Fourth International Geochemical Exploration Symposium

London
17-20 April, 1972

Organized by
The Institution of Mining and Metallurgy
For The Association of Exploration Geochemists

Handbook

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(Founded in 1892 and Incorporated by Royal Charter in 1915)

44 Portland Place, London W1N 4BR

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GENERAL INFORMATION

All scheduled technical sessions will take place in the *Lecture Theatre,* Institution of Electrical Engineers, Savoy Place, London WC2. Registrants are asked to take their seats at least five minutes before the start of each session. The *Faraday Room*, adjacent to the Lecture Theatre, will be available for those who wish to carry discussion of particular papers beyond the scheduled times.

Morning coffee and afternoon tea will be served in the *Kelvin* and *Common Rooms*. Luncheon facilities are not available on the premises, but the street map given in this *Handbook* shows the location of nearby restaurants.

Smoking is not permitted in the Lecture Theatre, but registrants may smoke in any other Symposium rooms.

Cloakrooms are located in the basement.

The Symposium office (telephone 01–240 1871, extension 322) is located in the *Maxwell Room*, and all enquiries may be made there. IMM staff will be happy to give assistance.

Authors of papers to be presented at the technical sessions (or their deputies) will introduce their work briefly (maximum presentation time, 20 minutes). Intending contributors to the discussion of papers are asked to sit near the front of the hall, and to announce clearly their name and organization.

No epidiascope is available, but there are facilities for showing slides of all standard sizes. Slides, clearly numbered and bearing the speaker's name, should be handed to a member of the Institution staff on duty in the Lecture Theatre before the session begins. A blackboard and chalks are also provided.

A volume of proceedings, which will contain the papers presented at the Symposium, together with name and subject indexes, will be published in the period August–October, 1972. It will be available to registrants at the special reduced price of £7·50 ($U.S. 20.00).

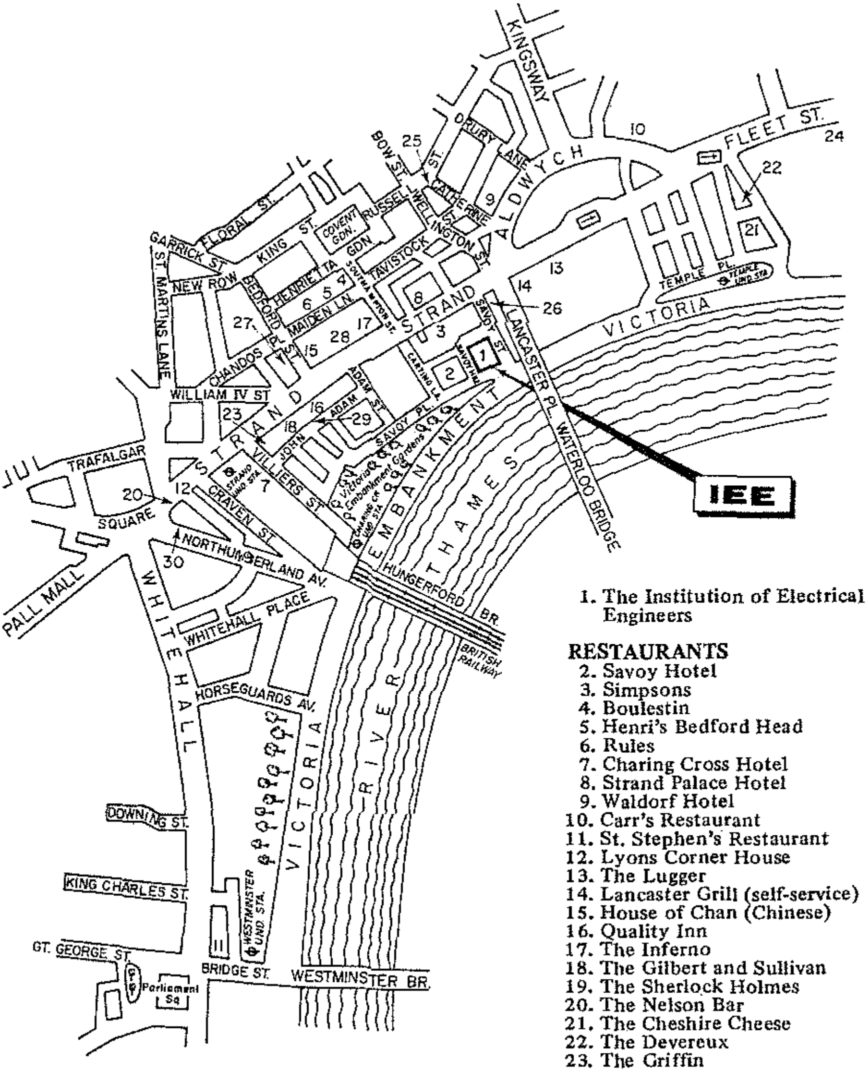
SOCIAL EVENTS

All registrants, and their wives, are invited to attend the Welcoming Reception (to be held at the Waldorf Hotel, Aldwych, London WC2, on Monday, 17 April, 1972, 6.30 p.m.–7.30 p.m.) and the Reception arranged by HM Government (to be held at Lancaster House, Pall Mall, London SW1, on Wednesday, 19 April, 1972, 6.30 p.m.–9.00 p.m.).

