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Abstracts
1.1 Regional Geochemical Exploration

1.1.1 Opening lectures

REGIONAL EXPLORATION ROCK GEOCHEMISTRY FOR MASSIVE SULPHIDES, N.B., CANADA

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In the Bathurst District of New Brunswick there are more than 50 known occurrences of base metal sulphides mineralization within an area of 2,600 km² of Palaeozoic volcanic-sedimentary rocks approximately bounded by the Rocky Turn deposit in the north, the Kay Anacon deposit in the east, the Heath Steele deposit in the south, and the Devil's Elbow deposit in the west. Only 4 of these occurrences are, or have been producing mines; 19 are classed as "major occurrences". The area is highly prospective for massive sulphide deposits of the Brunswick Mining and Smelting and Heath Steele type; it would obviously be of considerable importance to exploration to define the zone within the sequence where major occurrences should be sought.

To determine whether exploration rock geochemistry could be used on a regional scale, about 5,600 samples of volcanic and pyroclastic rock from the entire area of 2,600 km² (as far as outcrop and access permitted) were analyzed for both total and hot acid-extractable Cu, Pb, Zn, Mn, Fe, Na, K, Ca, and Mg. To compensate for the unequal geographic distribution of samples and to reduce the effect of local extreme variations the data were divided into blocks of about 10 km. Regional trends were best displayed by a measure of the central values (e.g., geometric mean, mode) in each block rather than arithmetic mean values. The results show that the present and past producing mines and the major sulphide occurrences tend to be in zones characterized by similar geochemical relations that typify the local halos around individual deposits (i.e., in zones enriched in base metals, Mn, Fe, K, and Mg, and depleted in Na and Ca). There are, however, no universal simple relations; for example, the Brunswick No. 12 deposit lies in a region depleted in Zn, whereas the Heath Steele deposits occur in a zone enriched in Zn.

Simple element ratios considerably enhance anomalous relations. The sulphide Zn:Pb ratio in the main deposits is about 2.8, regardless of grade (e.g., the Zn:Pb ratios at Brunswick No. 12, Brunswick No. 6, Heath Steele, and Key Anacon are 2.8, Caribou is 2.4 - 2.6); earlier studies have shown that the Zn:Pb ratio in rocks in the immediate vicinity of the deposits is similar. Extending this observation to a regional scale, it is demonstrated that all present and past producing mines and all known major occurrences lie within well-defined zones of Zn:Pb ratios of 2.4 to 3.2 as measured by the ratio of geometric means of Zn and Pb in rock samples in blocks of about 10 km².

The data are used to illustrate a simple interpretative procedure to identify regional trends without recourse to complex statistical manipulation, and the results define the most prospective zones in the area investigated.
Geochemical exploration in China started in the early 50's. In 1951, first experimental work was carried out in Yueshan, Anqing, and a geochemical exploration section was set up in the Ministry of Geology in 1953.

Regional geochemical reconnaissance (metallometric survey) was initiated in 1956 on a nation-wide scale. Soil samples have been collected, and analyzed with semiquantitative spectrographic method. The results were heavily biased and were not adequately processed and utilized. Renewed efforts have been made to reprocess the vast amount of data accumulated and to utilize them more fully in mineral prospecting.

Meanwhile, another nation-wide program of regional geochemistry using more refined techniques has been in its preparatory stage. It is the Regional Geochemistry-National Reconnaissance Program.

In this program stream sediment sampling with a sample density of one per km$^2$ will be used in China proper, and low density sampling of various kind of medium in different environments will be used in remote areas. Pilot surveys covering some thousands to the thousands square kilometers of area are being undertaken in several provinces.

Beside regional reconnaissance, geochemical prospecting has been virtually carried out at all phases of mineral prospecting in China.

A brief summary of current research in exploration geochemistry taken by research institutes and universities is given, including studies on regional geochemical survey's methodology, primary halos around various types of ore deposits, mercury vapor survey techniques, refinement of analytical methods and instrumentations, and computerized data processing and plotting techniques.

Several case histories are described which have led to success of ore finding in China by using geochemical exploration techniques.
1.1.2 Europe

GEOCHEMICAL PROVINCES IN SOUTHEASTERN EUROPE

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Taking into consideration the crystallogeochemical peculiarities of the ore-forming metals and their selective enrichment in the earth crust, their distribution in Southeastern Europe is explained in terms of (1) a primeval concentration of non-compatible elements in the protocrust, reworked remnants of which "float" amidst Variscan and Alpine orogenic girdles, (2) mobilisation of these elements through tectonic and thermal disequilibrium, usually accompanied by generation of magmas at different levels of the Earth's crust, the Upper Mantle as well, and (3) deposition in favourable geological setting. Exogenous processes may have contributed to superficial enrichment in former times.

A distinct temporal and lateral zoning is discernible both in the development of magmatic rocks (ultrabasic, basic and acidic to alkaline) and ore deposits, that outline corresponding geochemical provinces. The latter are traced first in connection with the peculiarities of the geoblocks (thickness, composition, relative elevation, and textural heterogeneity), and then in connection with stressed tensional deformation between and within these geoblocks, and with their relative saturation with magmatic bodies.

The principal trends of mineralization are NW-SE, NE-SW, E-W, less frequently N-S and arcuate, corresponding to deformations in the protocrust of the opposing African and European platforms. Considerable role in the transport of ore metals must have played volatiles (F, Cl, B, S, Se, Te, As etc.) and aqueous solutions most probably of exomagmatic origin. Older evaporitic and oil deposits may have contributed towards the activity of the so-formed hydrothermal solutions.
LITHOGEOCHEMICAL EXPLORATION DATA IN SULPHIDE PROSPECTING IN NORTHERN SWEDEN:

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Sulphide ores have been mined in Sweden since the 12th century. At the same time great efforts in prospecting have been made. When new methods of prospecting have been innovated a considerable amount of new sulphide ores have been found. Most ores which are easily accessible in the established mining districts have now been found, and therefore prospecting is now concentrating on deep seated blind ore bodies in these areas. One of the main methods used will be lithogeochemistry.

The Geological Survey of Sweden (SGU) has for some years been developing prospecting based upon studies of primary haloes. The distribution of trace elements in horizontal and vertical sections in the bedrock is studied. Investigations of drill cores from mining areas are carried out at several places in northern and southern Sweden in order to ascertain the distribution patterns of trace elements around different kinds of known ores.

In an area in northern Sweden, the Malanäs area, SGU is also making a regional surface lithogeochemical investigation for the purpose of finding target areas for sub outcropping and deep seated blind ore bodies.

The Malanäs area is situated in the forest- and bog regions in northern Sweden and has an areal extent of 200 square kilometres. The bedrock consists of precambrian volcanics (quartz, porphyries, agglomerates and tuffs with precambrian sedimentary phyllites and greenstones.

Prospecting in this area started in the beginning of the 20th century, and several ores and mineralisations have been found. Up to the 1950s electric, electromagnetic and gravimetric methods were carried out. In 1970 a regional lithogeochemical investigation was initiated. 1500 rock samples from outcrops were sampled, and they were analysed using emission spectrography and sulphide isoformation. The results were studied using factor analysis and other types of statistical treatment. This investigation has generated new investigations using boulder tracing, new geophysical measurements, sampling of organic stream sediments. (700 samples), peat (400 samples) and till 500 samples.

Results:

1. Distinct primary haloes have been indicated in connection with the already known ores.

2. Several additional raw value trace element anomalies were disclosed. After using statistical treatment some of these have disappeared, but some other areas of definite interest have shown up. They are supposedly haloes from unknown mineralisations or deeply situated ore bodies and have the same general appearance as the haloes around the already known ores. Diamond drilling has started.

3. 150 bedrock samples have been crushed and separated and the fraction >2.96 g/cm³ has been analysed. These results and all other analyses of the bedrock samples indicate in a regional scale the different types of ores present in the various regions in the Malanäs-area.
PROBLEMS OF METALLOGENY AND GEOCHEMICAL PROSPECTING IN THE
BOHEMIAN MASSIF

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The ore mineralizations of the Bohemian Massif differ in age, source, chemical composition, and in structural-geological position. The oldest of them is pre-Variscan in age; it encompasses the Moldanubian (Middle Proterozoic), Brioverian, and Late Paleozoic time-units. It is believed to have produced skarn deposits of minor significance, the Cambrian Cu-Ni deposits associated with the Ransko Massif, the deposits of low-grade Fe-sulphides with Mn carbonates (Chvaletice), and the Fe ores of the Jeseníky Mt., the sedimentary Fe ores in the Barrandian region, and possibly the Cu deposit Tisová.

The Variscan mineralization has produced the large stratabound Cu, Pb-Zn deposits with younger Au mineralization in the Jeseníky Mt., the Au vein deposits associated with early Variscan tonalites (Jilové type). The middle Variscan stage is connected with the genesis of skarns in the Krusně hory Mt. and in the Krkonoše Mt., with tungsten vein mineralization (Rotava), and with pyrite-bearing Mo mineralization (Hurky near Čistá), and with gold deposits (Roudný type). The most productive was the Saalian phase that includes the Sn-W-Li mineralization (Cinovec, Horní Slavkov types) with small intrusions of albitized granites, polymetallic mineralization that represents both the aftermaths of the magmatism of early Variscan tonalites and granodiorites (Ratíbrošské Hory) and of the Middle Variscan granites (Kutná Hora type), the uraninite formation (Jáchymov, Příbram). The Saxonian tectogenesis is associated with early Variscan Fe-Ba, Pb-Zn, Bi-Co-Ni mineralization. The latest rift activation and the young alkaline volcanism are associated with the genesis of F-Ba deposits and rarely also of polymetallic mineralization.

The specific features of geochemical prospecting in the Bohemian Massif are due to an one hundred years old tradition chemical composition of the usually small deposits that are often formed by the products of several mineralization stages, to the fact that several prospective areas are covered by sediments of a platform character (notably Cretaceous and Tertiary sediments) and by Tertiary volcanics and to the deep-reaching weathering and leaching of some areas. A large part of the territory has been affected by anthropogenous influences on the distribution of elements, notably in the weathering mantle.

The geochemical prospecting on a regional scale includes the measurement of clark values in the major lithostratigraphic units, heavy minerals prospecting, and the stream sediments method; prospective regions are studied using hydrogeochemical methods (this applies to F-Ba and polymetallic mineralization); other methods employed are lithogeochemical studies of rock fragments including those from the bedrock (Sn-W and polymetallic deposits), soil metallometry, mercurometry, and tentatively also atmogeochemistry. Considerable significance is also ascribed to the study of primary aureoles (polymetallic deposits and Sn-W formations).
MINERALOGICAL-GEOCHEMICAL PROSPECTION METHODS IN THE CENTRAL-EUROPEAN COPPER BELT

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The copper deposits of the southern border of the Central-European Zechstein basin are distinctly palaeotectonically controlled by the Mid-German crystalline zone, which is to be found beneath the Permosilesian molasse stage in the basement folded during Variscan and which forms the outer metamorphic rim of the Saxo-Thuringian zone of the Variscan orogens. Therefore the term "Central-European Copper Belt" is suggested for this belt of deposits. The lithological-palaeogeographical control of the deposits is not so strong, because the deposits occur with differing lithological forms of the Zechstein base sediments and in different palaeogeographical positions.

The application of efficient mineralogical-geochemical prospection methods is based on the knowledge of the ore-controlling zoning Fe³⁺-Cu-Pb-Zn-Fe²⁺ resp. hematite-chalcosine-bornite±chalcopyrite-galenite-sphalerite-pyrite. The ore-bearing zone at the Zechstein base is locked to the copper shale and the uppermost centimeters of the so called sandore only in the areas far from the deposits. Within the deposits the ore-bearing zone varies within a vertical range of about 10 m around the copper shale. Only in the traditional deposits of Mansfeld-Sangershausen the workable mineralization varies between the copper shale and the basal parts of the Zechstein limestone. This bears a resemblance to the remoter parts of the deposits.

Knowing the lithological structure of copper shale in detail, the mapping of the lateral and vertical distribution of the metals and parageneses leads to the proof of the diagonal intersection of the mineralization by the lithotypes. Thus, in the case of a relatively simple structure of the ore-bearing zone, lateral extrapolation of the copper mineralization becomes possible for several hundreds of meters beyond the bore holes or mine workings. By means of the zoning of the distribution of metals and parageneses it was demonstrated, that the metals were delivered syngenetically to diagenetically through areas with the hematite paragenesis (Rote Fäule-facies). The diagenetic solution transfer towards the sapropelite facies produces the parageneses with sulphides rich in copper (idaite-covellite- and chalcosine paragenesis). In the first instance only parageneses rich in chalcopyrite and bornite were formed early diagenetically.
AN EVALUATION OF GEOCHEMICAL TECHNIQUES IN THE EXPLORATION FOR STRATABOUND BARYTE AND BASE METAL DEPOSITS IN THE MIDDLE DALRADIAN OF SCOTLAND.

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A regional geochemical drainage survey of the Middle Dalradian metamorphic rocks near Aberfeldy in the Scottish Highlands located a stratabound zone of barium, zinc and lead mineralisation. Sampling of the fine fraction of the stream sediment was the most effective reconnaissance exploration method but heavy mineral concentrates were the most precise indicator of the mineralisation at the follow-up stage. A multivariate factor analysis model was used to assign an order of follow-up priority to the samples and to separate false anomalies due to contamination. Similar results were obtained by plotting cumulative frequency-probability diagrams. Subsequent sampling of the soils, glacial overburden and rocks was undertaken and is briefly discussed. Analysis of cores and rock samples for barium with a portable X-ray fluorescence spectrometer identified barium-rich schist outside the mineralised zone and this lithogeochemical approach has potential for further exploration of this horizon. A regional drainage survey is considered, however, to be the essential first stage in the exploration for further stratabound occurrences.
ON THE THEORETICAL AND PRACTICAL SIGNIFICANCE OF PRIMARY LITHOCHEMICAL HALOS

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It is known, that primary halos firstly attracted attention of geologists in connection with the problem of exploration for so-called blind ore bodies and deposits. The subsequent works revealed, that due to their characteristic features (substantial extension of supra-ore halos, geochemical zoning of halos etc.), primary halos can be successfully used in search for blind mineralization. The works carried out in several ore areas of the USSR, proved high geological and economical efficiency of primary halos used in search for blind mineralization. The recent investigations revealed, that the use of primary halos is rather effective not only in exploration for buried mineralization but in the assessment of ore showings too. The geochemical zoning of primary halos, which allows to estimate the level of erosion surface of ore showings and to determine the distinction between supra-ore level (promising in depth) and below-ore ones (deeply eroded) is used to solve this task.

It is considered that in exploration for blind and weekly eroded ore bodies the primary halos can be successfully used practically only in the areas of good exposure when ore-bearing bedrocks come to erosion surface.

The experience of geochemical exploration in the USSR allows to state that the primary halos are the basis of geochemical exploration both in the exposed and buried areas. This conclusion comes to some extent from the specific position of primary halos in a wide group of different types of geochemical anomalies; it is known that primary halos are nearest to ore bodies and they are in fact a primary source of other types of geochemical halos, particularly a wide group of hypergene halos. Thus, the task to estimate any of hypergene anomalies becomes the task of establishing characteristic features adequate to primary halos - the primary source of this anomaly - because transition from the anomaly to the ore body (the deposit) comes true only through primary halos.

The primary halos essentially are the integral part of ore bodies and deposits and this reason determines theoretical significances of the result of primary halos investigation; the characteristic features of composition and structure of primary halos, reflecting conditions of deposits formation, carry important genetic information.
The potential applications of As, Sb and Bi as pathfinder elements in geochemical exploration have been researched using a new, rapid technique for the simultaneous determination of the three elements. Following a warm hydrochloric acid sample leach, the volatile hydrides of the elements are generated and flushed into an inductively-coupled plasma linked to an emission spectrometer. The technique offers a combination of good analytical precision and detection limits of 100 ppb for each of the elements.

The principal sulphide ore minerals commonly contain traces of As, Sb and Bi, and concentrations of more than 1% of any one of these have been found in some sulphide specimens. During sub-aerial oxidation of sulphides, any As, Sb, and Bi present is released and forms dispersion patterns in the surficial environment. Soil samples collected along traverses across veins bearing base metal mineralization in the United Kingdom contain anomalous concentrations of some of the elements As, Sb and Bi over the projected suboutcrop of the veins. Anomalous dispersion trains of these elements were also detected in the sediments of streams draining the mineralized localities. In a geochemical reconnaissance covering 12,000 km of central Nepal, over 3,500 stream sediment samples were analyzed for As, Sb and Bi, and may known occurrences of Cu, Pb and Zn mineralization are reflected by As and Sb anomalies; however, bedrock lithology appears to be an important factor influencing Bi concentrations.

In the areas studied, some or all of the elements As, Sb and Bi produce soil and stream sediment anomalies that compare favourably in terms of contrast and extent with the heavy metal expressions, although none of the three elements has formerly been reported as a known associate of the local mineralization.
EXPLORATION FOR CHROMITE IN DIFFERENT TERRAINS OF INDIA

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Of the various stages of exploration for chromite in India, the geological mapping (stage 1) is completed in most of the chromite deposits. Geochemical exploration (stage 2) and geophysical exploration (stage 3) were felt necessary and completed recently in parts of Orissa and Karnataka. In case of other deposits, stage 1 is still incomplete and the necessity for the other stages is not yet felt.

The chromite in the chromitites of these deposits varies from 50 to 95% and is associated with various ultramafic and mafic rocks. Three types of geological settings for the chromits are found in India. Type 1 has chromitite having 80 - 95% chromite in association with limonitised and silicified ultramafic rocks, pyroxenite, serpentinite and peridotite, type 2 has chromitite having 60 - 80% chromite in association with hypersthene, diopsidite and type 3 has chromitite having 50% chromite in association with anorthosite - gneiss - amphibolite.

The alteration of ultramafic rocks and consequent development of soil profile is thickest (upto 100 m and more) in case of type 1 and thinnest (almost negligible) in case of type 3 with intermediate values for type 2. Experience shows that geochemical exploration (stage 2) was best suited for type 1 before and after the stage 3. In case of other types, only primary geochemical exploration is possible and meaningful and hence necessary after stage 1, whereas stage 3 may conveniently be skipped because of disadvantages involved. Drilling (stage 4) to prove three levels was possible only in case of type 1 of Orissa. Even though all geochemical studies have been employed before this stage, primary geochemical studies are still necessary even after stage 4 in such deposits.

It is concluded that geochemical exploration attains special significance in this context in establishing the nature and continuity of various types of chromite deposits as its value is immense at every stage of exploration for chromite.
ANOMALOUS GEOCHEMICAL PATTERNS FROM NORTHERN SUMATRA: THEIR ASSESSMENT IN TERMS OF MINERAL EXPLORATION AND REGIONAL GEOLOGY.

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Geochemical drainage sediment maps and anomaly maps are presented covering Sumatra, Indonesia, north of 4°N, an area of over 38,000 sq.km. The drainage sediment maps employ a grey scale format and the anomaly maps are based on a probability measure of the occurrence of anomalies in a unit area. The unit area (cell size) for the anomaly maps is 10 km x 10 km and the average sample density is 13 samples per cell.

In assessing the mineral potential of the cells it is necessary to compensate for variation in sample density. To achieve this probability measure, from the binomial distribution, is calculated which gives the likelihood of the number of anomalies occurring among the number of samples taken per cell. This measure is used to make a comparative ranking of the cells in which the lowest values indicate a high improbability of occurrence of that number of anomalies unless the cell was truly enriched or excessively depleted in the element concerned. In this case the low sample density excludes low probabilities due to depletion. However, the simple ratio of the number of anomalies squared to the number of samples per cell gives the same ranking as the binomial measure, on a different order of scale, and reveals only enriched cells.

Northern Sumatra has very distinct geochemical patterns. The copper distribution has its high analytical values along the axial mountain range of Sumatra and is derived from two main sources: one is the Sumatran ophiolite sequence, the other is the copper-rich calc-alkaline intrusives. Chromium patterns follow the ophiolite sequence but also indicate placer concentrations. Lead and zinc combine to give a distinct grouping which occurs east of the linear copper zone and borders the oil and gas basins. These clear patterns, when related to geologic information, allow rational selection of areas for detailed mineral exploration.

Apart from the economic aspects, other elements have patterns of regional geologic significance. High tin values occur between the copper-rich calc-alkaline intrusive axis and the subduction zone west of Sumatra: this would not appear to be the usual location for tin mineralisation. However, the lithium distribution distinguishes two major crustal blocks which are now sutured along the Sumatran ophiolite sequence. Thus the recognition that Sumatra is not a simple continental margin is fundamental in the interpretation of geochemical patterns for mineral exploration.
EXPLORATION FOR NICKELIFEROUS LATERITES IN HUMID TROPICAL TERRAINS.

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In humid tropical terrains laterites are fast becoming a useful geological material worthy of exploitation. The four main types of mineral deposits associated with lateritic weathering are: (a) Iron-ore deposits, (b) bauxite deposits, (c) manganese ore, (d) secondary nickel deposits over ultramafic rocks. Among these, the nickel potential of lateritized and serpentinized ultramafic rocks is of great interest and a large number of case histories are reported from Asia and Australia. Among the criteria that could be effectively used in the location of such laterites are special characteristics due to topographical expressions, soil, vegetation, weathering phenomena, type and distribution of opaque minerals and characteristic geochemical features.

These criteria and the geochemistry of weathering profiles used in exploration for nickeliferous laterites will be discussed in the paper.
GEOCHEMISTRY OF APATITES IN THE GRANITIC ROCKS OF THE MOLYBDENUM TUNGSTEN, AND BARREN PROVINCES OF SOUTHWEST JAPAN

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Four petrographic provinces have been recognized in Southwest Japan on the basis of distribution, mode of occurrence, age, and chemical and mineralogical composition of granitic rocks. The provinces trend almost parallel to the island arc and referred to, from south to north, as the Outer Zone, the Ryoke, Sanyo-Naegi, and Sanin-Shirakawa belts. The K-Ar ages of the granitic rocks in these zone and belts belong to 11-22 m.y., 50-95 m.y., 50-95 m.y., and 35-65 m.y. ranges, respectively.

Clear zonal arrangement of tin, tungsten, and molybdenum deposits is observed in Southwest Japan. Namely, the metallogenic provinces in Southwest Japan, such as the Tin, Barren, Tungsten, and Molybdenum provinces from south to north, correspond closely with the petrographic provinces aforementioned.

Recognition of the importance of chlorine complexing of metal sulfides in aqueous solutions has led to the view that the chlorine content of intrusive rocks could govern the ability of a magma to separate a metal-rich hydrothermal phase. This article presents the chlorine and fluorine contents of apatites in the granitic rocks of the Barren, Tungsten, and Molybdenum provinces of Southwest Japan.

The apatite analyses were done with a JEOL model JXA-5A electron microprobe using a PET crystal for Cl and a MYR crystal for F, an excitation voltage of 10 kV, sample currents of $10^{-7}$ A on MgO, integration times of 20 sec, and chlorapatites and fluorapatites as standards.

The granitic rocks in this article range from granite to quartz diorite, but include some diorites.

The abundance of Cl in apatite correlates negatively with rock D.I. (differentiation indices), while the abundance of F in apatite correlates positively with rock D.I. Abundance of Cl in apatite in the granitic rocks of the Molybdenum province is generally higher than that of Cl in apatite of the Tungsten and Barren provinces, while abundance of F in apatite in the granitic rocks of the Molybdenum province is generally lower than that of F in apatite of the Tungsten and Barren provinces, although it is apparent that individual districts exhibit characteristic chlorine-fluorine abundances.

Apatites in the granitic rocks genetically related to tungsten mineralization and granite pegmatite formation, and from the Barren province are fluorapatites.
Research on primary halos around sulfide deposits of hydrothermal origin (in its broad sense) was initiated in China in the late 50's. Terminology used is somewhat different from Soviet Union and Western Countries. The high content zone around a sulfide ore body is taken as a whole, and is divided into four parts: front part (front anomaly or front halo), developed in the channelways of egress; rear part (rear anomaly or rear halo), developed in the channelways of ingress; adjacent part (adjacent anomaly or adjacent halo), developed in the vicinity of a sulfide ore body; lateral part (lateral anomaly), developed at the terminals along the strike of a sulfide ore body.

Primary halo around a single ore body is termed single halo. But most primary halos are compound halos, which are formed by the incooperation of several single halos.

According to the relative positions of primary halos to their "concentration centers" (ore bodies), primary halos may be referred as concentric, eccentric, and peripherical.

Primary halos developed in one channelway system are termed simple halos, while those developed in more than one channelway systems are termed complex halos.

Internal structure of a primary halo is described in a standardized way. Element content $a^0T$, $a^1T$, and $a^2T$ zones ($a=2,3$, or $4$, T-Threshold) are contoured and referred as outer, intermediate and inner zones of a primary halo. Such specification avoid subjective contouring, and put primary halos of different origin and from various districts in an easily comparable basis.

Zoning of primary unielement halos or in other words, compositional zoning of a primary multielement halo shows different patterns over hydrothermal polymetallic, skarn copper and porphyry copper deposits. Emphasis has been placed on the relationship of "primary contrast" of various indicator elements on their positions in a zoning sequence.

Many examples for illustration are presented. Practical applications and case histories for finding blind ore bodies by study of their primary halos are briefly referred.
THE CONTINUOUS UNITED STATES MINERAL ASSESSMENT PROGRAM WITH THE THALLIS IDAHO 1° x 2° QUADRANGLE AS AN EXAMPLE PROJECT


The objective of the Conterminous United States Mineral Assessment Program (CUSMAP) is to gather, interpret, and disseminate information on mineral resources on a regional basis for land-use planning and mineral resources management by government and industry. The basic element of CUSMAP provides systematic assessments of the minerals resource potential of selected 1° x 2° 1:250,000 scale quadrangles (18,000 km²). The program began in October 1978, and 15 quadrangles are under investigation. Criteria for selecting quadrangles are (1) importance of known mineral resources, (2) amount of Federally owned land, (3) urgent need for resource information for land use planning decisions, and (4) known or possible critical commodity resources.

Every quadrangle has a multidisciplinary team of geologists, geochemists, and geophysicists under a team coordinator. They will produce a colored geologic map for each quadrangle, and overlays to show geochemistry, geophysics, and potential for mineral resources. The geochemical investigations include a regional sampling program to define broad background geochemical patterns and delineate anomalous patterns resulting from mineralization. Between 5,000 and 10,000 samples are collected for each quadrangle. A detailed program of rock and soil sampling is made of anomalous areas and areas of alteration and mineralization. Geophysical surveys including aeromagnetic, gravity, and remote sensing data are provided each CUSMAP quadrangle. In addition research will be carried out on geophysical technique development directed toward resource discovery and appraisal.

The ultimate objective of the program is to produce mineral resource assessment information that can be understood and used by Government and industry for land-use decisions and planning. The minimum product will be a map showing areas of various degrees of favorability based on our understanding of the geologic environment of the various commodities present as well as interpretation of the geophysical and geochemical data. In addition all the mineral resource data will be incorporated in the U.S. Geological Survey computer data banks.

