculated and the value coincide with the one measured by injection in drill-holes. Dolomite has the same behaviour. Gypsum is greatly over-saturated everywhere.

A first population of samples is characterized by a weak ionic strength (less than 0,15) and is composed of surficial infiltrations circulating in a karstic network. A second population represents the upper part of the aquifer under the recent influence of recharge waters and is characterized by ionic strengths between 0,2 and 0,4 but also by abundant sulfate complex (200-800 ppm). The third population corresponds to the deep aquifer sensu stricto. Sulfate complex abundance is a lot lower (less than 100 ppm). The ionic strength is higher than 0,5 and increases rapidly with depth. Strontium is abundant (300-1000 ppm). It originates from calcite whose solubility greatly increases with pressure.

The sulfate complex is the result of sulphides oxydation in the desaturated zone of the carbonatite. In terms of Eh-pH, the stable species of sulfur in the zone is effectively the sulfate complex. It is transported by surficial infiltrations, accumulated at the surface of the cone of depression and precipitated with strontium in celestite. The sulfate complex is a good marker of the interface between the desaturated and the saturated systems. Ferrous iron in the sulfurous species is also oxydated in ferric iron and it colours the fractures surfaces in which there is phreatic circulations. The acidity induced by the ferric hydroxydes precipitation is neutralized by the carbonates, pH being between 7 and 8.

The salinity gradient with depth can be related to the dilution of a very deep original brine saturated in halite. The dilution waters are meteoritic and the dilution rate decreases with depth. This dilution is at a regional scale and

acted for millions of years. The original salinity migrated upward by diffusion on hectometric, even kilometric distances.

Nevertheless, the salinity gradient, far more important at Niobec than in any other drill sampled locations in the Precambrian shield, suggests important ascent of deep brines due to 25 years of water pumping at the mine. The dilution water is the surficial recharge infiltrated in the cone of depression. The dilution rate, estimated by the salinity of surface water, is about one to one.

The influence of surface waters on the geochemistry of deep brines, induced by pumping, is confirmed by seasonal variations of the aquifer temperature at a depth of 300 meters.

DISCOVERY OF RADON POTENTIAL IN THE RINCON SHALE, CALIFORNIA -  
A CASE HISTORY OF DELIBERATE EXPLORATION

DONALD CARLISLE AND HAYDAR AZZOUZ

Elevated indoor levels of radon gas (Rn 222) are associated with excess lung cancer in humans. Risk estimates are currently derived from probability samples of houses over large regions and do not detect radon-prone subareas.

Geological exploration incorporating aeroradiometric data, soil-gas radon and soil-gas permeability has identified an unsuspected belt of abnormal indoor radon in southern California. Roughly 74% of houses on the Rincon Shale and soils derived from the Rincon exceed the US EPA guideline of 4 pCi/l (148 Bq/m<sup>3</sup>) and 26% exceed 20 pCi/l (740 Bq/m<sup>3</sup>) in standardized "closed-house" screening tests. Fifty three percent exceed 4 pCi/l in longer-term measurements under normal ventilation conditions.

Strong correlations between aeroradiometric data, soil-gas radon (adjusted for soil permeability), geology, and indoor radon reflect the unaltered character of sedimentary host rocks and a consequent tendency for anomalous uranium to occur throughout given rock units rather than in epigenetic mineralized zones. Under these circumstances, deliberate geological exploration may be a more efficient approach to indoor radon risk identification than simple random sampling or non-random testing of houses. By the same token geological parameters can facilitate radon risk assessment on undeveloped lands. Attention is drawn to multiple populations within radon test samples and the consequent problems in estimating regional parameters.

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## ULTRA-TRACE RARE EARTH ELEMENT ANALYSIS OF GEOCHEMICAL REFERENCE SAMPLES USING A RECYCLING NEBULIZATION SYSTEM WITH A DISPOSABLE SPRAY CHAMBER BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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In recent years, the precise and accurate determination of rare earth elements (REEs) in a range of rock types has become increasingly important. Interpretation of the REE geochemistry of igneous and metamorphic rocks and minerals is a prerequisite for the development of many petrogenetic models. Inductively coupled plasma-mass spectrometry (ICP-MS) is a multi-element analytical method having detection limits across the whole mass range which are superior to most conventional techniques, particularly for heavy elements. However, there are samples in which the REE concentrations are below the detection limits (0.01-0.1 ppm) of whole rock procedures (1) in which samples are prepared at 0.5 g rock per kg solution (0.1 g per 200 g solution). A procedure, such as ion exchange, which increases the concentration of the REE's while maintaining the total dissolved solids at less than 0.1% is required.

In this study, 15 ultra-trace rare earth elements have been determined in 5 international geochemical reference samples at ultra-trace levels, PCC-1 (USGS), AL-1 (GIT-IWG), FK-N (ANRT), NBS70a and NBS99a, using a recycling nebulization system with a disposable spray chamber by inductively coupled plasma-mass spectrometry (2), after preconcentrating the REEs from a 100 mg sample using cation exchange. Samples were dissolved, and a REE separate was obtained using 10 ml of cation exchange resin in a quartz column. Major elements were eluted using a 1.13 M HNO<sub>3</sub>-0.63 M HCl solution. The REE were collected using 8 M HNO<sub>3</sub>. The solution containing the REE's was evaporated to dryness, the residue dissolved in HNO<sub>3</sub>, and diluted to a final weight of 2 g using 0.2 M HNO<sub>3</sub>. Solid limits of detection are 0.01-1 ppb. Precision, accuracy and sample heterogeneity are addressed.

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## DETERMINATION OF PRECIOUS METALS IN SULPHIDE AND MAGNETITE MINERALS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY AFTER PRECONCENTRATION USING CATION EXCHANGE

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The determination of the natural concentrations of precious metals must take into consideration their occurrence in rare, discrete, and inhomogeneously distributed minerals. The analysis of rocks and ores for these elements is often performed on large (10-60 g) samples using fire-assay collection to obtain representative bulk concentrations. To examine the distribution of these elements within and between minerals requires analytical techniques using a more specific microsampling technique.

Serious interferences of base metal-argon polyatomic ions and matrix effects that hampered the accurate determination of precious metals by inductively coupled plasma-mass spectrometry (ICP-MS), require quantitative separations of precious metals from base metals. Solvent extraction (1) or Te precipitation (2) have been used for the separation of precious metals from the matrix elements in samples. These methods are not applicable for the milligram weights of samples due to the high reagent blanks.

A method for the separation of seven precious metals (Ru, Rh, Pd, Re, Ir, Pt, and Au) from large amounts associated base metals in dilute hydrochloric acid solutions using a strongly acidic cation exchange resin, Amberlite CG-120 is described. The method has successively been applied to the determination of precious metals in small quantities (2-20 mg) of high purity sulphide and magnetite minerals by high sensitivity of inductively coupled plasma-mass spectrometry using an automated 2 speed peristaltic pump speed controller for controlling sample solution uptake rate for analysis of small sample volumes (3). Solid limits of detection for a 20 mg of sample are less than 4 ppb for Ru, Rh, Re, Ir, Pt, and Au, and 29 ppb for Pd. Analysis of nickel sulphide fire assay beads of the reference material, SARM-7, shows good agreement with certified values with relative standard deviations of less than 8%. Poor accuracy for Au are due to sample heterogeneity of small samples of the nickel sulphide bead used for analysis.

Data from the analysis of sulphide and magnetite minerals from Sudbury copper-nickel sulphide ores demonstrate the ability of the method to make useful determinations of precious metals for the study of ore genesis.

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## **A GEOCHEMISTRY DATABASE FOR THE HAURAKI GOLDFIELD, NORTH ISLAND, NEW ZEALAND**

CHRISTIE, A.B.

Stream sediment geochemical analyses from exploration surveys of the Hauraki Goldfield, North Island, New Zealand, carried out by private mining companies, have been collated and assembled in a relational database termed REGCHEM. The database operates on an IBM-compatible PC microcomputer using an application programmed in dBASE IV. Data for more than 6000 stream sediment samples have been entered to date, giving a total of about 30,000 separate elemental analyses.

A study was made of analyses from a set of 1400 samples collected by AMOCO Minerals (NZ) Ltd during their exploration of a 200 km<sup>2</sup> area in the north-east part of the region (Whangapoua-Mahakiraua area). The prospect consists of Late Tertiary volcanic and intrusive rocks of intermediate composition and contains several epithermal deposits with small past productions of gold and silver. Sets of Cu, Pb, Zn and Mo geochemical analyses were statistically analysed using PROBPLOT (Association of Exploration Geochemists special volume 14). Thresholds separating background and anomalous sub-populations were determined as follows: 37 ppm Cu, 31 ppm Pb, 112 ppm Zn, and 2.3 ppm Mo. The largest anomalies are attributable to previously mined epithermal gold-silver deposits, whereas several smaller anomalies relate to areas of known alteration associated with past epithermal or porphyry style hydrothermal systems. This left a few isolated anomalous values to be explained. Molybdenum was the best pathfinder for the known epithermal deposits.

## APPLICATION OF AN ENZYME-LEACH TECHNIQUE TO DETECT THE BURIED MAG AND CLAY PIT ORE DEPOSITS, GETCHELL TREND, NEVADA, USA

Clark, J.R., Kretschmer, E.L.

Significant areas of bedrock in the Basin and Range Province of North America are buried by transported sediments. In this region selective chemical analysis of soils, which determines the amount of a trace element that has been added to the overburden rather than the total amount of that element in the overburden sample, is a technique that may detect mineralized bedrock. In arid climates trace elements released by oxidation of sulfide minerals at depth can migrate up through overburden by capillary action or diffusion of volatile compounds. These elements may be trapped in manganese- and iron-oxide coatings on mineral grains in the overlying soil.

Amorphous manganese dioxide, which is commonly a very small part of the total manganese oxides in soils, is one of the most efficient natural traps for trace elements that are moving in the surface and near-surface environment. A glucose oxidase leach has been used to preferentially leach and enhance anomalies associated with amorphous manganese-oxide coatings on mineral grains. This enzyme reacts with dextrose in the leach solution to produce trace amounts of hydrogen peroxide and gluconic acid. Dilute hydrogen peroxide readily reduces and dissolves amorphous manganese dioxide, releasing trace elements trapped in that compound, while crystalline  $MnO_2$  phases are only weakly attacked.

The Enzyme Leach technique was tested on B-horizon soils collected over the Mag and Clay Pit deposits, which are pediment-covered epithermal, Carlin-type disseminated-gold deposits in the Getchell Trend, northeast of Winnemucca, Nevada. Both deposits are hosted by Paleozoic shales and carbonates. The Mag ore body dips steeply to the east and is covered with about 60 meters of basin-fill gravel. The Clay Pit deposit is covered by approximately 60 meters of post-ore ash-flow tuffs and basalt, which are intensely argillized and are capped by about 7 meters of gravel and sand. B-horizon soil samples were collected along two traverses over each of the deposits, and the samples were analyzed for 56 elements.

Anomalous As, Br, Cl, I, Mo, Sb, U, V, and W concentrations were

found along both traverses at the Mag deposit. For samples collected along a traverse crossing the surface projection of the ore body, these anomalies were strongest at both edges of the deposit, and a central area of suppressed to weakly anomalous trace-element values occurs directly over the subcrop of the mineralized body. For this traverse the anomaly on the up-dip side of the deposit had a relatively low contrast and was restricted. Much stronger anomalies were found over a broader area on the down-dip side of the ore body. The anomaly at the south end of the Mag ore body seemed to be centered over a down-dip extension of unoxidized, mineralized rock.

Strong As, Br, Ce, Cl, I, La, Mo, Sb, Th, U, V, and W anomalies were found at both edges of the Clay Pit deposit along one of the traverses. However, the analysis of samples from the second traverse did not reveal any anomalies. This second traverse provides an excellent example of how an ore body can be missed because of a poor sampling design.

The Enzyme Leach technique was effective in locating these two buried gold deposits. We thus recommend that the technique be considered for geochemical exploration programs searching for buried gold deposits in other arid regions.

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## THE SIMULTANEOUS DETERMINATION OF ALUMINIUM, IRON (II) AND IRON (III) IN A FLOW INJECTION SYSTEM

NICHOLAS CLARKE and LARS-GÖRAN DANIELSSON

Aluminium and iron are elements of great geochemical and toxicological importance. We have tested the possibility of determining Al, Fe (II) and Fe (III) simultaneously using complexation by various reagents in a flow injection system, using a fast scanning spectrophotometer as the detector. A multivariate analytical method, Partial Least Squares, was used to separate the contributions to the signal from aluminium, iron (III) and iron (II).

Preliminary results showed that, using 8-hydroxyquinoline-5-sulphonic acid as the reagent, our system was able to measure iron (III) and aluminium correctly in each other's presence, but could only measure iron (II) correctly in the presence of aluminium if present at high concentrations. The sampling frequency was 100 injections/hour with a reaction time of 16.4 s. Serious interference was caused by humus, while  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  may also be present in natural fresh waters in quantities large enough to interfere. It's potentially possible to use the method for the speciation of aluminium and a more detailed speciation of iron. This can be done by choosing the reaction time such that only labile forms of the metals have time to react.

## DEVELOPMENT OF SYNTHETIC CHEMICAL STANDARDS FOR USE IN EXPLORATION AND ENVIRONMENTAL GEOCHEMISTRY

D.R. COHEN and R.W. BECK

In a range of exploration and environmental geochemical applications, it is essential that a high degree of accuracy is maintained for trace metal analysis. This is particularly true for environmental assessments associated with mining or exploration activities given the increasing stringency of environmental regulations. The determination of accuracy and precision for trace element analysis in geological materials is partly dependent on the monitoring of suitable geochemical reference materials or standards. As comparative analytical techniques such as ICP-MS and INAA are subject to a variety of matrix interferences, standards should ideally contain trace element concentrations and matrix compositions similar to the samples being analysed, exhibit the required level of homogeneity, and display long term physical and chemical stability.

It is difficult to achieve adequate levels of homogeneity in solid geochemical standards developed by milling rock, ore, sediment or vegetation samples. Gold presents special problems due to its ability to resist comminution and the particle scarcity effect. There is also the problem of preventing segregation of components of varying density or particle sizes within standards.

Establishment of the true element contents of "natural" standards is generally based on a statistical assessment of analytical data derived from one or more techniques. Reported data in collaborative programs are generally highly incoherent and often result in severely skewed distributions. A comparison of published data on gold contents of USGS standards BHVO-1, BIR-1 and DNC-1 using fire assay-INAA indicates relative standard deviations exceed 50% in some cases, at the 1g sub-sample size. Certified values for (natural) standards may closely estimate the true values but the true value is an ideal which cannot be perfectly known.

Silica gel techniques, based on an organo-silica reagent, have been used to create synthetic or partially synthetic standards whose chemical and mineralogical compositions are similar to soils or sediments. Two types of standards have been developed – high purity formulations and standard additions to geological materials such as quartz sand, iron oxides and lateritic soil.

Synthetic standards may be produced at relatively low cost compared with the cost of milling and mixing large quantities of natural materials. This allows for their routine use in monitoring within-batch analytical precision and accuracy.

SEM work indicates the trace metals (or their salts) are present as thin coatings on silica particles in the 0.1 to 5 micron size range. In the second type of standard, the silica gel particles are themselves loosely attached to the substrate rock or soil particles. The trace metals are readily attacked by acids. The effective gold particle size in the standards has been estimated as generally less than 0.2 mm by the GOLDCALC sizing method.

For most elements investigated, the relative standard deviation for analyses of sub-samples in the 0.1g to 30g range is less than 1%. The formulation of multielement standards presents some problems due to chemical interactions between species. An alternative method involving mixing of single-element standards to obtain the required composition appears feasible.

THE ROLE OF THE YELLOW-CLAYEY TOPSOILS (LATOSOLS) FOR GOLD  
GEOCHEMICAL EXPLORATION IN LATERITIC TERRAINS: AMAZON  
REGION, BRAZIL.

GOSTA, M.L., ANGÉLICA, R.S.

One of the most interesting features related to laterite research and geochemical exploration in low-latitude regions, mainly in the Brazilian Amazon region and in West Africa, are the widely spread yellow-clayey topsoils, which can be residual or locally transported latosols. They occur invariably covering older complete or truncated laterite profiles in both regions. In the Amazon region, where they are regionally distributed, several works dealing with the origin of these latosols have been done generally showing a good correlation with bauxite-bearing profiles. The allocthonists authors suggest different hypotheses for their origin: marine sedimentation; mud-flow deposits under semi-arid climate; terrestrial sedimentation and also as termite activity products. The autocthonists authors suggest that these soil profiles developed by chemical degradation from the former horizons (iron crust, bauxite and saprolite) under tropical climate during the present and also in the late Tertiary. Meanwhile, this material received no direct attention of geologists to understand the distribution (concentration and dispersion) of the chemical elements for practical use in geochemical exploration.

In the Amazon region, these latosols are called "Beiterra Clay". They can be correlated with the topsoils from lateritic profiles of West Africa, described also as H1 or loose-clay horizon by French geologists. Because these materials are found everywhere on the landsurface in lateritic terrains, they are the most common and important sampling media in geochemical soil surveys. They show a typical yellowish color, earthy aspect free of structures and are composed by kaolinite, quartz, Al-goethite and variable contents of gibbsite. In the Amazon region, this soil cover can reach up to 20 m depth and in such situation they seem to have been shortly transported and present a thin pebble sequence composed of iron crust and/or bauxite fragments at the base of the profile, as stone lines. These topsoils generally occur on old peneplanized and dissected landsurfaces (plateaus). They fulfil narrow paleocanals and other depressions. On the center of the plateaus they are some times absent and on hilling lowlands thin and may contain iron concretions and nodules as well as stone lines. The origin of this material is clearly related to chemical and biological weathering of the former top horizons from either mature or immature laterite profiles, deslocated during the periods of dissection and peneplanization to the pre-existing depressions developed on the lateritic terrains. On this transported overburden it is possible to delineate significant geochemical signatures using the low gold concentrations. Where high gold content persist even in overburden composed by deslocated soils, primary mineralization with the similar content can be found.

The geochemical dispersion haloes in such soils will depend

from which part of the profile the soils derived and of course, from the time of formation, and their degree of transport. The dispersion halo measured from the former contact between primary mineralization and surrounding rocks reaches 100 m for the soil derived from iron crust or bauxite, and as less as 20 m the for those derived from saprolite.

Geochemical surveys conducted on such top soils and paleosoils in the Amazon region, were obtained in the Cassipuré region, with bauxitic laterites, in the Carajás region, with lateritized gossans and in the Ipitinga river with laterites and gossans as well as in two older gold producer regions: Tapajós river with laterite and gossans and Gurupí region mostly with laterites of different composition. In all these regions the soils cover laterite profiles with different degree of truncation. The results reveal that the loose-clayey topsoils (and paleosoils) derived from the weathering of the former laterite profiles may be useful to detect underlying supergene (laterite or gossan) and/or primary gold mineralization.

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## **International Geochemical Mapping: present and future.**

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Systematic geochemical maps of the land surface are an essential component of any comprehensive geoscience database. Geochemical maps are directly relevant to economic and environmental problems involving minerals and mineral exploration, soil science, agriculture, forestry, animal and human health, and land-use planning. The data are needed by both developed and developing countries.

International Geochemical Mapping began as IGCP Project 259 in 1988 in response to the fact that the presently available database concerning the geochemical composition of the Earth's surface is substantially incomplete and inconsistent. In order to find ways to remedy the situation, existing methodologies have been reviewed, computer-based experiments have been undertaken with existing large regional data sets, and new experimental field surveys completed. From these studies comprehensive recommendations have been prepared by the project's Steering Committee\* to guide organizations which are, or may become, involved in the collection of large quantities of geochemical data. The recommendations relate to a proposed global network of geochemical reference samples and radiometric profiles, with sample collection and preparation specifications, analytical requirements and standards, and data management procedures.

International geochemical mapping is achievable in stages. It has been demonstrated through IGCP 259 that properly controlled wide-spaced sampling is valid and useful. Wide-spaced sampling is crucial to the concept of international geochemical mapping because it offers speed, economy and relative simplicity in execution. Supplemented by suitably located transects and radiometric profiles it provides a practical way of obtaining a global overview and providing a reference network for comparing detailed surveys in different areas. Work undertaken during the project by Xie, Bolviken, Bjorklund, Garrett, Davenport, Ridgway and others has demonstrated that to obtain representivity in the sampling of large areas it is possible to use materials which provide natural composite samples (e.g. flood plain sediment, till, or water) or materials (e.g. stream or lake sediment) where the sampling pattern can be statistically designed to provide representivity.

It is proposed that the acquisition and analysis of reference materials should be the first step towards establishing global geochemical baselines. A 160 x 160 km unit cell is proposed for the collection of specified reference materials (regolith, drainage sediment, water where available), requiring 5000 site-clusters worldwide. These samples will be split, part retained in the

country of origin, part analysed according to a strict protocol in international laboratories. The samples will provide analytical data and serve as future reference material. Wide-spaced sampling and transects are of high priority in regions of the world where there is a low probability of obtaining conventional geochemical surveys in the near future. However, a global reference network requires systematic wide-spaced sampling over all the Earth's land surface.

To produce atlas-scale maps and baseline data for environmental and geoscience purposes, the primary cells must be subdivided and sampled (later if necessary) in smaller blocks (e.g. 40 x 40 km, 20 x 20 etc.) according to the spatial definition that is required. Ultimately 70+ elements will be determined in solid samples, using methods which will provide total content and ensure detection limits significantly below the Clarke. Digital data management procedures are prescribed in the recommendations, to allow maximum flexibility in the format of products, with map scales determined by sampling density.

Appropriate institutional arrangements to facilitate continuing close international collaboration will be essential to accomplish these tasks. It is recommended that they should be initiated as Phase II of the International Geochemical Mapping project.

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\* The following members of the IGCP 259 Steering Committee participated directly in the final discussion leading to the recommendations; others have also made significant contributions:

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WATER QUALITY CHARACTERISTICS ASSOCIATED WITH FLUORITE  
MINING IN THE KERIO VALLEY, AREA, WESTERN KENYA

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ABSTRACT

This work aims at establishing the extent to which fluorite mining and the disposal of mine waste influence surface and groundwater quality in the Kerio Valley area. Several hydro-chemical parameters and their inter-relationships have been determined in order to identify pollution types and transport mechanisms. Adsorption and complex formation are shown to be important processes governing the behaviour of metals in these waters; the dissolved metal fraction is consequently often low and of limited toxicological significance. The levels of nutrients such as nitrates and phosphates are also within acceptable limits in relation to the quality of ecosystem that these waters can sustain. Because of the relatively high rate of soil erosion and leaching of associated bedrock, however, rather elevated values are found for dissolved solids, electrical conductivity and alkalinity. Indices of organic pollution such as biochemical oxygen demand (BOD) are up to 10 times their maximum permissible limits for domestic water supply. Organic pollution is attributed mainly to reagents used in ore processing.

## THE APPLICATION OF LITHOGEOCHEMISTRY TO GOLD EXPLORATION IN THE CASA BERARDI AREA, NW QUEBEC

Davies, J.P.E. and Nichol, Ian.

The Casa Berardi gold deposits, situated in the Abitibi greenstone belt, north-western Quebec, were discovered in the mid 1980's as a result of an intensive diamond and overburden drilling programme carried out to follow up regional geophysical anomalies. The area is characterised by thick glacial overburden, with few outcrops, a feature that hinders exploration. In addition, it has been found that the ore lenses are commonly boudinaged and dislocated by the strong deformation that has affected the area, further complicating the geology. An investigation was therefore carried out in order to determine whether lithogeochemistry could be used to improve the efficiency of exploration, which currently involves expensive diamond drilling of geophysical anomalies.

The Casa Berardi gold deposits are hosted by clastic and chemical sediments, pyroclastic units, volcanic flows and sub-volcanic intrusives of lower to mid-greenschist metamorphic facies, referred to as the Golden Pond Sequence. Gold mineralization principally occurs in quartz-carbonate veins and altered wallrock, spatially associated with the Casa Berardi fault, within the regionally extensive east-west trending Casa Berardi Deformation Zone which hosts other significant mineral deposits such as the Estrades polymetallic deposit.

The wallrocks to gold mineralization at Casa Berardi are characterized by zoned alteration, grading from sericite-ankerite alteration adjacent to mineralization, through sericite-chlorite-ankerite and calcite-chlorite alteration to unaltered greenschist mineral assemblages. Microprobe analysis was used to confirm the zonation of carbonate minerals as determined by staining techniques, and to determine whether silicate minerals displayed compositional variations related to mineralization. Sericite did not display systematic variations with respect to mineralization, whereas chlorite was found to vary from Mg-rich compositions in weakly altered rocks to strongly Fe-rich compositions in ore samples.

Ore-grade samples from Casa Berardi are characterized by the presence of pyrite and arsenopyrite, and commonly contain minor base metal sulphide minerals. Recognition of the occurrence of base metal sulphides in high grade ore zones can be used as a rough guide to Au

grades during core logging, and petrographic examination has revealed that sulphides from ore zones contain more inclusions of base metal sulphides than those from weakly mineralized samples. An attempt was therefore made to separate sulphide minerals from samples of mineralized and unmineralized wallrocks in order to determine whether dispersion haloes of base metals exist, and could be detected by geochemical analysis of such separates and this feature used in exploration. Results obtained indicate that weakly altered rocks distal to mineralization contained very little separable sulphide, necessitating the collection of large volumes of sample in order to obtain sufficient separable sulphide to analyze. Separates obtained from ore-grade samples contained relatively high concentrations of base metals (Cu, Zn, Pb, Sb), but no distinct dispersion halo was noted; in contrast there appeared to be a depletion of base metals in sulphide separates from samples collected at distances from 5 to 50 metres away from ore-grade mineralization. As part of the same study sulphide separates prepared from samples collected from various other lode gold and VMS deposits were analyzed, and distinct variations were noted between trace element concentrations of sulphides from different deposits. In particular, Se/S ratios and Co, Cr and Ni concentrations differed markedly between VMS and lode gold deposits.

Geochemical whole rock variations in the rocks hosting the Casa Berardi West deposit are consistent with the mineralogical patterns observed. A halo of > 100 ppb Au extending for up to 100 metres around the deposit had previously been described, and was confirmed in this study but found to be erratic on the hand specimen scale. Dispersion haloes of Ag, As, Sb and W were also noted; however these were found to have a lesser areal extent than the Au dispersion halo due to the greater sensitivity of Au analysis. These pathfinder elements could however be used in addition to routine Au analysis in order to reduce uncertainty caused by the nugget effect, and provide greater confidence during exploration by diamond drilling. Geochemical trace element analysis was also carried out, and the data used to assist in lithological discrimination of altered wallrock, and to study alteration processes related to mineralization in order to obtain an improved understanding of the metallogenesis of the deposit. In conclusion, litho-geochemistry was found to provide additional information which could be used to improve the confidence of geological interpretation during exploration.

## EFFECT OF SOIL pH ON ALUMINIUM AVAILABILITY IN SOILS AND ITS UPTAKE BY THE SOYBEAN PLANT (*Glycine max*)

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A greenhouse experiment was designed to investigate the effects of soil pH and other soil properties on the availability of aluminium and its uptake by the soybean plant. Six soils were compared that were developed over six contrasting bedrock types ranging widely in their total aluminium content and other chemical and physical characteristics. These soils were a silt loam developed over the Oxford Clay, a loam over Chalk, a silt loam over Lower Lias Clay, a sandy loam over Devonian Shale, a sandy loam over Granite, and a loamy sand over the Lower Greensand. The natural pH of the soils ranged from 4.2 to 8.0 and each soil was also amended to give two other pH levels using elemental sulphur and /or calcium carbonate.

The solubility of the aluminium in the soils and hence its availability to the plants was estimated using extraction with 0.02M CaCl<sub>2</sub> and 0.05M EDTA prior to determination by ICP-AES. Aluminium concentrations in the plant materials were similarly determined after acid digestion with concentrated nitric and perchloric acid. The quality of the estimates of aluminium concentration was assessed by estimation of the systematic and random errors originating from the sampling and analytical procedures using a Sampling and Analytical Quality Control Scheme (Ramsey et al. 1992). A method was developed to estimate semi-quantitatively, the proportion of the aluminium in the herbage that is contributed by soil or dust particles that can contaminate the plant materials, either during the life of the plant or during chemical analysis.

In the comparison between two empirical extractants, the best predictor of soil aluminium available for uptake into the soybean plant was found to be 0.02M CaCl<sub>2</sub>. This relationship appears to be linear with a correlation coefficient of 0.94 ( $p = 0.001$ ). The amounts of extractable aluminium in the soils and the uptake of aluminium by the soybean plants both increased as the soil pH decreased. These relationships are both non-linear with marked increases in extractability and uptake when the soil pH falls below 4.4. It is concluded that the speciation of aluminium in the soils changes at this pH value, and that the specie of aluminium taken up by soybean plants is the Al<sup>3+</sup> ion, which is the only stable aluminium ion at a pH less than 4.4. Soil pH has been identified as the major factor that controls the uptake of aluminium from soil into the soybean plant

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A geochemical survey of overbank stream sediment, till, stream water and humus from 49 large catchment basins (500-7000 km<sup>2</sup>) in Fennoscandia was conducted at Åbo Akademi University. The main objective was to test the usefulness of different sampling media at extremely low sampling densities (1 station/23 000 km<sup>2</sup>) in glaciated areas as a pilot study for a geochemical mapping of the whole globe. Results of humus are described in a separate contribution.

Overbank sediment and water were sampled from the downstream apex of each basin. One sediment sample was collected at the surface and another at depth (40-100 cm). Stream water was sampled once a month during one year. Within each basin till and humus were sampled from 10-20 randomly selected sites.

The fine fraction of the surface samples of overbank sediment are anthropogenically contaminated at some stations, especially where there are mining activities, whereas the samples from depth normally reflect the natural composition of the entire catchment basin. The element contents of the latter samples form regional patterns, only a few of which coincide with the major geological domains. For most elements the patterns and content levels are very similar to those displayed by till. The main difference is, that the contents of Mn, Fe and the supposedly co-precipitated Ba, Cu and Zn are higher in the sediment.

The content patterns of most elements in overbank sediment and till coincide closely with those of previous regional surveys at higher sampling densities, e.g., the geochemistry of till in Finland and Sweden and of overbank sediment in Norway. This coincidence is better for geochemistry based on total contents than that of Aqua Regia soluble contents.

Due to the large region investigated and the large basins sampled there are numerous factors affecting water composition and this results in a large variation within and between the basins. Such factors are climate, topography, bedrock and soil, atmospheric deposition, industries, population, agriculture, etc. Therefore, the contents of chemical elements in stream water do not form patterns related to geology. Only in anthropogenically unaffected environments effects of geology can be seen in the behaviour of elements in waters.

Most elements in water display broad anomaly patterns of contents, which correlate positively with the areal distributions of clays and arable land. High contents of easily soluble elements in clay and cultivation of these sediments are the probable causes of elevated contents in water. Also, many major and trace elements, including several heavy metals, are added to the cultivated soils with fertilizers, lime, sewage sludges and pesticides, which apparently contributes to this correlation. Atmospheric deposition is a large contributor of many elements, which is seen in the geochemistry of the waters of especially southern Fennoscandia.

With regard to the factors governing the regional variation of metal contents in overbank sediment and till, the low number of samples used does not allow far-reaching conclusions to be made. Contents in both media form distinct patterns for most elements analyzed and in general the patterns in the deep sediment agree reasonably well with the patterns found in the composited till samples, although there are some detailed differences. For the surface samples of the sediment patterns are affected by anthropogenic sources. Content variation in river water in Fennoscandia seem to be more related to land use, contamination and physiography than to bedrock lithology. For geochemical mapping at a global scale all three media dealt with, could be used for delineation of major geochemical provinces. The regional geochemistry of overbank sediment reasonably well depicts that of the fine fraction of till in the glaciated area studied. Water of streams could be a suitable medium for environmental purposes at a global scale, but for large areas of the globe considerable seasonal variation in content levels could require repetitions of the sampling during a year.

# CAN CHLORINE STABLE ISOTOPE RATIO VARIATIONS BE USED IN MINERAL EXPLORATION?

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## -Introduction

The stable isotopes of chlorine ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ) usually do not fractionate very much. A deviation larger than 1‰ from the standard (S.M.O.C., standard mean ocean chloride) is considered as large (e.g. KAUFMANN 1984). Most measured values of natural (water) samples, are negative relative to this standard (EGGENKAMP in prep.). This paper presents the first accurate  $\delta^{37}\text{Cl}$  data on minerals.

## -Materials and methods

16 different minerals were measured for chlorine isotopes. These minerals represent different mineral-forming processes i.e. evaporites, fumaroles, magmatic minerals and oxidation zone minerals. Minerals were dissolved in water (evaporites and fumaroles), molten NaOH (silicates) or nitric acid (other). To this solution  $\text{AgNO}_3$  was added to precipitate  $\text{AgCl}$ . This solid was reacted with  $\text{CH}_3\text{I}$  to form  $\text{CH}_3\text{Cl}$ , which could be measured on a mass spectrometer (after TAYLOR & GRIMSRUD 1969, KAUFMANN 1984, EGGENKAMP in prep.).