On Thursday, 20 April, 1972, an informal dinner-dance will be held at Quaglino's, Bury Street, London SW1, at 7.30 p.m. (for 8.00 p.m.). Tickets (price, £5·00 each, exclusive of pre-dinner drinks and wine) are available from the Institution of Mining and Metallurgy.

TOURS

Field visits have been arranged to Cornwall and Devon, Scotland and Germany. Full details will be made available to registrants who have indicated their intention to participate in the visits. Details of the one-day short visits to Government and University Departments on Friday, 21 April, 1972, will be available on registration.



1. The Institution of Electrical Engineers

RESTAURANTS

2. Savoy Hotel
3. Simpsons
4. Boulestin
5. Henri's Bedford Head
6. Rules
7. Charing Cross Hotel
8. Strand Palace Hotel
9. Waldorf Hotel
10. Carr's Restaurant
11. St. Stephen's Restaurant
12. Lyons Corner House
13. The Lugger
14. Lancaster Grill (self-service)
15. House of Chan (Chinese)
16. Quality Inn
17. The Inferno
18. The Gilbert and Sullivan
19. The Sherlock Holmes
20. The Nelson Bar
21. The Cheshire Cheese
22. The Devereux
23. The Griffin

BAR/RESTAURANTS

24. Ye Old Cock Tavern
25. The Opera Tavern
26. The Savoy Tavern
27. The Bodega Bar
28. The Nell Gwynn
29. The George
30. Shorts Bier Keller

LADIES' PROGRAMME

Monday, 17 April
10.00 a.m.–4.00 p.m.
Ladies' Information Desk: MINA members will be at the Ladies' Tours desk at the Institution of Electrical Engineers to advise on tours, shopping, museums, etc.

Tuesday, 18 April
Tour 18A 9.30 a.m.–12.30 p.m. London drive
A coach drive through London's West End and Hyde Park, including a guided visit to Westminster Abbey and the Changing of the Guard.

Tour 18B 9.45 a.m.–3.45 p.m. Brighton
Assemble at barrier to platform 13, Victoria Station, by 9.45 a.m. A coach will meet the London train and drive around Brighton, with a guide, finishing with a guided tour of the Prince Regent's seaside palace, the Pavilion. Luncheon at the Grand Hotel (cost included in ticket).

Wednesday, 19 April
Tour 19B 9.00 a.m.–3.30 p.m. (approx.) Knole House, Sevenoaks
After a guided tour of this Jacobean manor house, the coach will drive to Westerham, an interesting old town with associations with General Wolfe and Sir Winston Churchill. Luncheon at the George and Dragon Hotel.

Thursday, 20 April
Tour 20A 9.30 a.m.–12.30 p.m.
Drive around City of London, with short guided tours of St Paul's Cathedral and the Guildhall.

Tour 20B 9.30 a.m.–1.00 p.m. (approx.)
Visit to Hampton Court Palace with guide. Coffee at nearby sixteenth-century inn, The Mitre.

All tours will depart from the Institution of Electrical Engineers, except for the Brighton tour, which departs from Victoria Station (platform 13). Members of MINA, wearing blue and white rosettes, will escort all tours and will be very pleased to look after visiting wives in any way they can.

London's main Museums and Art Galleries

Usual opening times are 10.00 a.m. to 5.00 p.m.
British Museum, Museum Street, WC1. Current special exhibition:

'Treasures of Tutankhamun' on loan from Egypt in aid of UNESCO fund to save the Temples of Philae. Admission 50p. Open 10 a.m.–9.00 p.m.

London Museum, Kensington Palace, Kensington Gardens, W8. A collection illustrating the history and social life of London from the earliest times. Interesting collections of glass, jewellery, Chelsea and Bone pottery, Royal dresses, toys, etc.

Queen's Gallery, Buckingham Palace Road, SW1. The current exhibition from the Queen's paintings is: 'The Dutch Paintings'. Open 11.00 a.m. to 5.00 p.m., except Mondays.

Victoria and Albert Museum, Brompton Road, SW7. Museum of fine and applied art from all countries. The collection of British art contains furniture, silver, water colours, miniatures and the best collection of Constable's paintings. There is an unrivalled collection of French and Italian furniture. Visitors should note the delightful new display on the ground floor of eighteenth-century continental furniture and porcelain.