Examples of products published from a prototype study in Alaska and Arizona will be displayed, as well as description of current work in the Challis quadrangle.
THE LOS ALAMOS SCIENTIFIC LABORATORY APPROACH TO HYDROGEOCHEMICAL AND STREAM SEDIMENT RECONNAISSANCE FOR URANIUM IN THE UNITED STATES

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The Los Alamos Scientific Laboratory of the United States is conducting a geochemical survey for uranium in the Rocky Mountain states of New Mexico, Colorado, Wyoming, and Montana and in Alaska. This survey is part of a national hydrogeochemical and stream sediment reconnaissance in which three national laboratories will study the uranium resources of the United States to provide data for the National Uranium Resource Evaluation sponsored by the US Department of Energy. The reconnaissance will identify areas which have higher than background concentrations of uranium in their ground waters, surface waters, and water-transported sediments. The reconnaissance data will be combined with data from airborne radiometric surveys and geological and geophysical investigations to provide an improved estimate of the economics and availability of nuclear fuel resources in the United States and to make information available to industry for use in the exploration and development of uranium resources.

The Los Alamos Scientific Laboratory based its reconnaissance on an extensive review of the world literature on geochemical sampling, the results of pilot studies, and similar sampling programs in Canada, France, Sweden, New Zealand, and the United Kingdom. It consists of field operations, sample analysis, and data evaluation and publication. The standardized field and analytical procedures being used were designed to emphasize the determination of the uranium in water and waterborne sediments. The samples are collected by professional geologists or contractors at a nominal density of one sample location per 10 km² except for lake areas of Alaska where the density is one sample location per 23 km². Water samples are analyzed for uranium by fluorometry with a lower limit of detection of 0.02 parts per billion. Concentrations of the 12 other elements in water are determined by plasmasource emission spectrography. All sediments are analyzed for uranium by delayed-neutron counting with a lower limit of detection of 20 parts per billion, well below the range of uranium concentrations in natural sediment samples. Other elemental concentrations in sediments are determined by neutron activation analysis for 31 elements, by x-ray fluorescence for 9 elements, and by arc-source emission spectrography for 2 elements. The multielement analyses provide valuable data for studies concerning pathfinder elements, environmental pollution, elemental distributions, dispersion halos, and economic ore deposits. An average of 350 samples are analyzed by each analytical method each working day.

To date, all of the four Rocky Mountain states and about 80% of Alaska have been sampled. Over 220,000 samples have been collected from about a 2,500,000 km² area. The philosophy, sampling methodology, analytical techniques, and progress of the reconnaissance are described in several published pilot study, reconnaissance, and technical reports. The Los Alamos program was designed to maximize the identification of uranium in terrains of varied geography, geology, and climate and is one of the largest geochemical programs of its type in the world. Due to its diversity, its technology could be applied to any country.
REGIONAL GEOCHEMICAL EXPLORATION FOR MINERAL DEPOSITS IN THE APPALACHIANS OF CENTRAL AND NORTHWESTERN VIRGINIA, U.S.A.

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Regional geochemical exploration was conducted in an 11,825 km² area of the Appalachians in Central and Northwestern Virginia. Its purposes were to develop geochemical base maps for mineral exploration, establish element geochemical dispersion patterns in the secondary environment of soils and streams with respect to known mineralized areas and regional structural lineaments, find anomalous zones as targets for detailed geochemical prospecting.

Element concentrations for Ag, Au, Mo, Cu, Pb, Zn, Mn, Fe, Ni, Cr, and Co, were determined in 107 soils, 159 stream sediments and 159 corresponding stream waters, using atomic absorption spectrometry. The analytical data were evaluated using regional deviation analysis (RDA), Pearson correlation coefficient estimates, and 5th order trend surfaces. Geochemical maps were produced using the "SYMAP" computer program. RDA and SYMAP graphics are effective in presenting the geochemical data.

Geochemical anomalies (concentration values greater than $\bar{x} + 2$) and dispersion patterns were treated in three geographical regions: a) the Piedmont Province, b) the Blue Ridge and Valley-Ridge Provinces combined, and c) the composite region. The element anomalies and regional trends are well-delineated within all categories, but are more important in reconnaissance exploration projects when generated for the individual regions (a and b) than for the entire region.

Of the eleven elements studied, Mo, Cu, Pb, Ni and Co have the greater number of stream sediment anomalies and these are thought to be "pathfinders" to mineralized areas. In soils, Zn, Mo, and Co anomalies are useful in regional exploration. Coupled Mn-Co anomalies in both stream sediments and soils may be indicative of supergene cobaltiferous Mn deposits in the Valley-Ridge Province. In the study area, soil-anomalies of Pb, Au, Ni, and Cr were found to be the most important in prospecting since these elements are relatively less mobile than others studied and are generally located closer to related mineralization. Element pairs with significant positive correlation coefficient estimates are probably geochemically associated in mineralization.

On the basis of geochemistry, geology, known mineralization, anomaly interrelationship, regional structural lineaments, and anthropogenic input, targets for detailed exploration were selected.

In the Piedmont Province, target areas were found near Mineral, Mt. Pleasant, Culpeper, Orange, Charlottesville, Wilmington and Columbia. Target areas were delineated in the Blue Ridge and Valley-Ridge Provinces southeast of Elkton and Harrisonburg, and northeast of Shenandoah. The significance of these targets is emphasized by the 5th order trend surface and residuals. Localities with clustering of anomalies are characterized by converging structural lineaments and are considered to be important target areas.
REGIONAL AND LOCAL URANIUM ANOMALIES IN THE DEVONIAN CATSKILL FORMATION NEAR SANDSTONE-TYPE URANIUM PROSPECTS IN PENNSYLVANIA

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Several uranium prospects, at least one a roll-type deposit, are localized in sandstones of the upper Devonian Catskill red beds near Jim Thorpe in eastern Pennsylvania. Contents of U, Th, and La in 370 samples of sandstone and shale are directly correlated with Al and inversely with Si. Background values of U and Th in the mineralized uppermost member of the Catskill average 60 % and 33 % higher, respectively, than lithologically similar samples from an underlying member lacking uranium occurrences. Shales from the mineralized member of the Catskill near Jim Thorpe average significantly higher in U than shales from the same member at four localities 25 to 110 km to the southwest along the depositional strike. Zircon separates from the sandstones near Jim Thorpe include 13-26 % of high-U grains (2050 ppm) compared to 0-6 % in the three sites to the southwest. The anomalous values for U and Th are attributed to deposition of relatively U- and Th-rich detritus in the uppermost Catskill of the Jim Thorpe area, followed by reworking, into deposits, of uranium derived from the detritus and from leaching of the source area. Possible source rocks in the Precambrian are known to be at least locally enriched in U.

Oxidized paleoaquifers through which U was transported to the roll-type deposit contain about four times the background amounts of U and have very low Th/U ratios. Grund waters that formed the deposits evidently brought U into the deposits and nearby aquifer rather than leaching it from the oxidized part of the aquifer.

The regionally elevated U and Th contents in rocks and zircons furnish a possible means of recognizing units favorable for occurrence of sandstonetype U deposits and can contribute to regional anomalies in stream sediments and other media. The more strongly anomalous U values in oxidized paleoaquifers constitute a more detailed guide to sandstones in which roll-type occurrences may be found.

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METAL TRANSPORT, PARTITION AND FIXATION IN LAKE WATERS AND SEDIMENTS IN CARBONATE TERRAIN IN SOUTHEASTERN ONTARIO

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The use of lake sediment composition as an indicator of mineralization within the catchment area has found widespread use in recent years, particularly in Canada. Results have indicated however the existence of varying relationships between lake sediment composition and mineralization resulting from local features of the limnological environment. Accordingly it was considered appropriate to examine the nature of metal transport in the lake and stream environment, the partitioning of metal between the stream, lake waters and lake sediments to obtain some understanding of the factors that affect the lake sediment-mineralization relationship. This investigation was carried out over an area containing Pb-Zn occurrences of supposed "Mississippi Valley type" in Grenville and Paleozoic bedrock in southeastern Ontario.

The headwater drainage systems comprise active streams, swamps, beaver ponds and small lake-bog systems giving way downstream to open lakes. The beaver swamps and seasonal swamps act as drainage sinks for metals, restricting the extent of geochemical dispersion in drainage systems adjacent to mineralization. Selective extraction of bog, stream and lake sediments indicates that metals are preferentially complexed by organic matter. The adsorbing and chelating action of organic matter on lead and zinc makes organic-rich sediments from these small swampy areas an excellent sample medium for reflecting local mineralization. Recognition of the down drainage dispersion of these elements can be accentuated by selective analysis for the organic-held metal involving either a hydrogen peroxide or sodium hypochlorite extraction.

In contrast, within larger lake systems, the analyses of water samples has indicated that geochemical dispersion in surface waters in the high pH environment (pH = 8.0) associated with the carbonate hosted lead-zinc deposits is of an extremely restricted nature. In this environment anomalous metal compositions in lake water were not evident in lakes adjacent to mineralization while anomalous lake sediment composition exist only in lakes immediately adjacent to Pb-Zn mineralization and do not extend down the drainage system. The existence of these restricted anomalous drainage patterns necessitates basing geochemical reconnaissance surveys on the collection and analysis of samples from the headwater organic-rich swamps at a higher sample density and resulting higher cost than that in areas where a lower sample density is acceptable due to a wider dispersion.
Recent geochemical studies in the central Brooks Range, Alaska, have delineated a regional, structurally controlled, mineral belt extending from 147° to 158°, a distance of over 450 kilometers. Within this belt are several occurrences of copper and molybdenum mineralization and geochemical evidence for numerous additional occurrences.

Over 4,000 stream sediment and panned concentrate geochemical samples have been taken in the central Brooks Range, Alaska, over a period of four years from 1975 to 1979. The -80 mesh (-177 micrometers) stream sediment and the heavy (>2.86 SpGr) nonmagnetic fraction of the panned concentrates were analyzed by semiquantitative spectrographic methods. Results of these analyses indicate an east-west trending structurally controlled mineral belt in meta-igneous and meta-sedimentary rocks.

Within this belt several types of mineralization have been noted. In the metamorphic rocks are several meta-intrusives, one of which is a potential porphyry system. Skarn deposits occur in sedimentary rocks adjacent to the metamorphic rocks and massive sulfides have been found in some of the meta-volcanics. Other areas of potential mineralization are evident from the regional geochemical study.
Several zinc showings occur in the Grenville Supergroup Marbles of Ontario, Quebec and New York State. Four of them have produced significant quantities of ore (e.g.: Balmat-Edwards, N.Y.; Calumet, Que.; Montauban, Que.; and Long Lake, Ont.). By far, the Balmat-Edwards district is the giant of this family with a production, since 1915, of 20 millions tons of ore grading 10% zinc and reserves of approximatively the same amount and grade.

Regional and detailed studies of a group of eight zinc showings in Southern Quebec led us to define several useful exploration guidelines:

a) the stratiform zinc mineralization is invariably associated with dolomitic marbles and their transitional contact with metaclastics.

b) the stratiform zinc mineralization occurs in the basal marble unit of the Grenville Supergroup (Helikian age).

c) the Southern Quebec Zinc showings seem to occur in a belt extending for some 250 km along the Helikian-Aphebian unconformity.

Geochemical methods prove to be very useful at all scales of exploration. Several zinc showings have recently been found by the follow-up of stream sediment geochemical anomalies. Traditional geophysical methods seem of little interest because disseminated and massive zinc mineralizations give poor responses. Prospecting methods used also include: Geochemical soil surveys; E.M., I.P. and magnetometer surveys, and boulder tracing.

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GEOCHEMICAL PROSPECTING FOR STRATABOUND MINERALISATION IN PRECAMBRIAN SEDIMENTS OF EAST GREENLAND (72-74°N).

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As part of IGCP-project no. 60 - "Correlation of Caledonian Stratabound Sulphides" a geochemical project was carried out in a 14,000 m thick sedimentary sequence of late Precambrian (Eleonore Bay Group and Tillite Group). The project included investigations of rock samples and drainage samples. The drainage samples were heavy mineral concentrates and finegrained stream sediment samples. The rock samples (267) and the finegrained stream sediment samples (72) were analysed for Cu, Co and Zn by atomic absorption spectrophotometry and the heavy mineral concentrates (90) were analysed for Cu by emission spectroscopy.

The analytical results indicate that Cu exhibits a very good geochemical variation in all three media and enable definition of several anomaly values. The results of the drainage sediments distinguish between three well defined Cu horizons in the sedimentary column. Two horizons are indicated by the heavy mineral concentrates, whilst the third is reflected by the finegrained stream sediments. The lithogeochemical studies of quartzites, pelites and carbonates confirm that the anomalous values obtained in the drainage sediments are due to several Cu mineralized horizons in the Upper Eleionore Bay Group. The Cu content of the quartzites and pelites have peak values of 6430 ppm and 7388 ppm respectively, whereas the carbonates reach only 174 ppm. The host rock lithology and the physico-chemical characteristics of the copper minerals play an important role in the reflectance if Cu during secondary dispersion.

This study has shown that geochemical prospecting appears to be well adapted to Cu prospecting in Central East Greenland under arctic climatic conditions. A very low sampling density with one sample per 5-10 km² for the drainage samples, and one sample per 10-100 m of the sedimentary stratigraphic column for the lithogeochemical investigations defines several Cu horizons in the Upper Eleionore Bay Group.
THE USE OF PETROLEUM-WELL SAMPLES AND DATA FOR GEOCHEMICAL PROSPECTING OF METALS IN SEDIMENTARY BASINS

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Systematic sampling of petroleum-well cuttings and cores, their analyses for 14 elements, and the compilation of relevant descriptive data are currently being used by Petrobrás Mineracão S.A., a subsidiary of Petróleo Brasileiro S.A. (PETROBRAS) in the search for stratiform sedimentary mineral deposits and the evaluation of mineral potential of the sedimentary basins of Brazil.

This program involves the selection of material collected during the exploratory and development drilling of over 5,000,000 meters throughout Brazil in the past 40 years. Target areas-sedimentary basins, wells, strata-are selected in accordance with Brazil's mineral requirements and the geologic probability of their occurrence. Composite samples are prepared from cuttings representing 5 meters of drilling, and are analyzed for Cu, Pb, Zn, Ni, Co, Cr, V, Cd, Ag, Mo, Ba, Sr, Fe, and Mn. Analytical results, together with positional and geologic data are coded and recorded in logical arrays on magnetic devices for storage and subsequent data selection and processing. Interpretation of data for potential mineralization or its indicators entails progressive screening for anomalous values of first raw data then of data enhanced by calculating standardized values of sub-populations selected by geologic criteria, and finally of nes geochemical values created by using regression residuals, and ratios or vectors formed within standardize values. Evaluation of the mineral potential in each sedimentary basin is done empirically applying a "What, Why and Where-does-it-lead" technique entailing a typological classification of geochemical highs and subsequent attempts to trace them to areas likely to be mineralized, using geochemical-geologic profiles and low-order trend surfaces, where best-fit geologic solutions are sought by adjusting the time-space dimensions and positioning of the datum planes used for trend surfaces.
MARINE SAMPLES IN THE SEARCH FOR ONSHORE MINERALIZATION:
BOTTOM SEDIMENT, SEAWEED, SUSPENDED MINERAL WATER

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Recently, several studies have used a marine sampling approach in the
reconnaissance for onshore mineralization. A geochemical prospecting tech­
ique, operational nearshore from a boat, would be useful in remote areas
(difficult logistics) and in areas with steep and/or rugged topography
(difficult access) such as the Antarctic Peninsula, and fjord regions in
Scandinavia, Greenland, the Arctic, Canada, New Zealand, and Chile. Because
of the transportation economics associated with the development and
operational phases of a mine in such areas, the location of a mineral depo­
sit near the coast could be more attractive than a like deposit located in­
land.

Beach sand mineralogy and geochemistry have long been used in the explora­
tion for nearshore placer type deposits. Bay environment surface sediments
have given plots of metal concentration/clay content vs. clay content that
indicate anomalous metal concentrations in the direction of fine-grained
sediment dispersal away from known onshore mineralization (Slatt, 1975;
Slatt and Sasseville, 1976); however, chemical diagenesis in the surface
and nearsurface (subsurface) sediments can greatly alter the original metal
content. Biogeochemical prospecting with seaweed was proposed as a tech­
ique for targeting on land mineralization for a West Greenland fjord, but detailed
research indicated that local geochemical anomalies that increased towards
an adjacent sphalerite-galena-pyrite deposit were the result of foreign
mineral inclusions in the seaweed (Bollingberg, 1975). Similar results were
reported from a steep-walled fjord in Norway (Sharp and Ølviken, 1979), but
the researchers did not report on the possible presence of foreign mineral
inclusions in their seaweed samples as the source of geochemical signals. Any
such inclusions have entered the marine systems studied as suspended sediment
Jedwab (1979) identified sphalerite, malachite, tenorite and other
minerals in suspended particulate matter of ocean waters. This suggests that the sus­
pended sediment itself, or a fraction thereof, can be an excellent sample
from an inshore environment in the geochemical reconnaissance for onshore
mineralization.

Geochemistry of suspended mineral matter from the southern Argentine shelf
gave a Au anomaly that could be related to a Au placer located on a spit
(Siegel and Pierce, 1978). A subsequent study of mineral suspensate from the
Chilean Archipelago yielded, in addition to Pb-Zn-(Cu) targets, a Cr-Ni-(Co)
cluster anomaly (e stations) that may be related to a nearby ophiolite se­
quence (Siegel et al., 1979, and in preparation); onshore stream sediment
analyses in a geologically similar area to the south gave Cr-Ni anomalies
(M.Suarez, p.c.). Most recently, geochemistry of mineral suspensates from
around Giglio Island (Mediterranean) showed anomalous values for Zn, Cu, and
Pb offshore from a promontory where Zn, Cu and Pb mineralization is known
(Parassis, 1980). In all of these suspended mineral matter studies, geo­
chemical analysis of the 2 μm fraction of the corresponding bottom sediments
showed either muted anomalies or no anomaly thus indicating that there was
a dilution of the chemical signal and/or a chemical diagenesis that mobilized
metals away from the size fraction analysed. This may limit the uti­
ity of bottom sediment geochemistry in prospecting, but underscore the
great potential of the mineral fraction of suspended matter as an excellent
inshore marine sample in the reconnaissance search for onshore mineralization.
1.1.5 Africa

OPERATION RESULTS AND COSTS OF THE REGIONAL STREAM SEDIMENT SURVEY OF THE GEOLOGICAL SURVEY OF SOUTH AFRICA

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As a contribution to the mineral development of the Country, the Geological Survey of South Africa conducts since 1975 a country-wide regional multi-element stream sediment survey which intends to cover the 1,2 million square kilometres of the Republic at a density of one sample per square kilometre. The present sampling rate is 20,000 samples per year, but is intended to be doubled in the near future.

Samples are collected by either vehicle or helicopter transported field teams. The sample sites are pre-selected by a geochemist and marked in the office on 1:50,000 topographical maps or aerial photographs. The samples are not treated in the field but railed to a central laboratory where a -200 mesh fraction and a heavy mineral concentrate are recovered by mechanical sieving and manual panning with subsequent heavy liquid cleaning, respectively.

The fines are analysed for Cu, Zn, Pb, Ni, Cr, Mn, As, Ag, Sn, U, V, Mo, W, Y, Zr, Rb, Sr, Fe, Th by a simultaneous XRF-spectrometer and for U and cold-extractable U by delayed neutron activation. The concentrates - after mineralogical investigation for kimberlite-indicating minerals - are analysed by DC-arc direct reader for a number of still to be determined elements. At the moment the results are plotted manually, but for the near future computer-plotting as proportional circles on maps to the scale of 1:50,000 and grey-scale maps to the scale of 1:250,000 as well as computer listings are envisaged and will be made public.

The recently discovered base metal deposits of Aggeneys (5.9 mill t Pb, 2.8 mill t Zn and 0.8 mill t Cu metal content) and Gamsberg (6.9 mill t Zn and 0.7 mill t Pb metal content) in the Northwestern Cape Province form extremely prominent geochemical anomalies in this type of survey and can be picked up geochemically over a distance of 15 km downstream.

The total sampling costs under the conditions of this survey carried out in a scarcely-populated semi-arid area with sampling tours of about 7000 samples amounted to US $ 8.47 if vehicle transport is used and US $ 9.34 with helicopter transport. The positive effect on the field staff because of shorter field seasons and the better control of sample positioning favour the helicopter-based sampling despite the higher costs of US 0.87 or 10 %.
URANIUM REDISTRIBUTION IN WEATHERED WITWATERSRAND-TYPE
CONGLOMERATES INVESTIGATED BY MEANS OF THE FISSION TRACK METHOD

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A radiometric surface survey of conglomerates of the early
Precambrian Swaziland and Pongola Supergroups in southern
Africa showed the presence of variable low but significant
U-concentrations (5-160 ppm $\text{U}_3\text{O}_8$). U-contents of a similar
range are known from surface outcrops of conglomerates of the
Witwatersrand Supergroup which carry economical amounts of
uranium at greater depths. To study the spatial distribution
of uranium in the weathered samples, U-fission track micro-
mapping was used. This method - characterized by high re-
solution - permits to investigate U-concentrations in the
sub-ppm range.

The results of the investigations revealed that uranium was
leached and redistributed in the weathered surface material
which now is U-depleted. In the weathered samples residual
U-concentrations were found to occur with phyllosilicates,
altered Ti-oxides (leucoxene), and carbonaceous matter within
the conglomerate matrix. It is suggested that the employed
method may serve as a tool in the exploration of deeply
weathered uraniferous rocks.
A regional radiometric reconnaissance was carried out in the Southern Provinces of Sudan by means of a car-borne survey.

The investigated area is physiographically subdivided in three sectors: the Southern Clay Plain of the Upper Nile Basin, with Alkaline Clay Soils; the Ironstone plateau, with the soils of the Latosol Catenae; the Southern Mountains, with soils of the Humid Montane Catenae.

Climatically the area falls in the tropical Savannah Belt and rainfalls increase south-westwards from 800 mm/year to more than 1600 mm/year.

From a lithological point of view the studied area is constituted by: medium to high grade metamorphites, extensively migmatized and intruded by granitic bodies (Crystalline Basement); alkali-granites and nepheline-syenites, discordant with the basement, outcropping in the central-eastern part of the area; volcanics, similar to the ethiopian Trap Series, occurring at the border with Ethiopia and Kenya; residual (laterites) and clastic continental deposits (Umm Ruwaba Formation).

The Umm Ruwaba Formation is made up mostly of sandy-argillaceous fluvio-lacustrine deposits.

Samples of stream sediments, residual soils and rocks were collected.

The field operations involved a three fold procedure: determination of the geological setting of the formations or soils under study, radiometric analysis by a portable scintillation counter and a sampling for gamma-ray spectrometric determination.

Total gamma radioactivity and Th/U ratios were determined in the laboratory by means of scintillation gamma-ray spectrometry.

The data were computed using a moving average analysis by means of which maps of the regional trends and residuals were obtained.

A search area of 10000 sq.km with an average of 40 measurements per search area was employed.

The obtained results are discussed in connection with the main geological features, bedrock and/or surficial.
SECONDARY GEOCHEMICAL DISPERSION AND BEDROCK REFLECTION IN THE TROPICAL RAIN FOREST TERRAIN

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In the tropical rain forest terrain, chemical weathering progresses faster towards its final products due to a continuously high reaction temperature and humidity resulting in considerable accumulation of lateritic soil. The secondary geochemical dispersion of these areas, governed mainly by the adsorption capacities of clay minerals and colloidal oxid/hydroxid systems and the lack of mobilizing chelating agents, keeps the trace element concentration ranges nearly stable from the bedrock to upper B-horizon where sampling takes place.

Examples from the Guiana shield and Nigeria demonstrate that residual geochemical soil pattern do reflect not only exploration targets but also distinct bedrock units. Thus, geochemical soil surveys can also serve as a useful tool for geological reconnaissance mapping in the vast areas of tropical rain forest terrain where adequate coverage by modern exploration techniques is widely lacking.
3. Local Geochemical Exploration

THE BIOGEOCHEMICAL EXPRESSION OF A DEEPLY BURIED MAJOR URANIUM DEPOSIT IN SASKATCHEWAN, CANADA.

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Ten kilometers from the eastern edge of the Athabasca Sandstone, a major uranium deposit (grading up to 27 % U₃O₈) lies at the Athabasca crystalline basement unconformity at a depth of 150 m.

The vegetation coverage immediately above the ore zone is dominated by black spruce (Picea mariana), and labrador tea (Ledum groenlandicum), with leather leaf (Chamaedaphne calyculata) present in wetter areas. A biogeochemical study of the area was conducted over a one square km. grid, yielding 140 sample sites and a total of over 500 vegetation and soil (A_H and B_F) samples. Subsequent breakdown of vegetation into leaves, stems, roots, etc. provided about 800 samples in total.

Uranium concentrations in the ash of various species provided some surprisingly high results: spruce twigs up to 154 ppm U; labrador tea and leather leaf stems around 100 ppm. Conversely labrador tea roots yielded 5 ppm U and spruce trunk wood usually 1 ppm U. Soils gave values of 1-3 ppm U.

Profiles and geographic plots of the uranium distribution reveal that the highest values are coincident with the occurrence of uranium ore 150 m beneath the surface. Clearly, biogeochemical exploration in this environment has interesting potential.
LITHOGEOCHEMICAL EXPLORATION OF A PRECAMBRIAN BATHOLITH, SOURCE OF A CU-W MINERALIZATION OF THE TOURMALINE BRECCIA TYPE IN SOUTHERN FINLAND

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The Hämeenkyrö batholith is a round shaped plutonic body of an areal size of 150 km² composed of calc-alkaline to alkaline porphyritic rocks, which intruded the previously metamorphosed Svecofennian volcanogenic and sedimentary rocks 1840 ± 40 Ma ago. The Cu-W bearing tourmaline breccia of the Ylöjärvi deposit is emplaced in metavolcanic rocks close to the eastern contact of the batholith.

The batholith has been sampled on average 1 sample per km² and 180 samples have been analyzed for Cu, As, Sn, Mo, W, Ag, Ni, Pb, Co, Zn, S by AAS and for SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O and P by X-ray diffractometer. For each sample Barth mesonorms have been calculated and the rock type is determined according the Streckeisen classification. Element distribution are displayed on isoline maps of metal and oxide contents and the mineralization potential is expressed by a factor-score map.

The rock types of the batholith exhibit a concentric arrangement from the center towards the margin: alaskite, granite, quartz monzonite, quartz syenite, alkali-felspar quartz syenite, syenite and alkali-feldspar syenite. Anomalously high Cu, As, Sn and S contents are met on the eastern margin of the batholith in a N-S trending zone. Within this zone three peaks appear. One of them is clearly associated with the Ylöjärvi deposit and the other two are regarded as suitable exploration targets.
Geochemical investigations of lithomorphic soils in the Central Iranian Volcanic Zone indicate that porphyry copper deposits, enriched by supergene processes, may easily be outlined in soil surveys using copper, lead, and zinc as indicators.

The disseminated copper porphyry deposit of Sara and La Chah, north of the small town of Shar-e-Babak (Kerman region), belongs to several hydrothermally altered diorite porphyrites intruded into a volcanic and sedimentary rock sequence of Paleocene to Miocene age.

The geochemical distribution of copper, lead, and zinc in soils overlying these deposits shows the typical circular and horizontal section of a porphyry mineral system. The ore zone is well defined by strongly anomalous amounts of copper. The medium copper concentration in soils over the La Chah orebody amounts to 4750 ppm and at the Sara orebody to 1360 ppm. The ore zone is surrounded by halos of non-economic mineralization. Lead and zinc form well defined circular zones in soils with more than 300 ppm Zn and 200 ppm Pb. In the central ore zone Zn- and Pb-values are 100 ppm and 55 ppm, respectively. This element distribution in soils clearly indicates the limits of economic mineralization.