## -Results

Results are presented in the following table. In general it is found that the oxidation zone minerals have positive  $\delta^{37}\text{Cl}$  values, while the other minerals have negative values.

Oxidation-zone minerals		Non-oxidation-zone minerals	
Atacamite	+ 5.96 ± 0.17‰	Amphibole	-0.26 ± 0.12‰ / -0.06 ± 0.02‰
Boleite	+ 1.66 ± 0.32‰	Boracite	+ 0.10 ± 0.21‰
Conellite	+ 1.12 ± 0.16‰	Carnallite	-0.48 ± 0.07‰
Mimetite	+ 0.08 ± 0.20‰	Chlorapatite	-0.04 ± 0.18‰
Nadorite	+ 0.08 ± 0.22‰	Cotunnite	-0.46 ± 0.05‰
Paralaurionite	-0.05 ± 0.03‰	Eudialite	-0.23 ± 0.08‰
Pyromorphite	+ 0.25 ± 0.20‰	Halite	-0.10 ± 0.09‰
		Sal Ammoniac	-4.88 ± 0.08‰
		Sodalite	+ 0.13 ± 0.06‰

## -Discussion

The oxidation zone minerals generally contain large amounts of economic important metals (Ag, Cu, Pb). Measuring  $\delta^{37}\text{Cl}$  values possibly provide a new tool to explore for such oxidation zone minerals. As mentioned before the  $\delta^{37}\text{Cl}$  values of these minerals are generally positive relative to seawater. Especially in the important group of oxychlorides (atacamite, boleite, conellite)  $\delta^{37}\text{Cl}$  is found to be very high ( $\delta^{37}\text{Cl} > +1\%$ ). These minerals can dissolve relatively easy and because they have a high chloride content they will dissolve preferentially and increase the  $\delta^{37}\text{Cl}$  value of water. Sampling water from deposits containing



these minerals and measuring its  $\delta^{37}\text{Cl}$  might therefore be used as a prospectian tool.

This method needs to be tested on several well defined deposits. It is expected that water that has been in contact with the oxychlorides has  $\delta^{37}\text{Cl}$  values that correspond with those of the minerals. If such a  $\delta^{37}\text{Cl}$  relationship will be found this method could be useful for mineral exploration. A potential problem is to obtain enough water for the  $\delta^{37}\text{Cl}$  measurements since the oxychlorides generally occur in (very) dry places (deserts). The measurement of  $\delta^{37}\text{Cl}$  is relatively easy, it can be performed in serial analysis. On the other hand it is relatively time consuming and an advanced laboratory equipment is necessary. The analysis of 20 samples takes about 4 days.

#### **-Conclusions**

It is suggested that the method described in this paper can give valuable additional information in case of exploration for oxidation zone minerals. It seems worth while to test the method and establish the problems and benefits involved.

#### **-Acknowledgments**

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## MOLYBDENOSIS IN AN AREA UNDERLAIN BY URANIUM-BEARING LIGNITES IN THE NORTHERN GREAT PLAINS, U.S.A.

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In the fall of 1975, cattle grazing to the north of an abandoned uranium mine on Flint Butte in Harding County, South Dakota, showed signs of molybdenosis, a disease due to molybdenum-induced copper deficiency. To identify the source of the problem, plant, water, and soil samples were collected on a grid design over a 16 km<sup>2</sup> (~9 miles<sup>2</sup>) area around Flint Butte. Uranium, molybdenum, and copper concentrations were determined in western wheatgrass (*Agropyron smithii*) and sweetclover (*Melilotus officinalis*); molybdenum and copper concentrations and pH were determined in pond waters; and the pH of soils was determined. Ratios of copper to molybdenum in the forage were found to be below 2:1, the lowest value considered safe for cattle. Molybdenum concentrations in some surface waters were extremely high. These conditions are related to the outcrop of uranium- and molybdenum-bearing lignites at Flint Butte and in the nearby Flint Hills. Similar lignites are widespread, and it is likely that nutritional problems of the type encountered in the Flint Butte area exist in similar geologic terrain over a broad region of the northern Great Plains.

## A NEW APPROACH TO GEOTHERMAL EXPLORATION — INTEGRATING GEOCHEMISTRY WITH REMOTE SENSING

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A geochemical study and remote-sensing study of two adjacent known geothermal resource areas (KGRAs) in the northern San Luis Valley, Colorado (U.S.A.), were linked to seek surface evidence of any possible extensions of these partially concealed geothermal areas. The San Luis Valley is an east-dipping half graben, the geomorphic expression of the Rio Grande Rift in southern Colorado, and contains a complex system of aquifers. One KGRA, Mineral Hot Springs, occurs in valley fill between low foothills of the San Juan Volcanic Field to the west and the steeply rising Sangre de Cristo Range to the east. The other KGRA, Valley View Hot Springs, lies on the bounding fault of the Sangre de Cristo Range. Scarps of a series of Holocene-age faults, the Villa Grove fault zone, trend across the valley to the northwest.

In 1992, 139 samples of rabbitbrush (genus *Chrysothamnus*), which dominates this high semiarid valley, were collected in an approximate grid. More closely-spaced sample sites were positioned along traverses across the mapped faults or fault zones that may serve as conduits for mineralizing and geothermal fluids. At the same time, 120 soil-gas and soil samples were taken at 0.1-mi (160-m) intervals, mostly over several of the fault traverses where plants had been collected. Plant samples were analyzed by extended-count instrumental neutron activation analysis (INAA) for 35 elements, prompt-gamma INAA for boron, and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for 30 elements. Soils were analyzed for 10 elements by a partial-extraction ICP-AES method that used a concentrated HCl-H<sub>2</sub>O<sub>2</sub> digestion. The soil gases were analyzed for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> by gas chromatography, and for He by mass spectrometry.

A large airborne imaging spectrometer data set—about  $6.7 \times 10^9$  bits—covering the visible and near-infrared region of the electromagnetic spectrum was acquired in the hot-springs areas in August 1992. Imaging spectrometer data have been used to detect a large variety of minerals (many OH-bearing minerals, mostly clays; Fe-bearing minerals; and carbonates) and for vegetation studies (to examine stress). In this phase of the study we hope to identify certain epithermal minerals and vegetation effects that indicate geothermal activity. We are currently correcting and calibrating the imaging-spectrometer data.

High Li, B, and Mn concentrations in rabbitbrush combined with high soil-Hg concentrations and high CO<sub>2</sub> concentrations in the associated soil gases collected nearby suggest that a geothermal heat source may occur in the low hills of Lower Proterozoic granites just west of Mineral Hot Springs. Several other distinct geochemical spatial patterns, probably unrelated to geothermal activity, were also revealed. These include anomalous concentrations of Fe, Al, Sc, and the light rare-earth elements La, Ce, and Sm in rabbitbrush with a corresponding depression of the soil gases CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> along the Villa Grove fault zone. This depression in soil-gas concentrations may have resulted from fault-zone

plugging due to water saturation and/or mineralization. The corresponding element anomalies in rabbitbrush could have been caused by the oxidation of pyrite, which generates acidic solutions. Low-pH systems are known to dissolve rare-earth elements contained in surrounding rocks and thus make them available for hydromorphic transport to the near-surface environment. Significant Cd and Zn anomalies also occurred in rabbitbrush in an area where carbonate rocks of Paleozoic age are highly brecciated, altered, and faulted. Finally, Br-enriched rabbitbrush was located in presumably deep valley fill, an area where soils and soil gases were not sampled. Bromine is highly mobile under all pH/Eh conditions in the supergene environment. Two sources are likely: (i) tuff-laden lacustrine clays of the Neogene Alamosa Formation, which also consists of unconsolidated sands; and (ii) biogenic gases in the same formation or oil seeps in the underlying Precambrian rocks, which may have created redox conditions that are known to produce Br and I anomalies in soils.

## THE CONCEPT OF GLOBAL GEOCHEMICAL BASE-LINE SAMPLING: A PILOT STUDY OF THE APPLICABILITY IN PORTUGAL

A.M.FERREIRA, A.BJORKLUND AND M.PINTO

A large number of soil and stream-sediment samples has been collected in Portugal for local and semi-regional purposes of mineral exploration and environmental research but no low-density geochemical data of total national coverage exist. The usefulness of such multipurpose data has been demonstrated elsewhere. Therefore, the concept of national geochemical mapping as an integrated part of a Global Geochemical Base-line Sampling program, proposed by IGCP Project 259, was tested in a pilot study in Portugal. The funds provided by the National Board of Scientific and Technological Investigation allowed only for a restricted sampling program and the use of only one of the media proposed by IGCP 259.

The basins of Mira River (1600 km<sup>2</sup>) in southern and Vouga River (3000 km<sup>2</sup>) in central-northern Portugal were chosen for stream-sediment sampling. These represent different lithologies and in both basins mineralized provinces and contrasting bedrock geology occur. Samples from 17 sites, each composited from 5 grabs along 200 m of the stream, were collected at an average density of about one site / 270 km<sup>2</sup> from streams draining areas averaging 150 km<sup>2</sup> in size. Each site was sampled in duplicate for composite samples big enough to produce 200 g of each of the fractions 180  $\mu$ m (80 mesh) and 60  $\mu$ m (230 mesh). Both fractions were analysed with ICP after digestion for one hour in hot Aqua Regia. For quality control all duplicate samples of each fraction were analysed twice and, in addition, the analysis of one fraction of each of three samples was repeated seven times.

The error variance of 20 elements out of 32 reported by the laboratory was significantly lower than the total variance in the data. No major difference in the error variation was found between the two grain-size fractions. For 18 elements the mean contents were significantly higher in the finer fraction, while the opposite was true only for Ti. The higher contents of Ag, As, Cd, U, and W in the finer fraction gave a significantly better anomaly pattern than in the coarser one. The mean contents of 10 elements differed significantly between the basins. In the Vouga basin the high contents of Ag, As, Co, Cu, Ni and Zn are in a province of sulfide mineralization and anomalous contents of K, La, Ti, Th, and W, are in a Sn-W province while samples anomalously high in U occur in a uranium province. An Fe-Mn province in the Mira basin is indicated by anomalously high contents of Fe, Mn, Ba, Zn, As, Sr, Ca, and P. The different lithological units in the Vouga basin are depicted by different content levels of Al, As, B, Cd, K, Mn, P, Sr, Th, Ti, V, and W. There is an apparent relationship of the variation of Cr, P and Pb to pollution.

The results of the study indicate that sampling of stream sediments at a density of one site / 200 km<sup>2</sup>, giving some 450 sites for Portugal, would give a content-variation pattern of most elements, which could be related to lithology, mineralized provinces and features of pollution. Inclusion of other media proposed by IGCP 259 (alluvium, non-alluvial soil, and water) and a diversified analytical program would certainly give substantial new and valuable information on the geochemistry of the secondary environment in Portugal. Proper planning would enable part of such samples to be included in a future set of Global Geochemical Base-line Samples.

## USE OF A SENSITIVE ANALYTICAL METHOD AND THE -53 $\mu\text{m}$ FRACTION OF STREAM SEDIMENTS IN EXPLORATION FOR GOLD IN NORTHERN THAILAND

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Heavy mineral concentrates (SG > 3.3) from the Huai Hin Laep, Thailand, contain strongly anomalous concentrations of gold (Paopongsawan and Fletcher, in press). In contrast, the gold content of the associated -212  $\mu\text{m}$  and -53  $\mu\text{m}$  fractions of the sediment is generally less than the 5 ppb detection limit of fire assay-atomic absorption. Failure to detect the gold anomaly in the sediments is apparently caused by dilution of the sediments with large amounts of barren silt and clay that results from increased erosion of lateritic soils as a result of deforestation and agricultural land usage. Because of the costs and unreliability associated with the use of heavy mineral concentrates, it would be an obvious advantage if gold content of the sediments could be determined directly. We have therefore developed an analytical procedure that uses acid digestion, followed by preconcentration of the gold on a column and its determination with a new type of spectrometer which optimizes baseline analysis. This provides a detection limit of 0.1 ppb gold with a 30 to 50 g sample. Here we report results obtained using this procedure for determination of gold in the -53  $\mu\text{m}$  fraction of sediments from the Huai Hin Laep.

Gold content of the -53  $\mu\text{m}$  fraction ranges from 1.0 to 2.9 ppb versus concentrations that typically range from 10,000 to 50,000 ppb in the heavy mineral concentrates. However, despite gold concentrations several orders of magnitude lower than those in the heavy mineral concentrates, the downstream dispersion patterns are remarkably similar with gold concentrations increasing downstream away from the supposed source. This similarity in downstream dispersion of gold in the -53  $\mu\text{m}$  fraction and gold content of the sand-sized heavy mineral fractions is also shown: (i) directly, by a strong correlation between the gold content of the -53  $\mu\text{m}$  fraction and the gold content of all three heavy mineral fractions; and (ii) indirectly, by the correlations between gold content of the -53  $\mu\text{m}$  fraction, bed roughness, and stream width and velocity.

These results confirm the presence of a greatly diluted gold anomaly in the -53  $\mu\text{m}$  of the sediments and show that transport and deposition of this fine grained gold is controlled by the same sedimentological factors that control the behaviour of gold in the sand size range. Most important for exploration purposes, by using a sufficiently sensitive analytical method, it is possible to recognize the presence of meaningful gold dispersion patterns at concentrations less than 5 ppb. Insofar as use of a more sensitive analytical method can avoid the need to collect bulk samples and prepare heavy mineral concentrates, this has the potential to provide gold exploration programmes with very major savings in both field sampling and analytical costs.

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## QUALITATIVE TIME TREND ANALYSIS OF GROUND WATER MONITORING NETWORKS: EXAMPLE FROM THE NETHERLANDS

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The detection of (short term) trends is one of the prime goals of ground water monitoring networks. These trends can be used to recognize threats and to discern active geochemical processes that affect the ground water composition. Few case histories have been published, describing the difficulties and traps that occur in trend studies. In this paper a qualitative time trend analysis was performed on macrochemical parameters of the dataset of the Dutch Ground Water Quality Monitoring Network. This network is operative since 1979 and monitors the ground water composition at 350 locations at two depths (about 10 and 25 m below surface level). Samples are analyzed yearly for electro-conductivity (Ec), pH, Na, K, Mg, Ca,  $\text{NH}_4$ ,  $\text{HCO}_3$ , Cl,  $\text{NO}_3$ ,  $\text{SO}_4$ , and Total P (van Duijvenbooden, 1987).

Prior to the trend analysis, the dataset was divided into homogeneous groups with the aid of fuzzy c-means clustering (Frapporti et al., 1993). Each group is characterized by its distinct source of the ground water (seawater, surface water or precipitation) and its specific combination of dominating geochemical processes (mineralization of organic matter, carbonate dissolution and cation exchange).

To determine whether or not two variables are related an association statistic is commonly used. In this case the sampling date and the concentration of a parameter of ground water quality are correlated to study trends qualitatively. The nonparametric and outlier insensitive Spearman rank correlation coefficient is calculated per well screen per parameter. Combining the Spearman correlation coefficients of all individual wells within a homogeneous group, a distribution of correlation coefficients is formed. This distribution is tested for deviations of a theoretical zero correlation distribution ( $r=0$ ) by use of the Kolmogorov-Smirnov one sample test (Frapporti et al., 1990). One Kolmogorov-Smirnov statistic is obtained per group of wells. The characteristics of the deviations from the zero correlation distribution can be found in the histogram of the Spearman rank correlation coefficients (see figure 1).

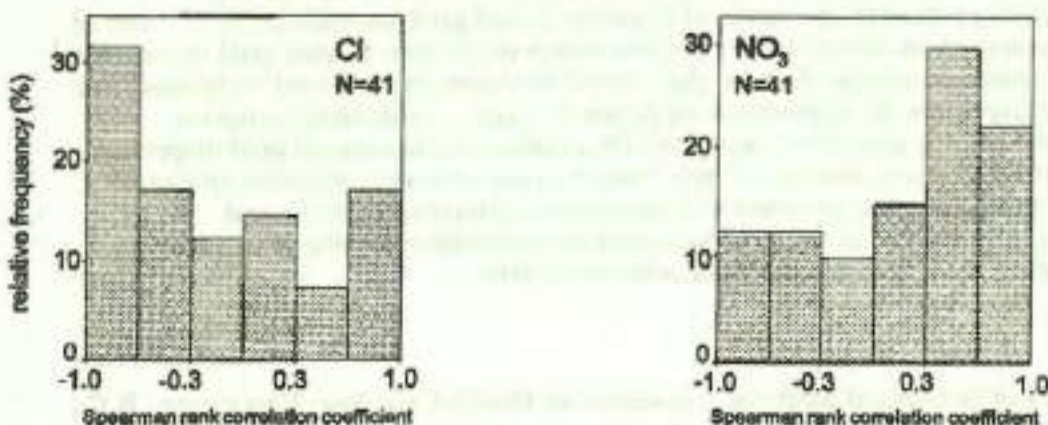


Figure 1: Histograms of Spearman rank correlation coefficients of chloride and nitrate of well screens allocated to the polluted cluster.

Most groups show statistically significant qualitative trends, many of which are caused by changes in sampling and analytical procedures. After equalizing detection limits, which varied in time for  $\text{NO}_3$ , total P, and  $\text{NH}_4$ , many trends were eliminated. In some clusters trends for alkalinity, pH, Ec, total P and  $\text{SO}_4$  can be explained by the variations in the procedures used, e.g. varying storage periods.

Other parameters show statistically significant trends, which can be explained by geochemical processes. In most cases quantitatively small, these trends are not necessarily linear, and should be closely monitored in the future.

The most interesting trends are found in a water type characterized by infiltrating rainwater with agricultural contaminants, the 'polluted cluster'. Surprisingly chloride decreases strongly in this water type, while nitrate increases, as illustrated in figure 2.

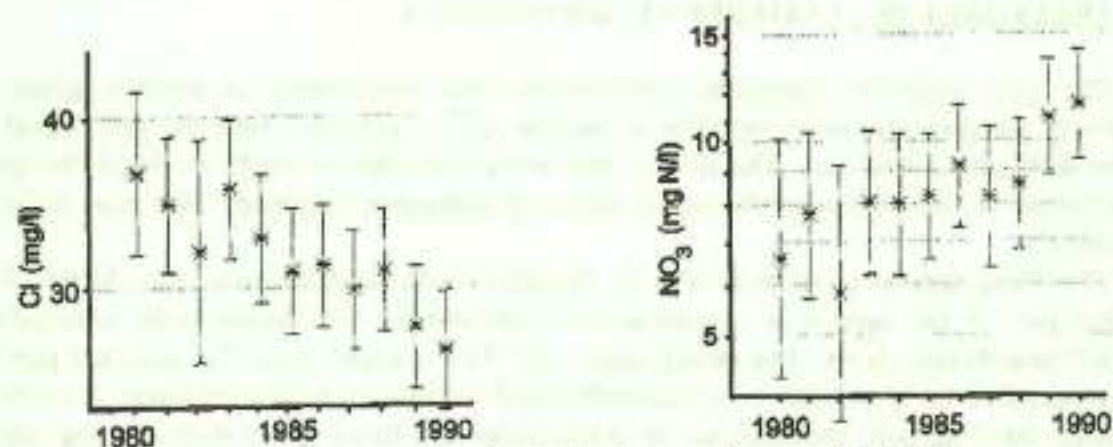


Figure 2: Annual geometric mean with standard error of mean of chloride and nitrate for the polluted cluster.

Increasing trends in nitrate are commonly explained as agricultural pollution by leaching of manure. From this study it seems that the lowering of the ground water tables plays an important role (figure 3). Nitrate produced through the mineralization of aerated organic matter in the enlarged unsaturated zone can not be taken up by vegetation. It is therefore leached into the ground water. Conservative parameters, like chloride, decrease because at lower ground water levels a smaller fraction of the infiltrated water is evapotranspired.

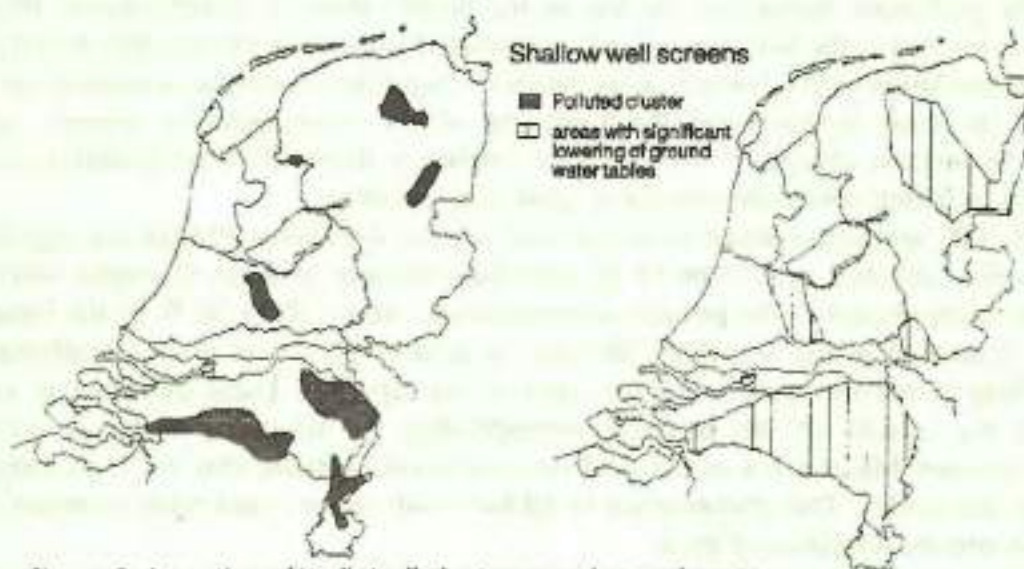


Figure 3: Location of 'polluted' cluster samples and areas with significant lowering of ground water tables.

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## GOLD MOBILITY IN EQUATORIAL RAIN FOREST LATERITIC PROFILES: THE EXAMPLE OF YAOU DEPOSIT (FRENCH GUIANA).

FREYSSINET Ph., LASSERRE J.L. and LOWELL J.

The gold cycle in supergene environments and particularly in lateritic zones is relatively complex due to its mobility in various type of profiles. Thus the gold signal is rather difficult to interpret. The aim of this work consisted to study in detail the gold distribution in rain forest conditions in terms of pedogenic processes and mass balance calculation.

The Yaou deposit is situated NW of French Guiana in Amazonian rain forest. The studied part of the deposit is composed of a sub-vertical trondjemite body intruded in mafic Precambrian schists. The morphology is of "half orange" type. The oxidized part of the mineralized body is made of a truncated profile at the top of the saprolite. An ochre-coloured ferralitic soil, characteristic of Amazonian rain forest zones is developing under the present equatorial climate.

The profile is composed of 3 main horizons from the bottom to the top: a saprolite (25-35m thick) with preserved primary textures, a uniform ochre-coloured horizon composed of kaolinite, gibbsite and goethite (2-4 m thick) and a humic layer (1m thick).

The gold mass balance calculation at the top of the profile has been estimated using the average gold content of the saprolite as reference. Gold shows an average absolute enrichment of 60% in the ochre horizon in comparison to the average gold concentration in the underlying saprolite. The gold accumulation mostly occurs at the contact between the ochre horizon and the top of the saprolite where the absolute enrichment can reach 200% up to 300 %. The humic layer is slightly depleted in gold in regard to the ochre horizon. The gold mass balance at the top of the profile shows a remobilization front where gold is leached in the humic layer and accumulated at the base of the ochre horizon. The gold accumulation at the contact ochre horizon - saprolite is mainly controlled by a decrease of the total porosity and the vanishing of the macro-porosity towards the saprolite. The textural change at this interface implies a decrease in permeability and probably less oxidizing conditions permitting gold reprecipitation.

Around 1000 samples obtained from a grid of vertical drill holes through the regolith enabled a well-established calculation of the gold mass balance in terms of depths within the saprolite with respect to the primary mineralization. About 40 to 50 % of the initial gold stock is leached in the saprolite. The loss of gold stock occurs at the weathering front. Leaching is not increased in higher parts of the saprolite. Local enrichments are noticed in the middle of the saprolite corresponding to Mn-enrichments. A good correlation between Mn and Au in the gold enriched levels indicate that Au is probably adsorbed by Mn-oxides. This phenomenon in relation with recent water table movements indicate post-lateritic migration of gold.

The global mass balance calculation for the Yaou gold deposit shows a loss of gold during the regolith formation of about 40% compared to the primary stock.

In conclusion, rain forest lateritic profiles are composed of two major remobilization fronts of gold: the top soil where rain forest pedogenic processes lead to absolute gold accumulation and the weathering front where 40% of the gold is leached out of the system.

In equatorial conditions, the gold accumulation effect in rain forest soils must be taken into account when selecting exploration targets.

## HYDROTHERMAL PROCESSES AND SHIFTING ELEMENT ASSOCIATION PATTERNS IN THE W-SN ENRICHED GRANITE OF REGOUFE, PORTUGAL

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### Abstract

Combined research in rock geochemistry and mineral chemistry of the hydrothermally altered, W-Sn specialized granite of Regoufe and its derivatives in Portugal was undertaken to gain insight in the mineralogical changes associated with hydrothermal processes and in the interaction of hydrothermal fluid and mineralogical rock composition within a single granite cupola. To this aim use was made of automated X-ray fluorescence spectrometry of unpolished rock sections (Integral Rock Analysis) and electron-probe micro-analysis on part of the same sections purposely selected on the basis of their rock chemistry. The study focuses on selected elements of interest that are measurable with the chosen techniques.

Major pervasive alteration within the Regoufe granite is virtually contemporaneous with mineralization in the form of Sn- or W-bearing quartz veins. Two phases of hydrothermal activity are discerned, characterized by different element-associations in the fluid. Fluids of the first phase are especially rich in Sn, Cs and F, whereas the second phase is marked by a W-Ta-Nb-Rb association and presumably carried less F. P (phosphorus) probably was an important fluid-component in both phases. The fluids are inferred to have fractionated from related magma at depth.

Sn, W, Nb and Ta are largely related to (inclusions in) biotite in the least altered part of the Regoufe granite. Tantaloniobian rutile is an important phase for the mineralogical distribution of Nb. Sn occurs in rutile and rarely as cassiterite. Muscovitization causes leaching of Ti and Zr from the granite. Sn, supplied or mobilized by the hydrothermal fluids, behaves differently from W, Nb and Ta. In the most altered rocks muscovite hosts significant amounts of Sn. Whereas Sn is still related to Ca and Ti, which elements probably represent altered biotite, W, Ta and Nb are related to newly formed Rb-rich muscovite. Columbo-tantalite was detected embedded in late muscovite. The fluid-supplied W, however, is predominantly deposited as wolframite in quartz-veins, the altered granite is not enriched in W compared to the relatively unaltered rocks.

Sr is preferentially hosted by K-feldspar in least altered granite, Ca in this rocktype is still partly contained in albite. Sr and Ca are released on increased albitization and muscovitization and are at least partly bound in newly formed apatite. Primary magmatic apatites have near ideal formula compositions. Mobilization of P during hydrothermal activity resulted in the formation of Mn-rich apatite in all parts of the granite. Mn-, Sr- and probably Li-rich apatites were formed in the most altered rocks. Eosphorite, and scorodite as the oxidation product of arsenopyrite are also formed as a result of P-mobility.

In the least altered rocks Cs is mainly contained in biotite. Cs- and Rb-enrichment in the most altered granite and aplitic rocks is evenly distributed over K-feldspar and micas. The processes that lead to increased Rb contents are partly independent of the Cs-enrichment, and apparently related to the W-Nb-Ta mineralization event separate from the preceding Sn-mineralization.

GEOCHEMICAL DATA FROM FLUID INCLUSION STUDIES AS EXPLORATION  
TOOL FOR GOLD DEPOSITS

GARCIA IGLESIAS, J., LOREDO, J.

Gold in many types of deposits has been transported by hydrothermal fluids, where some fraction of the gold precipitated to yield an orebody. Some fluid inclusion in gangue minerals contemporary to gold in these deposits will be a sample of the ore-forming fluids, preserved in the mineral for millions of years.

Independently of their use to the knowledge of parameters as temperature, pressure and density of ore-forming fluids, the study of these fluid inclusions give information about geochemical data of ore-forming fluids, and these data can help to the understanding of the processes that have been involved in the formation of many gold deposits and hence they can be useful in exploration.

In terms of understanding the geochemistry of the ore-forming processes, will be very important to have information about concentrations of the major solvents:  $H_2O$ ,  $CO_2$ ,  $CH_4$ , ..., and the major solute ions: Na, K, Ca, Mg, ..., between others.

A method to determine the chemical composition of fluids trapped as fluid inclusions in minerals, is the extraction of fluids from inclusions. These can be opened by fine grinding of the sample, which is leached with pure water; the leachate is then analyzed for such solutes: Na, K, Ca, Mg,  $SO_4$  and Cl (Roedder, 1958). Because of the very small size of fluid inclusion and the common occurrence of several different generations of fluid inclusions in a given sample, the problems of loss or/and contamination of fluids provide a major source of errors. Some qualitative and semiquantitative geochemical data can be obtained by identification under the polarizing microscope of any solids that have been formed inside the inclusion upon cooling by saturation of the fluids (i.e. daughter minerals) (Roedder, 1984a).

The composition of mixed fluid inclusion - $H_2O$ ,  $CO_2$ ,  $CH_4$ , and others-can be determined under the microscope by freezing procedures (Burruss, 1981; Roedder, 1984b). Raman microprobe is a powerful tool for such studies (Rosasco et al., 1975; Dhamelincourt and Schubnel, 1977; Guilhaumou, 1982). In the same way salinity of fluid inclusions expressed as NaCl wt. % equivalent, refers to the concentration of NaCl that corresponds to the observed depression of the freezing point in the NaCl- $H_2O$  theoretical system.

Because  $CO_2$  seems to be an almost universal constituent of the fluids involved in the transport and deposition of gold, the identification of  $CO_2$ -rich fluids will be very useful in exploration of gold deposits.

Another significant application of fluid inclusion geochemical data in exploration of gold deposits lies in the recognition of boiling of fluids, through the presence of presumably cogenetic vapour-rich and vapour-poor fluid inclusions, because in some deposits big changes in geochemistry of ore-forming fluids as results of boiling phenomena may be responsible for the deposition of gold (Kamilli and Ohmoto, 1977; Buchanan, 1981).

Therefore fluid inclusion geochemical data can be very useful

tool in the recognition of vertical or lateral salinity gradients within an ore-deposit or a mining district.

In spite of their limitations, fluid inclusion studies can help to the understanding of the processes that have been involved in the formation of many gold deposits and provided that they give interesting geochemical data at very low cost, the studies of fluid inclusions in minerals can be actually considered as a very useful tool in exploration for many types of gold deposits.

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## Ultra-Low Density Geochemical Mapping on the Canadian Prairie

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In 1991 two 1500 km orientation survey traverses were made across the Canadian Prairie, one roughly east-west (Winnipeg-Calgary) and one northwest-southeast (Edson/Edmonton-Winnipeg).  $A_p$  and C horizon soils were collected at sites randomly selected in 40 km traverse sections. One section in every 4 was selected at random and an additional site sampled, this sample was split and analyzed in duplicate. Mappable geochemical variations were detected using the ultra-low density sampling procedures and the analysis of the for many elements statistically significant variation was present between the means of 160 km sections.

In 1992 a systematic  $A_p$  and C horizon soil survey was undertaken across 850,000 km<sup>2</sup> of central North America. The majority of the sampling was undertaken in Alberta, Saskatchewan and Manitoba (735,000 km<sup>2</sup>). In cooperation with the U.S. Geological Survey an 80 km wide strip was also sampled immediately south of Canada in Minnesota, North Dakota and Montana (115,000 km<sup>2</sup>). The soils are dominantly Chernozemic and have developed for the most part on glacial tills and sediments. A stratified random sampling design was employed where 4 40x40 km cells were blocked into 80x80 km super-cells. Two sites in separate 20x20 km cells were randomly selected in 3 of the 40x40 km cells, in the randomly selected fourth cell an additional 3 sites were sampled. This design permits the variability of the data to be studied at the 40x40, 20x20, 10x10, within 10x10 km cell, and sample site and analysis levels.  $A_p$  samples were collected from 0-20 cm, and C horizon samples were collected from, on average, depths greater than 50 cm from a total of 1331 sites, at a density of no less than 2 sites per 1600 km<sup>2</sup>. After drying, the <2mm fraction of the soils was retained and a 50 g sub-sample ball milled. The total sample suite, with analytical duplicates and Control Reference materials, comprises 1447 samples. Aliquots of 88 USGS  $A_p$  horizon soils were included from their earlier surveys to facilitate data integration in support of IGCP Project 259 objectives. Instrumental Neutron Activation, Atomic Absorption Spectrophotometry (total decomposition), and x-ray Fluorescence techniques are being used to determine some 50 elements in the soils.