The Science, Geological and Natural History museums are opposite the Victoria and Albert Museum.

The Wallace Collection, Manchester Square, W1. It houses a once private collection of paintings, furniture, porcelain and a fine collection of armour.

The main public art galleries are the National Gallery and the National Portrait Gallery, both in Trafalgar Square, and the Tate Gallery and the Hayward Gallery, Millbank, SW1.

ANNUAL GENERAL MEETING OF THE ASSOCIATION OF EXPLORATION GEOCHEMISTS

The annual general meeting of the Association of Exploration Geochemists will be held at the Waldorf Hotel, Suites II and III, Aldwych, London WC2, on Tuesday, 18 April, 1972, at 8.00 p.m.

SYMPOSIUM PROGRAMME

Monday, 17 April, 1972

10.00 a.m.–1.30 p.m. Registration

2.00 p.m.–3.30 p.m. Official opening by Sir John Eden, Bt., M.P., Minister for Industry, Department of Trade and Industry, introductory remarks by Dr. J. A. Hansuld, President of the Association of Exploration Geochemists, and Ninth Sir Julius Wernher Memorial Lecture ('Basic and applied geochemists in search of ore') by Professor K. C. Dunham, F.R.S., Director of the Institute of Geological Sciences, London, and Emeritus Professor of Geology, University of Durham

4.00 p.m.–5.30 p.m. Session 1

Chairman: Professor J. S. Webb

G. B. Gott and J. M. Botbol: Zoning of major and minor metals in the Coeur d'Alene district, Idaho, U.S.A.

Sualbel

O. P. Razgonov: Geochemical zoning of copper–nickel mineralization and its endogenous haloes, with reference to the ore deposits of the Norilsk Group

D. M. Hausen, J. W. Ahlrichs and J. R. Odekirk: Application of sulphur and nickel analyses to geochemical prospecting

Tuesday, 18 April, 1972

9.00 a.m.–10.30 a.m. Session 2

Chairmen: Dr. H. E. Hawkes and Professor G. H. Friedrich (Sessions 2 and 3)

A. S. Dass, R. W. Boyle and W. M. Tupper: Endogenic haloes of the native silver deposits, Cobalt, Ontario, Canada

L. V. Tauson and V. D. Kozlov: Distribution and ratios of trace-element concentrations as a means of estimating the ore potential of granitic intrusions

P. H. Davenport and I. Nichol: Bedrock geochemistry as a guide to areas of base-metal potential in volcano-sedimentary belts of the Canadian Shield

11.00 a.m.–12.30 p.m. Session 3

R. J. Watling, G. R. Davis and W. T. Meyer: Identification of trace mercury compounds in rocks as a guide to sulphide mineralization at Keel, Eire

E. C. Smith and G. R. Webber: Nature of mercury anomalies at the New Calumet Mines area, Quebec, Canada

G. J. S. Govett: Differential secondary dispersion in transported soils and post-mineralization rocks: an electrochemical interpretation

2.00 p.m.–3.30 p.m. Session 4

Chairmen: Dr. R. W. Boyle and Dr. A. Kvalheim (Sessions 4 and 5)

R. E. Learned and R. Boissen: Gold – a useful pathfinder element for porphyry copper exploration in Puerto Rico

M. B. Mehrtens, J. S. Tooms and A. G. Troup: Some aspects of geochemical dispersion from base-metal mineralization within glaciated terrain in Norway, North Wales and British Columbia, Canada

U. McL. Michie, M. J. Gallagher and A. Simpson: Detection of concealed mineralization in northern Scotland

4.00 p.m.–5.30 p.m. Session 5

R. J. Allan, E. M. Cameron and C. C. Durham: Low sample density limnic geochemistry – a new technique for reconnaissance geochemical exploration within the Canadian Shield

I. R. Jonasson and R. J. Allan: Snow – a sampling medium in hydrogeochemical prospecting

Scratch

A. K. Banerjee, A. Z. Gedeon and J. C. Inasi: Problems of mineral exploration in the white sand covered Precambrian Shield of Guyana, South America

Wednesday, 19 April, 1972

9.00 a.m.–10.30 a.m. Session 6

Chairmen: Professor L. V. Tauson and Professor I. Nichol (Sessions 6 and 7)

L. N. Ovchinnikov, V. N. Sokolov, A. I. Fridman and I. N. Yanitskii: Gaseous geochemical methods of structural mapping and search for ore deposits

Scratched

M. M. Elynson: Gaseous surveys in prospecting for sulphide ore deposits

A. N. Eremeev, V. A. Sokolov, A. P. Solovov and I. N. Yanitskii: Application of helium surveying to structural mapping and ore deposit forecasting