Recognition of the foregoing relations is based on analyses of the -80 mesh fraction of samples from lithomorphic soils with weak or no differentiation in vertical sections.
GEOCHEMICAL SOIL PROSPECTING IN N-W KALIMANTAN, INDONESIA

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A target area, already defined by a geochemical stream sediment survey, has been selected within the framework of a technical cooperation program between Indonesia and Belgium. It has been further investigated by geochemical analysis of soils and samples from testpits.

Overlapping geochemical anomalies in the soils were found for Cu, Mo, Au and Bi. Through detailed geological mapping and mineralogical and petrographical studies the anomalies could be explained by a porphyry copper type mineralization in granodiorite rocks. Characteristics and type of the mineralization are discussed and implications for the mineral potential of W Kalimantan are given.
THE GEOCHEMISTRY OF THE LEACHED CAPPING OF THE LA GRANJA PROPHYRY COPPER DEPOSIT, PERU

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The La Granja Porphyry Copper is located in the Cordillera Occidental of Northern Peru. Copper mineralization is associated with a "feldspar quartz porphyry" which intruded andesitic and rhyolitic rocks of Tertiary age and Cretaceous clastic and calcareous sediments. Alteration consists of a central zone with a quartz-sericite and argillic mineral assemblage which is surrounded by a propylitic halo inside the andesitic country rock. Skarn formation is subordinate.

Weathering has been intensive in the phyllic-argillic zone, due to the over-all complete hydrothermal decomposition of feldspar, originally high pyrite content of the rock, intensive fracturing, topography and subtropical climate. Maximum drilled thickness of the leached capping is 200 metres. Outcrops with visible copper minerals, all of supergene origin, are sparse. Oxidic copper minerals, or less frequently copper sulfides, usually only occur near the margins of the phyllic-argillic zone.

90 surface rock-chip samples have been analysed for 30 elements as well as drill cores. The dispersion patterns of 14 of these elements (Na, K, Mg, Ca, Sr, Mn, Rb, S, Fe, Cu, Mo, Au, Zn, Ni) proved to be specially related to hydrothermal alteration and copper mineralization.

The elements Cu, Zn, S, Na, Ca and Mg are significantly depleted by weathering inside the phyllic-argillic alteration zone, copper as much as 10 to 20 times with respect to the hypogene ore; K and Rb are depleted in some areas. Mo, Sr and Mn seem to be relatively stable and Fe is enriched under weathering conditions.

Weathering has distorted the primary dispersion halo, subduing differences of original concentrations of Cu, K, Rb and S but amplifying already existing differences in Na, Mg, Ca and Zn concentrations. The resulting surface dispersion pattern is a central zone of 2,000 x 2,000 metres extension with low Na, Mg, Ca, Mn, Ni and high Cu concentrations compared with the surrounding. This central area can be further subdivided into zones with high Mo, high Au, low Fe, low Sr concentrations as well as high Cu/Fe ratios; areas with two or more thus defined zones overlapping proved to be overlying high grade supergene or hypogene ore.
GEOCHEMICAL EXPLORATION OF THE RIO ANDAGUEDA PORPHYRY COPPER SYSTEM, WESTERN COLOMBIA, SOUTH AMERICA

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Detailed geochemical studies of bedrock, soil, stream-sediment, water and pan-concentrate samples from the Rio Andagueda porphyry copper prospect in the Western Colombia, have defined two principally anomalous zones showing a good correlation of Cu-Mo anomalies. Geochemical profiles of various elements, constructed through the alteration zones, show that the elemental dispersion patterns do not follow any systematic variation, although very broadly Cu appears to be anti-pathetic to Ba and sympathetic to Ni. Hydrothermal alteration effects appear to be associated with the distribution of Ba, Sr, Mn, V, Cr and Ni. Geochemical patterns have not been strongly influenced by the primary lithology but more by alteration and to some extent by the mineralization. The high acidity of soil and water samples can probably be attributed to the high degree of precipitation and the resultant chemical transformation. Low Eh values reflect restricted drainage, stagnant bottom conditions and effects of circulating ground water. Eh-pH estimates show that the stability ranges from Cu^{++} and Fe^{++} to CuO and Fe_2O_3. Since most anomalies are barely above the threshold or directly related to mineralization, their economic significance is greatly reduced.
GEOCHEMICAL DISPERSION IN WALLROCKS ASSOCIATED WITH THE NORBEC DEPOSIT, NORANDA, QUEBEC

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Increasing emphasis is being given to the search for blind mineral deposits and the presence of geochemical dispersion halos associated with wallrocks may significantly enhance the chances of exploration success. Accordingly, the nature of wallrock dispersion associated with the Lake Dufaul Cu-Zn-Au-Ag massive sulphide deposit, Noranda, Quebec, was examined to see if any such patterns existed. On the basis of relatively well defined geology, the area offered an opportunity to establish the relation between geochemical alteration and metallogeny, texture, structure and mineralogy.

Results indicate that anomalous dispersion, spatially related to mineralization is confined to the stratigraphic footwall (Waite Rhyolite) where Na₂O, SiO₂, and possibly CaO depletions and total Fe, Mn and MgO enrichments can be related to the hydrothermal vent. Anomalous dispersion halos 150-500 metres in diameter are at least twice as wide as the obvious mineralogical alteration halo. Cu, Zn, Ag and S distributions show roughly similar patterns which are not obviously related to the main alteration pipe but do reveal broad enrichment zones in the general of mineralization.

There appears to be a certain amount of textural control over dispersion. Because of greater primary permeability, the halos produced in rhyolite breccia are wider and better defined than those in more massive rhyolites. On a wider scale (10 km²) it is possible to relate dispersion patterns to the fault and fracture systems of the area.

As many as five stages of metamorphisme have affected the area, altering all rocks to some extent. Petrographic examination allowed samples to be classified into alteration groups, both related and unrelated to mineralization. Comparison of the chemistry of these groups reveals the inadequacy of certain elements for outlining alteration related to mineralization. For example, the range of K₂O in relatively unaltered rhyolite extends over the range in composition of all other groups, including those related to mineralization. Similarly apparent is that the distribution of certain elements, e.g., Na₂O may adequately define one part of an alteration zone such as the sericite-rich zone, but not another.

It is concluded that careful use of lithogeochemistry in conjunction with detailed geological mapping and core logging can provide information otherwise obtainable only by time-consuming petrographic analysis. Thus it can be a potent weapon in the search for blind ore deposits.
THE MECHANISM OF ORE FORMATION AND PRIMARY DISPERSION OF PORPHYRY COPPER DEPOSIT OF TESHING, KIANGSI AND ITS GEOCHEMICAL EXPLORATION

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The geochemical exploration of porphyry copper deposits in particular, and of metallic mineral deposits in general, must base upon the following three essential aspects:

1) The physical chemical and thermodnamical conditions of ore formation and mechanism of ore formation and primary dispersion.

2) The spatial configuration of the ore-forming, ore-controlling and ore-transporting elements.

3) The temporal evolution of the ore-forming geochemical processes.

Selecting proper parameters to characterize the state of the mineralization system we can utilize Markov scheme to analyze time series or space series, and the resulting curves of trend factor would reflect the ore forming process, and thereby they may be used be to distinguish and predict various mineralization stages, as well as to indicate favourite regions of mineralization and depth of mineralization and denudation.
TREND SURFACE ANALYSIS OF GEOCHEMICAL DISTRIBUTION OF COPPER IN JAGPURA MINERALISED ZONE, BANSWARA DISTRICT, RAJASTHAN, INDIA

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In Jagpura, extensive old workings and slag dumps are present. The folded dolomitic marble and amphibole quartzite of Bhukia Formation of Aravalli Group (Pre-Cambrian) are mineralised along axial shears of the folds. Surface indications of mineralisation, apart from old workings, are development of gossan and wall-rock alteration manifested by silicification, chloritisation, sericitisation and development of rosettes of actinolite. The area experiences extreme climate with hot summer and dry and cold winter and is endowed with thick vegetation with a fluctuating water table. Geochemical sampling was carried out in a fluctuating water table. Geochemical sampling was carried out in a mineralised area of 2.4 sq. km. over sample lines laid 100 m apart. Samples were collected at every 20 m interval along these lines from the 'B' horizon of the residual soil derived from dolomitic marble.

Random local variation in the geochemical distribution of copper was observed in the area. To separate the systematic component of variation from erratic geochemical values, trend surface and residuals were determined. The residuals of different trends, are plotted in the trend surface map to delineate areas of local variations. Trend surface analysis indicates that geochemical relief of copper decreases from 600 ppm in the southeast to 100 ppm in the northwest which is also the regional topographic slope. Interpretation of the bed rock geology vis-a-vis geochemical high, indicates that zone of copper mineralization is confirmed to 300 ppm and higher trends. Residuals with 99 percent confidence levels represent sub-surface copper mineralisation as proved by drilling and at places show parallelism with the axial shears of folds.

The programme adopted in the study was primarily meant for regional geochemical surveys of homogeneous population and was proved effective in delineating copper mineralisation.
Acid volcanics and cherty sediments of the ordovician Tetagouche group host the "Captain North Extension" sulfide zone, which comprises 200,000 tons of 11.5 % lead plus zinc and 3.3oz/t silver. It was discovered in 1978 as the result of a systematical three dimensional sampling of soils, till and bogs. The zone is situated on a gentle east slope and covered by a four to five meter thick layer of till. The surrounding area is overlain by a rather thin till sheet of one to two meter thickness, exceptions are swamps and eskers where the overburden may exceed ten meters.

Vertical profiles in swamps were sampled by hand augers and auger drills, in soil and till by means of a backhoe. Samples were grouped in twelve different categories and statistics evaluated separately for the main groups. Several grain-size fractions were assayed, applying various chemical extraction techniques.

Anomalous high lead and zinc was first detected in swamps approximately one kilometer south and east of the mineralized horizon. Since decreasing lead content with depth indicated hydromorphic accumulation, the search for the source was concentrated on the higher land close to a shallow south and east draining swamp where the anomaly seemed to originate.

Till profiles from this area reflect up to three different ice directions within the late Wisconsin glaciation. The most common till is green, sandy, compact or fissile and has rounded pebbles or cobbles, indicating transport over several kilometers. Its base metal content is low and fairly uniform. Red brown till under two to three meters of green till carries angular, local derived rock fragments and is highly anomalous in copper, lead, zinc and silver. This till
THE GEOCHEMISTRY OF THE SEDIMENTARY ROCKS IN THE VICINITY OF THE TOM Pb-Zn-Ba DEPOSIT, YUKON TERRITORY, CANADA.

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A total of 138 samples of the Devonian sediments in the vicinity of the Tom stratiform Pb-Zn-Ba deposit were analysed for 14 major and 17 minor and trace elements by X-ray fluorescence. The results of these analyses are discussed in terms of:

1) the geochemistry of the sedimentary environment that was prevailing at the time of the formation of the Tom mineralisation, and
2) the identification of lithogeochemical haloes and other potentially mineralised areas.

The geochemistry of the footwall argillites is characterised by a concentration of elements that are typically associated with the detrital resistate minerals and feldspars (e.g. Al$_2$O$_3$, Na$_2$O, K$_2$O, TiO$_2$, Ce, Nb, Zr), which are contained within the interbedded silty layers of probable distal turbidite origin.

The hanging-wall shales are characterised by high V concentrations and anomalously low concentrations of TiO$_2$, Nb, Cr, and Rb. The depositional environment is thought to be that of a starved basin. The C-organic data and the V/Cr ratios suggest that sapropelic conditions may have been locally developed in the vicinity of the west zone mineralisation and in the hanging-wall shales. Very high concentrations of Ba were found to be present in the hanging-wall shales (>0.5 % Ba), the Ba is thought to be of hydrothermal origin.

Zn is more widely dispersed than Pb in the sediments around the mineralisation. There is no marked enrichment of Fe, Mn or Cu in the sediments close to the mineralisation.

A discriminant analysis of the sample data was used in an attempt to locate other areas with the same lithogeochemical characteristics as were found in the sediments surrounding the Tom mineralisation.
GEOCHEMICAL SURVEYS FOR LEAD-ZINC MINERALIZATION AND THE NATURE OF SECONDARY DISPERSION IN THE TROPICAL ENVIRONMENT, BENUE TROUGH, NIGERIA

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Lead-Zinc deposits occur as veins and minor replacement bodies in Cretaceous sediments of the Benue Trough. As part of an extensive programme of reconnaissance prospecting, approximately 350 stream sediments were analyzed for Cu, Pb, Zn, Mn, Fe, pH and organic matter. Results of orientation study show that cold-extraction techniques do not provide adequate contrast between background and anomalous areas in this humid tropical environment. This is attributed to the fact that anomalies mostly result from the erosion of metal-rich overburden.

Pb distribution is characterized by intense but restricted anomalies, whereas Zn and Cu are dispersed a considerable distance but with less intense anomalies. R-mode analysis shows that the factors controlling metal dispersion include organic matter content, pH and Eh of the environment and the scavenging action of Fe-Mn oxides. Fractional analysis indicates that Zn is partitioned dominantly within the clay and heavy mineral fractions, Cu within the iron oxide and heavy mineral fractions, and Pb dominantly within the heavy mineral fraction. Detailed follow-up stream-sediment surveys have outlined known mineralization and sources of some of the reconnaissance anomalies. Despite the extreme climatic conditions, stream-sediment surveys provide a suitable tool for rapid prospecting in conjunction with reconnaissance geological mapping.
Research on primary halos around sulfide deposits of hydrothermal origin (in its broad sense) was initiated in China in the late 50's. Terminology used is somewhat different from Soviet Union and Western Countries. The high content zone around a sulfide ore body is taken as a whole, and is divided into four parts: front part, rear part, adjacent part, and lateral part.

Internal structure of a primary halo is described in a standardized way. Element content $a^O_T$, $a^I_T$, and $a^2_T$ zones ($a = 2, 3, or 4$, $T =$ Threshold) are contoured and referred as outer, intermediate and inner zones of a primary halo. Such specification avoid subjective contouring, and put primary halos of different origin and from various districts in a easily comparable basis.

Compositional zoning of a primary multielement halo shows different patterns over hydrothermal polymetallic, skarn copper and porphyry copper deposits. Emphasis has been placed on the relationship of "primary contrast" of various indicator elements on their positions in a zoning sequence.

Many examples for illustration are presented. Practical applications and case histories for finding blind ore bodies by study of their primary halos are briefly referred.
GEOCHEMICAL INVESTIGATIONS ON LITHIUM-PEGMATITES FROM THE LEINSTER GRANITE (SE-IRELAND)

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Recently discovered Lithium-pegmatites of the Leinster Granite as well as aplites and granitic wall rocks were analyzed and their mineral resp. element contents evaluated for genetic conclusions. These geochemical investigations were done in context with studies on the distribution of alkaline and alkaline earth metals in granitic residues.

The granitic massif (about 80 km SSW of Dublin) corresponds with its NNE-SSW-extension to the caledonitic striking and is to NW and SE concordantly emplaced in a slate-greywacke sequence of Lower Palaeozoic age. BRINDLEY (1973) divides the pluton into five intrusive units, separated from each other by narrow schist septa with discordant granite-schist boundaries. Detailed structural survey of the granite and its contacts as well as relics of the roof area proved that the present day erosion level of all the units with about 600 - 800 m O.D. is close to the original roof. This observation is supported by the character of the given pegmatitic mineral paragenesis, which indicates by Li- and Nb/Ta-mineralization as well as by cleavalandite feldspar a relatively high preserved niveau within the individual intrusive bodies.

Still in granitic marginal zones and parallel striking to the eastern granite-schist contact of the Tullow Lowlands intrusive unit in SE of the massif vein-like Li-pegmatites of simple mineralogy and no well-developed zoning are found. These rocks indicate their occurrence less by outcrops but by extended areas covered with big in situ-boulders (Ø 2-3 m). Based on a systematic prospection work a lot of core drillings were done by the Irish Base Metals Ltd. (Dublin); the extension of at least 16 pegmatite occurrences could be stated by evaluating boulder accumulation maps and the drilling profiles. Closer examinations showed that these coarse-grained quartz-feldspar-pegmatites are mainly marked by high spodumen resp. Li-muscovite contents up till 60 wt.-%, the latter with high Rb-, Cs- and F-concentrations, and typically by a constant occurrence of Nb/Ta-minerals, which show radioactivity within the Li-muscovite-pegmatites (STEIGER & v.KNORRING, 1974). From the main outcrops survey and drilling samples were taken, the rocks as well as the minerals (spodumen, mica, and feldspar) were investigated and the element contents of Li, Rb, Cs, Bs, Sr, Ba, Na, K, Mg, Ca, Al, Fe, Mn, P, and F used to establish a genetic relationship to the granite of the Leinster massif.
THE SECONDARY GEOCHEMICAL DISPERSION OF SOME SELECTED ELEMENTS AROUND THE SCHEELITIC DEPOSIT OF CRAVEZES, NORTHEASTERN PORTUGAL

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Some geochemical data obtained during the performance of a combined geological-geochemical programme carried out by the DGGM of Portugal on the virgin scheelitic deposit of Cravezes (northeastern Portugal) are here presented. This ore deposit consists of some layers of skarn and calcosilicated rocks interbedded in silurian pelitic slates.

In particular, it was investigated the secondary geochemical behaviour of some selected trace and minor elements in stream sediments. Together with the tungsten anomalies, it was shown that good geochemical patterns were obtained for some other elements, which clearly delineate the deposit. These elements may then be utilized as useful pathfinders for further geochemical prospecting campaigns.
MOLYBDENUM MINERALISATION RELATED TO CARBONATITE-SYENITE IGNEOUS
ACTIVITY IN PARTS OF TAMIL NADU, SOUTH INDIA, A GEOCHEMICAL
CASE HISTORY

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The geochemical association of molybdenum with granitic suite of rocks
is very well known and has been studied in detail by many. Its asso-
ciation with carbonatite-alkaline complexes has received very little
attention. One of the recent publications Encyclopedia of Geochemistry
(1972) completely ignored this association which apparently reflects
the opinion of many earth scientists. It was way back in 1963 that
F.M. Vokes propounded that geochemically Mo has greater affinity to
alkaline rocks than to granitic rocks. Gold (1963) reported 42 % Mo in
Carbonatites. Deans (1966) said that the possibility of finding economic
Mo deposits in carbonatite provinces should not be precluded.

In Tamil Nadu peralkaline, alkaline and carbonatite igneous bodies are
found emplaced in a ill-developed rift system between Shevroy-Kalrayan-
Javadi hill ranges on the east and the hill ranges of Mysore plateau
on the west. These rocks are surrounded by a wide zone of fenites
derived from charnockites, their associated granulites and gneisses, and
migmatites. This zone extends over a length of about 200 km in a south-
west direction from Gudiyattam on the north to Bhavani in the south, and
extends further northwards into Andhra Pradesh.

Quartz-barytes and pegmatitic quartz veins are seen emplaced through-
out this zone of fenites and less commonly in the syenites. These veins
carry besides barytes occasional pockets and disseminations of galena,
pyrites and ilmenorutile. The first author discovered Molybdenum miner-
alisation in Alangayam area in 1975. Regional and detailed pedo-geochemical
sampling, and lithogeochemical sampling have established that the chief
carriers of Mo mineralisation in this area are the quartz veins and that
the fenites are also mineralised to a limited extent with Mo. This data
led the first author to develop the concept of a province of molybdenum
mineralisation related to the syenite-carbonatite activity in the 200 km
long zone of fenites and alkaline rocks. The first author established
this province by carrying out test lithogeochemical sampling in 1977.
This has brought out two more economic prospects, besides Alangayam,
for Molybdenum.

Detailed prospecting in Alangayam area brought out the spatial and para-
genetic relationship among Cu, Mo and the nearby Yelagiri syenite
batholith, which are in contrast with the features of Cu-Mo mineralisation
related to granitic rocks. The quartz-barytes veins contain minor amounts
of Pb, Bi, Ag, Sn, Ga, Ni, Sr, Cr, Mn and rare earths like Ce, La, Cu, Eb,
Y, Yb, Sc, Sm, Na, Dy, Nb and W are surprisingly in very low quantities.
Genetic inter-relationship of some of these elements and molybdenum has
also been brought out.

This paper deals with various aspects of the geochemical exploration and
the geochemistry of molybdenum in this geological milieu besides briefly
dealing with the geological and tectonic setting of the alkaline-carbona-
tite complexes.
GEOCHEMICAL INVESTIGATIONS OF TUNGSTEN DEPOSITS IN NORTH-EASTERN BRASIL

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The scheelite mineralization in the mining district Brejui - Zangarelhas, south of Currais Novos, is associated with Precambrian tactites (calcsilicate rocks) which form layers between marble and biotite-gneiss. High-grade ore with more than 0.5 % WO₃ can be observed at the contact between marble and tactite, where a type of "porous tactite" is developed. Highgrade ore also is found in irregularly shaped bodies within the calcsilicate rocks. In the transition zone to gneiss "compact tactite" is developed which contains less than 0.2 % WO₃.

This paper deals with new aspects of the genesis of scheelite mineralization revealed by geological and structural observations and the interpretation of geochemical investigations. In order to analyse them for main and trace elements, 170 samples were selected from cores of three drill holes in Brejui, together with some rock samples from Zangarelhas (64 samples of tactite, 36 of marble, 4 of amphibolite-gneiss, 49 of biotite-gneiss, 16 of pegmatite, and 4 of granite).

The tactites contain relatively high concentrations of Ba, Co, Cr, Cu, Nb, Ni, Rb, V, Zn and Zr, which show relationships to shist and clay. These tactite samples also have anomalously high values for W, Rb, Mo, Sn, and Ta, which are characteristic for residual liquid from primary magmatic differentiation. Accordingly, some trace elements in the tactite might originate from magmatogenic sources - probably from submarine volcanism.

Pegmatite and granite which are common rocks in the investigated area are not considered to be the source of the mineralization. They are poor in volatile elements such as W, Sn, Ta, Nb, and Rb.

The interpretation of geochemical correlations lead to the assumption that scheelite is concentrated by secondary enrichment such as by pressure solution activity and by metasomatic processes during high grade metamorphose.
ORIENTATION GEOCHEMICAL SURVEY OF TUNGSTEN MINERALIZATION IN ARID CONDITIONS, EASTERN DESERT, EGYPT

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24 bulk samples of the various genetic types of the anomalous detrital overburden in Abu Kharif area 40 km west of the Red Sea Coast were mechanically analyzed to 9 fractions. The heavy minerals (> 2.87 gm/cm³) of 4 sandy particle size classes were separated. The particle size, heavy and light fractions were microscopically studied, as well as, spectrographically analyzed semiquantitatively after grinding to detect the minerals and elements associating tungsten.

The most favourable particle size of the authochthonous debris to be analyzed is ≤1 mm, while that of the allochthonous debris ≤4 ≤1 mm. Mechanical weathering plays the dominant role in dispersion of tungsten. However, chemical dispersion displays a pronounced role as tungsten is adsorped in the hydrous manganese oxides and the clay minerals. The important metals associating tungsten is molybdenum and copper.
ZINC - A USEFUL ELEMENT FOR THE PROSPECTION OF PRE-CAMBRIAN CHROMITITITES?

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Proterozoic "alpine type" (geosynclinal) ultramafic rocks from the Itabira region (Minas Gerais, Brazil) possess Zn-contents as high as 1.400 ppm. These are anomalies of up to 25 times the average values of spinel peridotites (WEDEPOHL 1972). Similar earlier observations were generally interpreted as a result of hydrothermal alteration theoretically linked to granites postulated in the underground. Petrographic and chemical studies of some fifty ultramafic rock bodies of various sizes made evident a positive correlation between modal chromite and Zn-content. Microprobe studies confirmed the Zn to be bound in the chromite spinel structure (WIEDEMANN & SCHORSCHER 1978). Low- to medium-grade regional metamorphism and/or serpentinisation caused a marginal alteration forming rims in the chromites characterized by higher reflectivity. By the same processes the Zn is mobilised from the altered rims, carried to the superficial parts of the ultramafic rock bodies and fixed there in weathering products and soil. These characteristics would make Zn an excellent tracer for chromitites, better than Cr, since it is bound exclusively to the chromite and not also to paragenetic silicates like Cr. However, these results will be useful in geochemical exploration only if it should prove right that Zn-bearing chromites play an important role in the Pre-cambrian, either in a general, worldwide context or in large provinces. This seems possible. VILLAUME and ROSE (1976) for instance detected and placed importance on the high Zn-contents of Pre-cambrian ultramafics from South Africa and many recently published analysis of Pre-cambrian ultramafics report Zn-contents of 100-250 ppm, however, mostly without comment. Further regional studies in Brazil indicated occurrences of Zn-bearing Pre-cambrian chromites in an area extending for some 2.000 km from central Minas Gerais to the North, up to the Campo Formoso chromite deposits near the Serra da Jacobina in Bahia. Some interesting problems concerning the Pre-cambrian Geochemistry of Zn and its possible relations with komatiitic partial fusion arise in this context.


Geobotany involves the visual examination of vegetal cover to determine (1) the presence of characteristic flora and to identify indicator plants and (2) morphological changes in vegetation related to mineralised zones. Geobotany is much older than biogeochemistry.

Although geobotanical work has been carried out on experimental basis in some of the base metal deposits of India, it has been remarkably successful in deciphering nickel mineralisation in the ultramafics of the Sukinda Valley, Orrissa. Excessive nickel (around 1.0 %) contained in the substratum of the mineralised zones has caused poisonous effect on tall trees like Shorea rhobusta (Sal.). Terminalia tomentosa (Asan) etc. Shorea rhobusta, which forms thick vegetation outside the mineralised zone, completely disappears and Terminalia tomentosa becomes stunted within the mineralised zone. While Shorea rhobusta disappears and Terminalia tomentosa becomes stunted, close affinity of assemblages of creeper types of plants to the nickel enriched zones has been observed in this area. Out of the plant assemblages related to the mineralised zones, Combretum decandrum has been found to be predominant and may be taken as the "Indicator Plant" for nickel mineralisation. By geobotanical mapping of the areas covered by this plant, nickel mineralisation (0.5% to 1.0%) has been established in a number of new sectors. The Geobotanical exploration in Sukinda ultramafic belt has established its applicability for broad delineation of nickel enriched zone in other ultramafic belts with identical climatological and pedological environments.
THE USE OF SOIL GEOCHEMISTRY IN OUTLINING PHOSPHATE DEPOSITS, NORTHERN AND SOUTHWESTERN VENEZUELA

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Phosphate deposits had been outlined in Falcón State (Northern Venezuela) and Táchira State (Southwestern Venezuela) using geochemical soil methods. The phosphate deposits located in Falcón State constitute lenses and masses interbedded with tertiary limestone and shales. The area is covered by a thick soil with few outcrops and the region is characterized by typical tropical rainy forest. Soil samples taken every 1000 meters across complete stratigraphic sequences were analyzed for $P_2O_5$ content. An anomalous area with a $P_2O_5$ content ranging from 3.19 % to 9.04 % was outlined between areas with less than 0.83 % of $P_2O_5$. More than 11 millions M.T. of commercial phosphatic rock, were evaluated associated with that anomaly.

In Táchira State several stratigraphic sequences of potentially phosphatic rocks, with a thick cover of black soil, were geochemically investigated. Soil samples taken each 10 meters were analyzed for $P_2O_5$. Probably a sequence of phosphatic rocks was outlined showing a $P_2O_5$ content varying between 7.3 % and 9.2 %. Apparently the sequence is interbedded with phosphate-poor siliceous rocks showing a $P_2O_5$ content below 2 %.