The upper level of this design, 80x80 km, conforms to one of the proposed IGCP 259 Sampling densities, and the computed cell means will correspond to a composite of between 8 and 11 randomly selected sites (the uncertainty is due to the hierarchical spatial design, i.e., multiple samples in a single 20x20 km cell).

Regional geochemical maps based on 80x80 km cell means arising from this survey will be presented, and the results discussed in terms of their relationship to geochemical and metallogenic provinces, and environmental considerations. The results will also be reviewed in order to assess the appropriateness of the IGCP 259 recommendations implemented.

**DIFFERENT-SCALE GEOCHEMICAL MAPPING OF THE ENDOGENIC  
GEOCHEMICAL FIELDS OF THE KARIISK ORE KNOT (EASTERN  
TRANSBAIKAL REGION)**

GNILUSHA V.A., SPIRIDONOV A.M.

The revealed pattern of the geochemical field distributions within the ore zone, genetic nature, analysis of the associated haloes enable the geochemical methods to be applied for the assessment of ore-bearing potential of the area and revealing the hidden mineralization. In this connection the geochemical mapping was done. As a result, the series of the monoelement and polyelement maps of different scales was compiled.

The considered region is located in the north-western segment of the chamber dome-like structure. The area is composed of the granitoids of different ages (from the Proterozoic to the Mesozoic), effusive rocks and the dykes from acid to basic compositions. The mineralization are veins and veinlet-disseminated zones.

The main productive mineral associations, containing gold, are the following (from early to late ones): quartz-pyrite-tourmaline, quartz-actinolite-magnetite and quartz-arsenopyrite. The analysis of the medium scale maps (1:200 000 - 1:100 000) indicates that the formation of the regional geochemical field is associated with the dome-like structure generation. The morphology of the geochemical fields results from the structural-tectonic features, while the element composition is due to the composition of the dispersed mineralization. Gold and the associated Bi, W, Ag, Cu, As, B, Pb, Mo and Zn form a weakly-contrast field. This field rounds the central granitoid massif (rigid structure core) and possesses the fan-shaped pattern of the structure, which is associated with the radial and concentric fractures, controlling mineralization.

The observed zonation results in the displacement of geochemical fields relative to each other and to the central intrusion on the whole and is determined by the influence of the thermal field. The alteration of the element association from the center to the peripheral parts indicates the regular change of high-temperature parageneses to medium-temperature ones and is represented by the series: (W, Mo, Cu)-(Bi, Ag, Pb, B)-(As, B, Au)-(Ag-Zn).

The geochemical mapping of large scales (1:50 000 - 1:25 000) indicates the complicated inner structure of the regional field, which involves the anomalies of different types. These anomalies are characterized in addition to high element concentrations by different element composition. They are formed due to the substance concentration and redistribution under mineralization. The high-contrast geochemical fields spatially coincide with the distribution of the main mineral associations, which correspond to the successive mineralization stages. They are marked by the spectrum of typomorphic elements with the determined contrast coefficients (CC\*): quartz-pyrite-tourmaline, quartz-actinolite-magnetite, quartz-arsenopyrite. The separation of the productive mineral associations within the ore knot, which are mainly distributed on the separate sites (deposits) results from the pulse-like

development of the common ore-bearing center.

The detailed geochemical mapping (1:10 000) enables the specific features of gold and the associated element distributions to be revealed within the deposits, ore-bearing locations and separate ore intervals. The distinguished pattern probably corresponds to the deposition zonation within one stage. The zonation is observed relative to the center of the corresponding mineralization and depends on the composition of the predominant one. Bi, W and Cu are located near the gold concentration fields, Ag and As are observed further and Pb, Zn occur in the peripheral parts. The similar pattern is evident vertically, as well.

Thus, the interpretation of data of different-scale geochemical surveys and the study of the element distribution features in the endogenic fields provide development of the geochemical model of the ore deposit formation, which may be applied for the assessment of the ore-bearing potential and forecast of gold mineralization.

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\* Contrast coefficient indicates ratio of the average element concentration in the paragenetic association to the background content.

## IS GOLD REALLY BEHAVING AS A NOBLE METAL IN SOILS ?

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The nature, mobility and dispersion of Au in soils is generally poorly understood, despite the extensive use of soil sampling in Au exploration. Selective extractions and incubations with iodide and water have been used to examine the chemistry of Au in two common soils in semi-arid, inland western Australia. The soils were (1) a calcareous, kaolinitic red clay, in which Au is strongly associated with pedogenic carbonate and (2) a ferruginous, lateritic soil with little carbonate, both were collected from the Bounty Au deposit.

Coarse (jaw-crushed) and fine (pulverized) soil samples were shaken with potassium iodide (0.1 M, pH 7.5) for 24 hours. Results showed:

- (i) in the Fe-rich soil, iodide extracted more Au from the fine samples,
- (ii) in the Ca-rich soil, iodide extracted more Au from the coarse samples,
- (iii) iodide was more effective in extracting Au from Ca-rich than the Fe-rich soil.

The results suggest that Au is more mobile in the Ca-rich than the Fe-rich soil, but when adsorption sites are exposed (e.g., by pulverizing), it may be readily immobilized.

Soil material was incubated in water for periods of up to 6 months following a series of treatments (saturation with CO<sub>2</sub> (so as to simulate root and microbial respiration), irradiation (to remove the effect of biological activity), inoculation of irradiated samples with untreated material (to test further the effect of biological activity). Untreated samples were used as controls. A duplicate set of samples was similarly treated but, in addition, were spiked with Au chloride solution. Results showed:

- (i) significant quantities of Au may be dissolved by water alone: 5-10 ppb was dissolved after one week and up to 140 ppb after six months. The results indicate the potentially rapid and high mobility of Au in these soils;
- (ii) considerably more Au was dissolved from irradiated samples, indicating that biological activity reduces Au mobility. Saturation with CO<sub>2</sub> strongly suppressed Au dissolution in samples containing more organic matter, possibly because it altered biological activity in the soil;
- (iii) Au dissolution was greatest from the Ca-rich samples for all treatments and increased with time even for non-irradiated samples, with little effect due to CO<sub>2</sub>;
- (iv) in non-irradiated treatments, added Au precipitated within one day for organic-rich samples and within one week for Ca-rich samples. However, after one week the Au began to re-dissolve. For irradiated treatments, added Au also precipitated, but dissolution was considerably slower, implying that biological activity is promoting redissolution.

The results suggest that biological activity is important in the long term dispersion of Au away from an ore body and indicate that the dispersion mechanism is likely to be complex and dependant on several factors, including the level of biological activity, time and soil type.

The high solubility of Au in the weak extractants indicates that it should not be considered as a "noble" metal in the soil environment. Indeed, Au may not be behaving as a metal ion at all, but be tightly bound to organically-derived molecules such as cyanide, thiosulphate or amino acids. Furthermore, adsorption sites and/or biological activity present in the soil may immobilize or otherwise influence the solubility of Au. Gold present in Ca-rich soils appears to be the most mobile yet paradoxically, Au accumulates in the pedogenic carbonate horizon. One explanation is that Au distribution is at least partially controlled by evapotranspirative processes. Thus, after rainfall, Au may be mobilized in upper soil horizons, with biologically generated ligands but, as it percolates down the soil profile, it is immobilized when water is gradually removed from the soil by vegetation in much the same manner as Ca itself. Thus, the primary controls on Au distribution in these soils are postulated to be biological and physical, rather than purely chemical.

This research was conducted as part of Project 241 of the Australian Mineral Industries Research Association. The sponsors of the Project are thanked for their financial support.



**CORRELATION OF ORE COMPOSITIONS AND THEIR PHYSICAL-CHEMICAL  
PARAMETERS, EXEMPLIFIED BY THE KOMMUNAR GOLD DEPOSIT  
(EASTERN SIBERIA)**

GREBENSCHIKOVA V.I., PROKOF'EV V.YU.

The Kommunar gold deposit is located in the central part of the Kuznetskii-Altai gold belt, stretching for about 200 km. The common term is usually applied for a series of the separate deposits, which are similar by ore-bearing structure or ore fields and represented by the veined bodies, stockworks and dykes, containing gold mineralization.

Three productive stages of mineralization are revealed: gold-quartz, gold-quartz-pyrite (pyrrhotite) and gold-quartz-tellurobismuth.

The more productive gold-quartz mineralization is spatially and genetically associated with the Riphean tholeiitic basalts with low chrome contents and comagmatic gabbro-diabases. The ore bodies are stockwork zones. The host rocks, distributed near the ore bodies, are weakly altered (actinolite, albite). High Au/Ag values ( $>10$ ), low Te, Se concentrations (Fig.1) as well as other elements are common to the ores of this type. It differs these ores from the ores of other types, distributed in ore field.

The analysis of separate fluid inclusions (primary and primary-secondary) in the quartz from gold deposits was carried out using thermo- and cryometric methods. The obtained data indicate that the gold-quartz ores were crystallized from chloride magnesium-sodium solutions with salt concentrations up to 12-14.5 mas% equal to NaCl. High  $\text{CO}_2$  concentrations (up to 5.6 mol/kg of the solution) and low  $\text{CH}_4$  contents (0.3 mol/kg) and maximum  $\text{CO}_2/\text{CH}_4$  values are observed (Fig.2). The temperature range of mineralization is  $340-310^\circ\text{C}$ , pressure - 3.5-16 kbar.

The majority of the deposits within the ore field are ore veins with gold-quartz-sulfide (pyrite, pyrrhotite) association. Fresh actinolite, chlorite, epidote, albite, quartz, pyrite, carbonate are observed in the near-ore altered rocks (basalts, gabbro-diabases, schists). The low Au/Ag ( $<10$ ) and increased Te/Se ( $>0.1$ ) values are typical of these ores. The concentration increase of a number of elements (Cu, Zn, Ag, As, S), which are mainly concentrated in the sulfide minerals (pyrite, pyrrhotite, chalcopyrite), is evident. The homogenization temperature of ore quartz decreases to  $310-210^\circ\text{C}$ , while pressure decreases up to 1.9-1.1 kbar.  $\text{CH}_4$  is more significant as opposed to  $\text{CO}_2$  in the gaseous component.

Quartz-chalcopyrite-tellurium-bismuth mineralization is not typical of the Kommunar ore field, but it is common to other deposits of this region. The increased sulfide concentrations in the ore bodies, beresite occurrences, distribution within the zones of the rock increased permeability, spatial and genetic association with the granitoid batholiths of the andesite type are characteristic of these deposits. As compared to the above deposits, Au/Ag values are equal to 1 and Te, Bi, Sb, Ag, Cu concentrations increase. The supplementary deep source of the hydrothermal fluids is supposed.

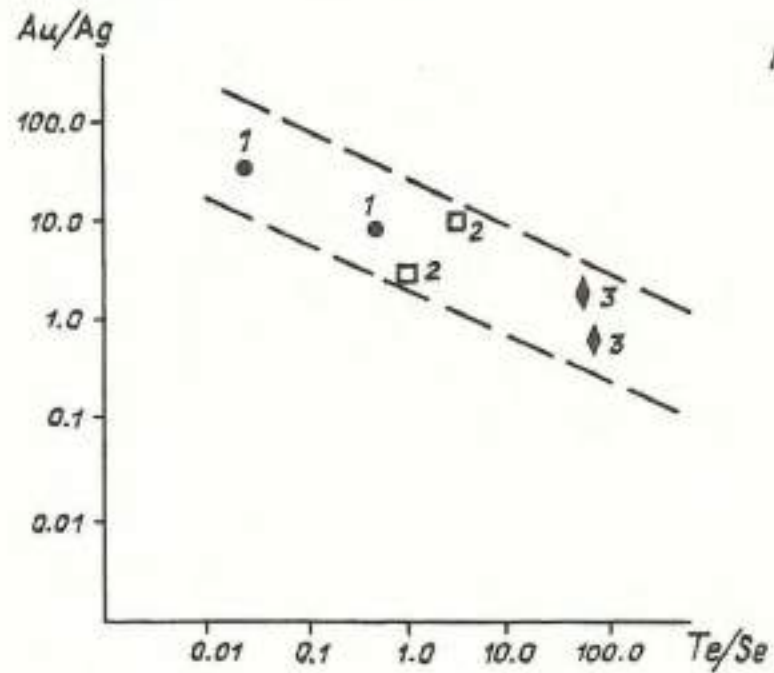


Fig. 1. Au/Ag and Te/Se correlation in ores from the Kommunar deposit

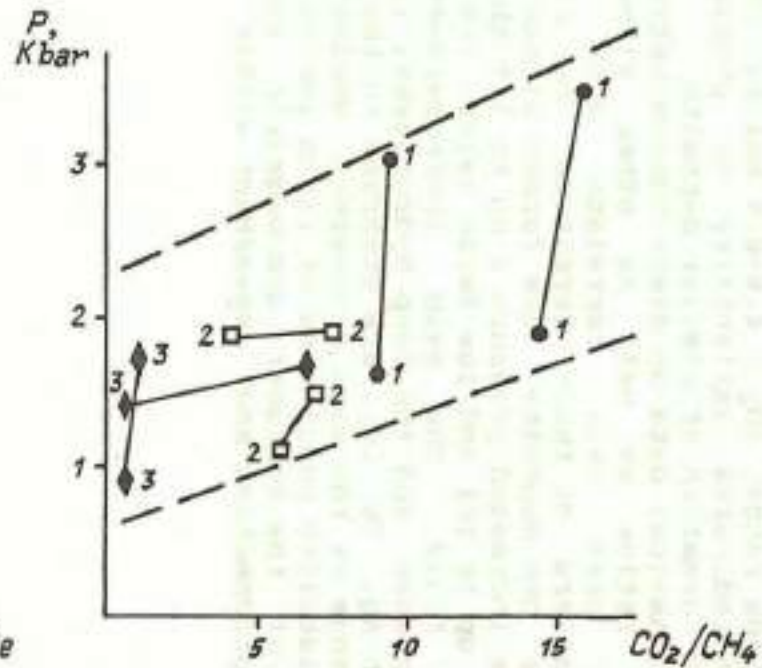


Fig. 2. CO<sub>2</sub>/CH<sub>4</sub> and P correlation under formation of ore quartz on the Kommunar deposit

The fluid inclusion investigations indicate low fluid pressure (1.7-0.9 kbar) as well as low solution density under fluid formation. The homogenization temperature of fluids is stable, equal to 330-310°C. The dissolved gas contents vary in a wide range: CO<sub>2</sub> = 4.6-0.6 mol/kg, CH<sub>4</sub> - 2.5-0.7 mol/kg, which indicates variability of physical-chemical setting under formation of similar deposits.

The obtained geochemical data on distribution patterns of Au/Ag and Te/Se ratios as well as other element-satellites in gold ores well correlate with the thermobarometric parameters of their formation. The high-temperature productive ore deposits were formed within the early stage under the increased pressure ( up to 3.5 kbar), high CO<sub>2</sub>/CH<sub>4</sub> values ( up to 16) and low Te/Se values (<0.01) in the ore-bearing fluid. The main thermobarometric parameters (T, P) decrease and the deep hydrothermal fluid supply, enriched with Ag, Te, CH<sub>4</sub>, are observed to the end of ore stage. Wide range of the main parameters variations is connected with variability conditions of fluid inclusion. The revealed pattern of the Kommunar ore-magmatic system development enables prospecting and assessment within the ore regions.

## GEOLOGICAL-GEOCHEMICAL FEATURES OF THE ZUN-KHOLBA GOLD DEPOSIT

GREBENSCHIKOVA V.I., SHMOTOV A.P.

The Zun-Kholba gold deposit is one of the deposits within 100 kilometer gold zone in the south-eastern part of the Eastern Sayan. This gold location is spatially confined to the ophiolite belt, which is controlled by the deep fractures (Dobretsov et al., 1989; Feofilaktov, 1992).

The Zun-Kholba deposit is located within the rocks of the Riphean layer, occurring between the Archean granite-gneiss block (polymetamorphic rocks of the plagioplerogneiss formation) and the Paleozoic granitoid batholith. The country rocks are diverse by composition and age: amphibolites, gneisses, plerogneisses and granite-gneisses of the Archean age, the Proterozoic carbonate-terrigenous rocks ( marbled limestones with the "coal schist" layers, quartzites), the Riphean ultrabasites and the Paleozoic granitoids. The near ore metasomatites occur within the above rocks and refer to different mineral associations of the beresite-listvenite formation. The connection of ore bodies with cleavage fractures and rupture zones, surrounding the deep fractures, results in blastomylonite and mylonite structure of the metasomatites. The intensive cataclasis is common to the rocks of the ore field (Shmotov, 1977).

The ore bodies are steeply dipping veins and mineralized zones of gold-sulfide formation. The age of ore bodies is estimated to be 1700-400 Ma. but it should be refined. The ore bodies are composed of quartz, carbonate, pyrite, galenite, sphalerite, tellurides, molybdenite and tourmaline.

The reverse correlation is observed between the concentrations of gold in the rocks and those in the metasomatites (Fig.1). It, probably, results from different physical-mechanic properties of the rocks. The rocks, primarily enriched with gold (ultrabasites, amphibolites, gneiss-granites), are intensively metasomatically altered on the contacts with ore bodies (serpentinites, serpentinite-talc-chlorite-carbonate metasomatites). As a result of it, gold is removed and enriches hydrothermal fluids. On the other hand, carbonate rocks and schists, originally containing gold in lesser concentrations, are enriched with carbon during the near-ore metasomatism, resulting from the deep hydrothermal fluids, and become good gold concentrators on the ore stage (Fig.1). High gold concentrations ( up to 4 ppm) in such metasomatites significantly increase ore reserves.

The increased Bi ( up to 80 ppm), Sb ( up to 30 ppm), Pb (up to n%), Te ( up to 40 ppm) concentrations, which are in accordance with the mineral associations, are observed in the ore bodies of the Zun-Kholba deposit. Au/Ag and Te/Se ratios are > 1. According to geochemical classification of gold deposits (Grebenschikova, 1990; Troshin, Grebenschikova, 1991), the considered deposit refers to gold-tellurium type, which is typical of the locations with the widely spread magmatism of femic type and deep fractures. On the triangle classification S-Se-Te diagram

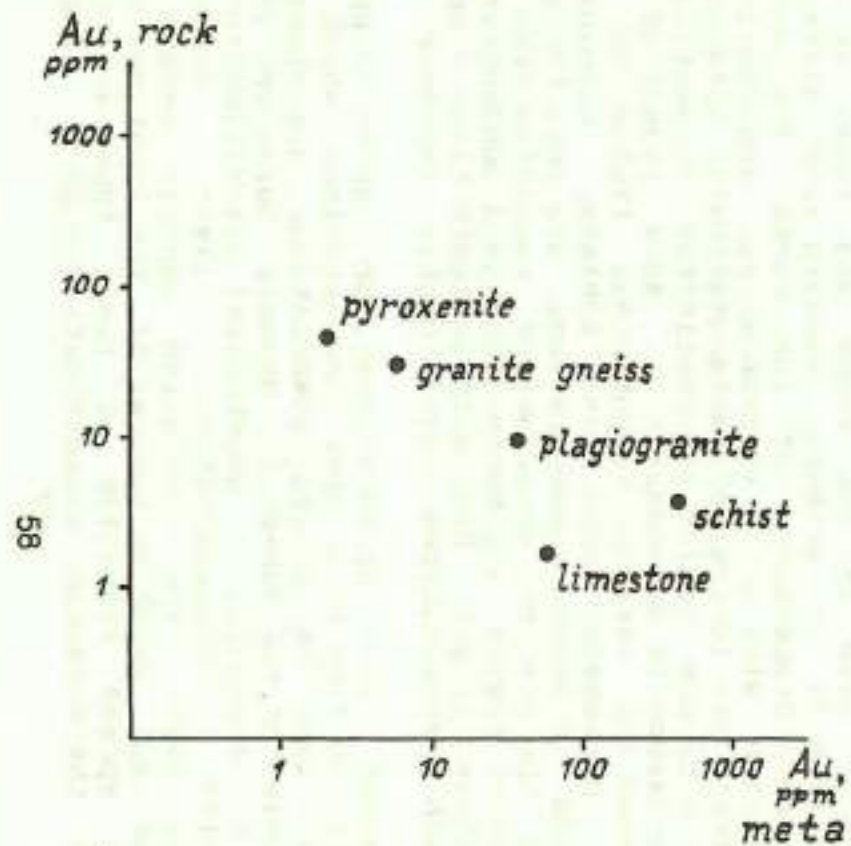


Fig.1. Correlation of gold concentrations in fresh rocks and metasomatites of the Zun-Kholba ore field.

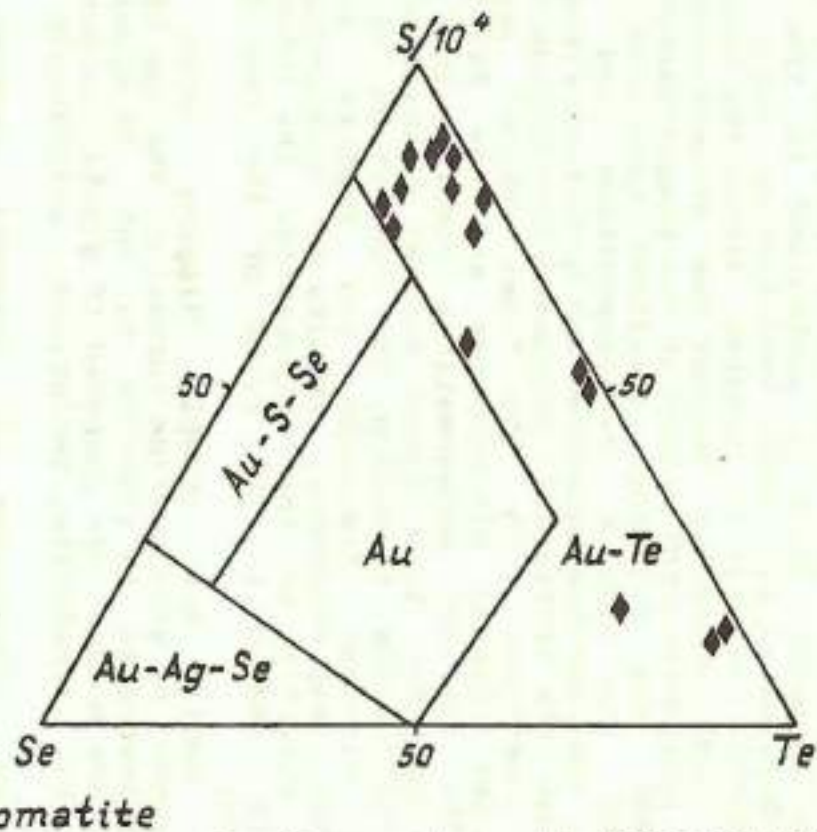


Fig.2. S-Se-Te diagram for some Siberian gold deposits. Rhombes indicate composition of ores from the Zun-Kholba deposit.

(Fig.2) the points of the compositions of the Zun-Kholba ores are close to Te-S side, distributing regularly. The deposits of such geochemical type are available in the Urals, Kuznetsky Alatau and other locations.

In addition to the above elements, the increased Ni (up to 200 ppm), Cr (up to 40 ppm) and Co (up to 50 ppm) concentrations are observed in the ore bodies of the Zun-Kholba deposit. The platinoids and chrome are observed in the gold nugget from the ore bodies (Dobretsov et al., 1989). These data indicate the influence of the rocks from the ophiolite belt on the ore process features. The reliable information on spatial and genetic association between mineralization and ultrabasites can be obtained via detailed geochemical investigations.

## GEOCHEMICAL MAPS OVER FINLAND AND SWEDEN

GUSTAVSSON, N., LAMPIO, E., NILSSON, B., NORBLAD, G., ROS, F. and SALMINEN, R.

Finland and Sweden belong to the same geological unit: The Fennoscandian Shield. The glaciological history has been the same in both countries: during the Weichselian Ice Age the whole area was covered by a till blanket. Most of the till blanket was derived from unweathered or only slightly chemically weathered bedrock. In this respect an exception makes the northernmost part of Finland, where the ice divide was situated and where the glacial erosion was therefore weaker.

Regional geochemical mapping programmes were carried out independently in Finland and Sweden during the 1980's using the same field methods and analytical procedures. Altogether 83 400 samples were collected using sampling densities 1 sample/4 km<sup>2</sup> - 1 sample/16 km<sup>2</sup>. The primary data sets consist of analytical results after aqua regia leaching of the finest fraction of till. The data sets from the two countries were put together and a common data set was compiled. The results from 14 elements (Al, Au, Ba, Ca, Co, Cu, Fe, K, Mg, Mn, Ni, P, Ti, and Zn) were accepted for this presentation. Map production methods developed at the Geological Survey of Finland were applied and shaded coloured surface maps were produced from the common data set.

The raw data were adjusted within both countries to avoid undesired effects and patterns caused by analytical fluctuations between batches. The corrections were based on data from regional transition zones along known or visually detected borders of batches. No attempts were made to adjust the large data sets to match the same level along the common border. Discordance across the border was visually inspected from dot maps of data covering a zone along the border. Most elements did not show any artificial discordance and could be treated uniformly on the final maps. Elements, which showed an apparently unnatural step across the border, were treated separately for both countries and are jointly presented on the same map.

The data were smoothed and interpolated to yield a regular grid with a distance of 1 km between adjacent points. The smoothing was based on the moving weighted median, (Björklund and Lummaa, 1983), computed within circular windows centered at the grid points. The window radius, 20 km, was constant over the whole area and for all elements. Each data point was assigned a weight according to its distance from the window centre. The bell-shaped weight function of Butterworth type, (Gonzales and Winz, 1987), was used. The smoother outlook of the surfaces on the Finnish side is due to a higher point density.

The compilation of the maps shows that combining of two independently created geochemical mapping data – in spite of same kind of field and laboratory methods applied – is not without problems. All analyzed elements could not be used in the compilation of maps because of different concentration levels due to very small differences in used procedures.

The tectono-stratigraphic features of the bedrock are the strongest control of geochemical anomaly patterns. This is seen especially clearly in the major anomaly

patterns of the lithophilic elements. Good examples of this correspondence are the Ladoga-Bothnian Bay zone and the Skellefte field, which both are connected with the boundaries of some major tectonostratigraphic units described by Gaál and Gorbatshev (1987), for example.

It is remarkable, that most of the main large lithological units do not coincide with the till geochemical anomaly patterns. The strong Ladoga-Bothnian Bay geochemical anomaly zone in Finland continues from the area of Proterozoic schists without any disruption over the contact to the area of Archaean granitoids. Only some Palaeozoic sedimentary rocks cause anomaly patterns, which differ distinctly from the surroundings: there are smaller sandstone areas in Finland showing very low heavy metal concentrations and limestone areas in Sweden showing exceptionally high Ca-concentrations.

These maps seem most useful for delineating target areas for gold. All known gold fields in Finland are situated in the areas of gold anomaly patterns. The situation is the same in Sweden, where the known gold ores cause nice anomalies. Single small mineralizations of vein type situated outside the anomaly zones cannot be detected in this scale and by this kind of mapping. Very remarkable is the gold anomaly zone (600 km), which continues from SW-Finland to northwest in Sweden. In this zone economical gold deposits were recently discovered in Sweden as well as new showings of possibly economic gold deposits in Finland.

The maps of the larger area (together 470 000 km<sup>2</sup>) shows the relations of anomaly patterns better than those of each country alone. The geochemical features are easier to understand and the maps are believed to be an excellent material for preliminary planning of exploration operations.

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## MULTI-PURPOSE GEOCHEMICAL MAPPING OF BOTTOM SEDIMENTS OF LAKE BAIKAL

GVOZDKOV A.N., WILLIAMS D.F., KARABANOV E.B., PAMPURA V.D

Bottom sediments of water reservoirs reflect the geochemical situation not only in the water reservoir itself but also on its watershed area. In addition, a sequence of correlative horizons characterizes the variability of geocological parameters in space and time.

Multi-purpose geochemical mapping is achieved by a rational use of analytical methods and determination of a wide spectrum of chemical, physical and biological parameters of bottom sediments.

Modern cartographic techniques can then be applied for studies of bottom sediments to provide both a visual and digital pattern of the spatial distribution of the present environment parameters and to perform the respective of older geosystems.

In the period from 1989 to 1992, surface bottom sediments were sampled at 120 stations on Lake Baikal to measure major and trace elements, ratios of stable carbon and nitrogen isotopes, and the content of some biogenic phases (biogenic silica, organic carbon and organic nitrogen). Cores of some stations were studied by radioisotope methods (Pb-210, C-14 and Cs-137) to define recent sedimentation rates.

These maps contain estimates of background geochemical parameters and demonstrate the geochemical classifications, geochemical and biochemical zonations of bottom landscapes of different hierarchic levels, including regions of antropogenic pollution.

Combination of some analytical maps resulted in synthetical geochemical maps reflecting the chemical and phase compositions of bottom sediments, the mechanism of their formation, and the intensity and character of sedimentations processes. This synthesis may be considered as a static model of the recent sedimentations in Lake Baikal. In addition this map may be used to create forecast, retrospective and scenery maps as well as for environmental paleoreconstructions and to establish the model of sedimentation on Lake Baikal.

Analysis of available geochemical data suggests the following conclusions:

1. Though morphologically divided into three depressions, Lake Baikal is a single basin of terrigenous-biogenic sedimentation with different rates of biogenic sedimentation in different basins with a similar composition of the terrigenous component of pelagic sediments. This is explained by a similarity of physico-geographic conditions, climate included, over the grater part of the watershed area.

2. Estimation of the trophic level of the three lake basins based on petrochemical data is the evidence of similar oligotrophic conditions at a somewhat higher trophic level of the northern basin.

## ULTRATRACE WATER ANALYSIS - A NEW FRONTIER IN GEOCHEMISTRY

GWENDY E.M. HALL

In the past several years the Analytical Method Development Section at the Geological Survey of Canada has been active in both designing and applying methodologies to determine, precisely and accurately, trace elements in surface waters at their 'natural' ppb and ppt ( $\text{ng l}^{-1}$ ) levels. Analysis is divided into 'packages' of compatible elements, all based on the technique of inductively coupled plasma mass spectrometry (ICP-MS) but grouped according to different pretreatments and sample introduction mechanisms. Detection limits as low as 1-2 ppt are achieved, for the rare earth (REE) and first row transition elements as well as for Pb and Cd, by fully automated preconcentration using a chelating resin and nebulization into an ICP mass spectrometer. The elements As, Sb, Se, Te and Bi are determined by flow injection hydride generation ICP-MS where potential interferences are removed by separation of the gaseous analyte from its liquid matrix. Speciation studies to quantify the amounts of element bound to organic ligands and present as free inorganic ions in different valency states are in progress. Both chemical and UV irradiation oxidation methods to liberate organically bound elements are under examination.

These methods are described in this poster together with the results of hydrogeochemical surveys conducted in the Baie Verte and Baie d'Espoir regions of Newfoundland Canada. Two objectives of these surveys are to: (1) establish a database of elemental concentrations in stream and lake waters largely unaffected by anthropogenic input, particularly for parameters (e.g., REEs) hitherto unmeasured due to analytical limitations; and (2) ascertain the factors (e.g., underlying geology, till cover, bulk water composition, sediment character) controlling the distribution of these elements in solute form. Terbium (and other REEs), for example, in the lakes of the Baie d'Espoir region delineates the bedrock geology clearly, even at the low and narrow range of 1-20 ppt. Subtle though definite anomalies in such gold pathfinder elements as Te and Bi are seen in streams collected in areas of high gold potential in Baie Verte. Daily variations in trace element composition of fast flowing streams have been found to be minimal, while spatial variation *within* a slow moving stream can be significant. These findings and considerations of sample preservation and in-lab contamination are discussed in this poster.

## THE DIAGNOSTIC CAPABILITIES OF SELECTIVE LEACHES IN ANOMALY RECOGNITION

HALL, G.E.M. AND KASZYCKI, C.

Interest in the use of selective extractions in exploration geochemistry was rekindled several years ago in Canada when a joint venture was formed between Scintrex (Concord, Ont.) and Rudgeofizika of the former USSR in order to demonstrate their 'geochemical' methods over different types of mineralisation in Ontario. Two of these methods are essentially selective leaches for (1) metals bound as humate and fulvate complexes in humus, and (2) metals adsorbed by the highly scavenging properties of amorphous Fe and Mn oxides and hydroxides present in soils and tills. The geochemical pattern thus obtained would then reflect that portion of element which had been present in a relatively labile (free ion) state as a result of secondary dispersion, as distinguished from that portion bound in insoluble organic matter (humus), sulphides, carbonates, crystalline oxides, refractory minerals, etc. The Analytical Method Development Section at the Geological Survey of Canada has refined these two leaches, based on the displacement properties of pyrophosphate (for soluble organics) and the reducing action of hydroxylamine hydrochloride (to liberate Fe/Mn oxyhydroxides), and has continued to develop a sequential procedure to also identify those metals/metalloids held in the following phases: (1) carbonate/exchangeable/adsorbed; (2) crystalline Fe oxides; (3) sulphides and 'insoluble' organics; and (4) silicates. It must be borne in mind that the results obtained are 'operationally defined', that is their accuracy and precision depends on the rigors of the experimental conditions applied; classifications used in describing the phases must accordingly be somewhat general.