11.00 a.m.–12.30 p.m. Session 7

R. Holmes and J. S. Tooms: Dispersion from a submarine exhalative orebody

R. G. Garrett: Regional geochemical study of Cretaceous acidic rocks in the northern Canadian Cordillera as a tool for broad mineral reconnaissance

W. R. Hesp and D. Rigby: Cluster analysis of rocks in the New England igneous complex, New South Wales, Australia

2.00 p.m.–3.30 p.m. Session 8

Chairmen: Professor F. C. Jaffé and R. L. Erickson (Sessions 8 and 9)

R. C. Obial and C. H. James: Use of cluster analysis in geochemical prospecting, with particular reference to southern Derbyshire, England

I. Nichol and J. O. Larsson: Comparison of multivariate techniques in the interpretation of geochemical data

R. J. Howarth: Pattern recognition problem in applied geochemistry

4.00 p.m.–5.30 p.m.

Session 9

R. I. Dubov: A statistical approach to the classification of geochemical anomalies

B. Bølviken and R. Sinding-Larsen: Sample error and other criteria of consequence for the interpretation of stream-sediment data

To #6

P. L. Lowenstein and R. J. Howarth: Automated colour-mapping of three-component systems and its application to regional geochemical reconnaissance

M. Dall'Aglio and F. Tonani: Correlations between sulphate and other constituents as an aid in hydrogeochemical exploration for sulphide deposits

Thursday, 20 April, 1972

9.00 a.m.–10.30 a.m.

Session 10

Chairmen: R. E. Stanton and Professor M. Dall'Aglio (Sessions 10 and 11)

J. C. Robbins: Zeeman spectrometer for the measurement of atmospheric mercury vapour

W. T. Meyer and Y. C. Y. Lam Shang Leen: Microwave-induced argon plasma emission system for geochemical trace analysis

C. L. Sainsbury: New system of geologic mapping and geochemical sampling by light aircraft

11.00 a.m.–12.30 p.m.

Session 11

H. Wollenberg: Fission-track radiography of uranium and thorium in radioactive minerals

S. H. U. Bowie, P. R. Simpson and C. M. Rice: Application of Lexan plastic fission-track registration method to geochemical exploration

Jane Plant and R. G. Coleman: Application of neutron activation analysis to the evaluation of placer gold concentrations

A. E. Hubert and H. W. Lakin: Atomic absorption determination of thallium and indium in geologic materials

2.00 p.m.–3.30 p.m. Session 12
Chairmen: Dr. S. H. U. Bowie and H. W. Lakin
(Sessions 12 and 13)

R. C. Leake and J. W. Aucott: Geochemical mapping and prospecting by use of rapid automatic X-ray fluorescence analysis of panned concentrates

H. Kunzendorf: Non-destructive determination of metals in rocks by radioisotope X-ray fluorescence instrumentation

B. Bølviken, Ø. Logn, A. Breen and O. Uddu: Instrument for *in situ* measurements of pH, Eh and self-potential in diamond drill holes

4.00 p.m.–5.30 p.m. Session 13
W. L. Plüger and G. H. Friedrich:
Determination of total and cold-extractable fluoride in soils and stream sediments with an ion-sensitive fluoride electrode

S. E. Kesler and J. C. Van Loon: Analysis of water-extractable chloride in rocks by use of a selective ion electrode

G. H. Friedrich, W. L. Plüger, E. F. Hilmer and I. Abu-Abed: Flameless atomic absorption and ion-sensitive electrodes as analytical tools in copper exploration

SYNOPSES

Given below are synopses of the papers which are to be presented at the technical sessions.

Low sample density limnic geochemistry – a new technique for reconnaissance geochemical exploration within the Canadian Shield

R. J. Allan, E. M. Cameron and C. C. Durham
Geological Survey of Canada, Ottawa, Ontario, Canada

Much of the Canadian Shield can be characterized as country of low relief dotted with abundant lakes. Although some areas are covered by thick glacial deposits, which partly mask the geochemical expression of the underlying rocks, most of the Shield is bare rock or is covered by thin Pleistocene or recent drift. This terrain is quite suitable for certain geochemical methods of exploration. The low relief has produced an often complex drainage system, within which inorganic sediments are irregularly developed. Thus, conventional methods of reconnaissance geochemical exploration, by use of stream-sediment sampling, are impractical for most parts of the Shield. An obvious alternative is to sample lake waters and sediments – limnic methods of geochemical exploration.

Because of the difficulty of travelling across typical Shield terrain, geochemical sampling must be carried out by use of aircraft – generally helicopters. Sampling costs are therefore high and to cover large areas economically a wide sampling interval must be employed.