As result of this preliminary investigation, expensive trenching, pitting and drilling works can be carefully planned.
A SIGNIFICANT TRACE ELEMENT DISTRIBUTION PATTERN IN SOME LATERITES OF GOA, INDIA: AN EXPERIENCE IN IRON ORE EXPLORATION

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For locating additional resources of hematitic iron ore as possible concealed ore deposits under cover of 3 to 30 metre thick laterite in Geo, a major iron ore producing area on the Arabian seaboard of India, a test geochemical survey was conducted. This was aimed at deciphering characteristic trace element assemblage, if any, in laterites covering known rich hematite deposits for distinguishing such laterites from other laterites capping associated but non-iron ore bearing Precambrian formations.

Out of a potential iron ore bearing area of about 500 sq km in Goa, a 50 sq km area within latitudes 15°25'-40'N and longitudes 73°50'-74'E in north Goa was covered by the survey. The -80 mesh fraction of 1385 latosol, rock and laterite samples collected along a measured rectangular grid from 35 traverse lines laid across the main iron ore bands and covering adjacent non-iron ore bearing pink phyllite formation as well, were analysed for major elements Fe, Mn, Ti and trace elements V, Cr, Ni and Zr in the Central Chemical Laboratory of the Geological Survey of India. For rapid non-destructive determination of Fe in these samples, a portable radio-isotope source X-ray fluorescence analyser was calibrated and used.

Correlation coefficients for the elements Ti, V, Cr, Mn, Fe, Ni and Zr were obtained from the analytical data of 1385 samples by using a programmable desk calculators.

The correlation coefficient values of Fe with Ti, Ni, and Zr have been found to be negative and highly significant at 99 % confidence level.

Rapid geochemical survey with matching analytical and statistical data processing facilities is thus indicated to be a possible tool for locating concealed iron ore bands in Goa.
GEOCHEMICAL STUDIES RELATING TO THE ENRICHMENT OF Ti, U, Ga, Zr FROM THE BAUXITIC PROFILES OF PENINSULAR INDIA

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Bauxites are associated with laterites which form a capping over basalts, charnockites, khondalites and other type of rocks in peninsular India. Bauxites are seen both as 'in-situ' and transported types and also seen in inland and coastal regions. Parent rock (Basalt or any other rock) → Altered zone → clay or without clay → laterites → Aluminous laterites/bauxites are seen as successive stages of weathering. Bauxites are seen as blanket deposits, pockets or local concentrations. Gibbsite is the major mineral and it occurs with boehmite, cliachite and halloysite. The geochemical studies show that leaching was the main factor and nearly 60 to 70% leaching took place to produce a residuum of laterite from parent rock. Among the major elements, alumina and titania records an enrichment, iron to an extent whereas silica was considerably leached out. Petrographical studies indicate 3 to 5 stages of weathering can be established. The distribution of trace elements in general is as follows: V 200 ppm, Cu 20 ppm, Ni 100 ppm, Pb 30 ppm, Mn 100 ppm, Sn 30 ppm, Cr 60-300 ppm, Zr 60-400 ppm, Ga 10-80 ppm. From the field setting and laboratory work, five zones are recognisable in most of the profiles with respect to the distribution of elements viz. (1) strongly depleted, (2) slightly depleted, (3) essentially unchanged, (4) slightly enriched, (5) strongly enriched. The enrichment of V, Zr and Ga are noteworthy. The trend and behaviour of the trace elements in relation to depth as well as against major elements and also in industrial qualities of bauxities are studies with the help of various charts. The principle of ionic potential, adsorption, and pH are fully discussed. Based on the detailed mineralogical and geochemical data, the geochemical gradient and weathering sequence have been drawn for the various profiles.

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Deposits of sparry magnesite (Spatmagnesitvorkommen) are widespread in the Eastern Alps, in particular in the low grade metamorphic carbonate rocks of the Northern Grauwackenzone. The genesis of these sparry magnesite deposits is considered either to be synsedimentary-diagenetic or metasomatic.

The magnesites generally contain low but appreciable amounts of Ca and are associated with calcites and dolomites. The REE contents of these carbonates in the magnesite deposits of the Northern Grauwackenzone can be used to distinguish between sedimentary and metasomatic formation. Remobilization processes as connected with the alpidian and/or hercynian metamorphism can also be observed.

The REE contents of the magnesites, dolomites and calcites from the deposits of Tux/Lanersbach (Innsbrucker Quarzphyllit), Entachen Alm, Spiessnägel and Hochfilzen (Grauwackenzone) will be discussed. It can be shown that the magnesite which is more or less finely dispersed in the country rock show REE pattern very similar to those of sedimentary carbonates. They are rather rich in LREE. The magnesites and other carbonates originating from veins show very low contents of the LREE. This difference is due to the fact that under the chemical conditions of in situ mobilization the LREE do not migrate so easily as the HREE. The absolute amounts of the REE and the similarity of their fractionation patterns with respect to the country rock contradict the hypothesis of magmatic hydrothermal formation. Both aspects speak in favour of a synsedimentary-diagenetic formation of magnesite and dolomite. In a later stage probably during hercynian and/or alpidian regional metamorphism in situ mobilization of these minerals took place.
USE OF MERCURY IN SOILS FOR PROSPECTION OF DEEP-SEATED Pb-Zn MINERALIZATION IN CARBONATE ROCKS, HERNAN P. EMPRESA NACIONAL ADARO

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The surveyed area consists of a lower Paleozoic sedimentary series where a carbonate dolomitised horizon (ore bearing) is overlaid by black shales. The area has been subjected to Hercynian deformations promoting the folding of the rocks into a gently synclinal structure elongate N 110° E. Some volcanic occurrences took place at that time interlayed within the sedimentary rocks. Alpine remobilization of the region brings the occurrence of small extrusive basatic bodies.

In order to estimate the availability of the area for the employ of this procedure, a review on the theory and some application examples of the method was previously done.

Main features of the area relevant to prospection are: this existence of a well developed soil profile extending overall the area with a B-horizon well distinguished of a clay nature, the subvertical schistosity of the overlying shales and the reasonable assumption of a maximum convergence of fractures in and about the neighbourhood of the hypothetically mineralised bodies.

The coexistence of these features and the confirmation of a highly sufficient concentration of Hg in the ores (250 ppm Hg in the sphalerite), led to the initiation of an orientation survey.

Three elements were analysed (Pb-Zn-Hg). Same samples were previously sieved to -80 and -200 mesh resulting that the smaller fraction offered a better contrast. The B-horizon exhibited for the three elements a higher response.

Some comments on the analytical procedure, discussion of final results and conclusions, will be included in the paper.
MERCURY VAPOR SURVEY OVER HEAVY OVERBURDEN DISTRICT

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Experimental work of mercury vapor survey carried out over a skarn copper deposit in the vicinity of Shanghai has given encouraging results. Thickness of the alluvial overburden in this district reaches to some 140-180 m. Soil gas samples were collected on gold wires in sults and mercury analysis was done with a mercury vapor detector in the camp. Soil and drill core samples were also collected and analyzed for Cu, Pb, Zn, Ag, Mo, Mn, Sn, W, Ba, Bi, Co, Ce with spectrographic or ion electrode method.

Results obtained were as follows

1. A distinct soil gas mercury anomaly was discovered over deeply buried skarn copper deposit. Surveys were repeated in different seasons. Shape, dimension and intensity of anomalies obtained in different seasons remained little changed.

2. Soil gas mercury high values relate closely with contact zones, fracture zones and faults.

3. Thermal release curves of mercury vapor obtained by heating rock, ore and alluvium samples have shown that mercury possibly possesses three forms of occurrence: easily volatile mercury, chloride mercury and sulfide mercury. Volatile mercury and mercury chloride are the predominant phase in alluvial samples.

4. Element zoning is well defined by the dispersion of Hg, Cu, Ag, etc. Calculation of the zoning index of mercury and other elements have shown that mercury is a typical "front element". Front halo of mercury is well developed and extents to the erosion surface.
THE OCCURRENCE OF MERCURY IN SOIL-GAS, SOILS AND UNDERLYING ROCKS

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In two areas of the Bensberg mining district east of Cologne, W. Germany, the mercury content in soil-gas, soils and rocks was analysed.

Secondary mercury dispersion halos were detected and defined by soil-gas analysis above known Pb-Zn-mineralization. Measurement of the mercury in soil-gas and long term in situ experiments established the effect of changing meteorological conditions on the mercury content. A positive linear correlation between mercury concentration in soil-gas and temperature of the air was observed. High amounts of rainfall or snowfall decrease the concentration of mercury in soil-gas; barometric pressure has no effect.

A mercury-release-apparatus was used for determination of the different mercury-compounds in soils and rocks: Hg-ionic (Hg-ion), Hg-adsorptive (Hg-ads), \( \text{Ng}_2 (\text{NO}_3)_2 \), HgCl, HgCl\(_2\), HgO, HgS and HgSO\(_4\). Organic-bound mercury (Hg-org) was analysed by a selective dissolution technique. In areas with sulphide mineralization, Hg-ads., HgCl\(_2\), HgS, HgSO\(_4\) and Hg-org. are the most important mercury-compounds.

Hg-ads., HgS and HgSO\(_4\) are enriched in soils above the Bensberg veintype ore deposits. Hg-ads. and Hg-org. decrease and HgS and HgSO\(_4\) increase with depth in the soil-profiles. Outside the mineralized area mercury occurs mainly as Hg-ads. and HgCl\(_2\). Organic mercury-compounds are enriched in soils with high water-content and low pH-values. The occurence of definite mercury compounds characterises the topographic influence on down slope dispersion and the direction of the veins.

A positive linear correlation between the distribution of the different mercury compounds in samples of soils and underlying rocks
GEOCHEMICAL PROSPECTION AND GENESIS OF MERCURY IN A SECTION OF THE WESTERN FLANK IN THE COLOMBIAN CENTRAL CORDILLERA

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In the western flank of the Colombian Central Cordillera between the localities of Aranzazu and Pacora in Caldas a detailed geochemical prospecting program for Hg was carried out. 613 stream sediment samples and 210 rock samples were collected which were analyzed by detector for Hg and by colorimetric methods of As and Sb; also 94 thin sections were studied.

In this area a north-south anomalous belt for Hg was found which is 1 kilometer wide and 27 kilometers long and includes the Nueva Esperanza Mine which is essentially a native mercury ore. The anomalous zone is located within the Quebradagrande Formation and is related to a metasediments-andesite contact.

The origin of the native mercury is apparently due to low sulfur solutions or to a later migration during the andesite intrusion.
APPLICATION OF VARIOUS GEOCHEMICAL PROXIMITY INDICATORS ON THE TIN BEARING OF SOUTH SARDINIAN GRANIDOIDS

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Only a little is known about Hercynian endogenous tin, tungsten and molybdenum deposits and a associated granitic host rocks of Sardinia. So a geochemical research of alluvial sediments and granitic whole rocks may be used are most likly to be tin, tungsten and molybdenum bearing. The research has been restricted on five distinctive granite intrusives within the Hercynian basement of South Sardinia. The alluvial distribution patterns of tin as well as the abundance of anomalous values of 17 hard rock proximity indicators allow the discrimination of probably tin bearing from barren intrusives. But the intensity of the geochemical specialization doesn't seem to be as high as in other known ore provinces. Nevertheless the used system of geochemical criterias is suitable for selecting tin bearing granite intrusives.
Geochemical investigations on the primary and secondary distribution of selected elements in areas of known ore deposits in the Federal Republic of Germany were carried out in recent years as research projects sponsored by DFG (Deutsche Forschungsgemeinschaft) and BMFT (Bundesministerium für Forschung und Technologie).

During the BMFT-exploration project "Rhenoherzynikum" anomalous heavy metal contents were found in soils above Lower Carboniferous sedimentary rocks of the Culm facies near Balve in the NE Rheinisches Schiefergebirge.

In a special study the distribution of Pb, Zn, Cu, and Mn has been investigated in outcrops of black shales (Liegende Alaunschiefer and Hangande Alaunschiefer) and limestones (Kulm-Plattenkalk).

The Liegende Alaunschiefer are characterized by a distinct Zn-Mn-anomaly possibly indicating the marginal zone of a sulphide mineralization with a manganese halo.

Anomalous Pb-, Zn-, Cu-, and Mn-values occur within tuff layers of the Kulm-Plattenkalk, an interstratification of pelitic layers and clastic limestones.

The Hangende Alaunschiefer (black shales) contain beds of iron-manganese mineralizations without anomalous Pb-, Zn-, and Cu-contents.

The primary contents of Pb, Zn, Cu and Mn in the sedimentary rocks were compared with their secondary dispersion patterns in the overlying soils: The primary dispersion is approximately reflected by lowermost B-horizons of soils overlying argillaceous shales.

In mineral exploration of stratiform ore deposits in the Rheinisches Schiefergebirge, the soil geochemistry is suitable for identification and delimitation of regional and local geochemical provinces and larger rock units. Final assessments of stratiform mineralizations require a systematic of rock geochemistry.
THE USE OF GEOCHEMICAL INFORMATION IN PROGNOSTIC-METALLOGENIC MAPPING

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The wide use of geochemical investigation at all stages of geological exploration is one of the most important aims of complex estimation for ore content prospects both in poorly studied and industrially exploited areas, especially from the point of view of possible buried mineralization.

In view of special actuality for discovery of buried deposits that are the significant source reserves increase in the areas of industrial exploitation, the main efforts in the applied geochemistry in the USSR were recently concentrated on the development and introduction into geological prospecting the effective exploration methods for search of buried deposits and ore bodies.

The estimation of outlook for the revealed geochemical anomalies is one of the most important problems in geochemical forecasting of blind mineralization. The scientific methodical investigations, fulfilled under varied landscape-geochemical conditions, revealed, that reliability of use of characteristic features and structures of primary halos in the interpretation of secondary dispersion halos of elements-indicators, depends, in the main, on the conformity of primary and secondary dispersion halos of elements-indicators. The conformity of primary and secondary halos is determined for each typomorphic landscape situation in the process of geochemical exploration by secondary halo dispersion flows of elements-indicators.

In areas with slow surface erosion and more distinct signs of hostrock terrains, the conformity of secondary and primary halos is often significantly disturbed.

In this case the choice of most contrast elements-indicators becomes very important in series of axial zonality of primary halos with similar features and migration aptitude in hypergenesis. The indicator ratios made according to these principles are characterized by the high conformity of primary and secondary halos. This approach is most effective for secondary halos in alluvial depositions of the oxidation zone up to several meters thick.

In the areas with significant crust of weathering of those overlapped by thick mantle of unconsolidated allochthonous sediments, the geochemical relationship between primary and secondary halos proves to be badly disturbed, and thus, the interpretation of the revealed geochemical anomalies requires more detailed investigations.

The use of geochemical data (zonality indexes, zonality coefficients, intensity, productivity, etc.) allows to distinguish the areas of "supraore" and "ore" erosive level of geochemical anomalies, which are promising for buried or overlapped mineralization in the region under investigation; to distinguish the areas without relation to ore anomalies, which are not promising for buried mineralization; and to contour, with different degrees of reliability, the areas promising for discovery of deposits and ore occurrences.
DEVELOPMENT OF GEOCHEMICAL PROSPECTING METHODS FOR ORES IN BULGARIA

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The geochemical methods have been applied to ore prospecting in Bulgaria since 1954. During the past 35 years they increased in volume, being also considerably ameliorated from methodical viewpoint.

A review of the application of the lithochemical (by means of investigation of the primary and secondary haloes), hydrochemical, biochemical and atmospheric prospecting methods is done. The problems of the conditions and the effectiveness of their application and their further development are discussed as well. Information on the analytical methods utilized by the geochemical prospecting is given.
RESULTS OF AN EXPLORATION ORIENTATION PROGRAMME DESIGNED TO LOCATE PRIMARY TIN MINERALISATION IN AN AREA OF INDONESIA

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The area selected for investigation contains rich alluvial and eluvial cassiterite deposits overlying weathered granite bedrock. The alluvials are currently being exploited by dredging and gravel pump mining techniques. Primary tin mineralisation occurs as cassiterite disseminations and as greisenbordered quartz-tourmaline-cassiterite vein swarms through the weathered granite.

The exploration orientation programme consisted of two distinct phases. The first was a soil geochemical survey, with samples taken by auger along widely spaced traverse lines. Samples were analysed for tin, tungsten, molybdenum and zinc by XRF and were also analysed for tin using a rapid colorimetric method to determine whether this would be suitable for future soil geochemical surveys. The survey indicated a major mineralised zone 800 m in length, and probably continuing into untested ground further along strike. Several smaller mineralised zones were also indicated.

The second phase consisted of coarse sampling in the major mineralised zone. Samples were taken from horizontal channels cut into the soft rock with a "parang" (bush knife), and from the dumps of material adjacent to the consteans. Samples were analysed by XRF and by panning. Grain size was determined by sieving following coarse crushing to liberate cassiterite. Mineral composition was determined by binocular microscope and several samples were submitted for petrographic and mineragraphic examination.

This initial work indicated a grade of between 0.15 % and 0.20 % Sn (about 2.5 kg Sn/m³) in a soft clay-rich host rock. The cassiterite grain size is very coarse (more than 50 % of grains + 20 mesh) hence coarse crushing of mineralised material to -8 mesh would liberate at least 93 % of the cassiterite. Overall the work demonstrated that the chosen exploration approach worked well in the area.
TRACE ELEMENT DISPERSION IN LATERITIC SOIL PROFILES APPLIED TO GEOCHEMICAL EXPLORATION

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Geochemical orientation studies in basic metasediments and around rare-metal bearing pegmatites of southwestern Nigeria demonstrate that residual geochemical soil pattern reflect potential source rock units adequately. The secondary geochemical dispersion processes of such tropical rain forest environments adjust the trace element concentration along lateritic soil profiles to narrow fluctuation ranges compared with average contents of differing rock units. In detail, pathfinders indicative for mineralization associated with acid magmatism may be rather depleted while elements associated with basic rock units are usually found to be enhanced due to adsorption effects of colloidal Fe/Mn-oxid/hydroxid systems.

The sample density in these surveys, averaging at 1 sample per km², favours inventories even at regional scale and shows great potentials to predict the bedrock composition of tropical terrain where rock outcrops are rather scarce.
PROBLEMS FACING THE CREATION OF A GEOCHEMICAL PROSPECTING DEPARTMENT IN A DEVELOPMENT COUNTRY: A CASE HISTORY IN VENEZUELA


The Mineral Resources Branch of the Venezuelan Geological Survey (Direccion de Geologia, Ministerio de Energia y Minas) had recently created a Geochemical Prospecting Department in order to carry out important programs concerning prospecting of base metals, tin and gold in the country. Although several universities in Venezuela have departments of chemistry which form geochemistry specialized people, the lack of professors constitutes one of the main problems. Actually a large faculties people from Canada, USA and England is engaged in these activities. Another problems facing universities is the low numbers of students in this career. A lot of people take different studies such as geology, mining engineer or petroelum engineer, which are extremely important in the country.

Actually the department have four geochemists, each one engaged in different projects and fields. Two of the people are responsible of programs under developing in the South (Precambrian Shield) Zone, and in the Perijá and Andes Cordilleras. Copper, Tin, Rare Earths, and Gold deposits are being prospected and outlined in those regions. New research programs are being carried put in complex fields such us primary dispersion in tropical areas, the use of metallometric studies in large areas, and the complicate geochemistry of the lateritic soils, which covers more than 40 % of the country.

The department have primary treatment laboratories in three locations of the country: the northern Cordillera Areas, the South Precambrian Shield, and the large Zulia State. The main laboratory with the main facilities including atomic apsortion equipments is located in the Andes Area. Two specialized chemical technitians are in charge of the analytical procedures, supervised by a geochemist.
EXPLORATION OF MINERAL DEPOSITS ACCORDING TO SECONDARY EPIGENETIC HALOS

Saiet Yu.E., USSR

The development and practical introduction of exploration methods for areas with buried bedrocks is an important task of the applied geochemistry. In these districts the ore bodies and their primary halos are buried under allochthonous sedimentary depositions.

It is generally known that overlapped and crypto-overlapped deposits are accompanied by epigenetic secondary halos of many chemical elements (copper, lead, zinc, arsenic, nickel, cobalt, mercury) which are spread for the whole thickness of the overlapping allochthonous loose mantle and are distinctly manifested in the humic horizon of soils.

The epigenetic secondary halos are natural generally shown indications of the overlapped and latent-overlapped deposits. They are observed in all types of the geochemical landscape and are formed with the existence of various lithologic and stratigraphic characteristics of the overlying beds. Particularly, they occur even in the case when deposits are overlapped by thick (profiles up to 150 m are investigated) series of waterproof clays.

Two varieties of epigenetic halos are observed; undisplaced, developing over the primary halos and displaced halos, confined to the outflows of ground waters.

Undisplaced epigenetic halos are formed at the expense of mechanisms providing rapid vertical migration of the chemical elements, even under conditions, when any intensive migration of water is impossible. The mechanism is the unfiltrated capillary memhraneous transport of ions (electrodiffusion) to the daylight surface, reflectable.

Displaced epigenetic halos are formed as a result of infiltrated streams of underground waters eluting ore bodies and their primary halos.

Epigenetic secondary dispersion halos are more contrast in the upper horizon of soil. For their exposure the use of the express method of the faze chemical extraction of sorptire-saline or organomineral forms elements-indicators is effective.

Peculiarities of the epigenetic halos depend upon the geochemical features of landscape, determining the level of background parameters, the degree of indicators concentration and morphology of halos.

Industrial approbation of this exploration method conducted in dry steppes of Kazakhstan and tundra-nashy landscapes of Karelia has shown it's high geological and geochemical effectiveness.
1.3 GEOCHEMICAL EXPLORATION IN CONTAMINATED AREAS.

GEOCHEMICAL PROSPECTING IN RIVER VALLEYS WITH RESPECT TO CONTAMINATION

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In river valleys the technogenical reactions on the alluvial lithogenesis have different forms, which characterized by specifical consequences of the chemical elements migration and concentration and differently influence on geochemical prospecting methods. In these circumstances the river valleys become important objects of geochemical prospecting.

In the Byelorussian territory the geochemical prospecting of the original deposits by buried alluvial dispersion haloes include a) elucidation of the valley's paleopotamology, b) determination of the paleostream hydrological regime and the alluvial transit, c) establishment of the relations between alluvium and original rocks by microelement's concentration in amphibolites, ilmenites and others minerals of the crystalline foundation and the river sediments, d) analysis of paragenetic associations and concentrations of the elements in geochemical haloes, e) calculations of possible natural and technogenous anomalies values, f) analysis of the geochemical anomalies. Statistical data and parameters are used. For elucidation of the haloes nature, with due regard for contaminations, the indexes of the elements distribution in the stadial extracts spectrum of the river sediments (forms: water soluble, ready exchangeable ions, carbonaceous, organic matter, amorphous hydroxides and of the ions adsorbed on them, etc) and other criterions are also used.

Theoretical problems of the classification of the technogenous reactions and contaminations in river valleys, the principles, methods and peculiarities of the geochemical prospecting and analysis of their data with respect to contamination are discussed.
ON THE CONTAMINATION OF STREAM SEDIMENTS IN SOME URBAN AND MINING AREAS IN FINLAND

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In immediate vicinity of the town of Kuopio in Central Finland was studied trace metal contents of the stream sediments with special emphasis on wastes produced by road and water traffic likewise wood processing industry. From contaminated areas were collected 57 organic and 75 mineral stream sediment samples and from unpolluted areas 64 organic and 49 mineral samples.

The effect of long continued mining industry on the metal contents of stream sediments was studied in the mining area of Outokumpu in Eastern Finland. The total of 82 organic and 51 mineral stream sediment samples were collected from the outflow of the waste area of the mine.

From all samples were determined Co, Cu, Mn, Ni, Pb and Zn by atomic absorption method.

At Kuopio was proved, that the lead content of stream sediments was greatly increased by the road traffic. But is was also proved that the influence of traffic was restricted to the immediate vicinity of the highway. The water traffic produces also an addition to the lead and copper concentrations, specially near the small boat harbours. The civilization as such produces an addition of zinc. It was not realized contamination in stream sediments caused by the wood processing industry. The metal contents of stream sediments in polluted areas correspond to the anomalies in geochemical exploration.

The effect of the waste waters of the Outokumpu mine to the metal content of stream sediments could clearly by verified as greatly increased concentrations of Co, Cu, Ni, and Zn in stream sediments as far as 7 - 8 km down along the river. The concentrations are multiple compared with ordinary high anomalies in geochemical exploration. On the other hand, when the stream from the waste area runs across a mineralized area, the metal content of the sediments increase considerably.
EXPERIMENTAL INVESTIGATION OF THE MIGRATE ABILITY OF SOME CHEMICAL ELEMENTS IN UPPER CRETACEOUS SEDIMENTATION BASIN OF THE TADJIK DEPRESSION

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X-ray fluorescence method may be used for determination of contents of the different chemical elements in adsorption complex of pelitic rocks to evaluate migrate ability of the different forms of elements in sedimentation. The migrate ability of line elements (K, Rb, Cs, Ca, Sr, Ba, Ga, Zr, Hf, etc) in Upper Cretaceous marine sedimentation basin of Tadjik depression was investigated.

The following forms of elements were studied:

- forms extracted by 60 % ethyl alcohol (easily soluble),
- forms extracted by 1 N NH₄Cl (ion-exchangeable),
- forms extracted by 5 % HCl ("salts").

The behaviour of these forms of elements is controlled by hydrochemical conditions in paleobasins and physicalchemical properties of the elements. Therefore these forms of elements show specific condition of sedimentation and they are effective geochemical indicators. We established a line of geochemical mibility of some elements using data according to contents of their different forms in Upper Cretaceous pelitic rocks of the Tadjik depression.

Paper Selection committee's Remark:
This paper is placed in the contamination section, as similar methods are used (cf. the paper of F. SONDAG): (Poster Presentation)
THE HEAVY METAL DISTRIBUTION IN SOME WELL POPULATED AREAS:
CONTAMINATION AND PROSPECTING PROBLEMS

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One of the main features of the modern geochemical prospecting is the necessity to deal with the deep buried ore deposits having weak haloes near the surface. On the other hand, at present very often the situation is complicated by contamination. Problems of prospecting in well populated areas have not been investigated sufficiently.

In this connection the authors of the report have been making experiments in some areas of humid region to clear up the geochemical associations of elements, their mode of occurrence in landscapes, the peculiarities of differentiation of elements in the haloes around the natural ore bodies and different technogenic sources (industrial enterprises, dumps, quarries and etc.). To analyse the nature of geochemical anomaly a complex of methods is used. With the aid of artificial sorbents (ion-exchange resins and others) placed in the streams and soils, the authors revealed the modes of occurrence of some elements to be different in the natural and technogenic haloes. For example around the ore body the mobile zink is present in the cation form, while in the anomalies in the waters from the populated areas the anion form is prevailing. These haloes are also different in the ratio value of Zn: Cd. The ion-exchange resins placed in soils for some time allow to detect weak signals from the deep buried ore deposits. To interpret the anomalies it is useful to investigate the distribution of elements in vertical sections of the soils and bottom deposits. Contamination mainly occurs in the upper parts of deposits. There are also differences in the distribution of Pb, Cu, Zn and other elements in various parts of plants (leaves and branches) due to the source of metals in the landscapes. This fact can probably be used for the further anomalies interpretation. It is advisable to draw a special maps of possible and revealed contamination factors in the prospecting area.