This poster describes these leaches and demonstrates their diagnostic usefulness in their application to humus, soil and till collected at the Chisel Lake mine (Zn-Cu mineralisation) in northern Manitoba, Canada. At a spacing of ca. 200 m, samples of humus, B-horizon glacial till (soil) and C-horizon glacial till (parent material) were taken at each site. Sequential extraction (five phases) was carried out on both the -80 mesh and 2 $\mu$ m fraction of soil and till and on the -80 mesh fraction of humus (six phases). Samples of C-horizon till reflect primary mechanical erosion and transport of mineralised bedrock. B-horizon till samples have been subjected to secondary chemical processes in the near surface environment and, as a result, may be depleted or enriched in metals relative to the C-horizon, depending on site specific weathering mechanisms. Humus reflects a combination of surficial geochemical, biogeochemical and atmospheric processes. At each site, the distribution of metals bound in various phases for each of the three sediment types was compared and interpreted with respect to location and type. Based on these observations, distinct geochemical signatures have been identified for anomalies created by glacial dispersal, hydromorphic/biogenic dispersion and surface contamination.

**GEOCHEMICAL PROSPECTING FOR GOLD IN THE EL SUKARI GOLD  
MINE, EASTERN DESERT, EGYPT**

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**ABSTRACT**

El Sukari gold lode is housed along fractures in a granite and metavolcanic-metasedimentary rocks, being largely controlled by a NE-SW trending fracture systems that affected the Eastern Desert. During these deformational events, faulting seems to have resulted in hydraulic fracturing. These hydraulic fractures have acted as favourable sites of localizing the gold-bearing quartz veins.

Primary dispersion haloes of Au, Ag, S, As, Hg, Cu, Mo, Zn, Pb, Sn, Be, Ni, Co and Ba were studied in the El Sukari gold mine area, Eastern Desert of Egypt. The study is based on 187 bedrock and 78 quartz vein samples, collected along twelve traverses across the mineralized zones, where Au-bearing quartz veins occur at the southwestern contact between a granitic body and the metavolcanic-metasediments. Anomalous gold in the surface samples is mostly observed over the shear zones containing quartz-carbonate-chlorite materials, or within albitized granite in the eastern part of the granitic body. Gold-content varied over a wide range (< 0.01-27 ppm). The results showed that S, Ag, Cu and Zn form relatively wide primary haloes on the surface, reflecting their usefulness as pathfinders in determining the extent of Au-concentration in primary haloes that influenced by superficial processes, in the eastern Egypt.

To study the variation of trace element contents with depth, 95 samples were collected from underground working at the El Sukari gold mine. The distribution of Au and Ag exhibited a high concentration in the lateral as compared with the vertical directions. Gold contents as high as 179 ppm were obtained from the quartz vein samples. In addition the Au-content range was high (5.8 and 20 ppm) in some of the altered granitic host rock samples collected from level I and shaft no.A.1, although values sharply decreased with depth. Thus, exploration activity should extend to quartz vein and wallrock alteration materials enriched by Au and Ag, instead of being restricted to the quartz vein material alone.

# Zinc Distribution Model in Wallrocks of Emarat Pb-Zn Mine and Potential Applicability in Local Exploration

by

*Ali.A.Hassani Pak\**

## Abstract

The Emarat Pb-Zn mine is located at about 50 miles south of the city of Arak , Iran . This Pb-Zn ore deposit has been classified as a lower-Cretaceous stratiform deposit . Thick bedded silicified limestone and yellowish limestone with shale and abundant of calcite veins make the footwall and hanging wall of the ore body respectively . Some evidence of recrystallization occur all over the area of study.

In the present mine-scale lithogeochemical survey 56 hanging wall samples and 37 footwall samples were taken from exploratory tunnels, drillholes and open pit. All samples were taken in the range of 0-40m from ore layer . The samples were analyzed only for Pb and Zn content . After statistical treatment of the obtained data, the relationship between three variables including concentrations of Pb and Zn in wallrock , distance from , and thickness of ore layer were investigated by plotting two sorts of scatter diagrams : (a) Plotting concentration versus distance for each sample while the thickness is constant; (b) Plotting thickness versus distance for each sample while the concentration is constant.

The Zn distribution model in footwall and hangingwall show the same trend , with about four times higher concentrations in footwall . The Zn distribution model curves ranging from 300 to 600 PPM shows a potential applicability in local-scale exploration while the Pb distribution model curves due to irregularity and lack of enough ordering is useless for such a purpose . By measuring Zn content in enough wallrock samples along the same path in tunnels or drillholes , and using the established Zn distribution model in the wallrocks , one can predict the distance from vein and the thickness of it.

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Regional-Scale Lithochemical Survey in Alvand Plutonic  
Complex, Hamedan, Iran

by

*Ali.A.Hassani Pak\**

Abstract

The Alvand plutonic complex located in middle west part of Iran, just south of Hamedan. It is also one of the plutonic complex which has been emplaced east of Zagross Range. The evaluation of ore-bearing potential or productivity of this complex and genetic relation to possible mineralization were the main aims of the present study. Granitic rocks and associated pegmatites are among the most frequent intrusive rock types in this complex.

Twenty eight pegmatite samples and fourteen granitic samples were taken and analyzed for 10 major elements and 13 trace elements including B, Ba, Co, Cr, Cu, Ga, La, Pb, Sc, Sr, V, Y and Li. Statistical analyses of single and multi-elements variables such as  $Li, Mg/Li, Na_2O/SiO_2, FeO(\text{total})+MgO+MnO+TiO_2$  were performed. Also relative comparison of the value of the above mentioned variables with those of barren and productive plutonic complexes were carried out. The results indicate that Alvand plutonic complex could be considered as a productive one.

To determine the genetic classification of these granitic rocks  $A_1 = (Na_2O/SiO_2)1000$ ,  $A_2 = FeO(\text{total})+MgO+MnO+TiO_2$  diagram was plotted. Eleven out of fourteen samples indicate the presence of I-type granitic rocks and only three samples were consistent with S-type granite.

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## **GEOCHEMICAL EXPLORATION FOR BASE METAL AND GOLD MINERALIZATION IN LOEI REGION, NE THAILAND**

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Loei region, NE Thailand, is well known as one of the most interesting area for base metal and gold mineralization. Series of geochemical exploration programs had begun in the Loei region since 1979 by Geochemical Exploration Section, Economic Geology Division, Department of Mineral Resources, covering the area of more than 8,300 sq km. The Loei region is underlain geologically by sedimentary and low grade metamorphic rocks of Palaeozoic age which were injected by Permian-Triassic volcanic and granitic rocks.

The stream sediment geochemical survey was undertaken in nine sub-areas and a total of 11,688 active stream sediments were collected using 200-500 m sample intervals. In addition, field panning survey for gold was carried out during the program.

The geochemical distribution patterns of Cu, Pb, Zn, Sb, and As show the anomalous patterns related to several base metal and gold prospects. The presence of visible gold grains in field panned concentrates are widespread and lead to the discovery of many primary gold occurrences.

The overall results of the geochemical exploration program in the Loei region indicated that a) geochemical anomalous patterns in stream sediments related to 12 copper, 22 lead, 4 zinc, 1 antimony, 29 barite and 6 primary gold occurrences, b) stream sediment geochemical survey in Loei region is very effective for base metal and gold exploration. Consequently, four special prospecting license areas (covering area of 2,400 sq km) were granted to private sectors for evaluation of these gold and base metal prospects.

## HUMUS AS A MEDIUM FOR LOW-DENSITY SAMPLING

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Various types of geochemical media were sampled from 49 large catchment basins in Finland, Sweden and Norway as a pilot study within IGCP Project 259 "International Geochemical Mapping", which averages one basin per 23 000 km<sup>2</sup>. A total of 523 humus samples were collected, ashed, leached in hot Aqua Regia for 1 h and analysed for 30 elements by ICP. The contents of the chemical elements were expressed on the dry weight basis and the median contents for each basin were plotted on maps. An attempt was made to correlate the chemical features of the humus-layer with geological factors and atmospheric deposition revealed by moss analyses.

High contents of Ca and Sr are closely related to the occurrence of limestones and dolomites. The low contents of Ca in humus from southern Sweden and Norway may be a result of leaching caused by acid rain. Chromium contents display a regional pattern that can be related to anthropogenic as well as natural sources. High concentrations were found mainly in the northern parts of Finland, where some of the basins receive anthropogenic Cr well reflected by contents in moss analyses whereas in other basins high concentrations reflect anomalous Cr in the underlying bedrock and till. Of the analysed elements Cr has the highest correlation between humus and till ( $r=0.48$ ).

Contents of Pb, Bi, Cd, As and Sb are all highly elevated in the southern parts of the countries, especially in Sweden and Norway. The anomalous patterns follow those of moss analyses and are therefore considered as anthropogenic. The source may be deposition due to long-range transport as well as pollution caused by a high population density in the area. The pattern of the contents of V coincides partly with that of moss analyses and may therefore to some extent be of anthropogenic origin. Zinc acts as a micronutrient and therefore it also reflects uptake by plants and internal cycling in the ecosystems to a certain degree which may explain the somewhat unclear pattern of this metal. This is also true for the Cu contents, which form no clearly defined patterns.

Concentrations of Na and Mg are high in Norway probably as a result of windblown sea salts from the Atlantic Ocean. The pattern of B seems to reflect both anthropogenic and sea salt deposition.

The distribution of the P and Al contents does not display features that could be explained by factors such as the geochemistry of till and bedrock. The low concentrations found throughout the southern part of the area might suggest leaching resulting from acid rain.

High contents of Ag are found in the southern and middle parts of Norway and in the middle and northern parts of Sweden, whereas high contents of Mn occur in southern Sweden. No explanation for the areal distribution of the contents of these and a number of other metals (e.g. Ba, Ni, Th and Ti) has so far been found.

The geochemistry of the humus horizon was found to reflect environmental changes, even at the very low sampling density used and may even reflect deposition of various elements which took place many years ago. Humus is an essential part of the ecosystems and it does not add much to the costs of geochemical surveys because it is easy to sample. Therefore this material should be included in multimedia surveys at low sampling densities.



GEOCHEMISTRY OF A SEDIMENT CORE AND APPLICATIONS OF CLUSTER ANALYSIS IN INTERPRETING DATA

KARHASSI, A. R.

Elemental concentrations (Cu, Zn, Pb, Ni, Co, Mn, Fe, Al and Ca), Loss On Ignition (LOI) and Magnetic Susceptibility (Xm) of a sediment core (GC-1) from West Coast of India were determined. Dendrogram of geochemical and physical parameters of core GC-1 was drawn through Weighted Pair Group method of cluster analysis (Fig. 1).

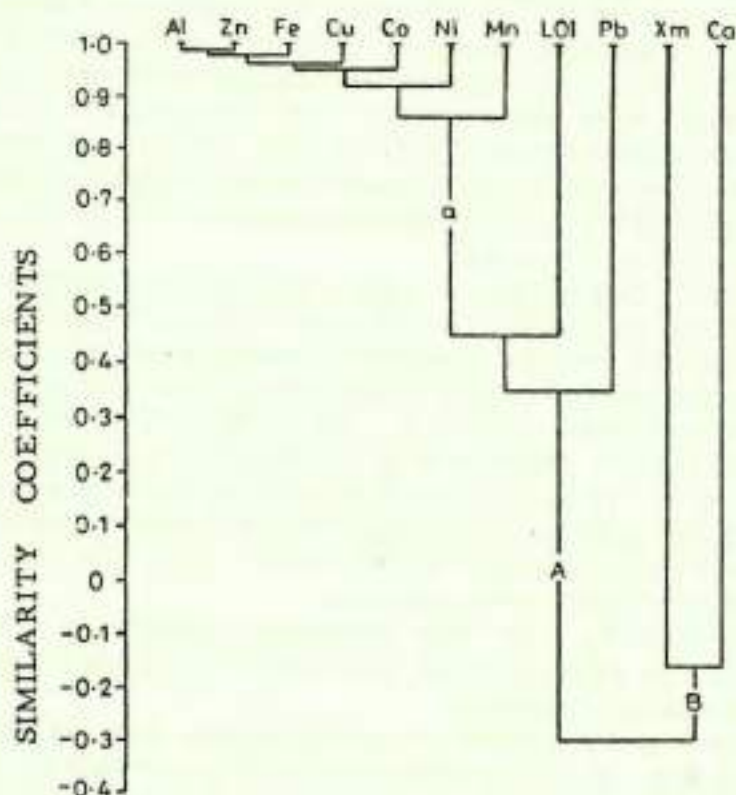


Fig. 1 DENDROGRAM OF GEOCHEMICAL AND PHYSICAL PARAMETERS OF SEDIMENT CORE GC-1.

Aluminium, Cu, Zn, Fe, Co, Ni and Mn cluster at very high similarity coefficients (>0.86) indicating that these elements have a principally lithogenous source. Compared to the high similarity coefficient for subcluster "a", LOI and Pb join at low similarity coefficients of 0.45 and 0.35 to form cluster "A". Therefore, organic matter does not significantly contribute base elements, nor does calcareous shells.

Magnetic susceptibility ( $\chi_m$ ) and Ca form cluster "B" at a negative similarity coefficient of -0.16. The two cluster join at an even more negative similarity coefficient of -0.30. Magnetic minerals do not appear to be derived from detrital sources.

Down-core variations of the parameters studied are controlled by the sediment type: Sandy silt (top 10 Cm) has lower elemental contents (except Pb and Ca) compared to clayey sediments in the rest of the core. The abundant shell fragments at 72 Cm depth are suggestive of a shell pavement/lag deposit.

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## SHALLOW GOLD DEPOSIT FEATURES AND THEIR PROSPECTING IN THE INTERMONTANE DEPRESSIONS

KITAEV N.A.

1. Gold mineralization in the zones of the Mesozoic tectonic-magmatic reactivation ( the Mongol-Okhotsk belt) is subdivided into three formations according to the depth i.e. middle-depth formations (Lyubavinsky), subvolcanic (Darasun, Ilinsk) and near-surface (Baleisky) ones. Each formation is located according to the main structural elements of gold-bearing belts and their erosion shear. The near-surface deposits are structurally associated with the intermontane depressions.

2. The rich gold deposits of the Baleisky type are mainly observed in the depressions. However, the prospecting of such deposits is very difficult, as these deposits are hidden and overlapped by the recent loose sediments. The geochemical methods were not applied as the prospecting from stream sediments was considered to be not efficient. The small-scale geochemical survey from the stream sediments of the solid (fine fraction) and liquid phases is appropriate to distinguish depressions and to discriminate the metallogenic types, using the statistical parameters of ore and rare element distributions. The inner pattern of the given structures is exemplified by the Undin-Dain depression with the near surface deposits.

3. The lateral zonation of the ore region is evident from the geochemical survey of the depression at 1:50 000 scale. It involves the successive changing of the major element associations with the displacement to the subsiding region part and decrease of deposit formation depth ( from the deposits, formed at the median depth, to near surface ones) in the following order:  $W_{5-40}Be_{5-10}Mo_{3-5}Au_{5-20}$  ---  $Au_{15-1000}As_{5-150}Ag_{10-30}B_{5-10}Bi_{3-5}Te$  ---  $Ag_{5-40}Au_{3-30}As_{5-10}BiPb_{2-3}$  ---  $Au_{15-300}Ag_{5-10}AsSb_{3-5}$  ( The numbers indicate average contrast coefficients of the elements i.e. ratio of element average concentration to the background content)

The data unite all facies types of mineralization into the common ore series and connect this series not with the certain intrusive bodies, but with the zonation features.

4. The near surface deposits are diverse by structure and composition as well as by the type of association with the volcanic structures. The structure of ore fields is exemplified by the Balei and Nizhneangarsk deposits, as the common features as well as the differences of the geological-structural, morphological, mineralogical and geochemical features are evident here. The patterns of the deposit primary haloes and ore fields ( qualitative and quantitative compositions, morphology, zoning) are presented. The total pattern of the substance differentiation on the deposits of near-surface formation and the summarized vertical zonation of the metasomatic column are considered.

5. The recognized geological-geochemical specific features of the deposits, zonation of the ore fields and ore regions in the intermontane depressions allow the revealing of the criteria of near-surface deposit prospecting:

metallogenic ( to distinguish depressions and to reveal the formation); structural (relations of mineralization structures of all ore zones); magmatic (polycycle pattern of ore-magmatic system development); geophysical ( gravitation and magnetic anomalies); mineralogical ( occurrence of mineralization zone and quartz near-surface formations); geochemical (formation relation of geochemical anomalies, qualitative alteration of element associations and quantitative composition, ore element ratio  $Ag/Au$ ,  $(As + Sb) / Au$ ,  $As/Ag$  as well as zonation of dispersion haloes of ore region, ore fields and deposits).

## MICROORGANISM PARTICIPATION IN GOLD TRANSFORMATION ON THE DEPOSITS AND GOLD EXTRACTION PROCEDURES

KOROBUSHKINA E.D.

The obtained data change the concept of gold migration in the hypergenesis zone of gold and placer deposits. The pattern of hypergene gold migration on gold-sulfide deposits and its concentration in the secondary gold subzone and in the zone of gold-sulfide enrichment, considering the microorganism geochemical activity, is represented for the first time. In the ecological niches of hypergene sulfides, microorganism biomass (sulfate-recovery bacteria, microscopic fungi, yeast, organotrophic bacteria) contains up to 70-120 ppm of gold. Biomass of ironbacteria (*Metallogenium*) concentrates gold up to 49 ppm. Gold in the biomass is mainly fine-dispersed (from 2 to 40 mkm). In the cells gold migrates and after their lysis it is removed to different rocks and minerals. The metal migration boundaries are found to be extended. Biocenosis and special microorganism significance in gold transformation is considered. The mechanism of gold transportation and gold origin in the *Thiobacillus ferrooxidans* cells, which are very active in the formation of oxidation zone, as well as in the yeast cells *Candida utilis*, which are the main gold concentrators, is studied for the first time. The main features of ionic, colloid, fine-dispersed and native gold influence on the physiological state of the bacteria cells are revealed. The data on mechanism and kinetics of process on bacteria solution, accumulation and "new" gold formation in the cells as well as on the surface of its primary particles are given. The obtained data are used for problems of fundamental and applied gold geochemistry.

Under microbiological and chemical sulfide oxidation, gold is extracted and dissolved as tiosulfate, halogen, gold-organic complexes, associated with iron oxides. Comparison of thermodynamic characteristics indicates that gold-organic complexes are stable (Eh from +0.7V - 0.2-0.5V) in a wider range as compared to tiosulfate (Eh from +0.4 + 0.8V) ones of the oxidation-reduction potential. The sulfates are reduced under the presence of sulphate-reducing bacteria, the complex gold compounds are destroyed and form the zone of secondary gold-sulfide enrichment.

It is shown, that gold was concentrated mainly via the biogenic method. It is proved by the prevalence of fine gold, associated with the sulfides, which results in the intensive sulfate reduction and gold solution. The majority of fine-dispersed biogenic gold mainly concentrates in the biomass and ore substance after cell destruction.

The microorganism geochemical significance is studied on Nizhne-Koshelevsk deposit of steam hydrothermae as well as on the recent gold-polymetallic deposit of active volcanism occurrences of the southern Kamchatka. The obtained data indicate that the formation of the recent volcanic-ore deposits is associated with caldera microorganism activity. Alga-bacteria assemblages contribute to formation of gold concentration fields in the hypergenesis zone and are the active agents in gold solution and recovery, which is accompanied by the "new" gold

formation and its grain coarsening.

The study on geochemical microorganism activity in gold transformation on the deposits of Siberia and Southern Kamchatka, are the basis for development of gold and silver extraction procedures i.e. microbiological leaching of fine dispersed gold from quartz-feldspar ores and sands, oxidized remains with fine gold; biological extraction of fine-disseminated gold from gold and silver-bearing ores and concentrates using the combined culture *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. This culture enables the increasing of technological procedures under the decreased temperatures; development of the recent procedures with high extraction of dissolved and fine gold using the convective dry biomass of the microorganisms from the technological solutions, untraditional gold-bearing substance.

The new ecologically safe procedures decrease the loss of fine gold to 20-60%, and in some cases they will enable almost the complete gold extraction from the untraditional gold-bearing substances, though the under up-to-date procedures the reworking of such material is impossible. The reserves of fine gold on each deposit are large.

MONITORING OF THE SNOW COVER AND SUPPLY OF HEAVY METALS INTO THE SOIL, EXEMPLIFIED BY THE SOUTH BAIKAL REGION.

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The main goal of the snow cover survey is assessment of pollution of near-surface atmosphere, waters, soils. The sampling of monitoring profiles are systematically conducted in agro-industrial zone of the Irkutsk region, starting from 1988. It is aimed at reliability of geochemical data on technogenic anomalies, their parameters and pollution of soils by the components of the snow cover. One of the profiles is observed in the south-eastern part of the region through the centers of heavy industry and agricultural zones. Another one occurs in the northwestern part of the Irkutsk region and crosses the large Bratsk water reservoir.

The water phase of the profile snow cover is represented by low mineralized waters of hydrocarbonate-sulfide and hydrocarbonate-chloride-calcium-magnesium compositions. The waters in Shelekhov and its vicinities are marked by high fluoride contents.

The solid phase of the snow cover is a complex mixture of silicate-coal-carbonate composition with high silica (to 69%), alumina (to 26%), calcium (to 9%) contents and high loss of volatile elements under ignition. The concentrations of microelements are higher than the background contents for podsollic soils of the taiga forest (zinc (to 590 ppm), copper (to 360 ppm), lead (to 390 ppm), boron (to 180 ppm), silver (to 1.4 ppm)).

Despite the significant difference in mineralization of the snow waters, depending on year of sampling (from 10-136 mg/l to 5-75 mg/l), the increase of micro- and macroelement contents is observed for the industrial centers and agricultural zones.

The bulk content of heavy metals, supplied with liquid and solid phases of the snow cover during the winter was calculated per unit of area. The Table gives the data on heavy metals supply (Q) and heavy metal contents in the humus horizon in the places of maximum man-made impact.

Microelements	Q solid phase g/km <sup>2</sup>	Q liquid phase g/km <sup>2</sup>	Contents in humus horizon
Pb	556.8-1667.0	10.0-34.0	100.0-150.0
Cu	576.6-3327.0	202.0-562.0	100.0-300.0
Zn	556.0-4000.8	304.0-2050.0	100.0-600.0
Cr	253.2-4000.8	15.0-31.0	80.0-150.0

**PROGRAMMES: "GEOECOLOGY OF RUSSIA" AND "GEOCHEMICAL MAP OF RUSSIA" (1991-2005)**

KOVAL P.V., BURENKOV E.K., GOLOVIN A.A.

The concept of "Multipurpose geochemical mapping (MPGM) of Russia at 1:1 000 000, 1:200 000 and 1:50 000 scales has been recently developed by IMGRE (Moscow) jointly with VSEGEI (Sankt Petersburg), Vinogradov Institute of Geochemistry (Irkutsk), DVIMS (Khabarovsk) and other institutes as a basis for the programmes "Geoecology of Russia" and "Geochemical map of Russia".

The main goal of the programmes is to compile the set

of multipurpose geochemical and geoecological maps, which can be used for the environmental studies, mineral exploration, soil geochemistry, geochemistry of geoecological formation and also for the nature exploration planning.

Considering the fact, that the recent activity of the humanity has an environmental influence on geological scale, the main subject to be investigated is additive geochemical fields, which are formed by both natural and anthropogenic processes. The concept of geocosystem is introduced as a geological media and man environment, related by substance, energy and information exchange. The geocosystems of different scales are the main objects of integrated geochemical studies in the considered programmes.

The sampling media are stream sediments, surficial waters, soils, bedrocks, plants, snow, atmospheric dust, biosubstrates. This list can be reduced after the pilot stage of the project and detailed investigations.

The recommended sampling density is 1 sample per 1 sq.cm. of the designed map. The design of the sampling strategy is recommended to be based on a quasi-uniform network of the sites, selected using the following preparatory maps: landscape-geochemical regionalization; functional zoning; structural-formation and metallogenic regionalization.

Before carrying out systematic geochemical mapping of Russia, the map of different geochemical landscapes will be compiled at 1:5 m scale. Initially, orientation studies must be carried out for both programmes. The orientations project entitled "Polygons of Russia" ("Polygon") is aimed at the development of multipurpose geochemical and geoecological mapping procedures.

The coordinated system of the analysis and quality control will be required for MPGM of Russia. The database and computer data management system should also be developed.

The experience advantages from other national and International Projects, particularly IGCP 259 one, are intended to be followed.

Both programmes are funded by the State Committee on Geology and Utilization of Mineral Resources.

Orientation studies began in 1991 mainly in 6 polygons: Kola, Moscow, Altai, Baikal, East Transbaikalian and Primorsky.

The main objectives of the "Polygon" stage (1991-1995) are to recommend techniques for multipurpose geochemical mapping



in different landscapes of the country and to prepare a set of the legends and map formats for 3 groups of geochemical and geocological maps. They are as follows:

1. preparatory maps:
  - inventory-geochemical regionalization;
  - functional zoning;
  - structural-formation and metallogenic regionalization;
2. intermediate maps:
  - single elements maps;
  - multielement maps;
3. final maps:
  - geochemical quality of the environment;
  - geochemical specialization of soils and the identification of agrogeochemical zones;
  - geochemical characterization of the primary geological formations;
  - geological-ecological;
  - land-use planning.

Standard models of the legends and map formats have been designed.

The most important feature of the "Polygon" orientation study is the flexibility and diversity of approaches on different polygons. The scientists involved are also free to develop and conduct their own experiments.

15 regional Geological Surveys and 10 Institutes, participating in the "Polygon" stage of MPGМ are coordinated by the interorganizational coordinating Council.

More details in "Polygon" Project are given in abstract devoted to the Baikal polygon subproject.

## MULTIPURPOSE GEOCHEMICAL MAPPING IN THE BAIKAL GEOECOLOGICAL POLYGON, RUSSIA

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The Baikal geoeological polygon is one of the several testing areas, chosen for realization of the initial stage (1991-1995) within the programmes "Geoecology of Russia" and "Geochemical map of Russia, funded by the State Committee on Geology and Utilization of Mineral Resources.

The principal aim of the programme is to develop scientific procedures for compiling multipurpose geochemical and geoeological maps (scales 1:1000 000, 1:200 000 and 1:50 000) as the basis for: the assessment of environmental pollution; the identification of mineral deposits; comparison of the distribution of chemical elements in coexisting natural media, including bedrock, soil and stream sediments, waters and botanical samples; land use with particular reference to agricultural and forestry, environmental geochemistry and health; the development of a system of geoeological monitoring ; implementation of sampling and quality control procedures; coordination with national and international projects such as "Global environment and climate changes", IGCP 259 "International geochemical mapping", etc.

The initial stage of the above programmes, entitled "Polygons of Russia" is scheduled for 5 years (completing in 1995). Initially, data will be collected for compiling maps at 1:1 000 000 scale and then at 1:200 000 (1993-1994) and 1:50 000 scales(1994-1995). The results will be summed up in 1993-1995.

Establishments executing the programme:  
Vinogradov Institute of Geochemistry, Irkutsk; Irkutsk Geological Survey; Buryat Geological Survey; Sosnov Geological Survey.

The Baikal polygon is one of the biggest polygons, included in the programme ( 10 km<sup>2</sup>). The unique fresh-water Lake Baikal is situated in this testing area. The polygon is characterized by a wide range of different geological settings, including platform structures, their basement and folded framing of different ages, orogenic depressions and troughs, both recent and paleorifts; a wide distribution of metalliferous and non-metalliferous mineral deposits; high seismic activity of a number of regions; a diversity of landscapes; a number of man-made water reservoirs, associated with hydropower stations; the frontier position; high industrial development of the considerable part of the territory. The pollution degree varies from minimum along part of the Baikal coast to extremely high in the vicinity of such towns as Shelekhov, Angarsk, Zima.

At the preliminary stage (1991-1992), a series of auxiliary maps was compiled to inventory the scope of geochemical studies, geological structures, landscape-geochemical zonation, functional zonation as well as the sampling , all used for planning works and selection of the sampling sites. Sampling is intended to be carried out at two site types: "ordinary" and "base" stations (sites). Spacing of ordinary sampling sites is accepted to be close to 1 point per 1 cm of the map to be compiled.

The active stream sediments (-0.18 mm fraction for analysis, 1 mm fraction for storing and experiments), stream water, 2 soils (one sample is from the floodplain, another one - from the slope, A and (B-C) horizons) as well as bedrocks (0.5-1kg) are sampled at ordinary sites for the maps at 1:1000 000 scale. The number of samples, collected at the base station is higher. In addition to the above mentioned, the sandy-gravel fractions of stream sediments, the branches of birches and willows, water mosses are also sampled. More detailed analytical and methodological studies are carried out at the base stations (repeated sampling, seasonal observations, study of distribution of the substance between fractions of the media to be sampled, comparison of different sampling techniques and different treatment and analysis procedures). A number of base stations is not less than 1/10 of the total station number. The base stations are of different levels, according to the problems to be solved: single sampling and repeated sampling (monitoring). The base stations should cover all typical landscapes, geological and anthropogenic settings and be consistent with the aims of the Global Geochemical Sampling (IGCP 259 Project).

Other studies also include:

- systematic geochemical study and mapping of the snow cover;
- experiments on biological testing of diverse environments;
- aerosol air and on-land survey;
- experimental survey of over-flood sediments;
- studies on geochemistry of water runoff and bottom sediments on Lake Baikal;
- geochemical study of bottom sediments and water of the water reservoir of the Angara River cascade.

The samples are analyzed for more than 40 chemical elements (OES, AAS, RFA, etc.). The field of application of different analytical techniques, including the approximately quantitative OES have to be assessed.

To provide the quality control, each batch of 33 samples will include: (i) one field duplicate (parallel sampling), (ii) one laboratory duplicate, (iii) one reference sample.

The results of 1991-1992 are illustrated with the set of auxiliary and geochemical maps at scales 1:1 000 000.

## THE NONBARRIER BIOGEOCHEMICAL PROSPECTING (NBP) - THE NEW DIRECTION IN THE SEARCHING GEOCHEMICAL EXPLORATION ON THE DAY'S SURFACE

KOVALEVSKII A.L.

Litho-, hydro- and biogeochemical searching explorations on the day's surface have the aim to reveal the perspective areas for the detailed geological-prospecting works with using of mine works - diggings, ditches, tranches and drilling cores. The most detail scale of such geochemical works is usually 1:10000 and very seldom 1:5000. The nonbarrier biogeochemical prospecting (NBP) is the detailed biogeochemical exploration in the perspective squares in prospecting scales 1:200-1:2000. They have the aims to reveal and to contour separated ore bodies and deposits and to evaluate the geological prognostic resources of the useful components in them.

NBP is based on the revealed, studied and approbated by the author linear correlation between the contents of chemical elements in nonbarrier bioobjects of plants and in their rootinhabited zone of soils, rocks and ores (Kovalevskii, 1978-1992). This dependence is established by us and other investigations for Pb, Ag, Au, Ra, U, Be, Mo, W, F. The preliminary data are received for Sn, Cd, Tl, As, Sb, Bi, Pt, La, Ce, Zr. It is undoubted that by the further special investigations the similar dependences would be established for other ore elements.

The elaboration of the concrete methods of NBP is possible only in the next conditions: 1) the presence in the dominant plants of the investigated landscapes the nonbarrier bioobjects for ore elements which are the objects of searching works; 2) the forming of the ore biogeochemical haloes by the lithobiogeochemical model of the root nutrition (Kovalevskii, 1991 in Russian; Kovalevskii, 1991 in English); 3) the displacing of the root nutritive horizon in the upper parts (in the undisplaced elubium) of ore bodies, which have contact with the lower parts of the investigated plants root systems.

The every elaboration of the concrete method of NBP is NOW HOW. It have great value as it make possible to reveal, contour and evaluate the geological prognostic

resources of separated ore bodies and deposits with the minimal expenditures of time and money. The important dignity of the NBP is its ecology as when using it take place the minimal disturbances of soil and vegetable covers which connected with the digging of short ditches for the verification of the supposed ore biogeochemical anomalies (SOBA) of the various geochemical types.