Sampling and analysis of lake waters has been carried out previously in the Coppermine area, N.W.T., for copper; for mercury in the Kaminak Lake area, N.W.T.; and for uranium within the Beaverlodge district of Saskatchewan. In all of these cases sampling at site densities as low as 1 sample per 10 square miles gave positive results. At Coppermine this density outlined a 200 square mile zone of copper mineralization in the Coppermine basalts. At Beaverlodge the regional pattern of uranium distribution at 1 sample per 10 square miles is essentially similar to that at 1 per square mile. Within the Kaminak Lake area the mercury in water distribution at 1 sample per 10 square miles correlates well with the known distribution of bedrock types underlying glacial drift. In addition to the study of lake waters at Coppermine, lake sediments were collected and analysed from the same 1500 square mile area. These samples successfully outlined the areas of anomalous mineralization at a 1 per 10 square mile sample density. The sediments of this area give far superior results: in part, this is due to the difficulty of analysing indicator elements at the low concentrations present in lake waters, and possible variations caused by spring runoff.

Concurrently with the lake water and sediment sampling programme at Coppermine, a geochemical study of the rocks of the area was made. This showed that parts of the Coppermine basalts contained widely distributed minor copper mineralization or 'micro-deposits'. It was suggested that the Cu deposits and micro-deposits of the Coppermine basalts are genetically related, being the extreme right tail of a more general frequency distribution of copper mineralization within the basalts.

By combining the two sets of data – those for the rocks and those for the lake sediments and waters – it was apparent that the enrichment of copper in the limnic materials throughout the 200 square mile anomalous area was not due to copper derived from known copper ore occurrences. Rather, it was caused by copper derived from copper sulphides widely distributed through the rocks of the anomalous area. Thus, the successful application of reconnaissance geochemical sampling programmes at a density of 1 sample per 10 square miles depends on there being a suitable dispersion through the rock unit of the economic trace element sought. This dispersion should be in the same mineralogical form as the element is expected to take in economic ore occurrences.

Prior to an extensive limnic geochemical survey planned for parts of the Bear and Slave Provinces of the Canadian Shield in 1972, a combined lake sediment and water and rock geochemical study was carried out during the summer of 1971 in a number of areas within these geological provinces. The purpose of the study was to establish the most generally useful indicator elements for a variety of mineral deposits and the types of deposits whose associated zones of mineralization could be picked up at a coarse sampling density. Eight areas were chosen and averaged 200 square miles in size: seven contained known or suspected mineral occurrences of varied type and one contained no known mineralization. The areas were chosen to represent other varied conditions: north and south of the treeline; discontinuous and continuous permafrost; and high and low relief.

The results of this work indicate that water methods are best used only to confirm sediment methods because the background levels of most interesting indicator elements in natural waters are often below present analytical detection limits. Future efforts in our laboratories to lower detection limits will increase the effectiveness of water sampling for exploration in the Shield. This is important because waters may be collected more readily, and, hence, more cheaply than sediment samples.

The sediment data successfully outlined anomalous belts around known economic deposits; again, this appears to be caused by the micro-deposit population associated with them. The size of the anomalous areas appears to be quite suitable for their discovery on a coarse sampling grid. For instance, around two known greenstone belt sulphide deposits of copper–zinc and lead–zinc–silver there were anomalous zones of 40 and 25 square miles, respectively, given by a number of different indicator elements. The range in trace-element levels defining an anomalous zone relative to background variations caused by different rock types is small. Thus, the interpretation of large-scale surveys of this type can be critical. Anomalous zones of element distribution in lake sediments were also found in areas so far only suspected to contain economic mineralization.

For the Bear–Slave Provinces limnic methods of reconnaissance geochemical exploration are effective for outlining zones of higher than background metal content. These areas, which are likely to be associated with mineralization, serve as foci for more detailed mineral exploration. At a cost of approximately $7.00 per square mile the methods are attractively economic. There is every possibility that the limnic method can be applied equally well to most areas of the Canadian Shield.

Problems of mineral exploration in the white sand covered Precambrian Shield of Guyana, South America

A. K. Banerjee, A. Z. Gedeon and J. C. Inasi
Guyana Geological Survey, Georgetown, Guyana (United Nations Technical Assistance Advisers)

The problems of mineral exploration in Guyana in areas covered by white sand of late Pliocene–Pleistocene age have received considerable attention during recent years. This cover of transported material forms the margin of the coastal plains and extends southwards to a distance of more than 100 miles from the Atlantic Ocean coast, the thickness varying from 50 to 200 ft. Northeastwards, the thickness increases to more than 6000 ft, and it has been divided into several sub-units by clay horizons. The total area covered by the white sand series amounts to more than 17 000 square miles – which is about 21 % of Guyana's land area. Of this, the areas with relatively thin cover, mostly towards the south and west, are of immediate interest from the exploration viewpoint.