The authors have also made some attempts to use snow to estimate contamination.
A STATISTICAL APPROACH TO THE CONTAMINATION STUDIES DUE TO MINING ACTIVITIES

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The 'natural' geochemical anomalies in stream water samples are contaminated by prolonged mining activities. Eight hypothetical idealized cases involving some are bodystream relationship are discussed. In terms of contaminating effects, these cases are examined in the light of a small mining area known as Dikchu in East Sikkim.

The Cu-Zn-Pb ore body at Dikchu has a stream flowing over it. This stream is a tributary to the Dikchu river which also traverses the ore. Downstream from the mine area, another small stream flows into the Dikchu. The discharge of water in all the streams is very high. About forty water samples from all the streams and from dripping mine water have been collected and analysed for twelve elements. A simple geochemical anomaly map is presented. Various practical situations are considered and sample regression models are followed to explain the effects of contamination statistically. Consequently an attempt is made to revise the anomaly map.
KINETICS OF SELECTIVE EXTRACTION OF METALS IN GEOCHEMICAL EXPLORATION SAMPLES

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Many selective extraction methods have been used in geochemical exploration with the aim of improving trace metal sensibility, enhancing contrasts in anomalies, and increasing economy in sampling. The kinetic approach to selective extraction is an advance on the empirical methods that have been used previously.

Concretions of crystalline iron (mainly goethite) from a gossan rich in lead and zinc were subjected to kinetic control during a sequence of selective extractions. Treatment of the kinetic curves indicates a liaison between zinc and iron. This liaison has been confirmed by electron microprobe studies which show a relative concentration of zinc with respect to iron at the margins of the goethite grains.

The kinetic methods thus established have been applied to samples, anomalous in lead, zinc and copper, taken from soils overlying carbonate and silicate rocks in various parts of Belgium. Lead and zinc anomalies in soils from carbonate environments can be explained by fragments of iron crust mineralised for these elements. Kinetic extractions of zinc from ore samples within a carbonate environment show that 40% of the zinc occurs in smithsonite, 30% in goethite and 30% in smectite. In the anomalous soils from a siliceous environment, copper is mainly associated with an amorphous phase containing iron and aluminium. In this case the amount of copper extracted varies directly with the square root of the duration of the extraction procedure.

The kinetic approach allows verification of the specificity of the reagents, provides information concerning the reaction time necessary to achieve a steady-state condition, and also facilitates planning of selective extraction methods. The shape of the kinetic curves can provide information on the mode of action of the reagents used. The method also enables the localisation of zinc, lead and copper in the
2. Chemical Analytical Methods in Geochemical Exploration

THE DETERMINATION OF URANIUM (VI), THORIUM (IV), TIN (IV), AND ANTIMONY (V) IN GEOCHEMICAL SAMPLES FOLLOWING LIQUID ION-EXCHANGE EXTRACTION

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A method is described for the determination of U (VI), Th (IV), Sn (IV), and Sb (V) in soils and stream sediments. Sample decomposition by hot digestion is made with a mixture of nitric and hydrofluoric acids for the silicate bound metals in rocks and soils. An acetic acid-hydrogen peroxide mixture or a hydrochloric acid solution is used for cold partial decomposition studies with soils and stream sediments.

Acetic acid and hydrogen are removed from the partial decomposition solution by evaporation at 85°C or less in the presence of a small amount of manganous sulfate.

Dissolution of the sample residue obtained from either of the above decompositions is made with 9M hydrochloric acid. An aliquot is extracted with Alamine-336 in chloroform to retain Th (IV) in the aqueous layer which is determined colorimetrically with Arsenazo III. Another aliquot or the remainder of the 9M hydrochloric acid solution is then extracted with Aliquat-336 in xylene to separate U (VI), Sn (IV), and Sb (V) into the organic layer. U (VI) is then back-extracted with 0.15 M nitric acid. An aliquot of this stripping solution is evaporated to dryness and the residue is fused with a carbonate-sodium fluoride flux to make a pellet which is examined fluorimetrically for U (VI). Sn (IV) and Sb (V) are then determined by conventional atomic absorption spectroscopy on the organic layer, if a cold, partial sample decomposition was used.
ORGANIC MATTER SCAVENGING OF COPPER, ZINC, MOLYBDENUM, IRON AND MANGANSE, ESTIMATED BY A SODIUM HYPOCHLORITE EXTRACTION (pH 9.5)

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The importance of scavenging by organic matter in geochemical samples was estimated using an alkaline sodium hypochlorite partial extraction to leach copper, zinc, molybdenum, iron and manganese from a variety of soils, and stream and lake sediments collected on the Nechako plateau, central British Columbia. The reagent oxidizes or dissolves most forms of organic matter and sulphide minerals to give strongly coloured extracts containing the associated trace elements at a pH where solution of other sample fractions is at a minimum. Metals precipitated due to alkaline conditions are redissolved by a succeeding distilled water leach (pH 3.0 ± 0.3).

A large fraction of the copper, zinc, molybdenum, and manganese held within the organic fraction of the 'A' soil horizon is liberated whereas only minor amounts of copper, zinc, and manganese are released from inorganic soil (B and C) horizons. Molybdenum, however, is soluble as the molybdate ion. Despite similar concentrations of organic matter in A horizon soils and stream sediments the latter release a lower proportion of their trace element content. Behaviour of the organic fraction of lake sediments varies from lake to lake and there is great variability in the association of copper, zinc, molybdenum and manganese with organic matter within the same lake.

The presence of organic matter in samples subjected to other partial extractions can be a deleterious factor if the organic fraction is not first removed by a hypochlorite extraction.
THE DETERMINATION OF MINOR AMOUNTS OF THORIUM AND NIOBIUM IN VENEZUELAN LATERITES FROM CERRO IMPACTO BY X-RAY FLUORESCENCE

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A method for determining minor amounts of thorium and niobium in Venezuelan laterites from Cerro Impacto by photon-induced, energy dispersive X-Ray Fluorescence will be discussed. Lead and zinc are also determined simultaneously by this method but are less important with respect to exploration. The major advantage of the present technique is that no sample decomposition is necessary whereas normally a complete sample decomposition is difficult and effectiveness questionable.

The X-Ray Fluorescence system consists of a 10 mCi $^{109}$Cd annular source for excitation of the K-lines of Zn, Nb, and Mo (the internal standard) and the L-lines of Pb and Th. A high resolution Si(Li) detector is employed with $<150$eV FWHM at 5.9 KeV. The data acquisition and analysis is performed by a PDP-11/05 processor.

The results of the determination of thorium, niobium, lead and zinc in typical laterites from Cerro Impacto are:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Percentage</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO$_2$</td>
<td>1% ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>0.8% ± 0.005</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.5% ± 0.04</td>
<td></td>
</tr>
<tr>
<td>PbO</td>
<td>0.15% ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

The values for lead and zinc are in good agreement with those obtained using atomic absorption spectroscopy. Finally, the accuracy of thorium determination has been verified by NBS standards.
CONTRIBUTION TO GEOCHEMICAL PROSPECTING FOR FLUORITE

N. John & H. Puchelt, University of Karlsruhe, Federal Republic of Germany

Using fluorine as an indicator eight different extraction methods have been tested whether they are suitable for geochemical prospecting for fluorite. The matrix to be analysed consisted of stream sediments from the SE part of the black forest (FRG). Previous investigations had shown that these samples can be regarded in first approximation as coarse grained clastic sediments of the bedrocks i.e. granites, gneisses and fluorite vein as well. This led to the conclusion that fluorine of the stream sediments is mostly bound to fluorine bearing minerals of these rocks. Anomalous samples contain fluorine essentially in fluorite from fluorspar mineralization.

In order to find the most effective extraction technique eight solutions were applied under various conditions to five of the most frequent fluorine bearing minerals: fluorite, mica, apatite, hornblende, and tourmaline. The two parameters which have been varied are: time of reaction and grain size of the minerals. Fluorine determination was accomplished by ionsensitive electrode. The ratio cxF (fluorite) vs. cxF (mica, apatite) was found to be a useful measure for the applicability of the respective method. Furthermore 41 streamsediment samples (-80 mesh) from the area under investigation were extracted with the eight extracting solutions. The contrast between CxF (anomaly) and CxF (background) was an additional discriminator for the extraction solutions.

With most of the extractions results for mineral concentrates and stream sediments are consistent. Nevertheless one solution (TISAB) proved to be not satisfactory for mineral concentrates but showed good results with stream sediments. This discrepancy may be explained by the assumption, that part of the TISAB extractable fluorine is not in the fluorobearing minerals.

The most suitable extraction solution - boric acid solution - was used for a reconnaissance stream sediment survey in an area of 500 km².
Rhodium metal occurs in association with gold and other precious metals. Due to its low concentration, some form of preconcentration is necessary before its determination. Most methods developed so far are based on fire assay where all precious metals are collected in the lead button.

A study on the presence of rhodium in association with gold in Kolar Gold Fields, Karnataka State, India, has been made. A new method has been developed in which a 10 g sample is treated with aqua regia and heated to near dryness. Perchloric and hydrochloric acids are added and again heated to near dryness. 50 ml 2N HCl is added, gently boiled and filtered. The solution is heated to boiling and 20 ml of 1 percent thiobarbituric acid in glacial acetic acid is added. After digestion on a hot plate for one hour, the solution is cooled and filtered. The residue is washed with water, dried and ignited in a furnace at 800°C. The residue is mixed with graphite powder and loaded into a graphite anode. It is arced using 10 amperes current in a 3.4 m. Ebert mounting Jarrell-Ash Spectrograph. Rh line 3434.89 is matched against standards similarly prepared. 0.1 ppm of rhodium can be easily determined by the method.

Lower limit of detection is possible by using a bigger sample.

Some sample from Kolar Gold Fields have been found to contain 0.4 ppm of rhodium. Further study on the distribution of rhodium in association with precious metals and other suitable environments is under progress.
The increasing use of delayed-neutron counting in uranium exploration requires a check of physical and elemental interferences of each facility in use.

Major physical effects influencing U analysis were investigated at the fully automated Risø delayed-neutron counting facility. Recommendations regarding sample form and size were evaluated. Changes in the physical conditions at the analytical facility can be greatly controlled.

A series of experiments with artificial, granitic and basaltic rock samples were performed to estimate the actual influence of Be, B, Li, Al, Mn, Fe, rare earth elements and Th on the U analysis. If Be is present in a sample additional neutrons may be produced by photo-neutron reactions. The amount of neutrons is increased by about 1 % per 1000 ppm Be in a 5-g sample. For Li often present in micas a correction factor 0.15 % per 1000 ppm Li was evaluated. For the strong neutron absorbers B and Cd the correction factor is about -1 % per 1000 ppm interfering element present. High-energy gamma radiation from Al may be counted by the neutron detectors, but no or only small effects are observed, even after addition of 10 % Al to the sample. Large added quantities of Mn and Fe do not alter the U analyses at all. Five rare earth elements with moderate to high neutron absorption cross sections, often present in heavy minerals, were investigated. For Gd a correction factor of -10 % per 1000 ppm Gd was found. This factor was about -2 % for Sm, but negligibly for La, Ce and Nd, and for Th often present in heavy minerals.
THE DIRECT SPECTROGRAPHIC METHOD OF DETERMINATION OF NB, TA, BI, IN AND TI IN SEDIMENTARY ROCKS

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For determination of clark concentrations of Nb and Ta in sedimentary rocks select evaporation of the metals from cavity of the large coal electrode (weight of the sample is 1000 mg) by transformation in easily volatile substances using independent heating of the electrode was proposed. The reagent is tetrafluorineethylen. Detection limits are $1 \times 10^{-5}$% Nb and $1 \times 10^{-4}$% Ta with relative reproduction of 5-10%.

For determination of clark concentrations of Bi, In and Tl in sedimentary rocks fractional distillation from a large quartz tube combined with coal electrode (weight of the sample is 600-800 mg) by transformation in easily volatile substances using independent heating was proposed. The reagent is CdJ$_2$. Detection limits are $5 \times 10^{-6}$% Bi and $3 \times 10^{-5}$% In and Tl with relative reproduction of 5-13%.

The use of these methods permits to find out the role of facial, climate conditions, chemical composition of the parent rocks, forms of the occurrences of elements in natural waters and other factors, controlling their distribution in deposits. These results may be used in paleoreconstructions.
METEOROLOGICAL NOISE IN CRUSTAL GAS EMISSION RELEVANT TO GEOCHEMICAL EXPLORATION

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The emission of gas from the earth’s crust is a complex process influenced by meteorological processes. The effective use of gas emission as a tool in geochemical exploration will require an understanding of these influences. Free mercury vapor emission and radon emanation are being measured at a single non-mineralized site to evaluate the influence of meteorological and other secondary variables. Mercury has been measured over 2 1/2 hour intervals and radon over weekly intervals for a period of one year. The measurements are made in a shallow instrument vault directly exposed to soil gas and regolith leakage.

Mercury concentrations in the instrument vault average 9.5 ng/m$^3$ and range from $\leq$ 1 ng/m$^3$ to 53 ng/m$^3$ with a strong seasonal effect. Radon has a correlation of 0.55 with mercury which is significant at the 0.01 level. The radon emanation tends to be noisy with more unexplained variance. Mercury emission has a direct relationship to air temperature, relative humidity, soil temperature, soil moisture, barometric pressure, and water table. The direct relationship to barometric pressure was unexpected but is possible under a particular mode of leakage of soil gas into the instrument vault. Diurnal cycles are common but do not occur on all days. A heavy precipitation event on a dry soil seals the soil resulting in a rise in mercury concentration. Precipitation on a soil that is already wet does not increase mercury emission because of the compensation caused by lowering of the soil temperature by the precipitation event. Frozen soil emits the lowest concentrations of mercury. Stepwise multiple regression of mercury as dependent variable and meteorological parameters as independent variables gives a cumulative $r$ value of 0.856 and $r^2$ of 0.733. An analysis of regression residuals indicates phase shifts or lag effects are important, particularly for temperature.
THE PARTITIONING OF COPPER AMONG CONSTITUENT PHASES OF GEOLOGIC MEDIA OF THE PORPHYRY COPPER DISTRICTS OF PUERTO RICO

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Our investigation represents an effort to determine the manner in which copper is partitioned among selected phases that constitute geological media of two porphyry copper districts. Accordingly we have applied the 5-step sequential extraction procedure of Chao and Theobald (1976) to the determination of copper in drill core, soil, and stream sediment of the Rio Tanama and Rio Vivi districts of Puerto Rico. The extraction procedure afford a convenient means of determining the trace metal content of the following fractions: (1) Mn oxides and "reactive" Fe oxides, (2) "amorphous" Fe oxides, (3) "crystalline" Fe oxides, (4) sulfides and magnetite, and (5) silicates. An additional extraction between steps (1) and (2) was performed to determine organic related copper in stream sediments.

The results of our investigation indicate that distinctive partitioning "signatures" are characteristic of particular geochemical conditions, and that partitioning among the three secondary oxide fractions is especially significant. Furthermore, our results show that anomaly-to-background ratios range widely among the fractions of each geologic medium investigated, and that at least one fraction of each medium yields substantially higher ratios than does the bulk medium. The particular fraction yielding optimal anomaly-to-background ratios varies by medium and by geochemical conditions.

We conclude that selective extraction procedures have important applications to the orientation and interpretive stages of geochemical exploration, and we recommend additional investigations of a similar nature.
The Track Etch system for radon detection has been successfully used for several years in a large number of uranium exploration programs. The Track Etch system employs passive, integrating, alpha-sensitive detectors to measure radon gas concentrations near the surface that may be associated with buried blind uranium deposits. Since the introduction of the Track Etch method several years ago, major improvements in the basic system have been made. These include a simple technique for thoron exclusion, improved detectors of greater sensitivity and thermal stability, and the ability to eliminate surface interferences using other geophysical techniques. In addition, a considerable number of successful uranium exploration surveys and tests have been completed. This paper will summarize these recent advances in the Track Etch method and the results that have been obtained.
APPLICATION OF RADIONUCLIDE - X RAY FLUORESCENCE ANALYSIS IN GEOCHEMICAL PROSPECTION

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For geochemical prospection a mobile and versatile equipment is available in form of the radionuclide XRF with semiconductor detectors (EDXRF) and on line computer data handling. This set up can be installed in a truck and allows simultaneous determination of several elements in the field with only minimal sample pretreatment. The parameters and performance of our system are discussed referring to experiences from extended test series.

Using $^{109}$Cd (5 mCi) our equipment allows simultaneous determination of Cu, Zn, As, Sr, Zr, and Pb from concentrations above 30 ppm and Ba above 300 ppm in geological samples. The time required for each analysis is less than 10 minutes. To determine Ba in lower concentrations (down to 20 ppm) and the light REEs $^{241}$Am radionuclide source (10 mCi) is used. For this type of analysis less than 5 minutes are required.

In order to minimize sample preparation the effect of grain size was both estimated and determined by comparing the fluorescence yield of subsequently ground samples. Effects of sample inhomogeneity were determined by measuring of several aliquots of the same grain size fraction and by repeated mixing of the samples. The comparatively large penetration depth of X rays excited by $^{241}$Am allows the use of bulk Powder samples of the fraction - 80 mesh. Grain size effects and sample inhomogeneity in most cases cause only minor acceptable errors under these conditions. Elements which can be analysed using $^{109}$Cd are affected in respect to accuracy both by grain size variation and sample inhomogeneity. In this case a finer grain size or ground sample material has to be used. Measurements are carried out with both nuclide sources using bulk powder samples filled in measuring containers to saturation height. Thus weighing of the sample material can be omitted.

Depending on the time required for sample preparation and measurement 25 - 100 samples can be processed per man day.

The applicability of the radionuclide EDXRF is demonstrated by a survey in a Hydrothermally mineralized area in the Black Forest (FRG).
The possibility of the determination of many chemical elements with high productivity and reproduction accelerates geochemical investigation and raises their reliability. We have elaborated highly sensitive and safe X-ray fluorescence methods for analysis of natural objects for a number of major and minor elements (K, Na, Rb, Cs, Cu, Ca, Sr, Mg, Ba, Zn, Al, Ga, some Tr, Si, Ti, Ge, U, Th, Pb, Zr, Hf, As, W, Mo, Nb, Ta, Mn, Fe, etc) using X-ray analyser VRA-2 (W-, Mo- and Cr-tubes, analysing crystals: LiF (002), Pe, KAP, EDDT, ADP). Detection limits vary from 20 to 0, n ppm for different rare elements, relative reproduction is 1-3 %. We have elaborated an X-ray fluorescence method of determination of F, S and P, which influence hydrochemical conditions of sedimentation basins and migrate forms of chemical elements. Detection limits vary from n0 to n00 ppm and relative reproduction is 3 - 5 %.

Calibrate curves were made up for individual types of rocks using standard samples taking into account matrix influence. Calculations were done on a computer.

The investigation allowed to find out the general trends and regularities of mesozoic sedimentation of the Tadjik depression. The value of their migrating ability and indicator properties were established, the value of their geochemical background was done, and it was found that these data can be used for paleo-construction.
3. Evaluation of Results, Statistical Methods

THE MEASUREMENT AND EVALUATION OF VARIABILITY IN STREAM SEDIMENT SURVEYS

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In the last five years a considerable effort has been expended on devising methods for efficiently measuring variability in the lake sediment surveys of Canada's National Geochemical Reconnaissance. The problems of assessing variability in stream sediments are somewhat different. A major factor which has to be considered is autocorrelation in data from a single stream, i.e. the memory effect exhibited by a sample collected downstream from another sample.

In order to investigate these problems a detailed exploratory survey of two stream basins was carried out in the Southern Yukon Territory. Two sampling schemes were utilized, one based on random nested designs suitable for study by analysis of variance methods, and the other, a systematic sampling design suitable for study using geostatistical methods.

The ball milled minus 177 μ (80 mesh) stream sediment samples were analysed for U, Zn, Mn and Fe by both total, or hot acid, methods and a partial cold extractable method. Additionally total W and loss-on-ignition, for organic content, were determined.

The data reveal certain systematic features and confirm that results from the two data analysis philosophies and techniques can be combined. If it is desired to determine the true variability in stream segments of the study area samples must be collected at least 100 m apart. In terms of aiding follow-up and exploration work more detailed levels of variability are often of interest when sampling sites are re-occupied. In order to assist data evaluation and interpretation a simple index of data reliability is proposed that can be easily determined from duplicate samples collected from a subset of sites in a regional reconnaissance survey.

Often in stream sediment surveys in mountainous regions it is difficult to obtain fine silt material from the central parts of the stream channel. In such cases it has become the practice in the North American Cordillera to collect entrapped silts from around mosses closer to the banks. In order to determine if this procedure introduces bias into the resulting data a number of sampling sites were sampled using both methodologies. The data were investigated using a mixed effects analysis of variance procedure. Although the data set is small and the investigation exploratory the conclusion is that except for partial Zn the moss sampling procedure introduces no significant bias. An improved and efficient data sampling and analysis procedure, which is presented, was developed as a part of this study which has general application in orientation and detailed surveys.
AN INVESTIGATION OF VARIABILITY IN LAKE SEDIMENT AND WATER SURVEYS

Eldon Hornbrook, Geological Survey of Canada, Ottawa, Ontario, Canada

The total area covered by Canada's National Geochemical Reconnaissance (N.G.R.) lake surveys is in excess of 750,000 km². In Canada, lake sediment and/or water surveys similar to N.G.R. are also carried out by Provincial Governments and the mineral exploration industry.

Several different methods have been and are being developed to satisfactorily monitor the quality and reduce the variability of regional lake sediment and water survey data by appropriate changes to the sampling design. The test survey described in this paper was designed to evaluate current sampling procedures and variability estimation methods used in N.G.R. surveys.

Utilizing an unbalanced nested sampling design, the variability at the analytical, site, basin, lake and sampling cell levels were computed for relevant study and comparisons. Certain characteristic aspects of drainage systems, lakes and lake basins were identified and their significance in increasing or decreasing data variability was evaluated.

Essentially, the effect of including or excluding data from one or more profundal lake basins in the same lake relative to another satellite single basin lake in the same sampling grid cell on the overall regional distribution of an element was determined and evaluated.

The test survey was carried out in a 500 km² area of northern Saskatchewan, Canada in the IAEA/NEA Athabasca Test Basin Study Area. Air-dried, ball-milled 177 u (80 -mesh) lake sediment samples were analyzed for U, Zn, Cu, Pb, Co, Ni, Ag, Mn, Fe, Mo and As and water samples for U, pH and conductivity. The pH, temperature, eH, conductivity and dissolved oxygen of surface water were also measured at the field site using a modified Martek V. Digital Water Quality Analyzer.

Data from two previous lake sediment surveys in the test basin area also provided an opportunity to assess variability at site, basin etc. levels due to annual efforts. Further, one other lake sediment and water survey was carried out independently of, but simultaneously with, the test survey: its data allowed for an independent check of the test survey data and variability.
APPLICATIONS OF COMPUTER MODELLING TO THE GENESIS, EXPLORATION, AND IN-SITU MINING OF URANIUM AND VANADIUM DEPOSITS

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The geochemical behaviour of uranium and vanadium are extremely complex. It is virtually impossible to adequately characterize the movement and deposition of these elements in nature without the aid of the computer. We have modified and enlarged an existing computer model, WATEQF, to include many dissolved species and solid compounds of uranium and vanadium. The enlarged model uses thermodynamic data and equilibrium calculations to compute the state of saturation of an aqueous solution with respect to approximately 213 solid compounds and 197 dissolved aqueous species. The results can be used to interpret the behaviour and interaction of aqueous solutions and minerals in such diverse situations as the genesis of uranium-vanadium deposits, in-situ mining of ores, and hydrogeochemical exploration for ore deposits.

Three examples are given in this paper of the use of the model. First, water analyses from the South Platte River in Colorado, U.S.A., are examined to see if the uranium-rich waters of this system are capable of precipitating uranium minerals in the arkosic alluvium of abandoned meanders. Second, analyses of groundwaters from two known uranium deposits are modelled, with the output displayed as contour maps of the state of saturation of the waters. And third, complex from an in-situ mining operation in Wyoming, U.S.A., are examined to determine the dissolved species of uranium and vanadium, as well as the solid minerals and compounds that may control the composition and efficiency of the leaching solution.

The computer model is only as good as the chemical analyses of the waters used as input. At a minimum, the chemical analyses should include the following parameters: field pH, field Eh, field temperature, Ca, Mg, Na, K, Cl, SO₄, PO₄, alkalinity, Fe, F, Al, SiO₂, U, and V. Additional minor elements can also be measured and modelled, such as Mo, As, Se, Ra, Th, Cu, Pb, and Zn.
1. Complex treatment of geochemical information is fulfilled by integration of n-dimensioned geochemical field and comes to the calculation of some degrees, functionally connected with anisotropy value of geochemical anomalies. The differentiation degree of element composition of geochemical field shows the anisotropy.

2. The geochemical research data control system (GRDCS) was developed for geochemical exploration of mineral deposits. It consists of information retrieval control system (IRCS), complex of geochemical data processing programs and some service programs.

IRCS performs the following functions: input of primary data and the analytical data (documents) in the non-volatile memory, checking of input data; multistage data storing, correction, search and listing of data storage.

3. Input data is presented on the punch cards or punch tape; in the International Telegraph Code (ITC-2).

The input action is accelerated by means of automatic analysers: the results of immediate spectrum measurements are being put directly into the data storage and calculation of elements concentrations is done by the computer (neutron-activation and x-ray radiometric analyses).

4. Raw geochemical information with the help of IRCS is divided into etalon file and work file.

5. Logical processing programs complex fulfills sequential processing of etalon files which is divided into K classes (subfiles). This complex defines the quality of analytical data and calculating values of the background level and abnormal concentrations for all N elements in all I rocks and also defines the set of L-distinctive and M optimal informative characteristics (elements) when comparing K classes. When finding non-linear decisive rules one teaches to distinguish K etalon classes.

The associations of elements are picked out of all the original L-elements and the hierarchical relation of associations is determined using the clusteranalysis method.

Comparing all K classes according to all L indications one can build a zonality sequence and determine a zonality coefficient taking into consideration L, M and hierarchies. The fields of pair vector relations in all K-classes are set up for the indications constituting the zonality coefficient.

The data of work files are also complex processing: the zonality coefficient is calculated as well as vector fields and the space points are classified for all the work files, ending with printing the plans using the plotter or the printer of computer.

6. The improvement of the system is connected with the introduction of some automatic analytical methods with the immediate input data into the data
A MICRO COMPUTER BASED SOFTWARE SYSTEM FOR COMPUTER ASSISTED INTERPRETATION OF EXPLORATION ORIENTED GEOCHEMICAL DATA

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The past few years have seen an increasing application of computer based procedures in the processing and interpretation of geochemical data. In many cases this has been carried out by non geologists using medium to large computers at centralized locations, remote from the exploration effort. In such situations, appreciation of the geological nature of the problems is often inadequate and in a number of cases this has led to the misapplication of procedures. The present paper describes the MICRO-GAS system consisting of a micro computer and a series of compatible interactive programs written in FORTRAN that can be used independently by a geologist with a minimum of experience with computers. This facility allows the geologist the opportunity to carry out personally the processing and interpretation of geochemical data and to ensure that the methodology used in the processing and interpretation is based on a firm geological framework. The system has the capability of (a) selecting subroups of samples that meet specified criteria (e.g., specific rock type, specific value ranges), (b) data transformation (addition, subtraction, multiplication, division, logarithms, and exponentiation), (c) statistical computations, (d) graphical display (e.g., histograms, X-Y plots, symbol maps etc.). Flexible disks are used for data storage and a video terminal is used for communications with the user. A small printer produces hard copy output. The system presently includes programs for data management, univariate statistics with histograms, correlation analysis, X-Y plots, line printer symbol maps, line printer geochemical profiles, multiple linear regression, discriminant analysis, and R-mode factor analysis. Attention is presently being given to developing programs that use a pen plotter for producing better quality maps and diagrams at any scale.