By the experience of our 15 years works the next modes of the NBP treatments are recommended. 1) The sampling of the nonbarrier bioobjects of plants by the crossed system of profiles over 20-60 m for simultaneous revealing ore bodies various directions. 2) The sampling of these bioobjects in the stripes to 40-60 m width for quaranteeng of the middle interval between samples in profiles 1-3 m. 3) The thickening of the sampling points to scales 1:200-1:500 when detailizing the SOBA of ore elements. 4) Opening by short ditches various geochemical types of the SOBA which are determined by the relations between ore elements and their companions. The aims of these openings are the verification of the SOBA, the receiving data on the plant-ore coefficients (POC) and the determination of the opened ore bodies and orebearing zones streaching. 5) The construction of the maps and sketch-maps of the nonbarrier biogeochemical haloes, anomalies and SOBA of the ore elements and their companions for separated localities. In these constructions the revealed direction of streaching is taken into account when anomalies on the neighbour profiles are correlated. 6) The constructions of the generalized biogeochemical maps and sketch-maps which make it possible to reveal the general structural plan of ore fields. The aim of these constructions is the choosing of the squares for the further searching works with using of NBP. 7) The complexing of NBP with other methods.

Our experience of the NBP for base metals, molybdenum, gold and silver is published partly. The most interesting results concern the NBP of the veined silverore bodies and deposits in the investigated by us region where early 4 times were conducted the detailed geological, soil-geochemical and geophysical exploration for silver in the scale 1:10000 by the Industrial Geologic Organization (IGO). Here with the help of NBP we have reveal 160 SOBA of silver with its contents from 70 to 3000

ppm in the background 0.5 ppm in the ash of *Pinus sibirica* and *Larix dahurica* old stumps. On 3 thickenings with 51, 35 and 18 SOBA here we prognose small deposits of silver with approximately corresponding quantities of silverore bodies. This experience would be discussed in details in this symposium.

NBP must be considered as the new direction in the searching geochemical exploration on the day's surface. It is stipulated by the fact that the geochemical works in the prospecting scales of 1:200-1:2000 early were not conducted. Taking into account high effectivity and perspectivity of NBP it is necessary to organize the elaboration and approbation of the concrete methods of NBP in various conditions of the earth's globe. NBP is of special interest for developing countries as it is the right, quick, economic and ecologic method.

BIOGEOCHEMICAL EXPLORATION AND PROSPECTING IN  
VARIOUS GEOLOGICAL AND GEOGRAPHICAL CONDITIONS  
KOVALEVSKII A.L.

More than 50 years of the biogeochemical exploration and prospecting elaboration and application show that they may be used in various geological and geographical conditions with vegetation covers.

In the last years three main models of the biogeochemical exploration were established. They are lithobiogeochemical, hydrobiogeochemical and atmobiogeochemical. In the practice the lithobiogeochemical and the complex lithohydrobiogeochemical models are predominant. Other combinations of the three main models are possible (Kovalevskii, 1991 in Russian; Kovalevskii, 1991 in English).

The lithobiogeochemical model take place when plant roots reach ore bodies or their eluvium and the water-tight horizons in the rootinhabited zone are absent. In these conditions the accumulation of ore elements and their companions take place by contact absorbing with the help of the acid root secretions. In our 35 year experimental works in the south of Siberia lithobiogeochemical model was observed in more than 90% of the investigated localities. When using the nonbarrier biological objects of plants in the lithobiogeochemical model the quantitative interpretation of the used analytical data is possible. This possibility was established for beryllium, molybdenum, lead, gold and silver (Kovalevskii, 1978, 1984, 1988, 1991 in Russian; Kovalevskii, 1987, 1991 in English). It is undoubted that by further investigations it would be established for other ore elements.

The hydrobiogeochemical model take place when plants accumulate indicator elements from ore hydrogeochemical haloes contacting with the lowest parts of root systems. By the factual data in the Canada and the China the depth of the hydrobiogeochemical exploration reach 200 m. By theoretical data it may reach 1000 m (Kovalevskii, 1975, 1991 in Russian).

Atmobiogeochemical model take place when plants accumulate indicator elements from their gaseous forms which are disposed in the rootinhabited zone. For the present time this model is most investigated for mercury (Kovalevskii, 1983, 1984, 1986, 1989, 1991 in Russian; Kovalevskii, 1984, 1986, 1987 in

English) and approbated for hydrocarbon gases (Stadnik, 1984 in Russian) and helium (Yurin, Stadnik, 1985 in Russian).

The experimental works with mercurybiogeochemistry in 28 various ore deposits of Siberia show that more than a half of mercurybiogeochemical haloes and anomalies are not accompanied by soil-geochemical ones, i.e. they have atmobiogeochemical origin. Many mercurybiogeochemical haloes are accompanied by Cd, Zn, Cu, Ag, Au, Tl, Sn, Pb, As, Sb, Bi. This may suppose their joint with mercury upward migration in the earth's crust and in loose covers in the form of their amalgames. Because of this atmobiogeochemical model may be possible for this complex and other chemical elements. Very important are our data that the contrast and the informativity of gasmercury anomalies in the underground soil air usually are much lesser than mercury biogeochemical ones (Kovalevskii, 1989, 1991 in Russian; Kovalevskii, 1986 in English), i.e. mercurybiogeochemical exploration have many predominances compared with soil gasmercury. By the theoretical data maximal depth of atmobiogeochemical exploration may reach 2-4 km. In the present time in Siberia its established depth is 100-200 m.

As it is seen from the discription of the main models the most importance have geological conditions, geochemical and mineralogical peculiarities of ores which are objects of exploration works; upward migration of indicator elements in water and gaseous phases; the depth and composition of loose covers; the hydrogeology of underground waters. They determine the effectiveness, the reliability and the depth of the biogeochemical exploration and prospecting - their main technical indices. Geographical and paleogeographical conditions which determine the climate, the conditions of native rocks and ores weathering and the character of the vegetation covers have significance in the choice of the indicator elements and in the choice of biogeochemical sampling objects. They have an influence also on the depth of biogeochemical exploration connected with the leaching of ore elements from soils and upper layers of loose covers.

The geochemical peculiarities of ores determine the choice of main indicator elements. By they may be not basic components of ores which have contents to tens of percentages, but their expensive components which determine the ore cost. The characteristic examples of this are precious metals of poly-



tallic, copper and sulphide ores. This is concerned also to some expensive rare elements.

Mineralogical peculiarities of ores also determine the choice of the main indicator elements as the chemical elements availability to plants depends from their mineral forms in the rootinhabited zone (Kovalevskii, 1974, 1984, 1991 in Russian; Kovalevskii, 1974, 1979, 1987 in English). In connection with this by the main biogeochemical indicators may be not main components of ores but their companions more easily available to plants. Examples of this may be using of molybdenum and fluorine in biogeochemical exploration for tungsten ores because of the unavailability of tungsten to plants when weathering crusts are absent (Kovalevskii, 1978 in Russian) and using of cadmium, silver, lead and mercury in exploration for lead-zinc ores in presence of the deep crusts weathering in Ozernoe pyrite-polymetallic deposit (Kovalevskii, 1974, 1984, 1991 in Russian; Kovalevskii, 1979, 1987 in English). This important question need special mineralogical investigations of the rootinhabited zone of soils, loose covers and oxidation zones of native rocks, ores and their primary haloes.

The depth and composition of loose covers determine in many cases the biogeochemical exploration conducting expediency. When loose covers absent or have little depth and eluvial type which not prevent the opened secondary lithogeochemical haloes forming more effective and expedient are exploration by soil-geochemical, eluvial or primary lithogeochemical haloes. Contact of plants with ores and their deeply buried lithogeochemical haloes is absent when depth of loose covers is significantly more than maximal depth of sampled plants root systems and when water-bearing horizons are absent. Because of this biogeochemical exploration in such conditions is uneffective and unexpedient.

The upward migration of indicator elements in water and gaseous phases is a factor which increase significantly the depth of biogeochemical exploration. In this cases the forming of the ore biogeochemical haloes take place by the models of the hydrobiogeochemical and the atmobiogeochemical root's nutrition. The question about the role of chemical elements upward migration in their accumulation by plants from deep situated sources was discussed detaily in the last author's monograph (Kovalevskii, 1991 in Russian).

Biogeochemical exploration and prospecting are expedient only when using high informative, nonbarrier and practically nonbarrier bioobjects of plants. They are revealed on the base of the systematic determinations of the quantitative barrier characteristics (QBCh) of plant species bioobjects suitable for sampling in exploration. These determinations were conducted in the present time for 24 indicator elements and 60-500 plant bioobjects of Siberia (Kovalevskii, 1991 in Russian). Determinations of the QBCh are started in China and must be organized in all countries where deep biogeochemical exploration and prospecting are possible and expedient. The practice show that nonbarrier bioobjects may be revealed in any geographical conditions with vegetation covers.

Geographical and paleogeographical conditions have the most influence on the biogeochemical exploration and prospecting effectivity connected with the peculiarities of the geochemical landscapes as they determine the peculiarities of soil-forming and also geochemical and mineralogical characteristics of the upper rootinhabited horizons of the weathering crusts and oxidation zones of rocks and ores. Because of this the investigations of geochemical landscapes must be the constitutive part of the biogeochemical exploration and prospecting. In the stage of planning these landscapes are used for the choice of the territories where biogeochemical exploration are expedient and during their conducting - for the interpretation of the revealed biogeochemical anomalies. The main aid of this interpretation is dividing the supposed ore biogeochemical anomalies from nonore landscape ones in geochemical barriers and determination of biogeochemical anomalies displacing because of their migration down slopes. This is concerning especially to hydrobiogeochemical anomalies on the slopes and to hydrobiogeochemical streams of dispersion in vallies.

Thus the effectivity of the biogeochemical exploration and prospecting are depended mostly from geological and partly from geographical including paleogeographical conditions. The knowledge and the accounting of these conditions are the necessary factor of the effectivity in exploration and prospecting for various minerals. The studying of the concrete geological and geographical conditions must be conducted simultaneously with any biogeochemical works and their results must be used in all stages of these works.

## NONBARRIER BIOGEOCHEMICAL PROSPECTING FOR SILVER IN THE LANDSCAPES OF THE TRANSBAIKAL SOUTH TAIGA

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The general scientific foundations of the detailed biogeochemical exploration with the geologic prognostic resources evaluation by the nonbarrier bioobjects of plants (the nonbarrier biogeochemical prospecting - NBP) for ore deposits as a new direction in the geochemical investigations on the day's surface are discussed in the special report of this symposium. The method of NBP is elaborated best for silverore bodies and deposits in the landscapes of the Transbaikal south taiga where our investigations were started in 1984.

The investigated silverbearing zone 20 km in the length is situated in the very favorable economic conditions. The distance from the railway station and the enriching factory is 20-40 km and 4-10 km from the asphalt road. In the south part of this zone the significant volumes of detailed investigations were conducted. They include biogeochemical, soil-geochemical, lithogeochemical, hydrogeochemical, biogeochemical, geophysical, biogeophysical (biolocation or dowsing), geobotanic, phytopatogenic, geoarchaeological, geoethnic and other. Notwithstanding that here in 1970-1985 years by the Industrial Geological Organization were conducted 4 times detailed soil geochemical and geophysical explorations for silver in the scale 1:10000 we have received principally new scientific data concerning geology, geochemistry, biogeochemistry, geobotany and other scientific problems of silver and also concerning methods of the nonbarrier biogeochemical exploration (NBE) and the NBP for silver ore bodies and deposits. Because of this we recommend to organize here the International investigating, testing and training polygone (IITTP).

In the elaboration of the NBP for silver in the investigating zone it was sampled and analysed for 47-70 chemical elements close to 20000 biogeochemical and more 3000 lithogeochemical and other samples, it was revealed 160 supposed ore biogeochemical anomalies (SOBA) of silver, 23 ditches are finished and new ones are conducted for the verification of silver SOBA. The drilling and exploration works are planning in which may take place foreign companies and firms.

In the process of NBP elaboration it was resolved here in consecutive order the range of problems. 1) It were revealed the quantitatively informative, nonbarrier bioobjects of dominant plants species. They are the suberized cones of *Pinus silvestris* and the wood of the *Pinus silvestris* and *Larix dahurica* old including rotten stumps. 2) By these bioobjects were revealed 160 local SOBA of silver to 8 m width and 20-200 m length with contents of silver in the wood of stumps ash from 70 to 3000 ppm. its increase the local background 0,5 ppm of silver are unique. Such concentrations of silver in plants were not known on the earth globe early. 3) In the arcshaped geological structure with area close to 2 km<sup>2</sup> it were revealed and contured 6 zones of thickenings areas 150-300 x 200-400 m with 51, 35, 19, 16, 9 and 6 SOBA of silver. 4) The rational nets system and intervals between lithobiogeochemical samples were established. It is recommended the crossed system of profiles with interval 40-60 m for the simultaneously revealing of the various directions probable ore bearing zones, the sampling of plants in the stripes to 40-60 m width along the profiles fastened on the investigated localities by pegs with 30-100 samples on 100 linear meters of the profile, i.e. with middle interval along profile 1-3 m. 5) Three approximations of the main

interpretation parameter - plant-ore coefficient (POC) were determined. This coefficient is calculated as the relation of the silver content in the plant ash and in the prospecting channal samples from the bottom of ditches 2-4 m depth. It is established that POC is depended from contents of silver in channal samples. It have maximal value (2.0) for poor ore with 20 ppm of silver ; it have value 1.0 for the limit content of rich ores with 200 ppm and decreased approximately to 0.5 for the most rich investigated ores with 6000 ppm. 6) It is established that the investigated silverbearing zone is situated in the limits of regional Vitim-Dzhida deep breaking more 1000 km of length. 7) By the verification of silver SOBA in ditches were opened 18 silverore bodies with contents of silver from 200 to 1700 ppm and more 40 silverbearing zones. The established reliability of the silverbearing zones revealing under SOBA of silver is equal 100% and of the rich ore bodies revealing under the SOBA with contents of silver 200-3000 ppm - 60%.

PECULIARITIES OF THE SCINTILLATION EMISSION SPECTRAL  
ANALYSIS (SESA) OF GEOCHEMICAL SAMPLES ON PLATINOIDS

KOVALEVSKII A.L., PROKOPCHUK S.I.

Analyses of ores, rocks, soils and plants for platinoids are the most complicated problem comparing with other ore elements. The especial complication have determinations of platinoids in biogeochemical samples as they have small weights  $\leq 1-3$  g.

Beginning in 1986 year scintillation emission spectral analyses (SESA) of various geochemical samples show that very characteristic for them is the presence of mineral forms - particles with sizes order 3-30 mkm which may be easily registered by the standard SESA. Such particles of platinoids - their microbioliths were revealed also in some bioobjects of plants (Kovalevskii et al., 1992 in Russian; Kovalevskii, Prokopchuk, 1992 in English).

The revealing of microbioliths of platinoids in plants open the possibility to use the automatized SESA in the very perspective biogeochemical exploration and prospecting for platinoids ore bodies and deposits. Microbioliths of platinoids are established mainly in the old dead plant parts - outer layers of trunk tree cork, in suberized cones of coniferous and in the wood of old including rotten stumps of coniferous. They are revealed also in branches of some tree species but are absent in young green parts of plants. Similar peculiarities of the microbioliths distribution were established for gold (Kovalevskii, Prokopchuk, 1978, 1990 in Russian; Kovalevskii, Prokopchuk, 1981, 1992 in English).

Data received for the present time show that microbioliths of platinoids in plants have smaller sizes comparing with rocks and ores. Because of this the sensitivity of their determinations may be increased and the detection limit decreased by registration microbioliths of lesser sizes than it is done in the standard SESA which registers platinoids with calculated diameters 2-4 mkm. This possibility was established for platinum and iridium.

The contemporary SESA (Prokopchuk, 1992, 1993) have next peculiarities when analysing geochemical samples on platinoids.

I. Detection limits of various platinoids are not equal.

The least detection limit was established for palladium (order 2-5 ppb) and maximal - for platinum, ruthenium and rhodium (10-30 ppb). The identical quantity of registered platinum particles correspond to their various contents. Because of this it is necessary careful standartizing SESA for various types and series of investigated samples.

2. The right correlation between contents and quantities of various platinum particles in cuttings of rocks and in biogeochemical profiles usually is absent. Because of this it is necessary to determine in the investigated samples all 6 platinum.

3. The analyses of interplatinum minerals by registering in SESA the pairs of coincided platinum particles are complicated but solved problem. In the experiences of osmium-iridium particles registering in lithogeochemical samples have been received very reassuring results. SESA in combination with mineralogical investigations is very perspective dealing.

4. The real way for increasing the sensibility of SESA is the registration of smaller mineral particles. This is possible in the present time only for biogeochemical samples as they have homogenous composition comparing with lithogeochemical ones. The first experience of platinum and iridium microbioliths of 0,5-1 mkm size registering was very reassuring. In these investigations it was established however the heightened unstability in time of the apparatus and the heightened influence of interfering chemical elements, for example lead on determinations of iridium.

5. In connection with the fact that the SESA give very valuable information about the sizes of platinum and interplatinum particles in various geochemical samples SESA should be used in mineralogical investigations. The main aid of this must be the choice of samples with the biggest sizes of platinum suitable for labour-consuming and high expensive mineralogical investigations.

The automatized SESA open the possibility of the mass determinations of platinum as one analyst may analyse 100-200 samples during 8 hours. By the present time after the main investigation works we have done close to 50000 SESA on platinum.

SCINTILLATION EMISSION SPECTRAL ANALYSIS (SESA) - THE  
PROBABLE DECISION OF THE MASS ANALYSES OF GEOCHEMICAL  
SAMPLES ON GOLD AND PLATINOIDS

KOVALEVSKII A.L., PROKOPCHUK S.I.

Scintillation emission spectral analysis (SESA) registers the analytical lines of studied chemical elements flashes of lights from their separated particles. Because of this SESA give information about contents of the analysed elements mineral forms. It is suitable for analyses of every samples which contain particles of studying elements sizes of which increase the detection limit of the apparatus. These sizes for the standard SESA is equal 2-4 mkm. By special methods they may be decreased to 0.3-1 mkm. SESA without chemical preparing of powdered samples was approbated for determinations of Au, As, Ag, Pt, Ir, Os, Pd, Rh, Ru, Nb, Ta, Zr, Pb (Prokopchuk, 1990, 1993). In the last time our SESA apparatus was automatized. This increase the objectivity and productivity of the received data. By SESA are determined simultaneously three selected elements with determining for every of them 2-5 sized of particles. After quantity and sizes of particles the contemporary SESA registers the coincided impulses of two-three various elements which may be used for the determinations of quantities and sizes of mineral particles containing the analysed chemical elements. This possibility may be used in geochemical and mineralogical investigations. By the present time we have much experience of the registering of coincided impulses of gold and arsenicum (goldcontaining arsenopyrite), of gold and silver (electrum, kustelit and goldbearing silver) with determinations of gold standard, and also preliminary experience of the interplatinoids particles registration.

Aur 16 years investigations of various geochemical samples - rocks, ores, soils, they various fractions and also plant's ash and their unashed phytoshlichs show that gold is presented in them fully or partly in separated particles which are registered by SESA (Kovalevskii, Prokopchuk, 1978, 1990 in Russian; Prokopchuk, 1990, 1992 in Russian; Kovalevskii, Prokopchuk, 1981, 1992 in English). In the last time it was established for the most hardly-determined platinoids. Very important are determination in plant ash of osmium which for a

long time could not be determined by other methods. In connection with this it was supposed that osmium volatiles significantly during the ashing of biogeochemical samples. Osmium determinations make it possible to finish the SESA elaboration for all 6 platinoids and to begin studying the peculiarities of SESA on platinoids and interplatinoids compounds in plants, soils, rocks, and ores. The results of these investigations would be discussed in the special report of this symposium.

Because of the high sensitivity (order 3-30 ppb) and productivity (order 100-200 during a day for one analyst) the determinations of precious metals by SESA may be recommended for mass analyses on gold and platinoids which need high expensive chemical preparing for other analytical methods. As for the present time SESA is approximately-quantitative method it should be used for the quick and economical revealing of samples with heightened and high contents of analysed elements. For some homogenous series of samples SESA have indices approaching quantitative methods. Because of this the nearest aid of SESA must be its standartizing for homogenous samples and gradual manufacturing of standards with determined sizes of the analysed elements mineral particles.

In our investigations SESA is mass analytical method on precious metals. During 16 years after scientific works we have analysed on gold more 100000 various samples including approximately 15000 samples of plant ash. Beginning in 1985 year to the present time were analysed close to 50000 samples on platinoids. The number of SESA on platinoids only in 1992 year was close to 15000 of various geochemical samples including more 5000 samples of plant ash with weight 0.2 g.

In the present time automatized SESA on precious metals is conducted by some chosen programmes. They include the determinations of the quantity and the 2-5 sizes of three choiced chemical elements for example Au+Ag+As, Pt+Os+Ir, Pt+Os+Rh, Pt+Pd+Rh and so on and at the same time the quantity of the analysed elements coincided particles.

Our experience make it possible to recomend SESA for wide using in geochemical and mineralogical investigations on precious metals tens of thousands various samples for one analytical apparatus. They promise to reveal and contour their geochemical anomalies quickly and with the minimal expenditures and to choose the most interesting samples with high contents of analysed elements for much more expensive quantitative and mineralogical analyses.



## **Application of limited Fuzzy-Clusters for anomaly recognition in complex geological environments**

**U.Kramar**

In geochemical mapping and exploration projects material from different geological environments is taken in most cases. Changing geological units, weathering- and climatologic conditions are modifying the geochemical background. Basic problems of data processing in geochemical exploration and mapping are to determine the different levels of background and to discriminate between background and anomalies. Non-hierarchical cluster analysis is often used to classify geochemical data by their taxonomic distance. The data set is divided into different clusters (groups). Each sample is then assigned to the nearest of these clusters (groups). In geological sense each cluster will represent a geological unit or a group of anomalous samples. One sample can be assigned to one cluster only.

In stream-sediment and soil surveys a part of the samples will be a mixture of components from different geological environments. Such mixed samples will be misclassified using conventional hard cluster methods. Fuzzy-clustering (BEZDEK et al., 1984) avoids these problems of misclassification. In Fuzzy-Clustering each sample is allowed to belong to several clusters. Starting from conventional hard clusters the contribution of each cluster to each sample is calculated. Cluster-centers and contributions are iteratively recalculated, until the system remains stable. Using this procedure for each cluster a contribution value between 0 and 1 is assigned to a sample. Similar to element concentrations, these cluster contributions can be displayed in contour maps (e.g. Kriging- maps). The amount of an element that is explained by the cluster contribution and element residuals can be calculated. The modified Fuzzy- clustering algorithm called "limited Fuzzy-Clusters" used in this paper avoids negative residuals.

Stream-sediment data of Sierra de San Carlos/ Tamaulipas/Mexico are used to demonstrate the possibilities of limited Fuzzy-clustering in geochemical exploration and mapping. The Sierra de San Carlos is located 150 km south-east of Monterrey and covers an area of ca. 300 km<sup>2</sup>. The Sierra consists of dioritic to gabbroitic rocks. Skarn deposits in the northern part of the Sierra

have been exploited extensively at the beginning of this century. From the different drainage systems 681 stream sediment samples were taken and analysed for 24 element.

A nineteen- element data set was used to divide the samples into 10 hard clusters. Starting from the centres of these clusters, limited Fuzzy clusters and element residuals were calculated. The contribution values for the clusters and element residuals are displayed in contour- maps. All geological units were outlined by the cluster- contributions. Extended anomalies are characterised by an own cluster. Small anomalies are clearly identified from the element residuals.

BEZDEK,C.J., EHRLICH,R. & FULL,W. (1984): FCM: the fuzzy c-means clustering algorithm. - *Comput.Geosci.*, **10**: 191-203.

**MINERALOGICAL-GEOCHEMICAL ZONATION IN PROSPECTING AND  
ASSESSMENT OF GOLD-SILVER DEPOSITS (NORTH-EAST OF RUSSIA)**

KRAVTSOVA R.G.

The study of geochemical fields on gold-silver deposits within the different structural-metallogenic zones of the Okhotsk-Chukotsk volcanogenic belt indicates that different mineralization types of the considered formation are marked by own mineralogical-geochemical zonation pattern. This pattern differs in the composition, structure and scale of near-ore metasomatite distribution (petrographic data, data of silicate chemical analysis as well as those of XRF) and anomalous concentration fields of ore elements (FAAS, AAS, OES, semi-quantitative OES data).

Three types of zonation are distinguished: zonation within the single ore stage ( monostage); zonation, resulting from the multi-stage pattern of ore association development ( polystage) and the zonation, typical of the zones with the telescoped development of the different-formation ores (polyformation). The monostage zonation is observed in the separate ore bodies, infrequently in the zones. The simple component composition and local pattern of the development is common to such zonation. The polystage geochemical associations possess the more complicated field compositions, the increased contrast coefficients and the increased degree of the metasomatic changes. The polyformation pattern of ore and halo distributions influence much on the vertical zonation of the deposits. The allogenic geochemical and metasomatic associations are widely distributed on the telescoping sites. They are marked by more complicated composition and structure.

The element distributions are expressed through different zonation indicators, which are based on the analysis of monoelement maps and sections. It is not always effective, particularly, on the deposits with the complicated polycomponent compositions of ores and haloes (polyformation type of zonation). The multidimensional geochemical field analysis is particularly efficient in these cases as it permits the element correlation to be made, polyelement maps and sections to be compiled. The geochemical element associations are used as the zonation markers. On the considered deposits, the zonation pattern of the haloes results from the alteration of the geochemical associations along the ore zones. When the zonation is monostage, the sub-ore intervals are Pb Ag (Zn), lower-ore - Ag Mo Pb (As, Au), middle-ore - Au Ag As Mo (Sb, Hg, Pb), upper-ore -Ag As Sb Hg (Au), super-ore - As Ag(Hg).

When the zonation is polystage the intervals are the following : Pb Ag [As'] (Zn, Cu) - Ag Mo Pb [Ag', As'] - Au Ag As Mo [Ag<sup>I</sup>, As<sup>I</sup>, Sb<sup>I</sup>] - Ag Au As Sb(Hg)-Ag As (Sb, Hg).

Under the polyformation zonation the intervals are: As Pb Ag Zn Cu Sn Bi Mn (Cd) - Ag As Mo Mn Sn Pb (W, Cu, Bi) - Ag Au As Mo Mn (W, Pb, Sn, Cu, Bi) - Ag Au As Hg Sb(Bi) - Ag As Sb Hg.

The main typomorphic element-indicators of gold-silver mineralization are Au, Ag, As, Sb, Hg, Pb, Mo, to lesser extent Zn.

The summarized zonation series for gold-silver deposits

is : (Zn)Pb-Mo-Au-As-Sb-Hg.

The location of a number of elements in the zonation series may significantly vary with the depth of gold-silver mineralization. In the deep settings Mo haloes, being very intensive, are distributed within the whole zone (under the low-ore locations of maximums), while in the near-surface ones, they are spread not higher than the middle-ore interval. As opposed to above mentioned, Sb, Hg, As, common to upper horizons, are more intensive in the near-surface settings and observed up to the sub-ore horizons. The observed deviations in the location of a number of elements probably result from difference of the thermodynamic conditions of the halo formation.

The zonal distribution of ore elements in the haloes well correlates with the metasomatic zonation, which indicates their similar genetic origin. The successive change of quartz-kaolin-hydromica, quartz-sericite-hydromica, quartz-adular, quartz-sericite-carbonate and epidote-chlorite-propilite associations are observed along the direction of the ore-bearing zone dip. The observed change of the metasomatic associations is typical of not only the studied deposits of the region but for the deposits of the considered formation of other regions (Trans-Baikal area, Kazakhstan). It indicates the common origin of the ore systems of such type. As opposed to the ore zonation, the metasomatic one is more stable. It permits the petrogenic and the associated rare element distribution patterns to be used for prospecting.

The study of the mode of element occurrences in the ores and endogenic haloes (mineragraphic and microprobe study, phase chemical analysis, AAS, OES) may increase the reliability of the revealed criteria and supplement the data on the vertical geochemical zonation, particularly, in case, with the polyformation ores. The changes of gold, silver and mercury mode of occurrences are evident with the depth. The fine dispersed native gold, proustite and pyrargyrite are common to upper ore horizons; electrum, argenite are typical of middle ore horizons and stromeyerite and tennantite - of lower ore ones. The gold, associated with the sulfide minerals, is significant on the lower ore horizons. It is considered to be the non-metallic form of gold occurrence into the sulfide (primarily pyrite) lattice. The maximum metallic mercury concentrations (including the isomorphous one) are observed in the upper horizons. The sulfide mercury occurs mainly in the regions of halo pinching out i.e. in the lower horizons. The zonal distribution of mineral forms (chemical compound groups) well correlates with the geochemical zonation.

**ENDOGENIC HALOES OF ALKALINE ELEMENTS IN PROSPECTING AND ASSESSMENT OF SILVER MINERALIZATION IN THE NORTH-EAST OF RUSSIA**

KRAVTSOVA R.G., SHANGINA N.N., SHATKOV N.G.

Study of geochemical fields on the veined gold-silver and silver-polymetallic deposits, occurring in the Cretaceous volcanogenic formations of acid and intermediate composition indicate that the majority of the deposits possess the complicated polychrone pattern of mineralization and halo development. It hinders the study of composition and endogenic geochemical field structures, complicates anomaly type interpretations and the revealing of zonation, based on traditional ore-forming and halo-forming elements. The investigation of the haloes of such alkaline elements as K, Na, Rb, Li, Cs is significant. Distribution and concentration of these elements strictly correlate with the compositions of the metasomatic parageneses.

Under the processes of hydrothermal rock alteration K (4-10%) supply and Na (0.01-2.5%) removal are observed in the zone of gold-silver mineralization. In addition to potassium, the metasomatites are enriched with Rb (52-50 ppm), Cs (2-25 ppm) and Li (25-60 ppm). Potassium concentration changes along the ore zones correspond to alteration of the prevalent low-temperature carbonate-sericite (propylite) complex in the lower parts of the section to quartz-sericite-adular in the middle parts and quartz-sericite-hydromica (illite) in the upper ones. Metasomatic process was developed under different K activity with maximum in the middle adulatory part. K, Au and Ag concentrations increase from the lower parts of the section to the upper ones. The zones of maximum Au and Ag concentrations are displaced to the upper parts relative to the maximum K contents. Na distribution in the near-ore zone area results from the primary plagioclase stability. The complete plagioclase destruction and Na removal from the lower parts to upper ones are observed in the mineralization zones. Rb distribution fully correlates with the specific features of potassium behavior. The moderate supply to all zones of syn-ore metasomatites typical of Cs. Maximum contents are observed in the quartz-sericite-hydromica zones while the minimum ones are typical of sub-ore propylite zones. The increased Li concentrations are observed in the supra-ore quartz-hydromica zones. Thus, the distribution of alkaline elements in the near ore area possesses the vertical zonation pattern: K, Rb-Cs-(Li). The values of K/Rb and K/Li + Cs ratios are steady, increasing with the depth (230-380 and 350-1600, correspondingly). They are the representative of sub-ore, supra-ore pattern of gold-silver mineralization development.

The near-ore metasomatites and ores of silver-polymetallic deposits as opposed to gold-silver ones are marked by insignificant K supply (2.7-4.2%), the increased Rb (120-400 ppm), Cs (4-40 ppm), Li (25-200 ppm) and lesser increased Na (0.12-2.5 %) removal. The dynamics behavior of Na and Rb significantly changes. In the zones of silver-polymetallic mineralization the heterodromous pattern in K and Na behavior is insignificant and Rb distribution correlation with the K distribution is not distinctive.

The zones of maximum Rb concentrations are significantly displaced to the upper parts relative to potassium. Markedly high Rb precipitation from the solutions is associated with the decreased K contents. The maximum Cs and Li contents are removed to the uppermost horizons. Alkaline element distributions along the silver-polymetallic mineralization zones possess the zonation pattern (K-Rb-Cs-Li) and well correlate with the composition and zonation structure of the near-ore metasomatites. Maximum K concentrations are confined to the carbonate-quartz-chlorite (lower middle-ore intervals), Rb contents - to the quartz-chlorite-sericite (middle-ore), Cs - to the quartz-hydromica-sericite (average upper-ore), Li - to quartz (montmorillonite) hydromica (upper ore) argillizites.

The K/Rb and K/Li + Cs values on the silver-polymetallic deposits are markedly lower as compared to gold-silver ones. It permits their using under the revealing of the anomaly type interpretation. They increase correspondingly with the depth: super-ore intervals - 75 and 125, upper-middle-ore - 160 - 330, lower-sub-ore - 230 and 870. Thus, K/Rb and K/Li + Cs values are the markers of the zonation, which indicate the level of mineralization zone shear.

The alkaline elements, primarily K and Na indicate the genetic nature of the observed features and like ore elements are associated with the physical-chemical conditions of ore formation. It may be presumed, that the features of alkaline element distributions such as stability, which is closely connected with the composition and structure of near-ore metasomatites and zonation are common to the majority of endogenic (hydrothermal) ore systems. In this sense, the developed methodological approach to anomaly type interpretation and zonation revealing is of common character and may be applied for prospecting and assessment in any ore region.