Bauxite is the most important mineral deposit under the barren transported material. Apart from the bauxitic materials, the white sand cover often conceals the strike continuity of known mineralized belts of the Precambrian Shield and, possibly, unknown mineralized ground. Biogeochemical studies in such areas with Cu–Au and Cu–Mo mineralization have provided interesting results in recent years. With 50–100 ft of cover of barren sand and clay soil sampling and hand augering serve very little purpose. On the other hand, in several cases, wood ash samples from the tall trees of the rain forests of Guyana have clearly reflected the nature of the bedrock mineralization beneath the cover of white sand.

One such tree, locally known as *Baromalli*,* has been used most extensively because of its deep-penetrating tap root. These trees reach heights of 100 ft or more and their 'sampling depth' is believed to be commensurable. The samples were collected from 5 ft above the soil by a ¾-in hand auger by drilling across the tree trunk and collecting the wood shavings in a plastic bag. The whole wood sample was dry-ashed at 400°C, homogenized and analysed spectrographically. The semi-quantitative concentrations were established by visual comparative estimation.

Samples were collected from areas of residual soil with known mineralization in the bedrock below, from areas with no mineralization and from areas with white sand cover, but in strike continuity of the known mineralized shear zone. The wood ash from the different areas reflected well the nature of mineralization in the residual soil and in the bedrock below. In a few such cases the biogeochemical findings were corroborated by ground geophysical data. The final test, by diamond drilling, has been carried out in some cases, but remaining areas await further investigation.

In areas of known molybdenum mineralization the Mo iso-concentration lines for wood ash and residual soil showed a close coincidence in the high values, and, similarly, low background values were reflected in both. Copper values presented a higher degree of scatter, and a somewhat subdued reflection in the higher ranges of values in wood ash was also observed.

In one case drilling in a white sand covered area showing strong anomalous

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**Bombacaceae: Catostemma commune, C. fragrans and C. Altsoni.*

Mo values in the wood ash failed to locate anomalous values in the residual soil or in the bedrock below the anomalous zone. The possible local behaviour of the *Baromalli* tree as a concentrator plant was studied, and extensive groundwater studies of the region were conducted. The possibility of the existence of deep-seated mineralization remains to be explored.

The available data suggest that for a successful exploration programme in the white sand covered areas of Guyana, especially with a relatively thin cover of sand, biogeochemical sampling could play an important role, together with the ground geophysical survey and the extrapolation of geological information from adjacent areas. The selection of more than one species of plant is desirable. Groundwater movement may be influenced greatly by the interbanded clay horizons of the white sand series.

It is hoped that with a better understanding of the various factors which influence the concentration of various elements in different plants in the tropical rain forest of Guyana and drill-hole data in remaining target areas mineral exploration activities in the extensive white sand covered areas of the Precambrian Guyana Shield will be advanced.

Instrument for *in situ* measurements of pH, Eh and self-potential in diamond drill holes

B. Bølviken, Ø. Logn, A. Breen and O. Uddu
Norges Geologiske Undersøkelse, Trondheim, Norway

At the Geological Survey of Norway an instrument has been developed for *in situ* measurements of the pH and Eh of groundwater in 46-mm diamond drill holes. The instrument, which can also be used for self-potential measurements, consists of a glass electrode, a platinum electrode and an ordinary self-potential electrode ($Cu/CuSO_4$) as reference electrode. The electrodes are mounted in a Perspex support, which is connected to a brass tube containing a small amplifier with high input resistance and low bias current. All electrodes have watertight electrical connexions to voltmeters at the surface, the glass electrode via the amplifier. The external pressure acting on the electrodes is compensated for by means of internal silicon oil separated from the exterior by a rubber membrane. If wanted, an auxiliary electrode of the same type as the reference electrode in the drill-hole can be placed in the top soil at the surface.

The instrument enables the following parameters to be recorded in the drill-hole: pH – by measuring the amplified voltage between the reference electrode and the glass electrode; Eh – by measuring the voltage between the reference electrode and the Pt electrode; and SP (self-potential) – by measuring the voltage between the reference electrode in the drill-hole and the electrode at the surface.

For calibration, the electrode housing is filled with standard buffer solution and sealed with a plastic tape, which acts as a membrane, and is then lowered into the drill-hole. The instrument has been tried in drill-holes at Joma, Nord-Trøndelag county, Norway. This is a copper- and zinc-containing massive pyrite deposit in metamorphosed volcanics with 5–10% $CaCO_3$. The mine is under development.

Results of preliminary measurements have shown (1) that the instrument can be used down to at least 350 m (approximately 35 atm); (2) the pH of the groundwaters in the drill-holes measured was found to be 6·0–9·5, depending on mineralization and depth: pH can vary by as much as 1 unit within a vertical distance of about 1 m; the reproducibility of the pH measurements appears to be within 0·1 pH unit; (3) Eh values between 0 and 560 mV were recorded; Eh measurements can be troublesome due to poisoning of the Pt electrode; and (4) SP readings clearly indicate both massive and impregnation types of pyritic ore; there appears to be a relationship between pH, Eh and SP.