Experience with the system thus far has shown that the similar programs for construction of maps, graphs, and diagrams can provide an immediate improvement in the quality, thoroughness, and speed of data interpretation as well as significantly reducing the tedium associated with manual methods. The multivariate statistical techniques, as always, require a higher level of expertise and many more man hours if they are to be used successfully, but offer the opportunity for identifying significant new features or clarifying features already recognized in the data.

The scope of the MICRO-GAS system is illustrated with reference to the processing of geochemical information relating to a set of bedrock geochemical data from an area of volcanic massive sulphide deposits in northwest Ontario.
GEOCHEMISTRY OF STREAM SEDIMENTS ALONG THE WESTERN COAST OF THE GULF OF ELAT (AQABA)

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Geological Survey of Israel

128 samples of heavy mineral fractions from sand-size sediments whose mineralogy has been studied by Ayalon (1976) were chosen for this geochemical study. The samples represent the stream sediments along the coastal belt from Elat to Sharm el Sheikh. The aim of this study is twofold: a) a reconnaissance survey of the catchment area and b) to try to correlate the analysed elements to specific minerals. This study complements the geochemical reconnaissance study of Zilberfarb and Bogoch (1977) on the Precambrian Terrain in Sinai where bulk stream sediments were analysed.

The samples were analysed mainly by DC emission spectrography. In the samples as a whole 14 elements were analysed. Table 1 lists the means and the standard deviations of the analysed elements in ppm (apart from Ti and Mn which are expressed in percent), the percentage of the heavy mineral fraction (HM) in the original samples together with the mineralogical composition of this fraction. Seven magnetic fractions were also separated in 20 samples and in these 14 to 20 elements were analysed according to the case.

The results were submitted to factor (SPSS) and to association (Gill et al., 1976) analysis. Since the environment is typically arid, there is relatively little chemical weathering and the combination of the results of both statistical analyses shows clearly that three types of catchment areas can be differentiated: sandstone, metamorphic and granitic terrain. Furthermore, a distinct Mn anomaly was found in the Sharm el Sheikh area.
POSSIBILITIES FOR GEOCHEMICAL CHARACTERIZATION OF TIN-GRANITES IN NORTHERN THAILAND

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Computer algorithms have been developed in order to calculate quantitative prospecting parameters. The user of this program can involve geological features, and technical conditions and calculate risks.

Geochemical results of rock-samples (tin granites in Northern Thailand) are used as a case-study.

The statistical method consists of three algorithms:

- A learning-algorithm, selecting significant elements in a known area which relate to rock features, and finding a rule to decide whether a sample is from the target of a tin granite or not.
- A simulation-algorithm to find the optimal sample design.
- A prospecting-algorithm which calculates the probability of being in a target area, basing on samples from a prospecting area.

The author will discuss the statistical method, first results, and point out additional algorithms.
GEOCHEMICAL STUDIES RELATING TO THE ENRICHMENT, BENEFICIATION AND OTHER ASPECTS OF FLUORITE, APATITE AND PYROCHLORE MINERALS FROM CARBONATITE BODIES OF AMBADONGAR REGION, GUJARAT STATE, INDIA

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The unique occurrence of huge fluorite deposits at Ambadongar, Gujarat State i.e. 12 million tons has attained its economic importance. The deposits are mainly seen as replacing, cavity filling types, display structures like comb and cockade. The mineralization is confined to 58 zones. Faults are common, at certain zones fault plane is almost vertical with well preserved slickenslides and the mineralization is seen with joints. This lucidly illustrates that faults and fractures acted as channelways for the mineral solutions. Fluorites occur as well developed crystals, the predominant form is cube but other combinations are also readily seen. Yellow, amber, green, colourless, blue and violet are the order of abundance. Laboratory data reveals that temperature of formation is between 115°C and 140°C, as observed from fluid inclusions; E.S.R. studies show the characteristic presence of Gd, Cu and Mn as paramagnetic impurities in fluorites of various colours, Be, La, Yt, Cu, Pb, Ba, Th, Mn, Ce, Co as trace elements, the isotope analysis of lead suggests a better potential for radio active minerals. In this context the minor occurrence of thorogummite, gummite and carnotite are worth mentioning. Fluorite, yittriofluorite, tysonite are identified. Apatite and pyrochlore are the other economic minerals which occur with quartz and calcite. The beneficication studies have been carried out on large scale carbonatite samples after obtaining the chemical and particle size liberation data of these economic minerals. The results suggest that the average grade fluorites can be upgraded to metallurgical grade. Though apatite and pyrochlore are low in their concentrations and uneconomical, they are recoverable as byproduct in this process. A flow sheet is presented which illustrates the significance of various stages. The economic aspects relating to this process are fully discussed.
THEORETICAL ESTIMATION OF ACCURACY IN MOVING AVERAGE OF BLOCKS

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The technique of moving average is often a useful tool in data analysis involving large number of samples and helps in the estimation of regional trend which is only an approximation of the true regional trend. The present work deals with the theoretical studies on the estimation of accuracy of the computed regional trend value, obtained through the technique of moving average. It is assumed that the sample points are arranged in the moving average blocks at grid points with equal spacing in X and Y directions and that the same exponential covariance function with components (local) and (regional) is valid in both the directions. Exponential covariance model has been used for its effectiveness to describe a rather irregular surface and is particularly suited to the problems of usual limited area geochemical surveys. In computing the variance of error, Var (e,e), different sizes of blocks are considered with gradual increase in the number of control of sampling points. The variances of errors, thus obtained for the different cases considered, have been reproduced in separate tables.

Analytical experiments with the variances of errors produced results which will help in minimising the amount of error from such operations. Two tables have been evolved wherefrom it is possible to directly read out the best choice of block-size with the corresponding optimal accuracy in moving average, provided the sampling interval and estimate of the covariance function are known. An example has also been given to demonstrate the usefulness of these tables.
ELIMINATING BIOGEOCHEMICAL BACKGROUND VARIATIONS BY NORMALIZATIONS

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1. Birch (Betula alba) twigs and leaves were analyzed along a profile crossing a nickel anomalous zone. The area is forested, in the south bordered by a road. Rock outcrops, as well as glacial drift and bogs make the ground surface, the underlying rock is a gabbro.

Using original dry weight data for leaves, the Ni-zone is clearly visible against a variable background. The figures were normalized against some combinations of main trace elements. Ba + Sr normalized data gave a 25-fold contrast to a rather smooth background curve. A small copper anomaly was seen at the same point, too.

2. In another area, a non-mineralized gravel pit, various trees and shrubs were regularly sampled during the vegetation season. Birch leaf samples from 1977 and 1978 were analyzed. The large-scale variations are different for different elements. Ca increases during the whole growth season whereas trace elements like Cu and Ni have their highest contents in the spring. Trying to eliminate both these large scale variations as well as smaller variations between single samples, different normalizations against the main trace elements were tried.

Only Ca and Zn got rather constant normalized values during the vegetation period. The smaller variations were compared with meteorological data. The Ba + Sr normalized data show a probable covariation between peaks and warm weather. The smallest weather correspondence was observed after normalization against Ba + Sr + Fe + Zn.
ON POSSIBLE ANALYSIS OF HETEROGENEOUS DISTRIBUTIONS OF CHEMICAL ELEMENTS AND GREAT POPULATIONS IN GEOCHEMICAL PROSPECTION

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In our method the analysis of heterogeneous distribution commences by selecting such a distribution of a heterogeneous population in which the most numerous symmetric class intervals can be found. In this interval the course of normal curve will be determined on the grounds of estimated parameters which will be treated more in detail in the paper. By prolongation of the normal curve course to the neighbouring classes of the symmetric interval the so-called estimated population will be found. By adding the resting values the population will be extended and by exclusion of added values it will be reduced so that the empirical distribution may correspond to theoretical normal distribution in accordance with the solver's demand. For this reason every modification of and estimated population to a defined population is tested by expressing the percentual agreement between the empirical and the theoretical distributions. Every new distribution is judged on the grounds of the most favourable number of classes.

Determination of number of classes is connected with the problem of treating large populations. The greater the number of values of a population the greater should be the number of classes. This is, however, limited by analytic sensibility of determination of contents. Surpassing of a certain number of classes results in empty classes which are undesirable in expressing the division. So analysis of extremely numerous populations must be based on treating populations limited in number. Such populations may be compared both according to arithmetic mean and dispersion. For identical or at least resemblant populations common values of arithmetic mean of dispersion and also common function of their distribution may be determined.
A NEW WAY OF INTERPRETING TRACE ELEMENT CONCENTRATIONS WITH RESPECT TO MODES OF MINERAL FORMATION

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The availability of multielement analyses provide unnumerous data on trace elements. These data complete petrochemical analyses in general and are often reported as averages although they vary over many orders of magnitudes.

As as result of a 4-years research project it can be shown that the variation of trace elements in ores can be related to fundamental processes during ore formation. As examples the fractionation of the lanthanoids in Ca-minerals (fluorite, calcite, apatite, phosphorites etc.), chalcophile elements in sphalerite and Ga, Sc, W and Fe in cassiterites will be discussed. Plotting of analytical data in variation diagrams (fractional index vs. chemical environmental index) help to decipher the mode of crystallization (pegmatitic, hydrothermal or sedimentary; primary or secondary crystallization; interaction of ore bearing solution with country rock). Anomalies in trace element distribution sensitive to oxidation or reduction processes give useful informations about the origin of the ore bearing solutions and environmental conditions during their migration.
EVALUATION OF LAKE SEDIMENT SURVEYS USING THE RELATIONSHIP OF METAL TENOR TO ORGANIC CONTENT

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In geochemical surveys, including those of lake sediment, it is convenient to classify logarithmic cumulative frequency distribution of the elements analysed as anomalous, uncertain, and background. The second, and commonest, group presents the dilemma -- is a given distribution in that group tending towards an anomalous or a background distribution? Data from a series of surveys suggest that the relationship of loss on ignition to metal tenor can be used as an indicator of an element's 'potential' or 'availability' in the region of the survey. In turn, increased availability implies an anomalous source, such as an ore deposit. Surveys with the best potential are considered to be those where particular element logarithmic cumulative distributions have the same or greater positive slopes than the associated loss on ignition distribution. The method does not define areas within the survey that can be considered more anomalous, only whether or not the region exhibits a greater than expected concentration of a given element.
REGIONAL GEOCHEMICAL PROSPECTING

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In the taiga-mountain regions of the far northeast of the USSR as well as in many other world-wide countries geochemical prospecting of ore-deposits are successfully carried out by stream sediments sampling.

These lithochemical surveyings are carried on a scale of 1:200000 with a density of one sample per sq.km. Usually these surveyings are carried out in areas of hundred thousands sq.km. and it is proved to be of higher geological effectivity.

More than 20 years ago the author offered a method for quantitative interpretation of lithochemical dispersion flows based on the study of their "productivity":

\[ P'_x = S_x (C'_x - C'_o) \]

where \( C'_x \) is the percentage composition of ore-element at the point of sampling \( x \); \( C'_o \) is the background composition of the ore-element in stream sediments and \( S_x \) - the area of water basin corresponding point \( x \) in sp.m. It was shown, that in the lower part of the stream below the ore-body

\[ P'_x = f(x) = \text{const.} = k'. P \]

where \( P \) is the productivity of the secondary-residual dispersion aureol located in the water-basin of the present stream. Productivity \( P \) is proportional to the productivity of ore \( P_p \), i.e. \( P = k P_p \) m\(^2\)/o where \( k' \) and \( k < 1,0 \) are local coefficients to be determined during the survey.

Later, this has allowed to calculate reserved of metal, on the discovered ore-manifestation:

\[ Q'_H = \frac{1}{k'k} \cdot \frac{1}{40} \sum_{i=1}^{m} P'_i \cdot H \]

where \( H \) is the depth of ore-evaluation generally fixed by geological considerations, \( m \) - is the number of neighbouring streams draining the ore-field, and subdivission by 40 agree with change from m\(^2\)/o to tons.

The function (2) is found to be good for first-order steams while it is not so in higher-order streams.

Correspondingly the apparent value of \( P'_x \) calculated from (1) deviating from (2) are converted to their actual values

\[ P'_{\text{actual}} = \lambda \cdot P'_{\text{max}} \]

Here \( \lambda, < 1,0 \) is correcting factor determined from the present data by special nomograph (1978).

Evaluation of \( Q'_H \) based on (4) and (3), regarding other data determining the value of discovered ore-manifestations is effectively used in the USSR.
4. EXPLORATION FOR HYDROCARBONS

USE OF LABORATORY SIMULATION EXPERIMENTS IN INTERPRETING THE CARBON-13 COMPOSITIONS OF NATURAL GASES

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The rate of formation and stable carbon isotope compositions of early methane formed during closed system pyrolysis of naturally occurring carbonaceous materials are considerably different than those compositions reported in the past for methan generation from model compounds such as \( \eta-C_{18}H_{38} \). A more rapid early methane formation from natural materials relative to model compounds makes possible studies at temperatures approaching 200\(^\circ\)C. Isotope fractionations for very early methane formed from four coal, six lipid-free shale and one topped crude oil samples are initially small, become as much as 10 \(^{\circ}/oo\) larger and then decrease as previously reported for the total accumulated methane generated from model compounds.

The experimental results on molecular and isotopic changes may be used to explain 1) reported values for the large differences between coal and shale-derived methanes 2) reported \(^{13}\)C rich coal associated methanes 3) increasing "wetness" of gases during the early stages of formation from the lipids in shales 4) the importance of carbon isotope heterogeneities in the molecular constituents comprising the source organic materials and 5) the minimum \(^{13}\)C values which may be expected during thermogenic methane formation.

Scenarios are presented to explain various reported natural gas compositions.
THE ORGANIC MATTER OF A GULF COAST WELL STUDIED BY A THERMAL ANALYSIS - GAS CHROMATOGRAPHY TECHNIQUE

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A thermal analysis - gas chromatography technique, previously described by Whelan et al. (1979) has been applied to a continental offshore stratigraphic Test (COST # 1) well drilled in the Gulf Coast.

The data allowed an evaluation of the degree of maturation of the organic matter and provided an accurate determination of the depth of the threshold of intense oil generation at 10,000 feet. Qualitative changes of hydrocarbons in the C1-C14 range were determined by Gas Chromatography - Mass Spectroscopy. These data are discussed in terms of generation and migration processes. The catagenetic evolution results in a strong tendency for a proportional increase in n-alkanes. Mass transfer phenomena may be responsible for updip movement of the lighter hydrocarbons.
ANALYSIS OF TYPE AND MATURITY OF THE ORGANIC MATTER AS A TOOL FOR THE INTERPRETATION OF THE GEOLOGICAL PROFILE

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Down to the depth of about 2890 m ("Lechtal nappe") the organic material of the sediments (Hauptdolomit and Raibler Schichten) consists mainly of bituminous matter, which can be finely dispersed or concentrated in thin lenses. The sparely occurring figurated organic particles comprise oxidized coaly material as well as algal debris. In this section the vitrinite reflectance increases very slowly from 0.4 to 0.6 % R.

At 2890 m a sudden jump of the vitrinite reflectance values to 1.5 % R is observed, which is accompanied by the complete disappearance of the fluorescence of the organic material. At the depth of 4186 m a reflectance value of 1.95 % R is reached.

In this part of the profile ("Zwischenschuppe"), above all between 3330 and 3800 m, coaly material is dominating.

Below 4186 m down to the depth of 6468 m the sediments contain organic material, which resembles that of the Lechtal nappe. Vitrinite reflectance increases from 0.6 to 1.15 % R.

The optical analysis are supported by pyrolysis data, which clearly demonstrate the separation of the profile into the above mentioned three sections.

Apart from the highly colaiyfied organic material in the Zwischen- schuppe, the organic matter of the other sections is able to generate oil, however the overall organic content is too low for real source rocks.

Additionally, data for the interpretation of the paleogeography and thermal history of the different profile section were received by...
$^{13}\text{C}/^{12}\text{C}$ and D/H Isotope Analyses on Drilling Stem Test Gases: Genetic Relationships to Natural Gases of Subalpine Basins

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Drilling stem test gases (DST) were found in 5000 and 6200 m depth in carbonaceous rocks of Karnian/Norian age (Hauptdolomit). In these strata the maturity of the organic matter increases from 0.6 % to 1.2 % vitrinite reflectance at 6200 m. The carbon-13 concentration of the gases was found to be higher in the 5000 m sample (-36 °/oo) as compared to the 6200 m sample (-40 °/oo). The opposite trend is expected taking the general relationship between maturity and 13-C concentration into consideration. This shows that either the upper sample was produced from terrestrial organic matter, or that mixing processes (short distance migration) has occurred.

The comparison of the D/H and $^{13}\text{C}/^{12}\text{C}$ patterns of natural gases from subalpine basins with the DST-samples from the wildcat shows that the DST gases exhibit the typical isotopic composition of Triassic gases from Hauptdolomit source rocks. This shows that the gases have been produced in situ and do not indicate a deeper source.
The amount of methane, the composition of light hydrocarbons and the carbon-isotope ratios of head-space gases from canned cuttings were analysed and compared with other geochemical data.

In the upper section ("Lechtal nappe") the amount of headspace hydrocarbons is low, the hydrocarbon composition varies considerably. The methane generally is enriched in $^{13}\text{C}$ compared to the isotope-maturity line for sapropelic organic material.

The section of higher coalification ("Zwischenschuppe") yields a large amount of hydrocarbons, predominantly methane (up to 4 - 6 %), in the head-space. The carbon-isotope ratios (methane) roughly match the "sapropel"-isotope-maturity line though the organic material in this section predominantly consists of humic particles.

The samples from the deepest zone ("Allgäu nappe") contain small amounts of hydrocarbons, mostly methane. The methane-carbon isotope data only partly match the isotope maturity line for sapropelic matter. They scatter by about ± 7 $^\circ\text{oo}$ possibly because of the mixed type of organic material (terrestrial, marine) in the rock and partly because of secondary fractionation effects during transportation of the cuttings in the borehole.

It is concluded that the hydrocarbons analysed originated in the drilled section of the well, they need not be generated in deeper or neighboured zones. In some depth intervals there are allochthonous hydrocarbons having migrated through strata of the drilled depth range of the well.
A CONTRIBUTION TO GEOCHEMICAL CRUDE OIL/SOURCE ROCK-CORRELATIONS IN THE MOLASSE BASIN (SOUTHERN GERMANY)

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Geochemical and isotopic results on crude oils from the Molasse Basin are compared with those on extracts and kerogen of drilling cores. The selection of the samples corresponds to the present state of industrial oil exploration in Southern Germany.

The results derived from these comparisons are discussed under following topics:

(i) Evidence concerning the method of isotopic type curves.

(ii) Correlation between these geochemical results and geologic considerations concerning the origin of crude oils in Southern Germany.
Gas chromatographic and gas chromatography/mass spectrometric analyses of certain Nigerian crude oil fractions have revealed the ubiquitous presence of $C_{24} - C_{27}$ tetracyclic alkanes likely to be degraded triterpanes. These tetracyclanes are not known natural products nor have they so far been reported present in petroleum or sedimentary rocks from elsewhere.

a) Two hypotheses of the origin of the oil polycyclanes were adduced:

The alkanes were formed from the transformation of naturally occurring seco-triterpenoids present in the source sediments which were deposited in the Niger delta basin during the Tertiary.

b) They resulted from the cleavages of either terminal ring of the pentacyclic triterpanes arising from thermal transformation of reservoired petroleum.

To test the first hypotheses, a $C_{27}$ seco-triterpane synthesized from $\beta$-amyrin was compared with the oil tetracyclane with the same number of carbon atoms. Similarly, to test the second possibility, a simulation of geological maturation of a crude oil sample initially rich in pentacyclic triterpanes was studied. The results of both investigations were discusses.

The relevance of the above study to oil exploration is that the degraded triterpanes might be useful for assessing the stages of thermal evolution of petroleum-in-the-reservoir. Specifically, the expected variations in the concentration of the tetracyclanes in crudes with different thermal histories could be utilized in distinguishing virgin (immature) oils from mature but biodegraded crudes found in the same basin.
ON THE SOURCE ROCK POSSIBILITIES OF THE JURASSIC SEDIMENTS, WESTERN DESERT, EGYPT.

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This work implies the evaluation of the Jurassic sediments as probably source rocks using a complex of geochemical analysis of organic matter extracted from these sediments. Special attention was paid to Wadi Natrun area where relatively thick Jurassic sediments were penetrated.

The marine Jurassic section in the Western Desert of Egypt represents a single transgressive cycle and comprises three formations namely (from base to top) Wadi Natrun, Khatatba and Massajid Formations, formed mainly of alternating shale and limestone beds, with fine-grained sandstone interbeds. Eghi group is the fourth unit, which is the continental facies of the Jurassic.

About 200 picked ditch samples from 4 wells, representing the Jurassic section were geochemically studied for their diagenetic order, organic matter content, bitumen type and content with separate extraction of more neutral and more acidic compounds by different solvents, and humic acid content.

This study allowed to conclude that the Jurassic sediments can be considered as potential source for oil as well as for gas. The section can be differentiated into intervals of more likely source for oil, for gas or for both oil and gas, whereas in other intervals the processes of petroleum genesis were incomplete.
The possible use of hydrochemical and isotope surveys of shallow groundwater sources as a tool for oil and gas exploration

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The possibility of using anomalous concentrations of carbon and sulfur species in shallow groundwater bodies, as a tool for oil and gas exploration is demonstrated in the present communication. The rationale for initiating the present study was the reasonable assumption that slow decomposition of organic compounds, under anaerobic conditions and in the presence of sulfates, releases CO\(_2\) and H\(_2\)S gases. Such gases might in turn, emerge along rock boundaries and produce a "halo" of geochemical anomalies in groundwater bodies above oil and gas reservoirs. Reliable screening of anomalous values from normal levels requires the use of advanced hydrogeochemical and geoisotope models.

This assumption was generally justified in the course of the research. The use of several geochemical and geoisotope criteria and indices, related to the carbon and sulfur systems, and developed especially for this study, made it possible to "locate" existing oil fields in the Gulf of Suez, and to demarcate the already proven boundaries of the Heletz-Kochav oil field in the coastal plain of Israel.
INTEGRATED GEOCHEMICAL, REMOTE - SENSING AND GEOLOGICAL APPROACH IN PETROLEUM EXPLORATION, MAVERICK COUNTY, SOUTH TEXAS, USA

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Geologic history, sedimentary sequence, and structural development of Cretaceous rocks in Maverick County, South Texas, U.S.A., are typical for the interior salt basins of the northern Gulf of Mexico. Such basins frequently contain significant reserves of oil and gas.

Predominantly platform carbonates and shales with lesser amounts of evaporites and sandstones were deposited in a restricted, evaporitic, platform basin, the Maverick Basin, in the eastern part of the Rio Grande Embayment during the Cretaceous. Subsequent deformation during the late Rocky Mountain orogeny in Late Cretaceous and Tertiary time produced a number of structures with associated faults and fractures some of which are discernable on conventional aircraft as well as Landsat imagery.

Photogeologic studies allowed the recognition of distinct sets of linear elements and several circular structures. A joint/fracture analysis performed utilizing data collected from the fractured surface rocks led to the recognition that the drainage network reflects structural conditions of the bedrock. The combination of photolineation and drainage lineation maps let recognize important intersections of individual lineations and lineation sets.

The determination of structural weakness as reflected by lineations bears a relationship to the occurrence of hydrocarbon accumulation. It is suggested that E-W lineations and their intersections with NE-SW lineations are of major importance with respect to hydrocarbon accumulation indicating subsurface fracturing and possible reservoir presence.

Actively upwards migrating hydrocarbons and related organic compounds moved along the deep-seated fractures and fracture zones identified and were confirmed by geochemical anomalies at the surface. Thus, an organo-chemical exploration approach with analyzing samples from 1 m to 3 m depth for adsorbed and interstitial methane, ethane and heavier, and pentane gases proved to be an essential exploration tool for the locating and delineation of several geochemical anomalies some of which are not suggested by field as well as photogeologic studies.
THE LOS ALAMOS SCIENTIFIC LABORATORY APPROACH TO HYDROGEOCHEMICAL AND STREAM SEDIMENT RECONNAISSANCE FOR URANIUM IN THE UNITED STATES

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The Los Alamos Scientific Laboratory of the United States is conducting a geochemical survey in the Rocky Mountain states of New Mexico, Colorado, Wyoming, and Montana and in Alaska. This survey is part of the National Uranium Resource Evaluation sponsored by the US Department of Energy. The purpose of the reconnaissance is to identify areas having higher than background concentrations of uranium in ground waters, surface waters, and watertransported sediments. The sampling procedures, analytical techniques, and data evaluation of this reconnaissance are portrayed in this poster session.

Sample densities, based on the results of pilot surveys, are nominally one sample location per 10 km² except for lake areas in Alaska where one location per 23 km² is used. Field procedures include collection, filtration, and acidification of waters; conductivity, pH, water and air temperatures, and scintillometer measurements; and collection of a watertransported sediment. Field observations include comments on the relief, geography, vegetation type, geology, weather, and contaminants. All measurements and observations are recorded on field data forms.

Samples are received and inventoried by Los Alamos personnel. Then, water samples are analyzed for uranium by fluorometry with a lower detection limit of 0.02 parts per billion (ppb). Concentrations of the 12 other elements in water are determined by plasma-source emission spectrography. All sediments were analyzed for uranium by delayed-neutron counting with a lower limit of detection of 20 ppb. Other elemental concentrations are determined by neutronactivation analysis for 31 elements, by x-ray fluorescence for 9 elements, and by arc-source emission spectrography for 2 elements. An average of 350 samples are analyzed by each analytical method each working day.

Data is reported by National Topographic Map Series quadrangle boundaries (1° latitude x 2° longitude), scale 1:250 000. A typical quadrangle has 1500 to 2000 sample locations and covers 15 000 to 20 000 km², depending on latitude. Data are presented in a formal report with brief sections on climate, geography, hydrology, known uranium occurrences, and geology and empirical and statistical evaluations. The uranium data is briefly discussed; however, multielement data is included only in the appendixes. Plates included with each report at a scale of 1:250 000 include a geological map, a sample location overlay, and graphic plots of uranium concentrations in waters, conductivities in waters, uranium concentrations in sediments, and thorium concentrations in sediment. All data is available to the general public on computer tape.
URANIUM GEOCHEMICAL PROSPECTING IN THE SOUTHERN BLACK FOREST, GERMANY

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A geochemical soil sampling survey was carried out over 500 km$^2$ in the southermost part of the Black Forest, underlain by Hercynian metamorphic and magmatic rocks. A total of 2,344 soil samples were collected, representing a sample density of 4.7 samples per km$^2$. The samples were taken at the foot of slopes in the transition zone to fluviatile alluvium. Uranium adsorption in clay minerals is enhanced in this zone due to a damming effect in the flow of the slope-groundwater. The clay fraction of the samples has been analyzed for U by paper-chromatography.

The technique described above allowed a cheap and rapid strategic prospecting of the large area. Its reliability was confirmed by a positive test over a known uranium deposit and by the discovery of several occurrences with anomalous uranium concentrations, partly coinciding with known hydrogeochemical anomalies (FAUTH, 1973). Follow-up surveys detected the occurrence of radiometric anomalies in the vicinity of clusters of geochemical anomalies.