FORMS OF OCCURENCE OF TECHNOGENIC RADIONUCLIDES  
AND THEIR TRANSFORMATIONS IN LANDSCAPES

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Various classifications of forms of chemical element occurrence, methods of their detection and analysis are presently used including those based on chemical extractions. Belarus scientists have developed a method of successive extractions, which makes it possible to distinguish seven forms of the element occurrence: water soluble, readily exchangeable, carbonaceous, bonded to the organic matter and some sulphides, sorbed by iron hydroxides, hardly soluble, and resistant silicate compounds.

Differences in the forms of occurrence of radionuclides related to global (observations of 1984) and accidental (Chernobyl, 1986) fallout have been revealed. The main form of global  $^{90}\text{Sr}$  is exchangeable - 46,1-71,0% of the total content, carbonaceous form - no greater than 38,1, organic and amorphous - inconsiderable - 7,6-16,5, resistant forms range within not detected - 23,7%. For  $^{137}\text{Cs}$  the ratio of forms is analogous: exchangeable form dominates - 37,5-87,5%, carbonaceous - less than 28,5, and resistant form varies within not detected - 54,1%.

Radionuclide forms during the Chernobyl accident were subject to primary differentiation, which was due to the reactor state, chemism of substances used for the emission inhibition, conditions and distance of wind transportation of radioisotopes. For accidental  $^{90}\text{Sr}$ , the amount of exchangeable form constituted 0,7-57,2%, carbonaceous - 1,8-40,7, and resistant - 9,6-50,6%, i.e. in most cases the content of the later increased, the first - decreased, intermediate forms show high variations.

Fallen radioactive isotopes essentially transformed the radiogeochemical environment of the region and formed a technogenic province of a complex structure with highly anomalous concentrations of radionuclides. Accidental radionuclides, involved in the modern geological and landscape - geochemical processes, were subject to: the secondary migration, disper-

sion and accumulation accompanied by the transformation of their forms.

It was shown that if during the accident concentrations of the carbonaceous form of  $^{90}\text{Sr}$  in valley soils were as high as 16,4-40,7% and were due to the dolomite application for the reactor emission inhibition, then by 1988 their content became 1,5-2 times lower because of a non-stability of carbonaceous compounds with this isotope in acid medium of landscapes. The Chernobyl range of radionuclide forms will approach with time to the present range of their forms from global fallout.

We distinguish the following aspects of the radionuclide forms transformation depending on the geochemical environment behaviour: facies, soil, biogeocenologic ones and that of geochemical barriers.

In silts within the 30 km zone,  $^{90}\text{Sr}$  shows similar contents of the water soluble form in sediments of the channel and oxbow facies averaging 2-4%, but sharply different from that in flood plain sediments - about 0,7%. Concentrations of the exchangeable and acid soluble forms occupy the intermediate position between the water soluble and resistant forms, but differ by increased limiting and average values in a facies series: "channel - flood plain - oxbow". The latter is there-with higher than the first one, especially in silts of the first two environments; it dominates over the other forms and averages 37,7-73,8%, but its content decreases in the above facies series. This is due to the "hot" particle weathering, which is very active under geochemical conditions of oxbow lakes and leads to the increase of exchangeable form.  $^{137}\text{Cs}$  shows the domination of the resistant form exceeding 90%, its concentrations tending to the decrease in a facies series however remaining at similar levels. This is explained by caesium involving in "hot" particles and fixation in the exchangeable and acid soluble forms in the crystal lattice of clay minerals. The behaviour of radionuclide forms range within the north-eastern trail shows similar regular trends. The difference in the content of some forms there is due to a peculiar pattern of the primary fallout in the remote zone (readily exchangeable forms average 20-35% in the channel and 13-37% in the flood plain facies sediments, etc.).



The transformation of radionuclide forms in the soil cover shows the decrease of the exchangeable and increase of acid soluble form of  $^{137}\text{Cs}$ , and increase of the exchangeable  $^{90}\text{Sr}$ , growth of a proportion of mobile forms of  $^{239,240}\text{Pu}$ ,  $^{106}\text{Ru}$ ,  $^{144}\text{Ce}$ . These form transitions depend on pedogeochemical conditions connected with soil types, depth of radionuclide penetration to humus and other horizons, fuel particles leaching, pedogeochemical barrier.

Transformations of radionuclide forms due to the processes occurring at geochemical barriers conform to the above pattern, however show some peculiar features. The experiments performed for revealing the relation between radionuclides with the organic matter, carbonate and iron compounds made it possible to explain the dynamics of their forms in landscape.

Results of studying the radionuclide migration in landscapes of Belarus based on forms of their occurrence contributed to the solution of some applied problems of radiogeochemical survey, water supply, efficient nature management, medicine and agriculture in contaminated territories.

LANDSCAPE - GEOCHEMICAL STUDIES OF SYNERGY OF  
NITROGEN COMPOUNDS AND RADIONUCLIDES

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Simultaneous action of the radiation and chemical factors on the human organism can essentially change the response, which is particularly shown by the synergy effect. The data available indicate that a combined action of nitrogen compounds and ionizing radiation is resulted in the formation of highly active carcinogenic substances with a simultaneous increase of metahaemoglobin concentrations in the organism. We study the problem of synergy of radionuclides and nitrates from in the context of landscape geochemistry using the data obtained before and after the Chernobyl accident.

Nitrates and nitrites are of particular interest among chemical compounds continuously affecting human organism. In some regions of Belarus before 1986 reliable links were established between malignant tumours cases and contents of nitrates in landscapes (soils and waters), as well as in foods (milk, potatoes). Areas with an increased, number of oncologic cases show the higher concentrations of nitrate nitrogen. High nitrate contents of drinking water of Belarus can result in metahaemoglobinemia.

Under the effect of economic activities, nitrogen concentrations sharply increase in all the landscape constituent, especially within populated areas, which result in the pollution of drinking water and foods by nitrates, and sometimes - by nitrites. About 80% of drinking water samples show nitrate contents which are 2-3 times the standard value (45 mg/l). Nitrate concentrations of ground drinking waters show a tendency for a decrease from the Southern to Northern geochemical province.

Natural radioactivity of cover sediments and soil marked by a low background value and subclark concentrations of radionuclides, as distinct from nitrates, was somewhat higher for the Northern province. Its minimal values were typical for sediments of the Southern province. In all sites where natural radio-

activity was relatively high, cover sediments are represented by morainic loams and sandy loams, and where it was low by glaciofluvial and alluvial sands. Average  $\beta$ -activity values of soil samples from allotment gardens were lower and,  $\alpha$ -activity values - higher than those of rocks of the appropriate province in general.

It is suggested to estimate the geochemical field of the above indices by the coefficient  $K_g$ , which show the relationship between radioactivity ( $n \cdot 10^{-9} \text{ Ci/kg}$ ) and nitrate nitrogen ( $\text{mg/kg}$ ).

Calculations made from the data of pre-accident observation show that average value of  $K_g$  for loams within studied areas of the Northern geochemical province is 5,5, for Central - 3,0; this value is considerably lower for loessial loams - 1,1.

This coefficient value sharply decreases in allotment plots, where nitrate nitrogen content is 1,5-8,0 times greater than in natural lands with an equal natural background radiation. For sandy loam soils from allotment plots of the Northern and Southern provinces this coefficient is 0,4, for Central - 0,5.

There is a difference in  $K_g$  values in test and carcinogenous allotment plots. In all three provinces this coefficient is 1,5-3 times less in carcinogenous plots. A comparison of plots with different sickness rates assumes that with the coefficient value of 0,50 and above the synergistic effect manifestation is highly improbable, from 0,50 to 0,30 - probable, and below 0,30 - more probable.

To check up the proposed coefficient, since 1987 observations are carried out in a landscape-geochemical stationary characterized by a minimal oncologic sickness rate in the pre-accident period and occurring now in the region adjacent to the 30 km zone with a high radiocontamination level from 15 to 40  $\text{Ci/km}^2$ .

The analysis has shown that the  $K_g$  value for soils of allotment plots within the stationary is 1,03 and synergistic effect is theoretically highly improbable. However, high concentrations of nitrates in foods and drinking water examined there (nitrate load is 1,7 times greater than the permissible stress value) in addition to a constantly high background radia-

tion are themselves dangerous for human health, especially for children.

The synergy manifestations are studied in the following ways: correlation of levels of geochemical indices of soils, waters and foods, on the one hand, and temporal dynamics of the oncologic sickness rate, on the other hand; determination of the importance of modes of radionuclides occurrence in landscapes and foodchain; assessment of the influence of landscape concentrations of trace elements responsible for endemic phenomena within the territory of Belarus. A network of landscape-geochemical test grounds was created within the north-western, western and north-eastern trails of the Chernobyl radionuclide fallout. The data of recent observations are discussed.

## GEOCHEMICAL PROCESSES IN AGROLANDSCAPES

### WITH INTENSIVE LIVE-STOCK FARMING

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Agrolandscapes of the northern humid zone typically are subjected to technogenic stresses of two types due to crop and cattle farming. Landscapes of the Belarus territory show the prevalence of drained soils and highly developed live-stock farming.

Ameliorated lands are used under cereal and hay crops with appropriate agricultural technology and chemicalization. Their impact upon the environment involves erosional losses (sediment runoff) and removal of untaken chemical ameliorants, which include nutrients - nitrogen, phosphorus, potassium, as well as admixtures - chlorides, trace elements as dissolved and suspended substances.

Dispersed agrochemical pollutants though increase the total salt content of natural waters and background concentration, but do not exceed maximum - allowable concentrations under existing chemicalization level.

Agricultural landscapes with developed live-stock farming are peculiar by a local effect of farm wastes upon waters, soils and plants. The volume of manure slurries, which are applied there every year are estimated at 500 m<sup>3</sup>/ha. Each cubic metre of manure slurries from pig - breeding farms with 54 to 108 thousand pigs includes 0,7 kg nitrogen, 0,4 kg phosphorus, 0,6 kg potassium, 5 kg salts, and up to 3,5 kg organic materials. Sewage waters contain as well manganese - up to 0,4 mg/l, zinc - 0,3, copper - 0,1, etc. The content of the above elements in wastes from cattle - breeding farms with 10 thousand cows is 2-3 times greater.

Manure slurries are utilized in agricultural irrigated lands (AIL) using sludge sprinklers, and mobile irrigators. Nutrients are intaken by soils and plants, so the nutrition value of sewages is utilized however not completely due to their excessive volumes. Therefore, the agrolandscapes discus-

sed are territories with anomalous technogenic levels of nitrogen, phosphorus, salts in waters, their concentrations are tens and hundreds times the hydro-chemical background value and there is the soil salinization hazard during drought seasons. Return waters from irrigated lands come to special drainage systems and are accumulated in settling basins for repeated utilization and natural purification before their discharge to the end receiving streams - rivers of the 3rd and 2nd order.

Hydrochemical monitoring relates the chemical element flows, dispersion, and concentrations to technological peculiarities of enterprises and natural conditions, as well as controls the regimes of the system functioning and ecological environment. Ex. gr., it was established that the ammonium concentration in the River Kabischanka - a receiving stream of the pig - breeding farm "Gorodoksky" - is as high as 5 mg/l (12 times the maximum - allowable concentration), which is an evidence of a negative ecological situation of these works. During the investigations it was found the pollution of AIL return waters by non-utilized waterwastes, silting and secondary pollution of settling basins, where the photosynthesis processes are depressed, salts, heavy metals and biogenic products are accumulated. During the vegetation period of dry 1992, from 20 to 280 tons of salts, including salt ammonium - up to 2 t, nitrates - 30, phosphorus - 4, etc. were removed from AIL to receiving streams of pig-breeding farms without appropriate technology of purification. A part of dissolved substances is intaken by natural vegetation of water bodies (macrophytes). Under specific conditions due to wastewaters, there are some species which can influence the content of pollutants. This is used for biological treatment of sewage waters.

The composition of AIL soils changes as a result of long-term irrigation. Dissolved elements saturate the absorbing complex, increase the concentrations of phosphorus, nitrogen, potassium, calcium, trace elements, change the mechanism and kinetics of processes contributing to the removal of one elements, and accumulation of the other in the plowing and subsurface layers. Soil phosphatization is observed, as well as the microelement redistribution depending on the wastewater application season, types of soils and their peculiarities.

Modes of occurrence of manganese, cobalt, chromium, vanadium and other trace elements were studied in peaty boggy and soddy podzolic soils irrigated by wastewaters. Some differences in the mobility of trace elements were determined: participation of easy-soluble, exchangeable, and organic-bound compounds increases; soils are saturated with biologically useful elements; portion of amorphous forms increases in peaty and loam sandy soils. Utilization of manure slurries results in the soil enrichment with microorganisms, formation of new microcoenoses.

Detailed studies within these territory make it possible to distinguish them as peculiar landscapes and efficiently contribute to the optimization of their ecological situation.

## THE APPLICATION OF REGIONAL ROCK GEOCHEMICAL DATA IN PREDICTING FAVOURABLE AREAS FOR MINERAL EXPLORATION: A CASE STUDY FROM TAMPERE-HÄMEENLINNA AREA, SOUTHERN FINLAND

LAHTINEN, R., LESTINEN, P.

A rock geochemical pilot study was conducted in the Tampere-Hämeenlinna area during 1989 to develop sampling strategies and methods, analytical methods and interpretation methods for the Rock Geochemistry Research Project (RGRP) begun by the Geological Survey of Finland in 1991. There are 403 samples included in this pilot study from an area of 9600 km<sup>2</sup>, with an average sampling density of one sample per 24 km<sup>2</sup>. The analytical methods included XRF, ICP, GAAS and INAA.

Gold and Ni mineralizations are the most prominent metallogenic features, but the study area is also known to have some Cu, W, Zn, Fe, Ti, Mo, U and rare-metal (Be, Ce, Cs, Li, Nb, REE, Sn, Ta and Y) potential. Exploration activity at present is focused on gold and many promising Au prospects have been located.

The background values of ore-related elements between different rock types vary markedly. For example, pelitic sediments are enriched in a number of elements and black schists in particular are rich in Mo, Te and Pd. In defining samples that may be indicative of ore grade mineralization, the background values of different rock types have been used.

The variation in Co, Ni and Zn data in this study is mainly attributed to differences in different rock type, and there appear to be only a few anomalous samples with mineralization effects. The Cu data show similar variation, but the tholeiitic volcanic association in the Hämeenlinna Schist Belt (HSB) contains higher values. Gold, As and Te data have many anomalous values forming potential areas that in part coincide with known gold occurrences. A noticeable feature is the possible zoning of Au + Te and As, especially in the western part of Tampere Schist Belt (TSB). Palladium contents are normally below detection limit, but there are some higher values associated with elevated Au concentrations in mafic rocks. Lithium data also indicate several anomalies including two earlier unknown potential areas, one in the HSB and one at the boundary of the HSB and the Microcline granite Complex (MC) to the south. The S-type microcline granites are considered to have potential for Sn mineralization and one possible target area from MC has been identified in this study. Some anomalous U and Pb values have been found for the microcline granites, too. Silver, Bi and Sb also show some anomalies, but their behaviour is rather irregular. Antimony is concentrated in calc-alkaline volcanics whereas the highest Bi values are recorded from S-type pegmatites and granites in the MB. Molybdenum and W contents are normally near or below the detection limits, but some anomalous values are observed.

Mineralized samples are normally avoided during sampling in this study and thus the anomalous samples probably represent extensive and pervasive mineralization effects and are reliable in a regional sense. This is seen in the combination map where anomalous trends and areas for elements such as Au, Te, As, Li and Sn are apparent. However, the low sampling density in most cases prevents the direct application of this data in exploration. This is especially, the case with magmatogenic Ni occurrences, where mineralization processes have not formed extensive alteration haloes. On the other hand, the recognition of plutons of depleted mantle nature in association with MORB-affinity volcanics could show regional scale potential areas. These samples have been combined with modified regional till geochemical data, which then delineates areas with a higher mafic component in till and areas of 'mineralized' mafic affinity.



## **ROCK GEOCHEMISTRY RESEARCH PROJECT (RGRP): A NEW REGIONAL RESEARCH PROGRAM**

**LAHTINEN, R., LESTINEN, P., KORAKOSKI, E., SALMINEN, R., SANDSTRÖM, H., SAVOLAINEN, H., VALLIUS, H.**

The Rock Geochemistry Research Project (RGRP) initiated by the Geological Survey of Finland (GSF) in 1991 is a seven year regional research program covering the whole of Finland. The main objective of the RGRP is to acquire a geochemical data base from different bedrock types in order to classify them into different tectono-magmatic and genetic groups with interpretations of their metallogenic significance. This data is also applied to combined till and rock geochemical data, and in studying the geochemical features of crustal evolution and origin of rock types.

The samples are taken from outcrops and the sampling density varies from one sample per 30 km<sup>2</sup> to one sample per 120 km<sup>2</sup> depending on the degree of lithological variation. Eventually total of 7000-8000 samples will be collected and analyzed. Sampling strategy is based on the available bedrock maps and all the major rock types are included. The sampling sites are distributed as evenly as possible and sampling is carried out by portable mini-drill with a diamond bit. Each sample is composed of five sub-samples all taken from the same lithological unit. Four sub-samples are used for analysis and the fifth is for petrophysical and petrographical studies. The sampling includes a detailed outcrop description with sample unit classification. The samples are analyzed in the GSF chemistry laboratory for over 50 elements including REE's, the main analytical methods being XRF, ICP-MS, ICP-AES and GAAS. As the sampling and analytical stages are critical an efficient quality control is used. Assessment of contamination during sampling and sample pretreatment are controlled by quartz samples. Systematic duplicate analysis system has been introduced including field and laboratory duplicates and a batch of control samples from the first year samples analyzed repeatedly every year, in order to eliminate the effect of possible annual drift and make the results comparable for the whole duration of the project. The results will be published as regional reports in the GSF report series. The field and analytical data including petrophysical data, are stored in the Alkemia-data base, enabling the simultaneous study of a large number of samples from a wide area and particularly, access to data from specific localities.

At present, about 3700 samples have been collected covering approximately 50% of Finland. Sampling is expected to be completed in 1995 and final results are to be published during 1997. The first sub-regional reports will be published in 1994.

## BRYOGEOCHEMICAL PROSPECTING FOR GOLD IN YAKUTIA

LAPAEV, G.P.

Bryogeochemical investigations in Yakutia were initiated in 1963. To the present for the search purposes more than 93000 samples of mosses have been collected on the area of 26000 km<sup>2</sup>.

Bryogeochemical prospecting for gold started from 1984 have been carried out on the area of 156000 km<sup>2</sup> and during that more than 55000 moss samples have been collected. Sampling density varied from 1.5-4 sample per 1 km<sup>2</sup> to 1 sample per 25 km<sup>2</sup>. Weight of dry moss sample was on the average 20-30 g. Its ashing was made by 480° C. Au content was determined by GFAAS after aqua regia digestion with an oil sulphide extraction. Also, the samples were analysed for 35 elements by arc-source emission spectrography.

The background values of Au are from 1.5-2 up to 4.5 ppb of different regions. A great number of bryogeochemical anomalies of Au and its pathfinders such as As, Sb, Pb, Zn, Tl, W, Cu, Bi and others was delineated. Maximum values of Au content do not usually exceed some ppm and sometimes they reach some tens of ppm.

Some tens of promising targets for Au have been discovered in Yakutia. Unfortunately, most of them has not a reconnaissance. The report has a description of some areas investigated.

The most interesting promising targets have been discovered in a district between rivers Yana and Omoloy. The area investigated is nearly 6000 km<sup>2</sup>. 35% of it is covered with overburden of diverse composition, thickness and source. Bryogeochemical anomalies of Au, Pb, Zn, As, Tl form jointly two large-scale zones. The central part of the first zone covers the known mineralized area involved several occurrences and placers of gold. The second previously totally unknown zone is discovered in the northern part of searching area and is covered fully with overburden. It is absolutely analogous to the first one.

It is recommended to use aquatic mosses for solving problems of prospecting and environmental geochemistry.

**TECHNOLOGICAL-GEOCHEMICAL CYCLES AND SPECIFIC FEATURES OF MICROELEMENT BALANCE FORMATION UNDER SULFATE-CELLULOSE MANUFACTURE ON THE SELENGA CELLULOSE PLANT**

LEONOVA G.A.

The procedures of different manufactures, studied by geochemical methods combined with the balance calculations, are significant. Such approach permits not assessing the consequences of manufacture influence on the environment separately, but revealing the specific features of their interaction.

The manufacture of sulfate cellulose is accompanied by the great amount of liquid and solid waste. The development of approaches, aimed at decreasing pollution, is impossible without analyzing geochemistry of waste. The following questions should be answered: is there toxic effect in the procedure itself or in the used chemicals; is it appropriate to change the procedure or to collect toxic compounds from the sewage and smokes.

As a result of conducted investigations, the pattern of mass transfer in the technologic cycle is developed. This pattern includes the outlet and inlet zones for chemical reagents, raw material, manufacture products and waste. The simplified pattern enables revealing the main sources of microelement supply into the technological cycle, their redistribution under the manufacture as well as substance-concentrators of the polluting agents.

The balance calculations indicate that the main sources of microelement supply into manufacture are raw material (wood) and chemical substances, used under the manufacture. The major part of Zn, Mn, Sr, Cd are supplied into the technologic cycle with the raw material. The major part of Al, Cu, Pb, Li, Fe are supplied with the chemicals.

The technological-geochemical background, the lower limit of which, results from the primary raw material composition, is revealed for sulfate-cellulose production. The toxic metal concentrations in chemical reagents may be decreased via preliminary cleaning but the microelement concentrations, supplied with the raw material cannot be controlled. Thus, the microelement concentrations in the wood is responsible for technologic-geochemical background formation. The background cannot be decreased without application of expensive and power-intensive procedures.

The toxic metals, when supplying into the technological cycle from raw material and chemicals, are redistributed and concentrated in solid waste (slime-lignin, redundant active mud, causticization waste) in the amount, significantly exceeding the technologic-geochemical background of the production (Table 1). The solid waste, being the reservoir of the accumulated toxic metals, is the main source of environment pollution. The concentrations of the heavy metals, discovered in the solid waste of the Selenga cellulose plant, should be controlled. Our data indicate that Pb, Cu, Zn, Cd concentrations in the plants, growing in the vicinity of sites of waste burial, are on the background level. As the places of solid waste burial are the alkaline landscapes, devoiding vegetation, the

above microelements are less mobile and inaccessible for the plants. The accumulation of molybdenum and boron is observed in some plants.

The proposed procedure on conducting investigations of toxic metals technological cycles and the creating the balance of chemical manufactures may be widely applied in geoecology.

Table 1

Concentrations of heavy metals in the waste of the Selenga cellulose plant as compared to technological-geochemical background of the manufacture (mg/kg of dry mass)

Micro elements	Analyzed objects				
	wood	slime-lignin	active mud	technologic slime	causticization waste
Cu	0.66	31.0	33.0	94.0	44.0
Zn	8.0	61.0	87.0	202.0	192.0
Pb	0.07	3.3	1.7	12.8	7.5
Hg	n.d.	0.008	0.008	0.015	0.01
Cd	0.023	0.15	0.27	1.7	1.8
Sr	16.5	48.0	63.6	196.0	450.0
Li	0.12	2.9	4.4	34.8	2.0
Mn	48.0	259.0	445.0	1224.0	1900.0
Al	37.0	41673.0	25606.0	106493.0	9000.0
Fe	28.0	4630.0	9383.0	5997.0	9800.0

## THE CHEMICAL AND MINERALOGICAL BEHAVIOR OF Pb IN POLLUTED SOILS FROM SHOOTING-RANGE AREAS IN MIDDLE SWEDEN

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### ABSTRACT

High Lead concentrations, up to 2300g Pb/m<sup>2</sup>, are found in some shooting range areas near Örebro, middle Sweden. The corresponding contamination from atmospheric deposition will only increase the Lead-content up to about 30 g/m<sup>2</sup> relative to background content in the surface soils. Lead pellets & bullets can readily decompose and transform into Pb-bearing minerals in contact with soil. The newly formed minerals are mainly Lead carbonate hydroxides (PbCO<sub>3</sub>-nH<sub>2</sub>O) in soil environment having pH value from 3-6.5. In neutral soil environment the transformation can produce cerussite (PbCO<sub>3</sub>). Compared with soils in Danish shooting areas, the Swedish acid soil environment is favourable for the formation of Lead sulfate (PbSO<sub>4</sub>) as well. Organic substances have a rather large capacity for degradation of Lead pellets & bullets. The degradation rate is environmentally dependent and is more rapid in soils rich in organic substances.

Soil minerals have however various capacities for adsorption of Lead in soil. Al-hydroxides are capable of retaining Pb via adsorption as an inner-sphere complex during their formation which causes more stable bonding of metal-mineral. Clay minerals, especially smectite and mixed layer chlorite, can be capable of adsorbing Pb via an outer-sphere surface complex. The EDTA extractable Pb in soil suggests the adsorption on the surface of clay minerals. The Lead pollutants appear to accumulate in surface soil horizons and the enrichment occurs within top several tens of centimeters. Adsorbed Pb on soil particles via ion-diffuse can be readily released into soil solution and can be mobilized down the profile by percolating water. From the soil profile studied it can be seen that there are smaller concentration of Pb in leached horizon(A) and slightly larger in accumulated horizon(B).

A special complex of Lead compounds was also found. The introduction of Lead into microstructure of soil particles can prevent the leaching of Pb from soil and the subsequent formation of new Pb-bearing minerals.

## PEDOGENIC CARBONATE - AN IMPORTANT SAMPLING MEDIUM FOR GOLD EXPLORATION IN SEMI-ARID AREAS

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Soil geochemical studies at several sites in the Archaean Yilgarn Craton of semi-arid south western Australia have shown a specific, highly significant and unequivocal association between Au and pedogenic carbonates. The region is characterized by the widespread development of a deep lateritic regolith which formed under humid, probably warm conditions during the early Tertiary and has been modified under subsequent arid climates that continue to the present. Although the regolith was strongly leached during the initial phase of weathering, the upper few metres are now commonly infused by pedogenic carbonates precipitated as evaporites in voids and as coatings, nodules and cements. Supergene Au deposits have developed in the ferruginous lateritic horizons and deeper in the saprolite, overlying primary mineralization. These have a strong surface expression where the laterite outcrops. Where the residual profile is partly truncated or buried, mineralization may be concealed by many metres of barren sediments and/or leached saprolite. Past exploration has relied on deep drilling, but such deposits can have a surface expression if soils are sampled correctly.

At the Bounty mine, the lateritic profile has been truncated and soils have developed from clay-rich saprolite. Gold is intimately and almost exclusively associated with the pedogenic carbonates (concentrations 50->500 ppb) that have developed in the top 2 m of the profile. Below the carbonate, the Au content declines to <10 ppb. A similar association occurs at the Panglo deposit, 250 km NE of Bounty, where significant supergene mineralization occurs at a depth of 40 m beneath strongly leached saprolite. Thin (<1 m) colluvial and alluvial sediments overlie much of the deposit, but to the south, the saprolite is buried by 10-15 m of barren ferruginous gravels, sands and clay. Mineralization is expressed by Au enrichments (50-150 ppb) in the carbonates in the top metre of soils on both the colluvium and the gravels. The Au distribution is more complex at Mulline, 110 km NW of Panglo, where the ferruginous lateritic horizon is being altered and partially disintegrated by carbonate precipitation. Dispersion of Au from primary mineralization has created a surficial halo characteristic of lateritic deposits but, in addition, Au is also present in the carbonates, so that both phases may contain up to 1 ppm Au.

Gold and carbonate not only have very similar distributions in soil profiles, but the Au associated with the carbonate is very soluble. This suggests that their dispersion is controlled by similar processes. A possible mechanism is that Au, Ca and Mg are brought to the surface by deep-rooted trees and are subsequently re-cycled in the soils. Calcium and Mg react with CO<sub>2</sub> produced by root and microbial respiration and Au forms a soluble complex, probably with organic matter, and all precipitate when the soil water is removed by evapotranspiration.

The strong association between Au and pedogenic carbonate suggests that the carbonate horizon should be identified and preferentially sampled during exploration, particularly where soils are developed from highly leached and/or transported substrates. Sampling that does not specifically select this horizon may be inappropriate because this restricted expression of Au mineralization may be missed. The depth and thickness of the carbonate horizon may vary, but it is generally within 1 to 2 m of the surface and may readily be identified using dilute HCl. The most cost-effective sampling procedure is by power auger drilling and compositing the cuttings through the carbonate horizon. Anomalies are, however, limited in lateral extent, so that close cross-strike sampling intervals should be used. This procedure has been successfully used throughout the southern Yilgarn Craton and should be applicable in equivalent terrains elsewhere.

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## THE STUDY OF HYDROCARBON DISTRIBUTION IN MARINE CYANOBACTERIAL MATS

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Microbial mat has been recognized as living fossil for its structural similarity with the ancient stromatolite. Thus, the study of chemical composition, especially the hydrocarbon in living microbial mat becomes very important in understanding the original input and transformation of hydrocarbon found in ancient stromatolite and fossil fuel. In this study, the distribution of hydrocarbon in a lagoonal cyanobacterial mat which was collected from Baffin Bay, Texas was studied by gas chromatography/mass spectrometry (GC/MS). Because of the irregularly seasonal and wind-generated tides, the intermittent growth of cyanobacteria at the bottom of the lagoons and the accumulation of mud brought into the lagoons by flooding have led to alternate organic-rich and mineral-rich layers. It is believed that the buried organic compounds were decomposed mainly by fermentative microorganism living in the mat. For this reason, the mat becomes a good model to study the change of hydrocarbon distribution owing to biodegradation effects in the environment.

The biomarkers from cyanobacteria such as n-heptadecane, monomethyl-hexadecanes and -heptadecanes, and heptadecene are the predominant compounds found in the upper part of the living mat (0-0.4 cm). However, with the depth increasing, the quantity of these compounds decreasing gradually. Decreasing the quantity of these hydrocarbon with depth in the mat implies that the effects of microbial degradation can heavily and rapidly alter the originally chemical composition in the environment.

It is interesting to find that a series of even-carbon number normal alkanes (from n-tetradecane to n-octadecane) were the predominant compounds in the bottom part of the living mat (0.9-2.0 cm). Similar compounds have been found in several marine sediments, therefore, the possible sources for these compounds may come from cyanobacteria or the bacteria lived in the mat.

C28 hopane (the number refers to the carbon number) is the predominant compound found in the buried mats. The possible sources of this compound may come from the cell decomposition of the cyanobacteria or other bacteria living in the buried mat.

## GEOCHEMICAL MAPPING OF STREAM SEDIMENTS OF THE BAIKAL LAKE BAIKAL TRIBUTARIES

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Geochemical mapping of the stream sediments from the Baikal lake tributaries was aimed at study of river drift influence on the recent sediments in the littoral and for the large tributaries for pelagic part of the lake bottom.

One of the main goal of the geochemical mapping is geochemical classification of the stream sediments of the near-mouth parts of the Baikal tributaries.

The sandy-clay fraction ( 0.5 mm in diameter) of the stream sediments was sampled from 250 constant tributaries of the Lake Baikal. The collected samples were analyzed for macroelements via the X-ray analysis and for microelements by atomic emission quantitative and semiquantitative analyses.

The data were interpreted via multidimensional field analysis as it enables the distribution patterns of chemical elements to be revealed i.e. the polyelement geochemical associations and geochemical types of sediments to be distinguished on the quantitative basis.

The study of macroelement distributions is particularly significant as they serve as the markers of phase and granulometric composition features, which determine the microelement composition of the deposits. The rate-setting of oxide sum of major elements to 100% were made to remove the irregularities in macroelement distributions. Then the oxide concentrations were calculated into element concentrations.

50% of the accumulated frequency was used as the background concentrations.