It is hoped that the instrument can provide data which may lead to a better understanding of the chemical processes in groundwater – particularly the electrochemical processes in the vicinity of ore deposits.

Sample error and other criteria of consequence for the interpretation of stream-sediment data

B. Bølviken and R. Sinding-Larsen
Norges Geologiske Undersøkelse, Trondheim, Norway

As part of a lead exploration project in southern Norway duplicate stream-sediment samples were collected from some 3000 sample sites near roads over an area of approximately 7000 km^2. The -80-mesh material of each of the 6000 samples was analysed for HNO_3-soluble Pb, Zn, Ni, Co, Cu, Mn, Fe and Ag by atomic absorption spectrometry.

By duplicate sampling an estimation of statistical parameters for the metal distribution within each sample site was made possible. As an estimate of the metal content at each sample site the arithmetic mean of each pair of analyses was used. The sample error within each site was defined as the standard deviation of the log-transformed concentrations.

Both the metal content and the sample error have been mapped. The statistical distribution of these parameters has been investigated, as well as their relationships with each other and their dependency on certain environmental factors. The average sample error varies within the sub-groups investigated and, moreover, the error may depend on the corresponding metal concentration and Mn and Fe contents.

The sample error has been compared with the overall data variability (F test) to obtain a measurement of the reliability of the geochemical pattern. The F test was carried out on all the data in one batch, and on sub-groups of data. Sub-groups of single samples yield levels of significance which vary from more than 99·9% down to nearly 50%.

For Pb the duplicate sampling is shown to be adequate. This is illustrated by an example of a lead anomaly which could have been overlooked if just one sample had been taken from each site, since only one of the duplicates showed an anomalous value. The follow-up of this anomaly led to the discovery of a Pb deposit. With the selected density of sample sites the collection of two or more samples at each site is justified.

Statistical treatment is essential for the evaluation of data from a stream-sediment survey with low density sampling sites. The sampling design should be chosen carefully, and knowledge of the reliability of the analytical methods at different concentrations is important.

Application of Lexan plastic fission-track registration method to geochemical exploartion

S. H. U. Bowie, P. R. Simpson and C. M. Rice
Institute of Geological Sciences, London

The application of the Lexan plastic fission-track method to geochemical exploration for uranium is evaluated in relation to the mineralization associated with sediments of the Orcadian cuvette and acid plutons in the underlying basement. An example of the latter includes the Helmsdale granite. Uranium in basal arkose derived from the Helmsdale granite and in flagstones higher in the sedimentary sequence is associated with secondary iron oxides, clay, organic and phosphatic phases. Primary uranium-bearing minerals, such as apatite and fluorite, also occur in the arkose. Some redistribution of uranium has taken place by the action of groundwater. The technique is also applied to a study of the uranium in the mineralized Dalbeattie and Cornwall granite and compared with granites from Aberdeenshire with which no uranium mineralization is known to be associated.

The method depends on the production of fission fragments of ^{235}U as a result of thermal neutron bombardment. Polished thin sections with a maximum dimension of 3 cm × 2·5 cm are prepared from rock or mineral specimens. These are overlain by Lexan polycarbonate film and assembled in batches of about 20, which are placed together with suitable standards and spacers in a screw-top aluminium container (maximum diameter, 4 cm; approximate length, 9 cm). The samples are irradiated at the Herald reactor, AWRE, Aldermaston, in a thermal neutron flux and receive a calibrated dose ranging from a minimum of 10^{15} to a maximum of 10^{17} n cm^{-2}, which is the highest dose compatible with the recovery of the Lexan plastic film. The samples are stored for approximately three weeks until the activity of ^{24}Na in the glass slide falls to a safe level for handling. The Lexan film is then etched in NaOH, and the induced fission-track distribution is compared with the sample. Quantitative results are obtained if the neutron dose is adjusted to generate an undersaturated track density for the sample which is compared with a standard of similar concentration exposed to the same neutron dose. The maximum dose is applied routinely to obtain rock texture 'prints' in the more general application of the technique to the study of uranium associations in rocks.

The main advantages of the method are high specificity for uranium and the low detection limit for uranium uniformly distributed over unit area (0·05 ppm). This is combined with a matching accuracy between print and rock ranging from 10 to 100 μm. No special facilities are required in the laboratory and the irradiation cost per section is about 50p. The technique provides information on the distribution and concentration of uranium which is not available by any other method.

The assessment of different acid igneous rocks by this method is discussed with particular reference to the likelihood of associated uranium mineralization. Factors which control the redistribution of uranium in erosion and redeposition of uranium-enriched granite as arkose are studied to evaluate the possibility of significant uranium concentration. Low levels of uranium distribution in other sandstone-type occurrences in the middle Old Red Sandstone of the Orcadian cuvette are also examined.