The relationship between uranium distribution and lithology, pedology, hydrogeology, and man-made contamination has been determined by statistical processing of the data (uranium content, morphology, soil characters, grain size, and depth of sampling).
POSTGRADUATE TRAINING IN GEOCHEMICAL EXPLORATION AT THE UNIVERSITY OF IFE, NIGERIA

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Based on a Technical Cooperation Agreement between the Federal Republics of Nigeria and Germany, 12 months lasting post-graduate programs in "Applied Geology", leading to the M.Sc. degree, were started at the Department of Geology, University of Ife, Nigeria in 1974. One of the options was in "Mineral Exploration" including both geochemical and geophysical teaching programs. The equipment for the geochemical facilities, incl. preparation, XRF and AAS, was financed in equal parts by the Nigerian and German governments; staff was sent from F.R.G. and a variety of scholarships for Nigerian and also for Tanzanian students were granted.

To get the students actively involved in practical exploration methods, a geochemical mapping program in the metasedimentary belts of SW-Nigeria and around the Sn-Nb-Ta-bearing Pegmatites of Nigeria was initiated. Within four years (1974-1978) 16 M.Sc. and 9 B.Sc. Dissertations were supervised, 2 Ph. D. thesis are in progress; 268 rock samples, 758 streamsediment samples and 1037 soil samples were studied by AAS and XRF totaling in about 24 000 geochemical data.

The geochemical mapping program did not result in new mineral findings but succeeded to improve the knowledge of the distribution and geochemical character of a variety of Precambrian Basement units within the metasedimentary belts of SW-Nigeria and served as a basis for further detailed petrological-geochemical investigations.
The general objective of the BMR geochemical surveys is to assist in mineral resource assessment of Australia. The BMR is currently investigating the mineral potential of metallogenic provinces in Australia, utilising geological mapping at 1:100 000 scale, regional geochemical surveys and geophysical studies, both regional and detailed.

Obtaining fresh rock, weathered bedrock or soil samples for geochemical surveys in much of Australia is difficult and expensive relative to the cost of collecting stream sediments. In many prospective parts of Australia weathering is deep, relief is low and streams flow only periodically, particularly in much of northern Australia where the climate is monsoonal. Thus, stream sediments are sought wherever applicable, and in Australia suitably drained areas comprise about 30-40 percent of the continent.

Parameters relating to sampling media, dispersion, sample density, and sampling techniques are thoroughly investigated by orientation surveys in the province of interest prior to conducting the regional survey.

Field procedures

The geochemical field program is commonly tied in with the geological field study of mineral provinces, and most sampling is done using a small turbo-jet helicopter such as the P 1 Jet Ranger.

In a typical sampling program sample points are plotted on 1:50 000 topographic maps to give a fairly even distribution of about 1 sample per 2.5 km², coverage being determined by drainage pattern; samples are taken from streams representing individual catchment areas, the sampling site being just upstream from the confluence with the adjacent stream.

Flight paths for the helicopter linking 20 sample localities are planned and transferred to overlays on 1:25 000 colour aerial photographs. Areas up to 200 km² can be covered by flying 4 sampling loops per day. Samples collected are a composite of active sediments near the centre of streams, and weigh 2 to 3 kg. A sample preparation unit is set up at a centrally located base camp in the survey area, where samples are sieved and treated to yield about 40 gm of 180 micron size fraction and about 100 gm of heavy mineral concentrate. The fractions are then returned to headquarters for analysis in a central laboratory.

Analytical procedures

In general as many elements as possible are analysed for in each sample using techniques that detect 'total' abundance. A typical range of element determinations would be Be, Cr, Co, Cu, Fe, Pb, Li, Mn, Ni, Ag and Zn by AAS, and As, Ba, Bi, Ce, F, Nb, Rb, S, Th, Sn, Ti, W, U and Y by XRF.

Heavy mineral concentrates are further refined by heavy liquid and magnetic separations, and then examined under a binocular microscope for the presence of important indicator minerals, checked by gamma-ray spectrometer for minerals such as monazite, and semiquantitatively analysed by optical emission spectrography for elements such as Bi, Cr, Co, Cu, Au, Mo, Ni, Ag, Sn, Zn, Pb, Nb, Ta and W.

Data presentation methods

A map format is used for the presentation of the survey data. A number of elements can be presented on each map without sacrificing clarity. The map is designed to have visual impact and highlight anomalies. A pie-chart type symbol is used to portray the analytical data. The values for 3 elements are depicted in each symbol by assigning a colour and a 120° sector of the circular symbol to each element. The portion of each sector blocked out is proportional, via a class-interval graduation scheme, to the element concentration. The actual analytical values in ppm corresponding to each
CONDITIONS OF FORMATION OF LA, Y, YB AND NB DISPERSION AUREOLES AND TRAIN IN ARID CONDITIONS, EASTERN DESERT, EGYPT

Mahmoud M. Hassaan¹) Mohammed M. Kaoud²) and Atif H. Sabet³)  
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The distribution of La, Y, Yb and Nb and the associated elements in the various genetic types of the allochthonous and autochthonous debris as well as their modes of Formation were studied in 12 bulk samples (3 kg) representing the anomalous detrital overburden in Wadi Baroud, 30 km west of Safaga in the Red Sea Coast.

Ti, Zr and Mn are the main associated elements, the distribution of which in the various particle-sizes are consistent with that of the rare elements.

Y and Yb are highly concentrated in 0.2 0.1 mm particle size of the autochthonous debris, while Nb- in 0.1 0.063 mm and La in 0.063 mm. In the coluvial-proluvium sediments, these elements are enriched in the particle size 0.2 0.1 mm. In the Alluvial-proluvium debris Y, Yb and Nb are enriched in 0.2 0.1 mm particle size, while La - in 0.1 0.063 mm particle size. These particle size fractions must be taken into consideration in lithochemical prospecting.

These elements are very highly enriched in the heavy (0.2445 %) relative to the light (0.0106 %) minerals of the sandy particles. They are more concentrated in the heavy fractions of the eluvium-deluvium and coluvium-proluvium debris.

The distribution of Nb, Y and Yb is intimately related to that of Mn and Ti and Zr, which may display their presence as polymagnite and columbite. However, the high manganese content in the fractions enriched by the rare metals is an indication that they are adsorbed on the hydrous manganese oxides. Monazite, fluorite and hydrous manganese oxides present may be responsible on the enrichment of La. Nb, Y and La are highly enriched in the very weak and weak magnetic fractions, while Yb in the very weak and non-magnetic fractions. This may display an economic importance of these dispersion aureoles and trains as placers.
STATISTICAL ANALYSIS OF STREAM SEDIMENT DATA FROM IFE-ILESHA AREA OF S.W.NIGERIA

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Statistical treatment of geochemical exploration data in the Ife-Ilesha area has not been fully utilized as an invaluable tool in their interpretation. The results of 176 stream sediment samples from an area of 1,800 km² analysed for Cu, Zn, Mn, Ni, Co and Cr after hot extraction were treated with both simple and sophisticated (R-mode factor) statistical analytical methods. All the elements were found to have density distributions closely approaching log-normal or a mixture of two lognormal populations.

They all show strong positive correlations with correlation coefficient values ranging from 0.5 between Mn and Ni, to 0.84 between Mn and Co, all considered to be real at 5% level of significance.

The R-mode factor analysis produced a three factor model which accounts for 85.6% of the total variance in the data. Factor 1 (Cu-Cr-Ni) correlates spatially with the area underlain by the amphibolite complex, thus reflecting the parent rock as a dominant influencing factor. Factor 2 (Mn-Co) and the strong positive correlation between Mn and Co are interpreted as resulting from the influence of coprecipitation activity of Mn-oxides. These results correlate with the earlier observed element associations in the area.
GEOCHEMICAL ORIENTATION SURVEY FOR COPPER MINERALIZATION IN WADI EL-URF, EASTERN DESERT, EGYPT

Mohamed A. Al-Hawary & Mahmoud M. Hassaan,
Geological survey, Abbassia, Cairo, Egypt and Al-Azhar University, Madinat Nasr, Cairo, Egypt.

An orientation survey was undertaken for copper in wadi El-Urf located near Ras Gharib on the Red Sea Coast. Where 6 bulk samples representing the eluvium, deluvium and alluvium were mechanically and spectrographically analyzed to detect copper and associated elements. Moreover 1000 samples collected from the dry channel draining the mineralization were also analyzed.

The favourable particle sizes to be analyzed are \(<0.5\) 0.125 mm and \(<3\) 2 mm. The chemical weathering plays the chief role in dispersion of copper. However mechanical weathering displays pronounced effect.

The detailed dispersion train survey indicated its efficiency and feasibility in revealing the copper mineralization in the arid conditions of the Eastern Desert.
In the last ten years, the application in Brazil of the geochemical exploration techniques, had a fast and well succeeded evolution. While in 1969 were collected about 20,000 samples in geochemical surveys, it is estimated to 1979 an amount of 300,000 samples to be collected. The two greater government owned companies of mineral survey, CPRM and DOCEGEO, are responsible about 70% of the geochemical exploration for programs in the country.

Presently, almost all the companies, private or government owned, have been using with good results the geochemical prospecting methods. The stream sediment sampling is often used in regional reconnaissance (1 sample to 5-50 sq. km). Several metallogenic provinces and districts were characterized based in geochemical data, especially in the northeastern, center/western and northern regions of Brazil. In promising areas, the combined use of prospecting methods has discovered occurrences of Cu, Au, Pb, Cr, and Ni. Several geochemical targets indicated as surely anomalous will be surveyed in detailed scale in the next five years, appearing to exist good perspectives of new mineral discoveries.
RECONNAISSANCE GEOCHEMICAL SURVEY OF GRANITOIDS IN THE NORTHERN PART OF EASTERN DESERT, EGYPT

Ibrahim Abu El-Leil & Mahmoud M. Hassaan,
Al Azhar University, Cairo, Egypt

93 Samples, collected from the Syn- and Late orogenic granitoids outcropping in the northern part of Eastern Desert (600 km²) were spectrographically analyzed, where, 26 elements were estimated. Mainly the Late orogenic granitoids comprise 2 phases, each of which is subdivided into 2 subphases.

The investigated granitoids comprise mainly 6 types: quartz diorite-diorite, biotite-hornblende-pyroxene, medium- and coarse-grained biotite-hornblende granites and medium- and coarse-grained leucocratic granites.

The relative concentration of the elements in the studied samples to their average content in the granites (concentration coefficient) was calculated, on the basis of which geochemical reconnaissance maps were done to measure the ore-metals potentials of these rocks.

All these granitic types, except the pyroxene-biotite-hornblende granites are Mo-bearing. However, the potential of the Late orogenic granites except the biotite-hornblende-pyroxene- and Um Salman biotite-hornblende granites for lanthanium is denoted. Arsenic recorded as direct path finder for gold in the Eastern Desert, was detected in 2 samples in each of Um Tweir and Hammad biotite-hornblende granites.

Nine samples mainly from the less differentiated granites of Late orogeny intensively invaded by intermediate and basic dykes contain relatively high copper content (sometimes with nickel).

Mo-Cu potential of the area may be of certain importance, particularly that nearby the area molybdenium and Copper mineralizations were noticed.
EXPLORATION FOR FLUORITE IN EASTERN BAVARIA

H. Fauth, Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Federal Republic of Germany

In the reconnaissance stage of an exploration program for new deposits in the fluorite vein bearing area of Eastern Bavaria a multielement program was started (Ca, Cu, Zn, Pb, Hg, F, etc.). After short time it became evident that exclusively the determination of fluoride - as well in water as in stream sediments - yielded clear indications for fluorite mineralized zones.

Consequently the detailed program was based on fluoride determination only. Soil samples were taken in profiles with 5 m distances. The investigation resulted in pronounced anomalies of up to 100 fold background values. Simple symbols proved to be more effective for representation than sophisticated statistical methods. One of the anomalies was investigated by two inclined borings, which met a fluorite vein so-far unknown of 40 cm thickness and at least 100 m length. It was investigated in detail by a reconnaissance mining operation with a shaft and galleries.
GEOCHEMICAL MAPS OF THE FEDERAL REPUBLIC OF GERMANY

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Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Federal Republic of Germany

Compilation of geochemical maps of surface water and stream sediment analyses for the Federal Republic of Germany commenced in 1977 and are planned to be finished in 1982. They are based on approximately 75,000 samples of each type, from a total area of about 150,000 km². For the waters, Pb, Cu, Zn, Cd, Co, Ni, U, and F contents were determined at the site in a mobile laboratory. In the case of the stream sediments, Ti, Cd, F, Ba, Co, Cr, Cu, Li, Mn, Ni, Pb, Sn, Sr, U, W, V and Zn were determined by emission spectrography and other methods in the Bundesanstalt.

In order to be compatible with the new geological maps of the same areas, the geochemical maps will be published at a scale of 1:200,000, but other scales can be made available on special request.

The first maps will be published at the end of 1980.
EXPLORATION FOR SCHEELITE IN EAST GREENLAND - A CASE STUDY

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An intensive scheelite exploration program was carried out in Precambrian crystalline and sedimentary rocks intruded by granitics of Precambrian and Caledonian ages in East Greenland (70-74°). Previous heavy mineral panning (2100 samples within an area of 100,000 km²) formed the basis for selection of scheelite anomalous semi-regions (1,550 km²).

In the semi-regions, pan concentrate samples were taken from first and second order rivers and from mid and side moraines of active glaciers. All samples were studied in the field under UV light, and scheelite grains were counted. A consideration of the distribution of scheelite in the samples together with the river and glacial drainage systems, enabled definition of the potential source areas of the scheelite to within localities of 2-5 km².

Within the localities, panning of scree fines (samples every 100-200 m along talus slopes) and UV light traverses at night led to the finding of outcropping or sub-outcropping scheelite mineralisation. Scheelite was observed associated with granite - carbonate contact zones, quartz vein stockworks, and fault zones in limestones, in four discrete areas within the 300 km long zone of investigation.

The heavy mineral panning method with the counting of scheelite grains in the field and the subsequent definition of scheelite potential areas has the advantage that it is possible to execute a program from semi-regional outcropping mineralisation stage in one field season. The investigation in this case was performed by five geologists during the 1979 2 1/2 month field season.
CONDITIONS OF FORMATION OF LA, Y, YB AND NB DISPERSION AUREOLES AND TRAINS IN ARID CONDITIONS, EASTERN DESERT, EGYPT

Mahmoud Hassaan 1) , Atif Sabet 2) & Mohammed Kaoud 3)
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Y and Yb are highly concentrated in <0.2> 0.1 mm particle size of the autochthonous debris, while Nb - in <0.1> 0.063 mm and La in <0.063 mm. In coluvial proluvium sediments, these elements are enriched in the particle size <0.2> 0.1 mm. In alluvial proluvium debris Y, Yb and Nb are enriched in <0.2> 0.1 mm particle size, while La - in <0.1> 0.063 mm particle size. These elements are very highly enriched in the heavy (0.2445 %) relative to light (0.0106 %) minerals of the sandy particles. Nb, Y and La are highly enriched in the very weak and weak magnetic fractions, while Yb in the very weak and non-magnetic fractions.

Ti, Zr and Mn are the main associated elements, the distribution of which in the various particle-sizes are consistent with that of the rare elements indicating their presence, most probably, as polymagnite and columbite. However, the high manganese content in the fractions enriched by the rare metals enhances their absorption on the hydrous manganese oxides. Monazite, fluorite and hydrous manganese oxides present may be responsible on the enrichment of La.

The high enrichment of these elements in the weak-very weak and non-magnetic fractions enhances the economic value of these dispersion aureoles and trains.
GEOCHEMICAL PROSPECTION IN FRANZ TAMAYO PROVINCE AREA NORTH OF LA PAZ - BOLIVIA

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This paper is a synthesis of the final report on regional Geochemistry Prospection carried out in the Apolo region (Franz Tamayo Province north of La Paz, Bolivia).

The regional geochemical survey was made to detect anomaly areas that are favourable for probable ore deposits. Also, this paper shows the relationship between the geological and geochemical studies that have been made in that region. Finally, the study indicates targets for systematic prospection.
GEOCHEMICAL EXPLORATION FOR URANIUM IN THE GREASE RIVER AREA, NORTHERN SASKATCHEWAN, CANADA

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During the reconnaissance and follow-up stages of a uranium exploration programme in the Grease River area, Northern Saskatchewan, Canada, several geochemical exploration techniques have been employed. These included lake water and lake sediment geochemistry, biogeochemistry, muskeg sampling, and rock geochemistry. Following first orientation surveys, a reconnaissance lake water and lake sediment survey was carried out over an area of 230 km². The sampling density was approximately 3.2 samples per km². The samples were analyzed for U, Cu, Ni, Zn, V, and As. In addition, Eh-pH-values and CO₂ content of the waters were measured and sampling depth and composition of the sediment samples were recorded. Both sediments and water revealed very strong uranium anomalies. None of the other elements proved to be useful as a pathfinder for U. The computerized data interpretation involved the calculation of background and threshold, regression analysis, computation of regional trend surfaces, and contour maps. Correlation between sampling depth, sediment type, and uranium contents was poor, thus indicating a relatively homogeneous sampling medium.

The effects of different sampling densities on the outlines of anomalies were investigated by computer. Results showed that no additional information could be expected from an increase of the sampling density.

Consequently, follow-up programmes consisted of muskeg sampling and rock geochemistry. Very strong uranium anomalies were found in muskeg. Moderate to high background rocks with a high percentage of easily leachable U proved to be abundant.

The detected anomalies are interpreted as the result of a subsequent enrichment of uranium in partly isolated drainage basins. The uranium is leached from high background country rock and scavenged by lake and swamp sediments, which are extremely rich in clay minerals and organic matter.
Geochemical Prospecting Criteria For Massive Sulphide Ores In Central Sredna Gora (Bulgaria)

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Investigations on the primary geochemical haloes of the El-shitsa copper-pyrite deposit (Panagyurishte ore district) resulted in the establishment of the following geochemical prospecting criteria for massive sulphide deposits: 1) elements-indicators of the ore mineralization; 2) geochemical indices for the prognosis of the composition of hidden ore bodies; 3) zonig coefficient - for evaluation of the level of revealing the geochemical anomalies by the present erosion surface or in bore-holes and galleries; 4) intensity coefficients - for prognosis of the economic importance of the hidden ore mineralization. The geochemical data can be used to solve some problems of the geology and the genesis of the deposits.
GEOCHEMICAL EXPLORATION IN INDIA: A FEW CASE HISTORIES

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Modern technique of geochemical prospecting were pursued intensively and systematically since 1953. The Geological Survey of India is the foremost among the organisations in India, followed by the Oil and natural Gas Commission and the Atomic Minerals Division, that use geochemical methods.

Soil and bed rock sampling have been the most commonly followed methods, while biogeochemical, stream sediment survey, gossan sampling etc., have been carried out on a limited scale. Recently atmo-geochemical method has been tried over a mercury field in South-west India. While integrated methods of landscape geochemical prospecting led to the discovery of economic deposits of nickel oxide in the Sukinda ultramafic belt, Cuttack district, Orissa, indicator plants like Shorea robusta, Tenoinalia tomentosa were used to determine the economic levels of nickel mineralisation.

Litho-geochemical prospecting followed by drilling in selected sectors established a direct correlation between the high copper anomaly zones (4,000 ppm or more) in the overburden of residual soil and the workable copper sulphide lodes underground in the Singhbhum copper-uranium-nickel-molybdenum-phosphate field in Bihar.

Gossan sampling was found to be more useful in locating the Zinc-lead deposits of Dariba in Rajasthan and their evaluation (Pb over 150 ppm and Zn up to 800 ppm). True gossans were differentiated from false gossans by statistical studies of the geochemical data and true evaluation of the ore prospect was possible. Contrastingly, no primary dispersion was shown around Pb-Cu ore bodies of the Agnigundala lead-copper-zinc deposits even though soil, water and bed rock sampling was done.

Geochemical soil surveys over the gold-bearing lodes of the Kolar gold field (Karnataka) indicated arsenic values of 50 to 1,000 ppm, the higher values corresponding to the sulphide-bearing Oriental lode. However, in the Champion gold-quartz reef, no geochemical anomaly of any path finder element was recorded.

Fluorine was used as a direct indicator in a local geochemical survey of the Chandodongri mineralized belt area consisting of quartz fluorite with minor lead-zinc sulphide association.

Geochemical prospecting by soil and bed-rock sampling in the extra-peninsular region of India has generally been found to be a discouraging experience.

The Field Research Technique Unit of the GSI is now trying to develop a vapour-phase geochemical technique and a Mercury vapour trap for exploration of concealed base metal mineralisation.
THE TOPOLOGICAL GROUPING OF THE GEOCHEMICAL DATA

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We have proposed method of grouping classified objects \( n \in \mathbb{N} \) by plurality of signs \( m \in \mathbb{M} \) in multidimension space of signs in geometrical interpretation. All signs are transformed to discrete ones \((1,0)\). The boundaries in multidimension space are determined by average \( \bar{x}_m \) of signs \( (d_{im} = 1 \text{ for } x_i \geq \bar{x}_m \text{ and } d_{im} = 0 \text{ for } x_i < \bar{x}_m) \).

This matrix of "object-sign" with discrete values is transformed to matrix of distances "object-object". To evaluate the measure of distance between objects (samples) the following formula is used:

\[
d_{ij} = L_{ii} + L_{jj} - 2L_{ij}
\]

\((L_{ii}, L_{jj} - \text{number of units in } i,j\text{-set}, \text{ } L_{ij} - \text{number of signs having values } 1 \text{ for } i,j \text{ objects simultaneously})\).

If we use \( m \) signs in discrete \((1,0)\) form, the space has \( 2^m \) equal elements. If there is

\[
2^m \gg n \quad (m \gg \log_2 n)
\]

then grouping in this space depends on the sum total signs.

The graph is built up from the matrix "object-object". The tops of the graph are samples. If we pass from the measure of distance to the measure of similarity and if we sum of measure of similarity we receive multiequational and hierarchical distribution of samples into groups which have genetical meaning.

The method was tested on different geological objects.
TRACE ELEMENT DISTRIBUTION AND ITS IMPLICATION IN THE WESTERN EXTREMITY OF THE SINGHBHUM SHEAR ZONE, EASTERN INDIA

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The association of copper sulfides, apatite-magnetite and uraniferous minerals with the feldspathic schists, gneisses ('soda-granites') and other associated rocks along a zone of intense shearing, popularly known as Singhbhum Cu Belt - a 130 km. long arcuate strip of country between Chakradharpur and Baharagora in Eastern India, is remarkable (Dunn, 1937; Banerji, 1962; Talapatra, 1968). The eastern end of this shear zone is narrow and quite well defined. But, towards west it is wider and its extension further to the west of Chakradharpur is not precisely demarcated (Banerji, 1975; Sarkar and Saha, 1977). To establish some geochemical signatures for defining the western extension of the shear zone and its mineral potentiality, the present study was made based on the analytical results of 160 bed rock samples collected from three parallel narrow strips running across this shear zone near its western end around Chakradharpur. The samples were spectrographically analysed for 25 elements, namely Cu, Pb, Zn, Ni, Co, Cr, Zr, Mn, V, Sr, Ga, Ba, Mo, Li, Rb, Nb, Ti, Cd, Bi, Cs, B, Ta, As, Ag, and Y. It appears from the result that excepting the elements underlined in the above list, other elements do not show significant values within the various lithological units of the different strips. Out of these only Cu, Ni, Co and V show some anomalous values close to the minor sulfide occurrences. It is also observed that distribution of individual elements like Cu, Zn, Ni, Co, Ba, Cr, Sr and V within the different lithological units of the three strips do not show any definite pattern. But ratios like Cu/Ni, Cu/Co, Cu/Cr and Cu/Sr show a gradual and marked increase of values towards the sulfide lode zone in the eastern strip near Kharaswan, while in the two other strips distinctly high ratios of the above pairs of elements were noted along the northern and southern fringe areas. These roughly correspond with the western extension of northern and southern boundary of the shear zone, in the two strips, respectively.

From the detailed study of the geochemical results of bed rock samples along these three strips and their statistical analysis it is evident that the elemental ratios of some significant pairs of elements, rather than their individual distributions pattern, may be more helpful in locating the anomalous areas of copper sulfide mineralisation, which also possibly help delineate the zone of deformation and shearing along the extension areas of this belt.
INTERPRETATION OF GEOCHEMICAL PATTERNS IN LAKE SEDIMENTS AND WATERS IN THE VICINITY OF THE KEY LAKE U-NI DEPOSITS, NORTHERN SASKATCHEWAN

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In 1977, an area of approximately 800 km² centered on the Key Lake U-Ni deposit in northern Saskatchewan, Canada was the object of a lake sediment and water geochemical survey. Sediments from the deep basins of lakes and surface waters were collected at an average density of one every 2 km². The waters were analysed for U, conductivity and pH, and the sediments for U, Zn, Cu, Pb, Ni, Co, Ag, Mn, As, Mo, Fe, Hg, and loss on ignition.

The most abundant elements to form the ore minerals, U, Ni, and As, all generate well defined anomalies in the vicinity of the orebodies and their extension in the direction of glaciation. These elements, along with Co, constitute the most prominent factor in an R-mode factor analyses of the data and their distribution, particularly that of uranium which has the strongest loading in the factor, seem to be directly related to the mineralization and associated glacial dispersion fan. Of the other elements that are found in accessory amounts in the ore, Zn, Cu, and Pb have their secondary dispersion patterns controlled largely by variations in the organic content of the sediments. Mo as well as some of the As, Co, and Zn are controlled partly by the distribution of iron and manganese hydroxides.

The highest uranium values in the sediments, in the order of 1500 ppm U, occur in Zimmer Lake, about 10 km southwest of the ore zones. The strongest uranium anomaly in the waters (5-14 ppb) occurs in Karl Ernst and Seahorse lakes over the Gaertner orebody. Both these lakes also show strong uranium anomalies in their sediments (500 to 1000 ppm). Key Lake, on the other hand, which is underlain by the Deilmann orebody, shows only slightly higher than background concentrations of uranium both in its water (up to 0.4 ppb) and in its sediments (up to 8 ppm). All three lakes, Key, Karl Ernst and Seahorse, show Ni anomalies of comparable magnitude (100 to 200 ppm). It is thought that reducing conditions associated with the ore are preventing uranium from dispersing hydromatically through about 50 m of Athabaska sandstone and 10 m of glacial till into overlying Key Lake. Nickel, which is mobile in the reducing environment, disperses to generate the anomaly in Key Lake. The Ni and U anomalies in Karl Ernst and Seahorse lakes may have developed due to the fact that these two lakes occur over a basement window and are separated from the ore only by glacial till (about 50 m thick). The absence of the Athabasca formation in that area would allow the oxidation of the upper part of the orebody thus inducing dispersion of the metals. Alternatively, the anomalies in Karl Ernst and Seahorse lakes may be related to a mineralized boulder train that begins west of Key Lake and extends to Zimmer Lake where it is known to be at the origin of U-Ni-As anomalies in the sediments and U anomalies in the waters.
SELECTIVE EXTRACTION PROCEDURES APPLIED TO GEOCHEMICAL PROSPECTING IN AREAS CONTAMINATED BY OLD MINE WORKINGS

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The region of La Calamine - Moresnet, in Belgium, was one which was actively mined during the 19th century. Geochemical prospecting in the area is now difficult because materials from the mine working were often used for such purposes as construction of road and railway embankments, and infilling of marshy areas. A geochemical soil survey in the vicinity of the known ore body at Lontzen has revealed numerous anomalies some of which exceed 10,000 ppm Pb and/or Zn. Three soil profiles were selected in this area and examined for possible contamination. Two anomalous samples from one profile were obviously contaminated (brick fragments). A sequential selective extraction procedure was applied to these soil profiles using a modification of the method of Gatehouse et al. (1977). The following dissolution sequence was utilized:

1) Ammonium acetate 1 M pH 4.5
2) Hydroxylamine hydrochloride 0.1 M pH 4.5
3) Hydrogen peroxide 130 vol.
4) Ammonium acetate 0.175 M - Oxalic acid 0.1 M pH 3.3 in the dark
5) Ammonium acetate 0.175 M - Oxalic acid 0.1 M pH 3.3 under U.V. light
6) Hydrochloric acid - hydrofluoric acid leach of the residue.