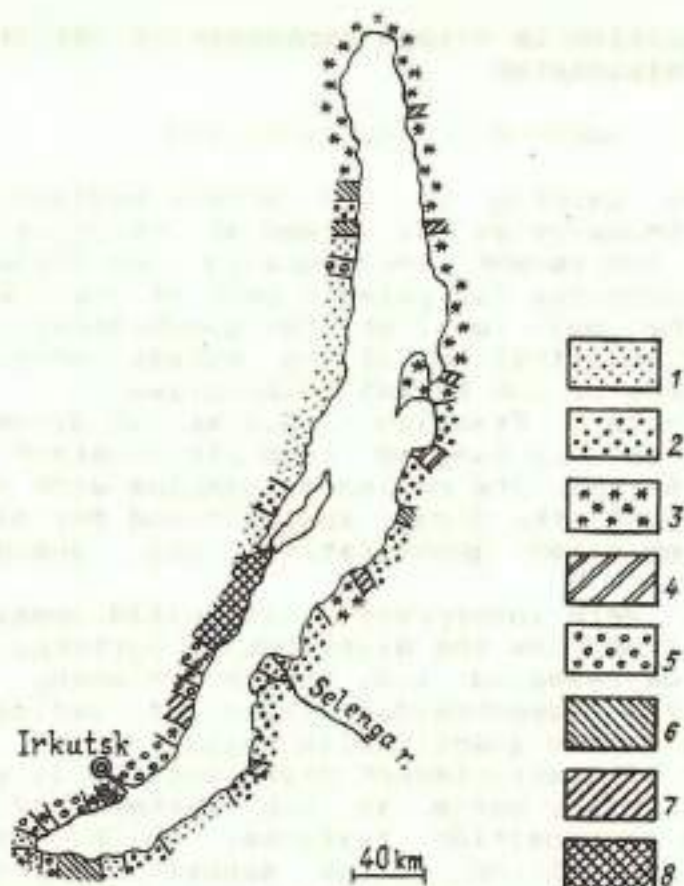
The background element concentrations in the stream sediments of the Baikal tributaries for the macroelements (weight percentages) are: Si -28.05; Ti - 0.42; Al -7.94; Fe - 3.70; Mn - 0.08; Mg - 1.51; Ca - 2.36; Na -1.71; K -1.91; P - 0.10; S - 0.07; Ba - 00.7; for the microelements (ppm): Ag - 0.06; Pb - 6; Zn -50;Cu - 27;Ni - 10; Co - 8; Mo - 2.0; Cr - 40, Li - 1; B - 10.

The polyelement geochemical map-scheme of the stream sediments of the Baikal tributaries.

Geochemical element association (in brackets are the contrast coefficients):

1. Li(13)B,Cu,Ni(1.8) Mn,Ti(1.2) Mg,Si,Al,Fe(1.1) Ca(0.7) Na(0.7)
2. B(2.2) Ag(1.6)Cr(1.5) Mo(1.4) Mn,Mg,Si,Ti(1.1) K,Al,Fe(1.0)
3. Sr(1.4)Na,Ba(1.3)Ca(1.2)Si(1.1)
4. Ba(11) Cu(2.1)S,Sr(1.9) Ca(1.7)Mn,Mg,Ti,P,Mo,Ag,V(1.5) Fe(1.3)
5. Li(20) S(1.6) Pb(1.4)Mn(1.3)Fe(1.2)Ca,P,Mg,K(1.1)Ti,Al(1.1)Si(1.0)
6. Cu(2.8) Ni,V(2.3) Mg(2.0)Ti(1.9)Mn(1.7) Fe(1.6)Ca(1.3) Na(1.1)
7. S(6) P(3.4)Mn(1.9) Ca(1.7)Fe(1.2)Al(1.2) Si,Ti,K,(1.0) Na,Mg(0.9)
8. Ag(108) Pb(5.7)Ni(2.6) Ca(2.4)Mg(1.8)Na(1.4)Mn(1.3) Fe, Ni(1.2)Al(1.1)Si(0.9)K(0.5)





For all distinguished groups, the main petrochemical coefficients were calculated. It permits to describe the revealed groups in detail (group numbers correspond to the numbers on the figure).

groups	$\frac{(Na_2O + CaO)}{Al_2O_3}$	$\frac{(Na_2O + K_2O)}{Al_2O_3}$	$\frac{(Al_2O_3 + TiO_2 + Fe_2O_3)}{SiO_2}$
1	1.67	0.251	0.379
2	2.19	0.291	0.345
3	3.02	0.353	0.344
4	5.06	0.251	0.444
5	2.16	0.264	0.427
6	4.94	0.261	0.518
7	3.33	0.243	0.451
8	9.68	0.265	0.486

The petrochemical features of the revealed groups characterize the stream sediments of the Baikal Lake tributaries as clay-sandy aleurites, which are different in the main phase ratio.

Thus, the stream sediments of the tributaries are similar by geochemical features. It results from the similarities of the landscape-climate conditions of the drainage basin.

CONTRIBUTION OF MASS BALANCE TECHNIQUE TO THE KNOWLEDGE OF GOLD ENRICHMENT IN GOSSANS: APPLICATION TO IBERIAN PYRITE BELT.

LOREDO, J., GARCIA IGLESIAS, J.

Gold-rich gossans are formed as weathering products of primary sulphide deposits containing native gold, which is a stable mineral under supergene conditions, and it is usually retained in the gossan as residual mineral. Gold is an immobile element, however some transport of small-size gold particles is possible (Boyle, 1979; Plyusnin et al., 1981; Webster and Mann, 1984). In these conditions must not be underestimated a gold transport in solution as complex ions, provided that the solubility of gold under supergene conditions is known (Maichairas, 1967; Warren, 1982; Cloke and Kelly, 1964; Lakin et al., 1974; Boyle, 1979). In conditions of supergenic alteration some protore minerals turn unstable and happen the solubilization of chemical elements. In these conditions the geochemical behaviour of the different elements is function of the mineralogical stability and the geochemical mobility of each one. So elements as Ti or Zr, which minerals are very stable in these conditions behave as immobile elements and they conserve their mass. Elements as Cu, Pb and Zn solubilize in these conditions, and some of them -Pb and Zn- have a great mobility and leave the system. Elements of low mobility as Fe, reprecipitate and neofom stable minerals -iron oxides- in these conditions.

The weathering of protore can be described as a closed chemical system assuming as simplification that lateral flux of elements is negligible. In this conditions the mass of an immobile chemical element contained in a protore volume, will remain retained in this volume after their transformation in gossan.

On the basis of that meteoric water flux and transport of elements are vertical, in moderate homogene ore deposits is possible to use mass balance models (Brimhall et al., 1985; Brimhall and Dietrich, 1987), which combines data about bulk density, chemical composition and volumetric properties (strain) of weathering products to those of the protore. Defining the strain (s) as the difference between gossan length ( $H_{i,g}$ ) and protore length ( $H_{i,p}$ ) divided by protore length :

$$s = (H_{i,g} - H_{i,p}) / H_{i,p}$$

In this case the residual enrichment factor ( $C_{i,g}/C_{i,p}$ ) for retention of an immobile element (i) from protore ( $C_{i,p}$ ) to gossan ( $C_{i,g}$ ) during weathering, is a function of the deformation of the system ( $H_{i,p}/H_{i,g} = 1/1+s$ ) and the density ratio ( $D_p/D_g$ ) of the protore ( $D_p$ ) to that of the gossan ( $D_g$ ):

$$(C_{i,g}/C_{i,p}) = (1/1+s) \times (D_p/D_g)$$

Gold enrichment in gossans occurs by isovolumetric residual concentration as it is retained in the weathering products as an immobile element and effectively enriched by complete depletion of sulfur and partial depletion of iron in solution. Iron is locally mobile and is transported and partially reprecipitated by oxidation as goethite and hematite. Other elements are more mobile such as copper, lead and zinc, and are leached from the gossan. Titanium was assumed to behave as an immobile element and used to compute the amount of strain due

to dissolutional collapse of the porous ferrogenous matrix.

The weathering of massive sulfide deposits from Iberian Pyrite Belt have produced ferruginous gossans with reduction of bulk dry density and average mineral grain density and increase of rock porosity by dissolution of minerals containing mobile elements. Residual enrichment of Ti and Au occurs, and is occasionally augmented by enrichment due to volume loss by dissolutional collapse.

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Application of artificial sorbents  
in prospecting

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Adsorption and ion exchange onto colloidal particles is one of the major processes governing the mobility of chemical elements in the surficial environment.

For more than 15 years artificial sorbents have been developed by the author for studying natural processes and for applied geochemical prospecting and environment monitoring.

We successfully combined the hydrogeochemical, atmochemical and lithochemical methods by the use of absorbing material. The method allows the fixing of the mobile forms of many elements by cation- and anion-exchangers, in order to estimate their contents more confidently. It also permits the selection of sorbents with highly selective properties. Cellulose polyphosphate, as well as other sorbents were used (carbon fibers, zeolites, ion-exchange resins etc.). These sorbents were submerged in streams or buried in the ground, or they were left for a period of time in soil at a depth of about 1 m at stations 25-200 m apart in regions where prospecting was going on. In some experiments we attached sorbents to branches of trees 1-3 m above soil level. Several case histories illustrate some of the different environments where the use of artificial sorbents was compared with other prospecting methods.

Artificial sorbents were used to search dispersion patterns of gold in soils and water streams from small- and average-sized sulphide-gold-quartz ore deposits in Archean-Proterozoic and Paleozoic granites in treeless mountain landscapes of Siberia. Glaciers, stone streams, solifluction, and glacial and fluvio-glacial deposits were widely developed here. After 3 months of keeping sorbents in soils their concentrations of gold above the ore manifestation were 30-40 times the background. Anomalies of silver were not so clear.

In 1986, during the 44th expedition of the research vessel

"Akademic Kurchatov" in the Baltic Sea, the author tested sorbents for measuring metal contents in gas-liquid fluids emanating onto the seafloor from craters (pockmarks) and other features. A series of experiments was carried out with artificial sorbents that were: 1) attached to a rope and pulled by the vessel in its passage; 2) submerged for four days in plastic tanks containing 5 liters of seawater from gas-crater zone; 3) submerged in the sea to different depths on ropes attached to buoys (floats). The distribution of Be, Ti, Cr, Mn, Ni, Cu, Zn, Y, Yb, Pb was studied in bottom sediments and waters around gas seepages. Differences in the contents of Ni, Cr, Mn, Ti were detected, which may be related to deep thermal sources and presence of oil.

Other experiments were carried out under difficult prospecting conditions in a region of the Byelorussian crystalline shield covered with 150-200 m of overburden (sandstones, chalk and tills). Here several geophysical anomalies with (iron, graphite and sulphide) mineralization have been proven by drill data. We have carried out investigation by burying sorbents in soil for periods of 3 to 12 months. Increased content of Ni and Cr observed on the sorbents are thought to be from magnetite, as well as pyroxenes and garnets, which are closely associated with iron ore in the deposits. Concentration of these metals in the ore zone are ten times greater than those of background. Anomalies of chalcophile elements (zinc and copper) which are seven times the background value are thought to be from buried sulphide minerals. Anomalies of gases (carbon dioxide and helium), which were also detected, are thought to be the main carriers of these metals to the surface.

Recent investigations show that the gases can transport finely dispersed metals or volatile compounds such as metal cyanides, carbonylic complexes etc. Bubbles discharging from an ore body can carry on their surface certain metals and organic compounds.

Some other factors are also involved: deep weathering; the activity of microbes in pore solutions, movement of metals in water films in clay strata and in frozen ground; and electrochemical processes. The mode of occurrence of elements in the secondary environments require further thorough investigation.

GEOCHEMICAL MAPPING AND TERRITORY ZONATION  
OF QUARternary DEPOSITS IN BYELORUSSIA

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In Byelorussia the investigations on geochemistry of Quarternary deposits and lithogenesis were carried out by K.Lukashev and his collaborators for more than 40 years. In this region Quarternary deposits cover the whole territory and exceed 350 m in thickness. The key problems were:

a) geochemical peculiarities of different genetic types of sediments (till, loess, lacustrine sediments etc.);

b) study of soils, vegetation, water chemical composition and zoogeochemistry;

c) mapping and territory zonation;

d) applied geochemical problems (prospecting, medicine, agriculture, environmental protection, Chernobyl fall-out etc.).

In Byelorussia three geochemical provinces are distinguished which differ in the content of some essential and trace elements (Ti, Cr, Ni, Mn etc.). The origin of these provinces is due to bedrocks, tectonics, glacial history, weathering processes and landscape geochemistry after the deglaciation.

A statistical treatment of 900 mechanical and 700 chemical analysis of loess, silt (sand loam and loam), and clays of moranic, alluvial and limno-glacial origin was made.

In Byelorussia, loess covers about 10 percent of the territory which is equal to 207,000 square kilometres. The thickness of the loess sheet is variable from 0.5 to 12 meters. As a rule, Byelorussia loess is macroporus. Its average porosity value is 42 percent. The loess deposits are commonly nonstratified and unconsolidated, but some of them have well-laminated features. Loess rock originated in periglacial regions and their formation was due chiefly to washout and eolian differentiation of other Quarternary deposits.

A comparison of the data shows that the Byelorussia loess sediments are characterized by very good grading, by predominance of 0.01 to 0.005 mm size fraction, by a high content of  $\text{SiO}_2$  and by low content of  $\text{Fe}_2\text{O}_3$ .

The comparison of data also shows that silt and clay of

alluvial type are the closest to loess by their granulometric and chemical composition, moraine sediments chiefly by their chemical composition, and limno-glacial deposits only by their granulometric composition. Loess rocks from different areas of Byelorussia vary in trace elements content (Ti, Cr, Ni, Mn, Cu etc.). The mineral and chemical compositions of loess in Byelorussia and Central Asia have been also examined and their physical and mechanical properties compared. As a result, material has been gathered characterizing the influence of zonal factors upon the lithochemical properties of loess in both regions. Environmental factors affects the some properties of loess rocks, especially the content of carbonates and easily leaching components. Loess deposits cover vast area of the Earth surface, including that with arid and semiarid climates where irregular river streams sediments and undeveloped soils are sometimes not good sampling media for successful mapping and comparison with other regions. The geochemical mapping of world loesses may be a new important branch or subproject in framework of the IGCP project 259.

## TILL GRINDING EXPERIMENTS AND SOME GUIDELINES FOR INTERPRETING TILL GEOCHEMICAL DATA

MÄKINEN, J.E.M.

Several types of till from Central Finland were sampled for grinding experiments aimed at simulating the genesis of the natural fine fraction (FF) ( $< 64 \mu\text{m}$ ) under different physico-chemical conditions. A Fritsch-P-5 centrifugal mill with zircon oxide chambers and balls was used. Before wet grinding a feed was sieved into 64 - 8000  $\mu\text{m}$  fraction.

It was observed that the production of artificial fine fraction (AFF) increased as the grain-size distribution of the feed was coarsened, i.e. 60 g of the fraction 64 - 500  $\mu\text{m}$  was replaced by the fraction 500 - 8000  $\mu\text{m}$ . The proportion of micas relative to quartz and feldspar also increased significantly, reflecting the growth of Co-, Cu-, Fe-, Mn-, Ni- and Zn-concentrations and decrease of UW (Fig. 1).

Decrease of pH also promoted the production of AFF, but mineralogical and geochemical trends were less unambiguous as than the coarsening of the grain-size-distribution (Fig. 2). Comparisons between AFF produced in neutral and acid solutions reveal that geochemical scatter was greatest for Co and Cu.

Increase of redox-potential and NaCl-concentration also promoted production of AFF.

On the basis of these observations mechanical and physico-chemical models were formulated to explain the genesis and composition of the fine fraction in glacial circumstances.

In the mechanical model the relation between boulder entrainment and the velocity of ice flow controls the quantity and composition of FF (Fig. 3). When the boulder entrainment is large in relation to the velocity of the ice flow, production of FF is effective, and micas are enriched in the FF relative to quartz and feldspar. That is reflected in high Co-, Cu-, Fe-, Mn-, Ni- and Zn-concentrations and low UW-value in FF. The converse applies when boulder entrainment is low in relation to the velocity of the ice flow. The boulder entrainment has usually been great in areas of compressive flow (e.g. rogen moraines) and smaller in areas of fast free flow of ice (e.g. drumlin fields).

In the physico-chemical model the production of FF is promoted by decreasing pH, increasing redox-potential and electrolyte concentration (Fig. 4). These factors are moreover dependent on the mineralogical and geochemical composition of the basal debris which acts as an ion exchanger.

The experiments revealed the inter dependencies between the geochemical and mineralogical composition of the AFF and physico-chemical conditions during grinding. The latter corresponds partly to glacial activity, and interpretation of the geochemical data therefore requires separation of the information derived from the bedrock and glacial geology. This can be partially achieved by using data processing based on element ratios or by standardizing the values by UW. Separation of the data according to glacial subareas is also recommended because better correlation exists between till and bedrock composition in the case of A than in the case of B (Fig. 3).



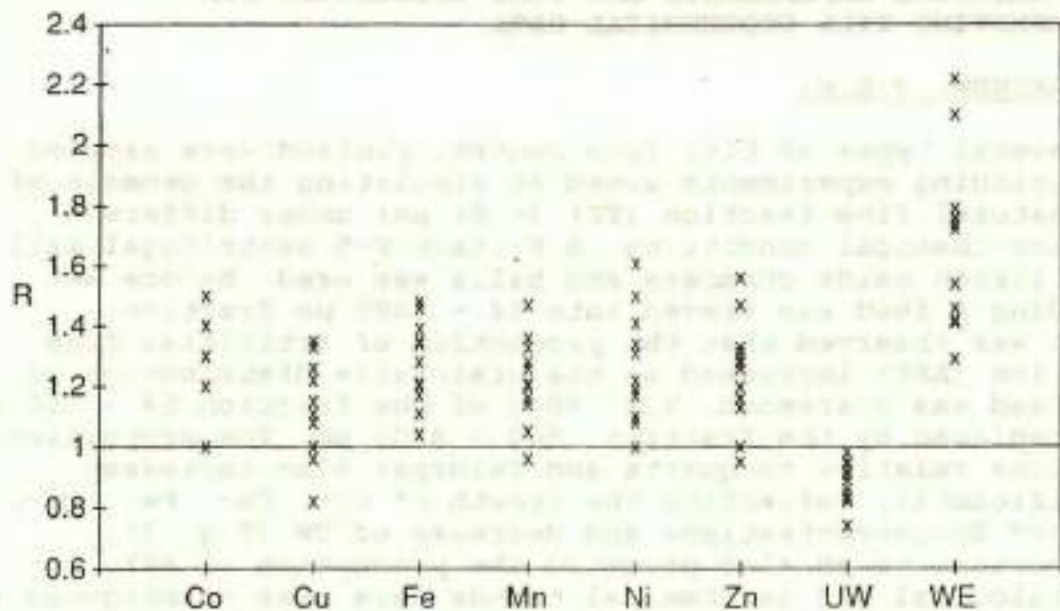


Figure 1. The ratio (R) of Co-, Cu-, Fe-, Mn-, Ni- and Zn-concentrations, unit weight (UW) and weight (WE) between AFF produced by coarsened and normal till samples. The value is calculated between experiments having the same production of AFF. UW expresses the amount of micas to quartz and feldspar. UW decrease as the proportion of micas increase.

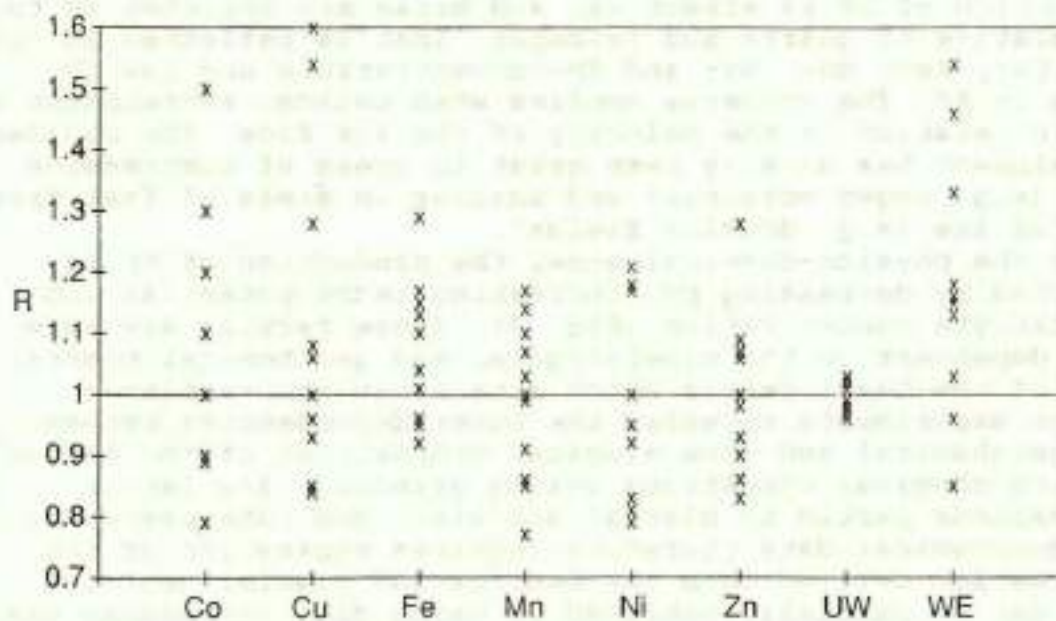


Figure 2. The ratio (R) of Co-, Cu-, Fe-, Mn-, Ni- and Zn-concentrations, UW and WE between AFF produced at pH 4 and at pH 7. See explanations in Fig. 1.

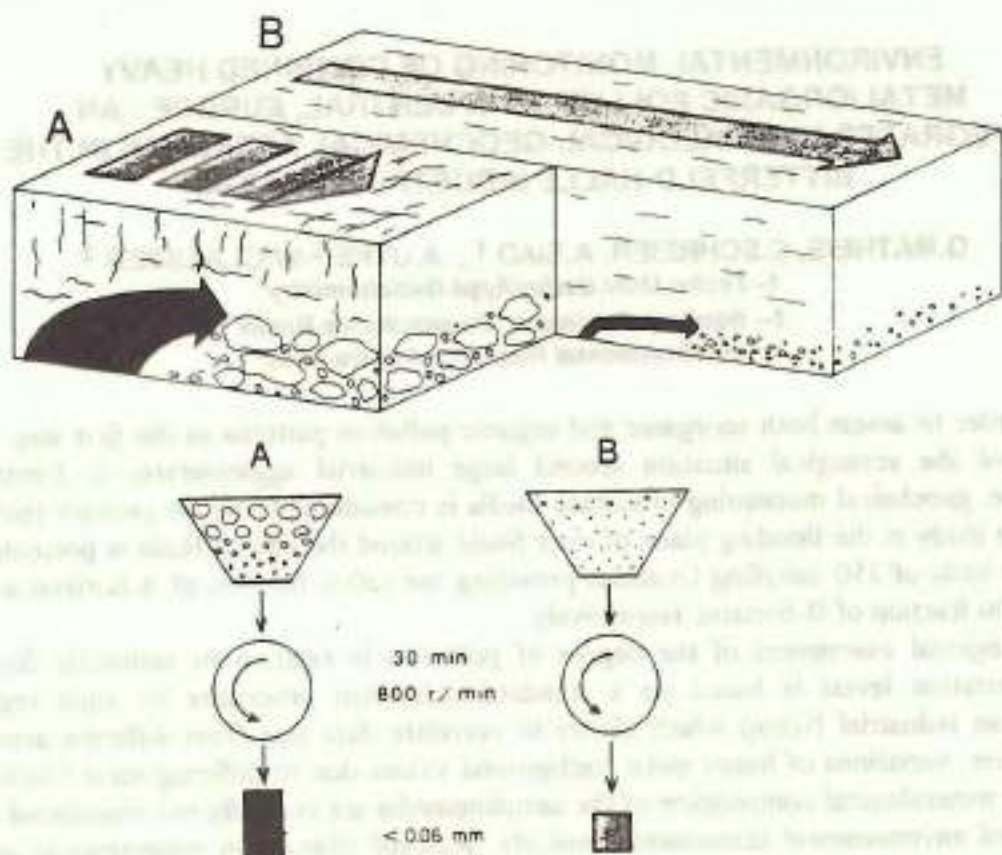


Figure 3. Mechanical model explaining the variations in the quality and quantity of the fine fraction of till. The magnitude of debris entrainment is great (A), minor (B) relative to the ice flow velocity - upper part in the figure.

The average grain size of the feed in A is greater than in B. The same energy supply produces more fine fraction in A than in B. Proportion of micas relative to quartz and feldspar is also greater in A (black) than in B (gray) -lower part in the figure.

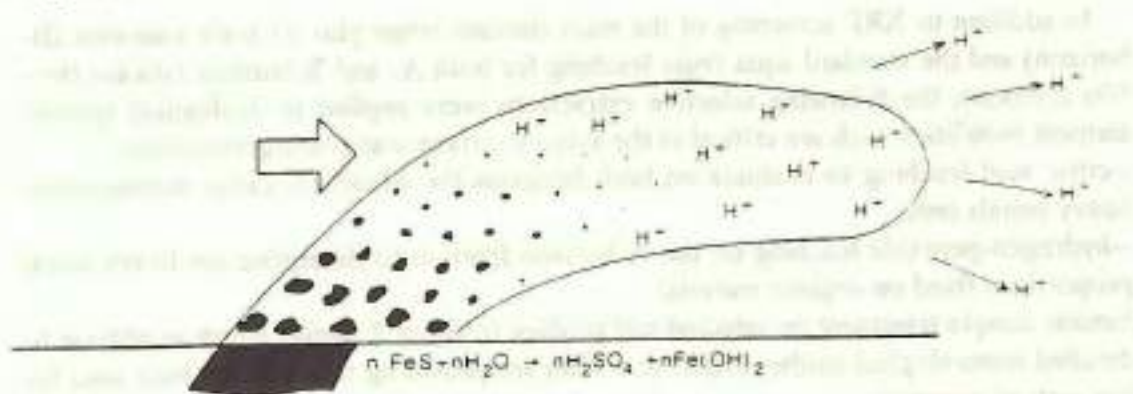


Figure 4. The physico-chemical model representing the effect of pH on the quantity of fine fraction in till. Weathered sulphides increase the  $H^+$ -concentration in the glacier along with the effect of glacial comminution. Production of the fine fraction increases concomitantly.

**ENVIRONMENTAL MONITORING OF COMBINED HEAVY  
METAL/ORGANIC POLLUTION IN CENTRAL, EUROPE - AN  
INTEGRATED MINERALOGICAL-GEOCHEMICAL APPROACH IN THE  
BITTERFELD-HALLE INDUSTRIAL REGION.**

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In order to assess both anorganic and organic pollution patterns as the first step to improve the ecological situation around large industrial agglomerates in Central Europe, geocheical monitoring in surface media is considered to be the primary tools. A case study in the flooding plane of river Saale around the city of Halle is presented on the basis of 350 sampling locations providing the -200u fraction of A-horizon and the -80u fraction of B-horizon, respectively.

Regional assessment of the degree of pollution in relation to nationally fixed concentration levels is based on a standard extraction procedure by aqua regia (German Industrial Norm) which allows to correlate data sets from different areas. However, variations of heavy metal background values due to differing local Clarkes and/or mineralogical composition of the samplingmedia are normally not considered in standard environmental assessment. Similarly, seasonal changes in mineralogical and geochemical concentrations, which are particularly sensitive in drainage surveys, are hardly monitored.

Such inventories have to incorporate at least semiquantitative information on the mineral composition (clay species, Fe/Al/Mn-oxides/hydroxides) of stream sediments, floats and soils, respectively, as one of the most important- and usually neglected factors to understand chemical speciation and adsorption effects. Regional monitoring prevents the application of the traditional mineralogical analytical tools as XRD and IR-Spectrometrie, however, factor analysis of XRF main element concentrations from powder pellets provides sufficient information on such mineralogical dispersion patterns.

In addition to XRF screening of the main element range plus 21 trace elements (B-horizon) and the standard aqua regia leaching for both A- and B-horizon (always the -80u fraction), the following selective extractions were applied to distinguish specific element mobilities wich are critical in the system surface-water/soil/groundwater:

--citric acid leaching to evaluate on both horizons the adsorbad, easily exchangeable heavy emtals only;

--hydrogen-peroxide leaching on the A-horizon fraction to determine the heavy metal proportions fixed on organic material.

Similar sample treatment on selected soil profiles to about 2 metres depth in addition to detailed mineralogical studies (XRD & FTIR) are providing the required base data for the vertical migration.

The resulting data sets are sufficient for statistical and geo-mathematical treatment and interpretations targeted both on the regional environmental pollution levels and the critical interaction between flooding plain and hydromorphic dispersion respectively. Cartographic networking and display of the data sets is achieved through integration into a geo-information system.

## COMPARISON BETWEEN STREAM SEDIMENT (SILT) AND HEAVY MINERAL GEOCHEMISTRY IN REGIONAL SURVEYS

MAURICE, Y.T.

Extracting and analyzing heavy mineral concentrates (HMCs) from stream alluvium is undeniably a more costly means of carrying out regional geochemistry than the more commonly used silt surveys. However, it is well documented that when the target is gold and/or platinum group element deposits, heavy minerals show greater contrast and clearer dispersal patterns than those from silts, making them a superior medium. When it comes to other metals, though, both media show different, but often equally useful aspects of the geochemical landscape.

In this paper we compare the signals (statistical data, distribution patterns, etc.) of both media for about 20 elements, based on a 3200 km<sup>2</sup>, 310-sample regional heavy mineral / silt drainage survey in the Appalachians of southern Quebec. The area was heavily glaciated and is characterized by a wide variety of mineral occurrences and lithological units ranging in composition from arkosic and carbonaceous sediments to basic volcanics and serpentinites. The HMCs and the silt samples were collected at the same sites.

The differences that can be observed in the geochemical signals are attributed to differences in element abundance, mobility, dispersal mechanism and/or mineralogy. Elements such as Cr and the rare earths, which occur mostly as detrital resistate minerals, tend to show similar patterns but the highest contrast in concentrations between the two media. The base metals, on the other hand, which are mobile with a strong tendency to disperse hydromorphically, show very distinct dispersal patterns with much less contrast in their concentrations. Other elements, such as Ba, occur in different mineral phases in HMCs (barite) and in silts (replacing K in feldspars) giving rise to similar concentration range values but highly contrasting distribution patterns. The influence of glacial dispersal is recognizable in the distribution patterns of most elements in both media, but it is more easily interpreted in the HMCs because of the absence of an hydromorphic component. On the other hand, the silt data displays numerous anomalies (hydromorphic?) which are not found in the HMCs but which could be important to the explorationists.

THE DEVELOPMENT AND APPLICATION OF AN ANALYTICAL METHOD FOR  
THE DETERMINATION OF GOLD IN GROUND WATER

MC HUGH, J.B., AND GRIMES, D.J.

An analytical technique was developed to determine low levels of gold in ground water samples collected around disseminated gold deposits in Nevada. A one-liter water sample is filtered, acidified, and brominated, and the gold-complex is extracted with an anion resin. The gold on the resin is eluted with an acetone/nitric acid solution and evaporated to dryness. The evaporite is taken up with a hydrobromic acid/bromine solution and extracted with methyl isobutyl ketone. The extract is electrothermally atomized in an atomic-absorption spectrophotometer. The limit of determination is 1-part-per-trillion.

Ground water samples were collected from drill holes near the Pinson, Rabbit Creek, and Summer Camp disseminated gold deposits in northern Nevada. The water samples were analyzed for gold at the 1-part-per-trillion level to determine if gold is being hydromorphically mobilized from these deposits. Analytical results indicate the presence of hydromorphic dispersion anomalies of gold in the ground water associated with the buried disseminated gold deposits.

## GEOCHEMICAL SPECIALIZATION OF HYDROTHERMAL - METASOMATIC FORMATIONS OF THE ALDANIAN SHIELD

MOLCHANOV A. V.

The Aldanian shield is an exposed part of crystalline base of the south - east part of Siberian platform. Tectonic history of the shield is divided into 4 stages (AR<sub>1</sub>, AR<sub>2</sub>, PR<sub>1</sub>, MZ) every of which is characterized by its own set of hydrothermal - metasomatic rock associations (HMRA) jointed in 4 genetic rock association series (GRAS) corresponded with tectonic stages. Geochemical and metallogenic characteristics of HMRA and GRAS are shown in the Table. However, there is direct correlation between geochemical and metallogenic patterns of HMRA and initial geochemical patterns of hosted rocks being especially distinct for such elements as U, Th, Au, Ag, Cr, and Co. Investigations of behaviour of some ore - forming elements (U, Th, Au, Ag, TR, polymetalles etc.) show hydrothermal - metasomatic processes to be leading to intensive activity of above mentioned elements, their transfer and subsequent concentration in favourable thermodynamic (high temperature for TR, Sn, Nb, Th, U and low temperature for Au, Ag, Cr, Co, U) conditions and structural (zones of brecciation and intensive fracturing, volumetric cataclasis, structural - stratigraphic unconformities) position. The result of this processes is formation of naturally observed metallogenic zonality of the region.

Usage of the method of A.A.Marakushev for determination of acidic - alkaline parameters of rocks in gumberte HMRA allow us to show that gumbertes contain alkaline (mostly adularic) as well as acidic (mostly quartz - adularic) subdivisions with clear tendency of concentration of uranium in the former and that of gold in the latter. During formation of GRAS of hydrothermal - metasomatic rocks significant changes in character of shape of concentrations of ore - forming elements (in particular, uranium) took place. For example, it is established transition from hosted rocks to high - temperature silicium - alkaline (quartz - plagioclase - orthoclastic or quartz - albite - microclincic or phenites) metasomatites and to low - temperature alkaline and subalkaline (gumbertes, zeolitites etc.) correlates with transition from dispersed uranium and thorium - bearing minerals to stockworks and viens of uranium - bearing minerals as well as with changes in character of correlation between uranium and other elements.

Study of geochemical characteristics of HMRA of Aldanian shield as well as behaviour of some ore - forming elements allow to establish hydrothermal - metasomatic activity as the main factor of ore genesis in the region.

Table of hydrothermal - metasomatic formations of the Aldanian shield and their geochemical specialization.

RAGS and their age	HMRA	geochemical specialization (ore deposits)
tectonic-magmatic activation (Upper Jurassic-Lower Cretaceous)	zeolitites	$U_{5,9}^{70}$ $Th_{3,8}^{70}$ $Sr_{2,2}^{70}$ $Pb_{2,0}^{70}$ $Y_{1,2}^{10}$ $Zr_{1,1}^{10}$ $Zn_{1,0}^{10}$ $Yb_{1,0}^{10}$ (zeolite-phosphorus-radioactive)
	gumbeites	$Bi_{1,0}^{95}$ $Se_{1,0}^{50}$ $As_{1,1}^{100}$ $Ag_{4,4}^{210}$ $U_{5,0}^{245}$ $W_{2,3}^{210}$ $Co_{1,5}^{90}$ $Mo_{1,6}^{120}$ $Th_{2,1}^{250}$ $Ge_{2,9}^{20}$ $Y_{2,7}^{100}$ $V_{2,5}^{125}$ $Nb_{2,1}^{100}$ $Pb_{1,9}^{250}$ $Sc_{1,8}^{45}$ $P_{1,6}^{70}$ $Sn_{1,2}^{100}$ $Zr_{1,0}^{50}$ (gold-rare metals-radioactive)
	propylites	$As_{2,5}^{35}$ $Pb_{2,1}^{35}$ $Zr_{1,8}^{50}$ $Mo_{1,5}^{35}$ $Be_{1,5}^{55}$ $Ti_{1,0}^{50}$ (polymetallic)
	phenites	$Sb_{1,0}^{10}$ $Nb_{5,3}^{60}$ $Ag_{5,0}^{100}$ $Zr_{3,7}^{100}$ $Mo_{3,3}^{100}$ $Sn_{2,5}^{85}$ $Be_{2,6}^{65}$ $Ca_{2,0}^{50}$ $U_{1,8}^{50}$ $Th_{1,7}^{70}$ $Pb_{1,6}^{60}$ $Zn_{1,3}^{70}$ $Ge_{1,8}^{50}$ $Y_{1,0}^{10}$ (polymetallic-rare metals-rare earth)
proto-tectonic-magmatic activation (Lower Proterozoic)	aseites	$Yb_{1,0}^{10}$ $Th_{1,7}^{35}$ $U_{5,0}^{70}$ $La_{1,1}^{20}$ $Cu_{5,8}^{10}$ $Mo_{2,1}^{40}$ $Pb_{1,0}^{70}$ $Ce_{2,5}^{25}$ $Nb_{2,2}^{95}$ $Ag_{1,4}^{10}$ $Sc_{1,6}^{20}$ $Sn_{1,6}^{70}$ $Zn_{1,4}^{70}$ $Be_{1,2}^{5}$ $Y_{1,2}^{20}$ $V_{1,0}^{10}$ $Ni_{1,1}^{10}$ $Sr_{1,0}^{5}$ (iron ore-phosphorus-radioactive)
	propylites	$U_{5,0}^{55}$ $Nb_{5,0}^{50}$ $Pb_{3,0}^{10}$ $Th_{2,0}^{40}$ $La_{2,3}^{35}$ $Cu_{2,5}^{75}$ $Be_{2,2}^{35}$ $Mo_{2,2}^{50}$ $Sc_{1,5}^{10}$ $Y_{1,5}^{15}$ $Zr_{1,1}^{100}$ $Sn_{1,0}^{50}$ (iron ore)
	quartz-albite microclinalic metasomatites	$Sc_{3,0}^{50}$ $U_{2,1}^{50}$ $Be_{1,5}^{25}$ $Ca_{1,4}^{40}$ $Th_{1,1}^{80}$ $Sn_{1,1}^{55}$ $Cu_{1,0}^{50}$ (rare metals-rare earth-radioactive)
proto-geosinclinal Upper Archean	quartz-plagioclase orthoclastic metasomatites	$Yb_{1,1}^{85}$ $Zn_{2,4}^{200}$ $Sn_{1,8}^{85}$ $Cu_{1,7}^{100}$ $Nb_{1,7}^{70}$ $Th_{1,8}^{40}$ $U_{1,4}^{95}$ (rare earth-radioactive)
nuclear (Lower Archean)	quartz-plagioclase orthoclastic metasomatites	$Y_{6,9}^{200}$ $Sn_{3,5}^{85}$ $Ca_{1,2}^{75}$ $Sr_{1,0}^{60}$ $U_{1,0}^{85}$ $Ti_{1,5}^{45}$ $Th_{1,0}^{100}$ (rare earth-radioactive)
	magnesian-iron-calcium metasomatites	$Cr_{3,3}^{10}$ $Ni_{3,7}^{90}$ $Ge_{1,5}^{60}$ $Co_{3,5}^{50}$ $Zn_{3,0}^{90}$ $Mo_{2,2}^{30}$ $Sc_{3,2}^{30}$ $Sn_{1,1}^{10}$ $Y_{1,0}^{10}$ $V_{1,5}^{50}$ (iron ore)

lower index in geochemical formulas shows clark of the element concentration whereas upper one shows coefficient of variation.

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The integrated use of electron paramagnetic resonance spectroscopy (EPR) and trace element analysis by particle induced gamma ray emission (PIGME) and particle induced x-ray emission (PIXE) of quartz and altered wallrock in exploration geochemistry.

Several types of natural quartz can be characterised by their electron paramagnetic resonance powder spectra and/or their trace element content, if properly purified prior to analysis. For example EPR spectra from various types of gold, zinc, copper and tin mineralisation and associated trace element distributions are typical for these types of deposits. More importantly the intensity of the spectra and the trace element of the quartz increases when the quartz contains or is close to ore. It was found through experience that silicious wallrock may be used as an alternative to quartz. This makes the integrated use of EPR spectroscopy and trace element studies much more generally applicable.

Quartz is an ideal material for electron paramagnetic resonance observations, which can be made with a conventional analogue EPR spectrometer. Because of the low level of trace elements encountered in quartz and of the inherent difficulty in dissolving the material without losing elements, either through precipitation or through volatilisation, we used particle induced gamma ray emission (PIGME) and particle induced x-ray emission (PIXE) conducted on pressed quartz pellets bonded with spectrographically pure graphite. The method allows simultaneous determination of up to sixty elements down to ppm level.

Because of its economic importance a large data bank was created of 3800 EPR spectra and 800 corresponding PIXE/PIGME analyses of quartz and silicious rocks, mainly associated with several types of mineralisation. A persistent positive correlation emerged between EPR signals and some trace elements, usually K, Na, Li and Ge, sometimes Mn, Fe, Cu and also Ti and Sr. Individual assemblages of other elements allow further chemical grouping. The EPR spectra show also considerable variations, but always consistent with the geological and petrological variations in the quartz or silicious rocks studied. Both EPR spectra and trace element concentrations can be linked to proximity of the samples to a mineralisation.

The explanation of these observations is that quartz associated with mineral deposits grows rapidly and usually in concentrated solutions. Similarly wallrock alteration products are generated in hydrothermal brines rich in trace elements. The resulting anomalous electron paramagnetic resonance spectra are either directly or indirectly the result of lattice substitutions in the quartz.

A large number of epithermal- (Waihi, Karangahake, Rodalquilar), mesothermal (Beaconsfield, Bendigo) and replacement gold (Carlin) gold deposits, VMS zinc-lead deposits (Rosebery, Hellyer) and some tin deposits



(NE Tasmania) have been studied in detail. As an example may serve the Rosebery VMS deposit. A survey based on whole rock geochemistry as determined by XRF analyses was conducted on the mine lease by Naschwitz and van Moort (1991) at a density of 5 samples per km<sup>2</sup>. A pattern of Si, K and Rb enrichment with an associated pattern of Na, Ca and Sr depletion was observed over an area of 2 x 0.7 km. After having been leached with hot concentrated HNO<sub>3</sub>, the same samples were reanalysed by PIXE/PIGME and also EPR (Aung Pwa et al.,1992). Unexpectedly a far better definition was obtained of the position of the orebody within the previously defined broad alteration zone. Two types of EPR and geochemical haloes were detected. The first type, related with primary massive sulphide and wallrock alteration processes, trends NE-SW and consists of an enhanced electron paramagnetic resonance [AlO<sub>4</sub>]<sup>0</sup> centre, chemical Na-Ca-Sr depletion patterns (feldspar destruction) and K-Rb enrichment patterns (sericite formation), measures 2 x 1.5 km and extends 500 m into the hanging and footwall ..The second type of haloes is probably not only related to primary processes but also to late stage remobilisation of elements. This second type of haloes trends NS, consists of enhanced spectroscopic Mn<sup>2+</sup> EPR signals and chemical Ba and Mn enrichment patterns, measures 3 x 1.2 km and extends 700 m into hanging and footwall. It is likely that a similar definition of the orebody would have been achieved by XRF analysis if the original material had also been acid leached. The simple EPR analysis proved to be the most efficient and accurate method compared with the supporting trace element study.

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THE JOINT USE OF GEOSTATISTICS AND IMAGE ANALYSIS IN THE  
INTERPRETATION OF GEOCHEMICAL AND REMOTE SENSING IMAGERY

Muge,F\*; Vairinho,M\*\*; Sousa,A.J.\*; Pina,P\*; Mariano,C\*

ABSTRACT

A methodology based on the joint use of geostatistical and image analysis techniques is presented in this paper applied to the interpretation of geochemical and TM LANDSAT images.

In order to highlight spatial features of the data, several smoothing and filtering methods were used. The first group of methods concern the use of moving average filters and robust alternatives such as the median filter and ATM filter.

The second group of methods is based on the calculation of variograms in order to model the spatial variability (detection of anisotropies,etc...). These variogram models were used to perform ordinary kriging as well as factorial kriging that allows the decomposition of each variable into 3 or more spatial components.

In order to evaluate the ability of both methods to highlight significant geochemical patterns as well as to reveal subtle features that were overlooked before (linear features related to bedrock structures, alteration along a linear zone, etc.), image analysis techniques were used to transform the geochemical as well as the TM images produced by each method stressing and quantifying those spatial patterns.

The second part of the work intends to study the spatial correlation between the geochemical and the Landsat TM images. In a first step, PCA was used in order to identify the combination of TM channels best correlated with the geochemical variables. In a second step, cross-variograms were calculated in order to model the cross-regionalization between the TM and geochemical data.

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In this study the resulting images were also compared from the morphological point of view by calculating morphological parameters obtained through morphology based image analysis techniques in order to take into account spatial continuities.

The study was carried out on geochemical data (Cu and Zn in soils), coming from Exploration Surveys undertaken by DGGM/SFM, covering an area of about 50 Km<sup>2</sup> in between Moura and Ficalho villages in Alentejo, South of Portugal at the Magnetitic-zinciferous Belt, metalogenic province within the Ossa Morena Zone.

The area contains mainly Zn-Pb (Cu) sulfide mineralizations hosted in Cambrian Dolomites. The oxidation of some sulfide deposits has led to significant gossan development during which enrichment reached economic values (Preguiça, Vila Ruiva).

## GEOCHEMICAL MAPS - TOPICS, TYPES AND PROBLEM

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The totality of chemical phenomena of a determined part of the earth's crust is defined as its geochemical field. In distinction from geophysical fields (e.g. gravity, magnetism) the geochemical field is always bound to a medium (rocks, soils, water etc.)

Geochemical maps allow to reflect only certain features or some components of this geochemical field, but never the whole of it. Commonly contents of chemical elements or compounds are represented in maps, but also composed or derived parameters as quotients or factors are used. In primary environment the contents mostly refer to the whole rock, whereas in secondary environment such regard often is impossible. The use of different fractions of superficial formations (e. g. grain size fractions, chemical extracts of soils or stream sediments) effects that geochemical maps created on that base, show only special, but nevertheless essential aspects of the geochemical field. Standardization of applied fractions and used fractionation techniques is necessary to attain equivalence of results and comparability of geochemical maps.

Geochemical mapping is a complicated process of sampling, analysis and data handling. Concerning the sampling two main procedures can be distinguished: statistic sampling of the whole area or sampling within subareas previously selected after non-geochemical criteria (geological units, rock formations, pedological units, land use areas, catchment basins administration units etc.). In the first case the resulting maps are called geochemical maps, in the second case maps are called semigeochemical. In the latest mentioned maps subareas are characterized as homogeneous, whereas internal inhomogenities are not reflected. In this case results are strongly influenced by the criterion of subdivision. The achievement of total new knowledges by this method is limited. Nevertheless both types are applicable and useful in geochemical practice in dependence on the foreseen purpose. Some examples of different types of geochemical maps are demonstrated.

## DETECTION OF PLATINUM GROUP ELEMENT DEPLETION IN LAYERED MAFIC INTRUSIONS: A POTENTIAL AID TO EXPLORATION FOR PGE DEPOSITS.

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In layered mafic intrusions, economic PGE deposits are the result of the collection of PGE's from the silicate melt by NiS droplets, and subsequent settling accumulation of PGE-bearing NiS droplets. An important consequence of NiS collection of PGE's from a silicate melt is PGE and Au depletion of the silicate melt. The ability to recognize PGE depletion in rocks crystallized from a depleted melt would be useful in exploration for PGE deposits. PGE depletion could be used to discriminate between favorable environments (those containing PGE depleted silicates) and unfavorable environments (those that did not experience NiS collection of PGE's).

Dry-chlorination was applied to drill core samples of the Fox River Sill (Canada) in order to remove metallic minerals. The remaining (silicate) fraction of each sample was digested by microwave heating in a mixture of HF-HCl-HNO<sub>3</sub>. The digestates were evaporated to dryness, re-digested in *aqua regia*, and reconstituted in distilled de-ionized water. The solutions were analyzed by inductively coupled plasma mass spectrometry for PGE's and Au. For PGE's and Au in the silicate remainders, the detection limits by this method are sub-ppb.

Relative to PGE content of silicate fractions of samples collected from non-mineralized horizons, the PGE content of silicate fractions of samples collected from the mineralized horizon is significantly depleted of PGEs and Au. The presence of PGE depletion in the silicate phase distinguishes the mineralized layer from the non-mineralized layers.

CHANGES OF THE LANDSCAPE - ECOLOGICAL AND GEOCHEMICAL ENVIRONMENT IN THE RIVER PRIPIYAT BASIN

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In recent years, the ecological situation in the River Pripyat basin in the south of the Republic of Belarus changed considerably. The increase of intensity of land use was accompanied by the drainage amelioration of vast overmoistened and marshy lands, construction of big drainage systems, live-stock farms, etc.

Before an intensive development of valley bottom lands, the ecological situation in the Pripyat valley was in a relative equilibrium. Effective fertility of prevailing sandy soils is mainly due to humus horizon its thickness ranging from several centimetres - in the near-channel areas to 40 cm - in the central and terrace floodplain. The content of humus varies between 0,5-9,3%. Soils are more often acid, or weakly acid (pH averages 5,0) with a low absorbing capacity, poor in exchangeable calcium, magnesium and potassium. Silica dominates (averaging 86,10%), the content of other macroelements is low:  $Al_2O_3$  - 3,62%,  $Fe_2O_3$  - 1,25, CaO - 0,45, MgO - 0,39,  $K_2O$  - 0,65,  $Al_2O$  - 0,30%. Concentrations of microelements are low. Peat lands of the floodplain valley usually occur at a small depth and are underlain by sands, have a small absorbing capacity, acidic and weakly acidic reaction, low content of nutrients and trace elements.

Hydrochemical environment is characterized by hydrocarbonate - calcic composition and a low salt content (from less than 100 to 300-400 mg/l). The quality of the Pripyat water is described by the following indices (summer-autumn low - water period) : salt content - 300, suspended substances - 15, soluble oxygen - 9,5, iron - 0,2, phosphorus - 0,01, sulphates - 20, chlorides - 15, ammonium nitrogen - 0,25, nitrate nitrogen - 0,20.

A widespread bog occurrence in this territory greatly influences the hydrochemical environment: waters of high bogs are less mineralized than those of low - level bogs (6-75 and 150-160 mg/l, respectively), less hard (alkaline-earth element content is 3-20 against 20-250 mg/l), less ferruginated (iron concentrations

are 0,1-2,5 and 0,3-6,0 mg/l), include smaller contents of soluble organics (120-560 and 130-995 mg/l, respectively).

Economic development of the region gave rise to ecological problems involving the environmental deterioration: most of ameliorated lands were overdrained, wind erosion of sandy and peaty soils increased, as well as water salinization, thickness of fertile humus horizon decreased, radical changes in the natural course of geochemical processes in landscapes and in the natural background of geochemical environment became evident.

The floodplain topography noticeably changed, underlying sand outcrop and deflation increased, shape and course of water streams changed, plant associations show some alternations, deep geochemical transformation of soil, rock, plant, river and ground water contents occur. So, the drainage amelioration and intensive cultivation, of peat soils within 1961-1985 resulted in the land degradation: 46% decrease of the peat layer thickness, increase of the ash content in the organic layer from 7,8 to 80,5%, and growth of its bulk density from 0,1 to 1,0 g/cm<sup>3</sup>, decrease of the organic content from 810 to 648 t/ha, 6 times decrease of the peat moisture capacity, increase of mobile forms of phosphorus from 4 to 75 mg P<sub>2</sub>O<sub>5</sub>/100 g of soil, potassium - from 9 to 66 mg K<sub>2</sub>O/100 g of soil, decrease of total nitrogen from 20,3 to 16,3 t/ha. Drained peat soils lose annually as much as 1,5 t of materials from a hectare with water runoff, and in addition 3-16 t - due to soil mineralization, which results sometimes within 25-30 years in a complete exhaustion of a fertile layer.

Geochemical changes occurring in mineral drained floodplain soils should be noted too. These changes stimulate the organic material mineralization. It is especially active in the first years after the virgin land development. Within ten years after the floodplain banking and soil utilization under perennial grasses the humus content decreased by 1-2%, and under crops - by 3-4%. Chemical indices of soils change considerably, which result in increase of soil acidity, decrease of absorbing capacity by 2-3 meg, exchangeable calcium and magnesium by 2-4 and 0,5-0,5 meg/100 g soil respectively; the ratio of these elements increases, and soil percentage s<sub>a</sub> saturation with bases decreases by 7-11%. Mobile forms of potassium, phosphorus, nitrogen are removed from the soil profile, as well as copper, cobalt, manganese and other biologically important trace elements; bound forms of silicon and aluminium are accumulated, iron content of drained soils increases.

Live-stock farms unfavourably influence the floodplain ecology. So, after the land irrigation with manure slurries the soil content of nitrate nitrogen increases by a factor of 3-4, potassium - 10, phosphorus - 5-7, calcium and magnesium - 2-3. Depending on the salt accumulation character, the sodium, chloride, sulphate and mixed salting types are distinguished. Chemicalization of lands resulted in the increase of the Pripyat water concentration of sulphates by a factor of 2, chlorides - more than 3.  $\beta$  times sodium and 6 times potassium increase is noted sometimes in river and ground water.

The data stated above indicate by far that during a large - scale drainage amelioration carried out in the Pripyat basin, several natural, especially geochemical processes were neglected, which negatively impacted the ecological situation. Efficient nature management requires at present a systematic control of the environmental quality dynamics in order to reach a good agreement between the man economic activities and natural processes.



LANDSCAPE-GEOCHEMICAL MAPPING OF TERRITORIES  
CONTAMINATED BY RADIONUCLIDES AS A RESULT OF  
THE CHERNOBYL ACCIDENT

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Measures for the elimination of the Chernobyl accident consequences necessitate the use of various maps, which give a comprehensive presentation of natural, social-economic, and radioactive situation within contaminated territories. At present, the most important task of works involves the more detailed spatial study of redistribution and secondary migration of radionuclides within contaminated areas with regard for modes of their occurrence and mobility due to natural conditions.

Landscape-geochemical investigation data represented as maps make possible an assessment of the radionuclide migration and can be used for adjusting the stress values depending on specific natural features of territories.

Special - purpose middle- and large-scale landscape-geochemical mapping aimed at forecasting the radionuclide migration with the recognition of zones of their secondary migration and dispersion is necessary to give a comprehensive assessment of the Chernobyl accident consequences. The results obtained can be a ground for both making substantiated decisions, and carrying out works for the contaminated territory management.

A landscape-geochemical map on a scale of 1:200 000 was compiled for a part of the Belarus territory subject to radionuclide contamination as a result of the Chernobyl accident. The map represents the real ways and pattern of land - use, material mass transfer, distribution pattern, modes of occurrence and migration of artificial radionuclides and its variation in landscapes.

As the migration of radionuclides depends on many factors and is observed in various natural environment, so, to assess the environmental conditions of the region, the information from a series of source maps which include topographic, geo-

logical, hydrogeological, geomorphological, hydrographic, solid runoff, vegetation, soil and landscape <sup>was used</sup> ones. Aqueo - physical and chemical soil indices controlling the range and conditions of the radionuclide migration in landscapes were considered too.

The migration of radionuclides in landscapes was studied in three aspects:

- migration of elements and geochemical barriers laterally;
- migration of radionuclides in vertical profile and geochemical barriers in soils;
- biomigration, removal of radionuclides with vegetation, and biogeochemical barriers.

Basing on the above indices, five types of geochemical landscapes characterized by similar processes and conditions of the radionuclide migration have been distinguished:

Eluvial type (removal dominant)

A dominant process is removal of radionuclides with runoff and biomass of agricultural plants. This landscape type can be related to territories showing a moderate self - purification capacity with the absence of additional radionuclide supply. There is no danger of groundwater contamination.

Transeluvial type (transition dominant)

Maximal radionuclide removal with surface and runoff is observed in slopes of morainic plains. Crop removal of radionuclides from arable lands is more active there, than in eluvial landscapes. Landscapes of morainic plain slopes are territories with the highest self - purification capacity, and those of second floodplain terraces of big and medium rivers are conditionally related to geochemical landscapes with a high, and under forests - moderate self - purification capacity.

Superaquatic (accumulation dominant)

Radionuclide removal with agricultural biomass is rather active. Their secondary accumulation in the sod cover and litter should be noted. Similar landscapes can be related to territories with moderate, more seldom poor self - purification capacity. Superaquatic landscapes being areas of possible accumulation of fallen radionuclides are at the same time territories of their most active removal outside the landscape sphere.

Subaquatic (outside the flood-plain)

Within drained lands the radionuclide removal from the

landscape is possible due to wind erosion and amelioration flow. In nonagricultural lands there is a danger of radionuclide washing by groundwaters. Their accumulation in the sod cover and litter is noted.

Subaquatic (flood-plain)

Accumulation and transition of radionuclides with flood waters are typical. Removal with agricultural biomass is poor. Self-purification is due to flood water wash-out.

The analysis carried out permits to conclude that the type of a landscape depends on the rate, direction and conditions of removal and accumulation of radionuclides in soils and plants, which are due in their turn to both natural landscape properties, and geochemical peculiarities of migrating elements themselves. An important problem of the secondary redistribution of radionuclides can be solved only with considering the landscape - geochemical pattern of contaminated territories.

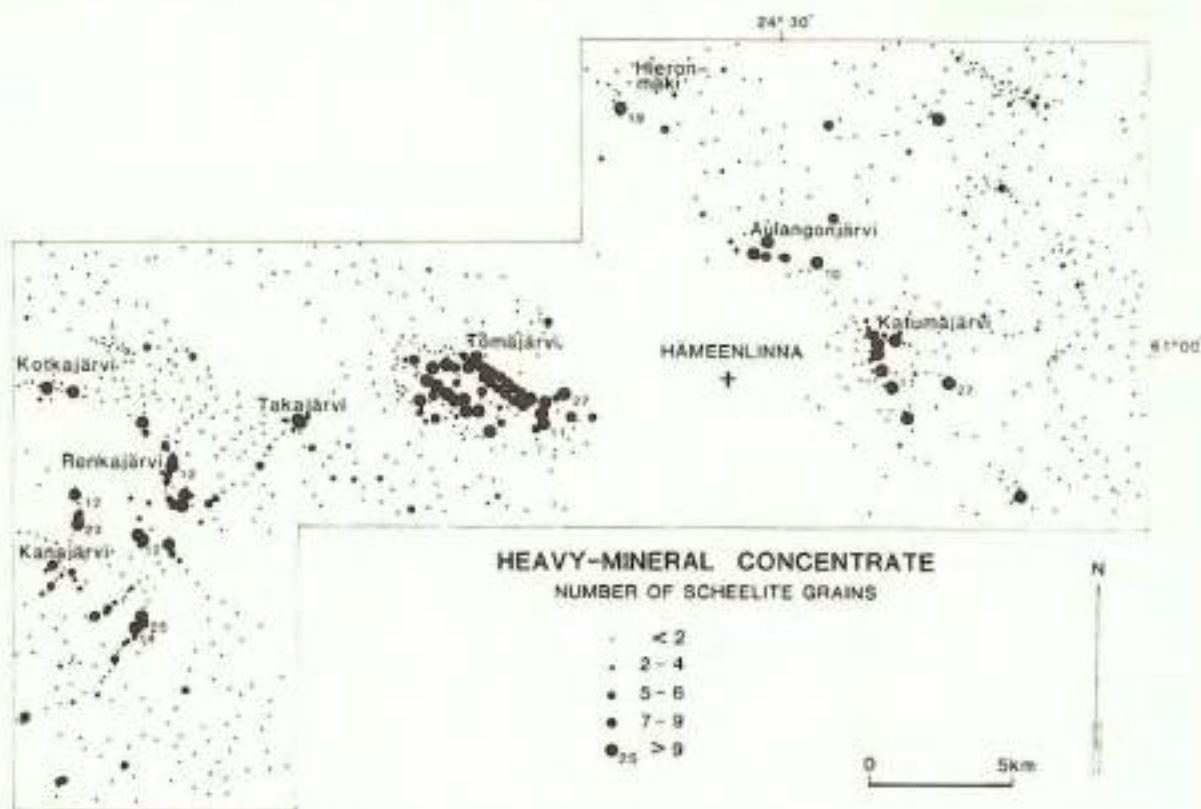
## USE OF REGIONAL AND DETAILED TILL GEOCHEMISTRY IN EXPLORATION FOR TUNGSTEN IN SOUTHERN FINLAND

PEURANIEMI, V.J., AARIO, R.T.

Heavy mineral till geochemistry was used for tungsten exploration in the volcanic-sedimentary schist area of Hämeenlinna in southern Finland. The area falls within the Pyhäjärvi ice lobe and was predominantly characterized by deposition during the deglaciation. Two of the sites are in cover moraine, one within ground moraine and one in hummocky active-ice moraine. Altogether 3500 heavy mineral till samples were gathered from a depth of 0.5-1 metre from an area of 2700 km<sup>2</sup> using a sparse sampling grid. Some deeper test pits were also dug using a tractor excavator, mainly in ore-critical areas. A denser sampling grid was employed in areas where ore boulders or mineralized outcrops were known to occur.

The heavy minerals were concentrated in the field by sluicing with a riffle box and then panning. The wet-sieved -2 mm fraction was concentrated, dried and sieved into two subfractions: -0.5 mm and 0.5-2 mm, and the number of scheelite grains present was counted. The concentrations of 30 elements were analyzed by XRF.

Conventional fine fraction till geochemistry was used in the detailed phase of the exploration. In some places a very dense sampling grid was adopted (point spacing 5 m) in order to obtain an exact picture of the dispersal pattern.



The heavy mineral geochemistry results showed that the sampling density used (0.5-2 samples/km<sup>2</sup>) was generally satisfactory, so that at least one sampling point would hit the dispersal train. One scheelite deposit known earlier from an outcrop (Hieronmäki) was nevertheless not found by means of this regional sampling grid. This deposit is located in the cover moraine area, where the glaciogenic dispersal was from 10-30 metres to 200 metres.

Another scheelite prospect, also situated in the cover moraine area (Vahervuori; not on the map), was found in the form of a one-sample heavy mineral anomaly. A narrow,

coherent fan-shaped tungsten anomaly 600 metres long was located in the fine fraction of the till as a result of detailed prospecting.

One of largest and most intensive scheelite anomalies ever found in Finland occurs around Lake Tömäjärvi. The area can be regarded as a ground moraine with a moderate thickness of till. The small drumlin field nearby is indicative of an active ice flow. The tungsten content was highest in the fine fraction of some of the sieved till samples from Tömäjärvi and in the coarser fractions of some others. Thus the behaviour of scheelite in the face of glacial milling differs from that of sulphide minerals, which are very quickly ground to a fine grain size, as also seen at Tömäjärvi. The influence of sampling density on the form and size of the predicted heavy mineral anomaly could also be tested at Tömäjärvi.

The heavy mineral survey revealed a clear scheelite dispersal train in the active-ice hummocky moraine area of Kanajärvi, whereas the dispersal pattern in the fine fraction of the till was quite incoherent.

Several promising scheelite occurrences were found as a result of geochemical exploration. The scheelite deposits of the Hämeenlinna area are mainly of two types: 1. Scheelite in skarn rocks within the basic volcanics, and 2. Scheelite disseminations and parallel bands in the basic volcanics. It may be said on the strength of this research that the Hämeenlinna volcanite area is one of the principal tungsten provinces in Finland.

Heavy mineral till geochemistry is a fast and reliable method for exploring vast areas of glaciated terrain for scheelite and also for other weathering-resistant heavy ore and industrial minerals.

## DISTRIBUTION OF SELECTED MAJOR AND TRACE ELEMENTS IN THE VOLCANIC HOST ROCKS OF THE RIO TINTO MASSIVE SULPHIDE DEPOSITS

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Available data on the study of hydrothermal haloes shows that numerous geochemical indicators can serve as mineral exploration guidelines. This work presents the results of a litho-geochemical study carried out on the mineralogical and geochemical signatures of the basal volcanic formations (footwall) in the vicinity of the Rio Tinto massive sulphide deposit (part of the South Iberian Pyrite Belt of late Proterozoic). The behaviour of K, Mg, Ba, Tl, Sb, Se and Rb in the proximal and distal host rocks of the massive sulphide body was studied.

The massive sulphide bodies in Rio Tinto are hosted by acidic volcanic formations (rhyolite to dacite) made up of pyroclastite, breccia and lava flows and domes that crop out in an east-west anticline. Samples were collected solely in the footwall of the mineralized bodies from the mineralized zone outward for several kilometres. The neogenic minerals formed after the deposition and emplacement of the volcanic rocks result from two successive events: (i) a hydrothermal alteration related to the massive sulphide emplacement, and (ii) a greenschist-type metamorphic alteration.

Three major alteration facies are distinguished on the basis of petrographic studies and whole-rock chemical analyses: (1) a feldspathic facies (albite and/or K-feldspar) with subordinate white mica, (2) a mica-(chlorite) facies, and (3) a mica-abundant facies corresponding to the inner haloes of hydrothermal alteration around the massive sulphide body.

Many elements in the footwall volcanics show significant anomalies related to the hydrothermal alteration and sulphide deposition. The highest concentrations of the chalcophile elements (Mo, As, Cu, etc.) are located in the inner part of the halo, close (0-500 m) to the massive sulphide body; their distribution is very erratic and shows a "nugget effect".

The elements in the aluminosilicates and carbonates show more regular positive anomalies (e.g. Mg) or negative anomalies (e.g. Na) extending over several kilometres. The Na, Mg and K distribution anomalies are explained by a leaching of the volcanic rocks in the hydrothermal zones with a partial redistribution due to mineral neogenesis. The Mg anomalies in the outer zone of the hydrothermal halo can be explained by a precipitation of sea-water Mg in alteration phyllosilicates.

A second type of anomaly with Sb and Se representative of a probable scarce distributed sulphide phase appears as well kilometric regular haloes superposed on the Mg anomaly.

Tl represents a valuable proximity pathfinder. But two contrasted Tl behaviour can be distinguished: strong proximal anomaly with  $Tl/Rb = 0.25$  and weak distal anomaly with  $Tl/Rb = 0.6 \times 10^{-2}$ . The first group (micas carriers) was obtained from rock that had been strongly altered under high-temperature conditions with high water/rock ratios. The second group (micas and K-feldspars carriers) derives from rocks which are weakly or not disturbed by the feeder zone.

The litho-geochemical study has revealed several hydrothermal-alteration pathfinders that resisted to later metamorphic events. In a homogeneous lithological background, the positive (Mg, Sb, Se, Tl) and negative (Na) anomalies resulting from hydrothermal alteration around the Rio Tinto massive sulphide deposit are sufficiently strong to be used as pathfinders of hydrothermalism in the footwall formations. The haloes show: (i) an inner zone (0-500 m) in which the rhyodacite has been leached of Na (total feldspars breakdown) in favour of Mg and K (strong aluminous white micas neogenesis), (ii) an outer zone (1000-2500 m) characterized by stronger Fe-Mg white mica neogenesis, albite, as well as the presence of Sb and Se enriched sulphides.