Using this procedure, anomalies related to a known galena - sphalerite vein appear in every dissolution step. In contrast, contamination of a sample produces no metal anomaly in the first five steps: it only appears in the final acid digestion (step 6).

One may thus suppose that contamination of the sample adds metal in the form of a resistant phase which is only dissolved by strongly acid reagents. It should be noted that the contrast between anomalies and background is about the same for all dissolution steps. So, in areas where contamination by old mine workings exists, ammonium acetate extraction may usefully replace the classic acid digestion procedure.

Literature:
The geochemical characterisation of soil anomalies round a gossan can help to improve geochemical prospecting methods in carbonate environments: it can also help to establish the mode of surface dispersion of lead and zinc.

Samples of the iron crust and its adjacent sulphide vein (marcasite, sphalerite and scarce galena, in a calcite gangue) were collected from cores. The gossan consists of dominant goethite alternating with lepidocrocite and hydrohematite in a type of "box-work" structure. Cerussite is rare. The oxidised ore contains about 0.6 % zinc and 0.2 % lead. Sequential selective extractions and electron microprobe analyses show that the zinc which accumulated in the iron crust is localised in the goethite either as microscopic inclusions or by isomorphous substitution for iron. Lead occurs either as lead oxide inclusions or in association with manganese oxides.

Soils with anomalous values in lead and zinc lying adjacent to the iron crust contain ferruginous masses with dimensions ranging from hundreds of microns to several centimeters. Mineralogical and chemical analyses show them to be fragments derived from the iron crust. However, certain masses appear to have been modified by pedological processes. They contain more goethite (with colloform structure) and hydrohematite as well as a small quantity of an amorphous iron phase containing 10 % of total zinc and 20 % of total lead.

As zinc is not very mobile and is mainly associated with residual goethite from the iron crust in anomalous soils, a separation and geochemical analysis of this mineral phase should optimise geochemical exploration methods. In the carbonate environment there exists a mechanism of dispersion by mechanical means like that recently proposed by several authors with reference to other geochemical environments.
DIRECT DETERMINATION OF URANIUM IN ORE OR SOIL SAMPLES
(A COMPARISON OF METHODS)

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As well for prospecting purposes as for investigations of the genesis
of uranium deposits it is necessary to use fast and reliable analy­
tical methods for the uranium determination.

We have prepared a standard set with different amounts of uranium and
used the following analytical methods:

1. Direct $\gamma$-counting
2. X-ray tube excited fluorescence
3. Cobalt-57 excited X-ray fluorescence
4. Laserinduced fluorescence (after fusion)
5. Delayed neutron counting

These 5 methods are compared as to time and cost of the analysis and
as the reproducibility and precision. The above mentioned factors are
a function of the concentration of uranium.
ELIMINATING MANGANESE DIOXIDE INTERFERENCE IN THE ATOMIC ABSORPTION DETERMINATION OF GOLD

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Manganese dioxide interference in the atomic absorption determination of gold can be eliminated by the simple process of heating the sample to remove the excess unreacted bromine prior to the addition of the methyl isobutyl ketone (MIBK).

Experimental data has shown that the presence of as low as 3 to 5 percent manganese dioxide in a sample can cause false readings for gold up to 1 ppm gold in a gold-free environment. This false reading is caused by an interference at the normal 242.8 nm wavelength used to analyze for gold on the atomic absorption spectrophotometer.

With the increase in value of gold, and the subsequent increase in demand, old mining properties not economic a few years ago are being reexamined by exploration geochemists. Many of these exploration companies are using panned concentrate samples as a means of evaluation, a technique that might also concentrate the manganese up to this interference level.
A pilot study was conducted in the vicinity of known uraninite-bearing quartz veins near Kenosha Pass in the Front Range of Colorado. Sampling media included minus-80 mesh alluvium ("total" digestion; partial digestion with 3% oxalic acid), Fe-Mn oxide boulder coatings (partial digestion with hydroxylamine hydrochloride followed by partial digestion with 3% oxalic acid), and aquatic bryophytes ("total" digestion of ashed residue). All samples were analyzed for Fe, Mn, Cu, Pb, Zn, Co, Ni, Mo, and U.

The results indicate that the combination of sampling media and partial digestions may provide valuable interpretive information in evaluating areas for uraninite mineralization. In sediment, "total" U may be significant if a substantial portion of U is soluble in 3% oxalic acid, or if the U/Fe ratio is high in 3% oxalic acid extracts. Sediment analysis mainly reflects uranium derived from soils and outcrops in the drainage basin. Concentrations of U in boulder coatings and aquatic bryophytes, on the other hand, reflect dissolved U introduced into the stream in groundwater. Anomalous U concentrations in these media tend to confirm the presence of uraninite mineralization if coincident with sediment anomalies, or suggest the presence of concealed uraninite mineralization if sediment anomalies are absent.
The in situ interaction of water and sulfide minerals yields dissolved species which can be used to trace back the presence of sulfide minerals and associated minerals. Field and laboratory results show that the most characteristic are the sulfur species, hydrogen sulfide ($H_2S$, $HS^-$), polysulfide ($S_{n}^{2-}$) and thiosulfate ($S_2O_3^{2-}$), issued from the hydrolysis of sulfide minerals. Typical concentration ranges are: $10^{-5} - 10^{-7}$ mol/1 for hydrogen sulfide, $10^{-6} - 10^{-9}$ mol/1 for polysulfide and $10^{-5} - 10^{-8}$ mol/1 for thiosulfate. The chemical reactivity of these species make them difficult to assess unless determined immediately after sampling.

These sulfur species can be determined rapidly and accurately in field conditions by simultaneous titration with mercuric chloride employing an Ag/Ag$_2$S electrode for the determination of the end points.

The application to ore exploration is exemplified by the case of the research of roll-type uranium deposits in the south west of France.
DETERMINATION OF NANOGRAM QUANTITY OF MERCURY IN SILVER WIRE SPIRALS USED IN GEOCHEMICAL PROSPECTING FOR THE DETECTION OF MERCURY HALOS

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Mercury, being a chalcophile element is associated with many sulphide minerals. The natural property of vaporisation of mercury at ordinary temperature and pressure results in formation of mercury halo in the soil-gas phase in surrounding area of primary mineralisation. For establishing the presence of such mercury halos, vapour of mercury present in soil-gas is trapped with silver spiral in field condition by special arrangements. Determination of a few nanograms of mercury trapped in such silver spiral requires special analytical operations for attaining the low detection level and also to have acceptable precision.

Two methods of determination of mercury amalgamated in silver wire spirals studied by the authors are described. Of these, one is direct method in which the silver wire spiral is placed in a silica tube and mercury is vaporised by heating with a movable tubefurnace. The mercury vapour is swept by careful regulated current of purified air through a silica absorption cell fitted in the lightpath of an AAS instrument. In the other method of determination amalgamated mercury is vaporised in the same manner but the vaporised mercury is allowed to be absorbed in acidic KMnO₄ and mercury determined in the solution by cold vapour AAS.

In the direct method mercury can be determined in the range of 3 - 125 nanogram whereas in the other method it is in the range of 20 - 500 nanogram. Calibration was done from a solid spike made from mercuric chloride and silica powder. The mercury in the spike was determined by acid decomposition and comparing with a primary liquid standard. For cross check, mercury in the two standard U.S.G.S. rocks G-2 and GSP-1 was determined comparing with this liquid standard and agreeable values were obtained.
Interpretation of geochemical anomalies with the help of stream sediments needs consideration of a number of special factors. Different grain sizes in the stream sediment differ in their abilities to collect trace elements from various types of rocks. The choice of one particular size fraction of stream sediment for sampling is found inadequate for interpretation of trace element distribution between the bed rock and stream sediment. This problem of selection the proper size fraction is also directly related to the choice of suitable analytical method.

The authors have studied samples from some areas in Bhutan, with little known detailed geology. More than 500 samples were analysed for Cu, Pb, Ni, Co, V, Cr, Zr, Ba, Sr, Y by spectrographic method. Cu, Pb and Zn were also analysed in some of the samples by atomic absorption spectrophotometry. Size fractions -80, -60, -40, -20 mesh and also heavy fraction were analysed. Comparison of the AAS and spectrographic results show that in case of Cu the spectrographic values are somewhat higher than the AAS values. This can be due to the reason that the treatment of the sample with acid for AAS analyses does not always decompose many mineral components, while spectrographic values indicate the total metal content. However, in case of Pb, emission spectrographic values tend to be lower than AAS values. For Zn, of course, AAS is the only suitable method because spectrographic method of Zn is unsatisfactory.

Study of the analytical results in relation to size fraction shows interesting results. On one area, contents of many elements, such as, Cu, Ni, V, Zr, Ba, Y showed the tendency to increase with grain size from -60 mesh to -20 mesh. In another area, similar trend was observed in samples for -80 mesh to -40 mesh, but in the samples of -20 mesh size, the enrichment was not so marked. Elements like Cr & Zr showed a higher concentration in finer fractions in some cases. The details of the results have been discussed.
USE OF THE SCINTREX UA-3 URANIUM ANALYZER FOR BIOGEOCHEMICAL PROSPECTING

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A preliminary study of the biogeochemical prospecting potential for locating uranium occurrences in the Marfa Basin, Texas, was conducted in 1978. A conventional fluorimetric method for uranium analysis was used at first, but the results were disappointing owing to the low concentrations in the plants that were sampled. Only 6 of the 74 samples collected in the reconnaissance survey showed levels above the detection limit of 0.4 ppm in the ash. We therefore considered using the Scintrex UA-3 analyzer for plant-tissue analysis and experienced a high degree of success. The UA-3 was designed primarily for direct analysis of uranium in natural waters and has proven beneficial for prospecting purposes because it can be used quite easily in a mobile laboratory. The improvement in sensitivity (0.05 ppm, about one order of magnitude) that resulted from use of the UA-3 gave us detectible uranium in all but 1 of the 75 samples. Accuracy and precision were evaluated and considered quite satisfactory. In brief, the method involves acid digestion of ashed tissue, extraction of uranium into ethyl acetate, destruction of the ethyl acetate, dissolution of the residue with 0.005 % nitric acid, and measurement. We recommend the use of this method especially when the uranium concentrations are generally below the detection limits of the conventional fluorimetric method, but also when results in the field are necessary for the success of the investigation.
THE BIOGEOCHEMICAL METHODS CLASSIFICATION BY THEIR EXPLORATION INFOMATIVITY

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The classification of various biogeochemical methods has been begun elaborated by the author since 1973-1974 years (Kovalevskii, 1974). The basis for this - the accumulated data about the plant's quantitive barrier characteristics as regards to high (toxic as a rule) concentrations of chemical elements in the nutrition medium (Kovalevskii, 1971-1974). The sum of knowledge about these barriers is considered as a doctrine about the plant's unconcentrational barriers (Petersburgskii, 1977).

The biogeochemical methods are divided into three groups on the basis of the quantitative barrier characteristics for various species and parts of plants: 1) the nonbarrier, quantitatively informative methods recommended for the wide practical use; 2) the barrier, qualitatively informative methods recommended for the limited use in cases when nonbarrier biological objects are absent in the concrete landscapes; 3) the background barrier, uninformative biogeochemical exploration methods which are not recommended for practical use. The last may be named the pseudobiogeochemical exploration or to be more precise the biogeochemical pseudoexploration.

The nonbarrier biogeochemical exploration (NBE) are realised with the help of the published tables of grouping for 50-250 biological objects by their exploration informativity (Kovalevskii, Kovalevskaya, 1979) or by the special investigations with the purpose to make grouping and finding of nonbarrier and practically nonbarrier species and parts of plants in the concrete landscapes.

The possibility to receive the quantitative information by means of NBE has been confirmed by the present time by various investigators (Baskinskii, Radchenko, 1977a; Kovalevskii, 1979; Radchenko et al., 1977; our unpublished data). In accordance with these data the linear correlation coefficient (r) for Be, F, Mo, W, Pb, Cd, Hg, Ag and Au contents in the systems "the nonbarrier biobject - the ore bodies eluvium" and "The nonbarrier biobject - the native rocks and ores" are on the level of 0.80 - 0.99 and the standard multiplier ±1 =1,8±1 - 2,7±1.

NBE were used earlier in the limited scales because of the lack of the exploration informativity determination method for various biological objects. In Canada the molybdenum deposit Endako Mine and copper-molybdenum deposit Bethlehem (Warren, Delavaul, 1970) and in the USSR the molybdenum deposit in Siberia were discovered by these methods.

Most of the biogeochemical exploration programmes carried out earlier may be attributed to the barrier biogeochemical exploration. These methods permit to discover the biogeochemical ore haloes which, as a rule, can not be interpreted quantitatively because of the use of the decabackground biobjects. In the system "the decabackground biological barrier - the ore bodies eluvium" the typical values of r=0.3-0.7 and the indicator element contents in the biogeochemical haloes are 3-30 times approximately into 10 times higher than the local background. In particular, the biogeochemical exploration programmes for uranium in the USA in 1950-1960-th years (Cannon, 1952-1971) may be attributed to such barrier biogeochemical exploration.
A new technique has been developed and tested for the rapid and efficient digestion of geochemical samples prior to analysis. Crushed or sieved sample material is weighed into a unique design of borosilicate test-tube which incorporates a glass flange around the rim. After addition of the leaching reagent (normally an acid or acid mixture), the test-tube is sealed by a crimp-on cap with an inert liner, and seated in a hot aluminium block. When adequate sample dissolution has been achieved, the cap is removed, and the leachate diluted for determination of trace and major elements by atomic absorption spectrophotometry, inductively-coupled plasma emission spectrometry and/or other methods.

Experiments on the digestion of a variety of soil and stream sediment samples show that a mixture of nitric acid and hydrochloric acid under pressure at $175^\circ$C for 1 hour generally produces a heavy metal leach comparable with that attained with fuming perchloric acid at atmospheric pressure. In addition, volatile sample constituents are not lost from the sealed tube as they are from conventional test-tubes, and are largely retained in the leachate for subsequent determination provided the tubes are allowed to cool prior to removing the cap.

Pressure digestions have capital investment and environmental advantages since no fumes escape from the sealed tubes. This eliminates the need for fume extraction systems and obviates the exhaustion of noxious gases to the atmosphere. For safety reasons, pressure digestions should be carried out in an isolated space, such as a cupboard, but no tube failures have been experienced to date. The procedure is amenable to the digestion of large batches of samples usually encountered in geochemical exploration programmes.
GEOCHEMICAL MAPPING OF CHARACTERISTIC ASSOCIATIONS OF ELEMENTS, PARTICULARLY OF HEAVY METALS, IN THE WESTERN HARZ MOUNTAINS

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For the purpose of geochemical prospecting for mineralizations which are not immediately accessible to investigation the dispersion and migration of elements is utilized. A further advantage accrues from the consideration of physiological activity of plants, which have the ability of absorbing and concentrating elements which have migrated to their vicinity. In this case, however, biogeochemical prospecting requires that certain conditions on constancy of plant species, etc. be fulfilled.

In the present investigation the relative concentration behaviour of two widespread plant species was studied in order to provide a basis for more extensive geochemical prospecting work. The Harz was selected as test area since it exhibits a highly varied geological set-up. Complications ensue from contaminations resulting from mining operations which have been conducted for centuries. In order to permit an assessment despite the difficult circumstances a multielement method was developed and refined to such an extent that the geochemical set-up could be resolved into distinguishable element associations. Of these, certain heavy-metal associations are conspicuous in the mineralized or contaminated zones on the basis of their elemental constitution; these permit conclusions about the type of mineralisation present. Since the resulting associations can be ascribed directly to the geochemical set-up a means is provided for recognizing and interpreting the so-called pseudoanomalies. For later prospecting work as well as for detailed investigations the resulting geochemical multielement maps furnish useful indications.
DETERMINATION OF HG-CONCENTRATIONS IN HARD ROCK AND SOIL BY FLAMELESS AAS
- A PROSPECTING METHOD FOR CONCEALED SULFIDE MINERALIZATION -

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The analytical equipment consists of
- small tube furnace
- flameless atomic absorption spectrometer (HGC-3/Scintrex Canada)
- computer integrator.

250 mg of the prepared sample (pulverized, sieve fraction < 0.112 mm) are rapidly heated up to 700°C. The Hg-vapour phase is carried into the sample cell of the spectrometer by a permanent nitrogen flow. The results are listed up and converted to "ppb" by the integrator.

The maximum analysis time is three minutes for one sample.

As an example, Hg-dispersions of two areas in hard rock and soil are shown:

- training area: Woodlawn stratabound ore deposit/Australia;
  Hg-concentrations in acid volcanic rocks.
  The Hg-dispersion related to ore body and tectonical structure of the rock unit.

- prospecting area: Menez Albot/France; Hg-concentrations in the soil.
  The Hg-dispersion relates to the striking of the geological unit, in which a stratabound sulfide mineralization is supposed to be found.
In a preliminary study, a variety of pigmented bacteria were tested for color changes in response to several trace metals. The red pigmentation of *Serratia Marcescens* was sensitive to the presence of copper in its growth medium. *Chromobacterium violaceum*, a strain of purple bacteria, when grown on plates containing from 1 to 12 ppm sodium molybdate, deposited an outwardly diffusing yellow substance, the color intensity of which was proportional to molybdenum concentration.

Since then, we have learned how to conduct such research in a more efficient way. By using one petri dish containing a concentration gradient of a given ion, and by the use of the Lederberg replica plating technique, seven species can be tested on three gradient plates in three motions of the hand. Information gathered formerly from 126 plates and requiring, say, five operations per plate, can now be gathered from three plates in three motions. We are thus in a position to rapidly assess the color sensitivity of standard strains of pigmented bacteria to a wide range of indicator trace metals. I thus hope to have substantial additional information about these bacteria in the next few months.

The end idea is to produce simple bioassay kits by means of which semiquantitative analyses can be conducted in remote areas without other chemicals or instrumentation. A good deal of basic research, however, is first required.
THE METHOD OF STUDYING INFORMATIVITY AND INDICATE PROPERTIES OF CHEMICAL ELEMENTS IN SEDIMENTARY PROCESSES

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The informativity of chemical elements may be evaluated by the formula:

\[ \Delta, \% = \frac{\bar{x}_{12} - \bar{x}_{11}}{\bar{x}_{\min}} \times 100 \% \]

(\( \bar{x}_{11}, \bar{x}_{12} \) - average content of an element in comparable assemblages 1 and 2).

If there is

\[ \sum \Delta > 3 (\Delta_s + \Delta_r) \]

(\( \Delta_s \) - standard deviation of sampling and preparing samples for analysis, \( \Delta_r \) - standard deviation of analytical determination and \( \sum \Delta \) - sum deviation) the element is informative or typomorphic.

The classification analysis of geological objects using typomorphic elements may be done by double system (1,0) relative to average of comparable assembles. For this purpose the averageweight (according to the number of samples) of Bul's functions was used.

The treatment of results for determination of a number of elements in mesozoic deposits of the Tadjik depression by X-ray fluorescence analysis permitted to find out typomorphic association of elements for different lithological types of rocks and their fractions. The typomorphic association of the elements reflected conditions of the sedimentation (composition of parent rocks, facial and climate conditions, migrate forms of the elements, etc). The error of the geochemical classification is 5%.
COPPER DISPERSION STUDIES IN CONTAMINATED LATOSOL FOR DEFINING A TARGET AREA OF BASEMETAL MINERALISATION IN EASTERN INDIA

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Old mine workings and waste dumps occur fairly continuously along the disposition of copper mineralisation in the Precambrian schistose rocks of the Iron-ore Group occurring in the Kesarpur East Block of Mayurbhani district, Orissa in Eastern India. Drilling has proved lensoid basemetal sulfide bodies of limited strike length, averaging 1.59 % Cu along the eastern limb of a synformal structure here. The test-area comprises the adjacent Dudhiasol West Block and Kesarpur West and Middle Block, forming the western limb of the synformal structure. Possible concealed mineralisation in this area is indicated by presence of detached old workings and waste dumps. Outcrops of schistose rocks, the host rocks of mineralisation, are scanty. Geochemical prospecting in the area suffers from contamination of soil from the old mine dumps. Since upper part of A horizon of the latosolic profile is most affected by surface contamination, restricted soil sampling was resorted to from a depth of 0.3 to 1.5 m either from B horizon soil matrix away from the area of contamination, or from fish-egg sized ferruginous nodular concretions close to the vicinity of old mining activity, for giving a reliable picture of mineralisation (Bose, 1975).

Geochemical anomaly maps for copper based on 180 samples from Dudhiasol West Block and 165 samples from Kesarpur West and Middle Block comprising B horizon soils and ferruginous concretions taken in grid pattern were prepared. Cumulative probability plots (after Sinclair, 1973) have indicated bimodal density distribution for the Dudhiasol West Block and polymodal complex distribution for the Kesarpur Block. While 68 % of the anomalous values in Dudhiasol West Block range from 310-435 ppm Cu, the identical percentage of values in the higher anomalous range in Kesarpur West and Middle Block lie between 820 and 1500 ppm Cu, suggesting poor concentration in former, and relatively higher concentration of copper in the latter block. Based on the upper threshold values of partitioned populations on the probability plots, priority areas for follow up exploration has been suggested. Geophysical prospecting carried out in these areas has broadly corroborated the geochemical data. Subsequent drilling (Mohanty, 1976) has substantiated much of the geochemical findings.
The important indexes of the informativity for various geochemical sampling objects (the definite fraction of the soil horizon, the local plant parts etc.) are the quantitative characteristics of the concentration curves in the system "the ore body or its residual litho-geochemical haloe (the ore) - the sampling object of the investigation". The main feature of these concentrational curves is the diapason value of the linear direct proportionality expressed in relative values - in contrast coefficients (CC) - the relationship of the anomalous values associated with the ore to the local geochemical background. The additional characteristics are: 1) the dispersion values of the separate variants as regards to the middling curves (the standard or the quadratic mean deviation - $\pm \sigma$ for the normal law of distribution and the standard multiplier - $\pm \sigma$ for the lognormal law of distribution of the investigated parameter); 2) the values of the linear correlation coefficients ($r$) for the investigated system; 3) the exposure probability of the ore ($P_0$) and nonore ($P_n$) anomalies.

Our 1973-1979 years experience of the exploration informativity investigations for 50-350 biological objects shows that it is the convenient for the exploration and prospecting practice to divide the investigated objects into four groups of the informativity: 1) the quantitatively informative group with the most wide direct linear diapason, $CC=300-3000$ and more; 2) the approximately quantitative informative group with the linear proportionality until $CC=30-300$, approximately 100 in geometric mean; 3) the qualitatively informative group with the linear proportionality until $CC=3-30$, approximately 10; 4) the group of the uninformative sampling objects in which the statistically trustworthy geochemical anomalies are absent over the ore bodies. According to the school system these four groups may be named as: 1) excellent, 2) good, 3) satisfactory and 4) unsatisfactory, useless (forbidden) for the use for exploration and prospecting of ores. The use of these quantitative characteristics for the concrete conditions make it possible to group various geochemical sampling objects. This grouping allows to choose the most informative sampling objects and to limit them by the optimal quantity. The values of $\pm \sigma$ or $\pm \sigma$ and $r$ give the quantitative information about the linear proportionality in the system "the ore - the sampling object".

The $P_0$ values for various geochemical sampling objects are determined as the relative quantity (4) of the anomalous points corresponding to ore mineralisation on the concentration curve for the every indicator element. $P_n$ is determined as the relative quantity (4) of the anomalous points corresponding to nonore diapason in rocks and their eluvium on the concentration curve.

The determination of $P_0$ and $P_n$ on the Malo-Oynogor molybdenum stockwerk and its neighbourhood showed that the more informative geochemical sampling objects for molybdenum are characterized by the values of $P_0=80-96$, $P_n=4-6$ % and the mean ratio of $P_0:P_n=16-19$. Qualitative informative objects of sampling have the values of $P_0=30-50$ %, $P_n=10-20$ % and $P_0:P_n=2,0-3,3$ and noninformative objects - $P_0=14-28$ %, $P_n=7-20$ and $P_0:P_n=1,2-2,0$. The use of the $P_0$ and $P_n$ values is effective for the exploration of ore stockworks in the conditions of eluvial landscapes and undisplaced...
THE APPLICABILITY OF THE CHI-SQUARE DISTRIBUTION TO GEOCHEMICAL EXPLORATION DATA

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The chi-square distribution appears to have useful application to the evaluation of geochemical exploration data in testing whether a given distribution differs significantly from an assumed theoretical distribution, and therefore warrants further analysis to identify anomalous values. The chi-square procedure can also be useful in setting threshold values at a predetermined level of confidence.

A computer program has been developed to generate a theoretical distribution which simulates the observed data and compares the observed data with the theoretical data using the chi-square statistic. The practical use of this procedure in the identification of anomalous values and in the setting of threshold values is illustrated through the interpretation of geochemical data for the Fox orebody in Manitoba.
AUTOMATIC COMPLEX PROCESSING OF GEOCHEMICAL INFORMATION USING COMPUTERS OF ES-SERIES

V. S. Voronov, G.L. Rubo, USSR

1. Complex treatment of geochemical information is fulfilled by integration of n-dimensioned geochemical field and comes to the calculation of some degrees, functionally connected with anisotropy value of geochemical anomalies. The differentiation degree of element composition of geochemical field shows the anisotropy.

2. The geochemical research data control system (GRDCS) was developed for geochemical exploration of mineral deposits. It consists of information retrieval control system (IRCS), complex of geochemical data processing programms and some service programms.

IRCS performs the following functions: input of primary data and the analytical data (documents) in the non-volatile memory, checking of input data; multistage data storing, correction, search and listing of data storage.

3. Input data is presented on the punchcards or punch tape in the International Telegraph Code (ITC-2).

The input action is accelerated by means of automatic analysers: the results of immediate spectrum measurements are being put directly into the data storage and calculation of elements concentrations is done by the computer (neutron-activation and x-ray radiometric analyses).

4. Raw geochemical information with the help of IRCS is divided into etalon file and work file.

5. Logical processing programms complex fulfills sequential processing of etalon files which is divided into K classes (subfiles). This complex defines the quality of analytical data and calculating values of the background level and abnormal concentrations for all N elements in all I rocks and also defines the set of L-distinctive and M optimal informative characteristics (elements) when comparing K classes. When finding non-linear decisive rules one teaches to distinguish K etalon classes.

The associations of elements are picked out of all the original L-elements and the hierarchial relation of associations is determined using the clusteranalysis method.

Comparing all K classes according to all L indications one can build a zonality sequence and determine a zonality coefficient taking into consideration L, M and hierarchies. The fields of pair vector relations in all K-classes are set up for the indications constituting the zonality coefficient.

The data of work files are also complex processing: the zonality coefficient is calculated as well as vector fields and the space points are classified for all the work files, ending with printing the plans using the plotter or the printer of computer.

6. The improvement of the system is connected with the introduction of some automatic analitical methods with the immediate input data into the data storage and with the expansion of the processing programms complex,
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