Correlations between sulphate and other constituents as an aid in hydrogeochemical exploration for sulphide deposits

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A hydrogeochemical reconnaissance survey for uranium has been carried out, 949 stream samples being collected throughout the Tuscany region (approximate area, 20000 km^2). The samples were analysed for Ca, Mg, Na, K, HCO_3, SO_4, Cl and SiO_2. The automatic processing of the data obtained, based on simple and multiple correlations and regression analysis, has shown that it is possible to achieve a good approximation in discriminating between the SO_4 ion in water that originates from the oxidation of sulphide and the part of the SO_4 ion that originates from the dissolution of gypsum. The aureoles are sufficiently wide to be detected by large-scale exploration – 1 sample per 20 km^2.

Thermal springs also yield in stream waters aureoles of the same kind. Study of the distribution of certain indicator elements enables the two types of haloes mentioned to be distinguished.

Endogenic haloes of the native silver deposits, Cobalt, Ontario, Canada

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The economic mineral deposits of the Cobalt area are extremely rich silver-bearing veins cutting Cobalt Series sediments, Nipissing diabase, Keewatin greenstone and associated rocks. The mineral assemblage of the veins is complex, consisting of carbonates, native silver and a great variety of nickel–cobalt arsenides.

Wallrock alteration haloes enclosing the native silver–nickel–cobalt arsenide veins are well developed in the Nipissing diabase, Keewatin greenstone, rhyolite porphyry and lamprophyre, but are much less pronounced in the Cobalt Series sediments. Chloritization, sericitization, carbonatization, albitization, pyritization and arsenopyritization took place in the wallrocks adjacent to the veins. H_2O, CO_2 and Fe_2O_3 increase and SiO_2 decreases in the wallrocks towards the veins. The iron content in chlorite increases, the sodium content of plagioclase increases and the calcium content of plagioclase decreases towards the veins.

The primary dispersion pattern of trace elements is coincident with the zones of vein clusters. The dispersion of Ag, As, Ni, Co, Sb, Mn and Hg outward from the vein in the Cobalt Series sediments is broad, and veins may be indicated as far as 80–100 ft away by these elements. The dispersion pattern in the Keewatin greenstone can be traced 50–60 ft outward from the vein. Haloes are very much restricted in the Nipissing diabase. The dispersion patterns of Cu, Pb and Zn are also broad and coincident with the veins.

A close association of silver–nickel–cobalt ores with the Keewatin sedimentary interflows and certain volcanic flows has been recognized. Furthermore, the Keewatin greenstone and interflow sediments contain higher than average background amounts of Ag, As, Sb, Ni, Co, Hg, Cu, Pb and Zn. These rock units may be the source of the ore constituents, the younger Nipissing diabase serving as an energy source for their mobilization. Thus, the most favourable prospecting localities may be restricted to areas where the Keewatin interflows adjoin the Nipissing diabase, or where they underlie the Cobalt sediments adjacent to the diabase. The pronounced trace-element dispersion patterns in the wallrocks can be used to locate the narrow silver veins in the rock units.

Bedrock geochemistry as a guide to areas of base-metal potential in volcano-sedimentary belts of the Canadian Shield

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In 1969 a high-grade Zn–Cu–Ag orebody was discovered by Selco Exploration in the Birch–Uchi Lakes Belt of northwest Ontario within the Superior Province of the Canadian Shield. The orebody was one of a number of mineral deposits which gave rise to geophysical anomalies, but, to date, no other deposit of economic importance has been located in the area. The object of this study was to determine whether geochemical techniques might assist in determining areas of potential economic mineralization, and thus provide a basis for the selection of geophysical anomalies for detailed investigation.

The volcanic rocks of this belt belong to the basalt–andesite–dacite–rhyolite association, characterized by the calc-alkaline trend, and relate to three cycles of volcanic activity. The belt is fairly typical of the Archaean volcano-sedimentary belts of the Canadian Shield. The character of the sulphide deposits spatially associated with the acid volcanic rocks is consistent with their formation by volcanic exhalative processes, as has been suggested for similar types of deposit in other Archaean volcanic belts. This mode of formation would imply that these deposits represent an integral part of the suite of volcanic rocks comprising the volcanic cycle within which they occur. Differences in the metal associations of the deposits, therefore, may be reflected in trace-element variations in the associated volcanic rocks.

To test this hypothesis a portion of the Birch–Uchi Lakes Belt, some 70 square miles in extent, was selected. The nature of the mineral deposits and their geological setting are quite well known and, thus, it provides a suitable study area. It contains portions of two volcanic cycles, in both of which sulphide deposits are developed within the upper acid volcanic units or within immediately superjacent sediments.

Samples of drill core from several sulphide deposits in each cycle and some 300 bedrock samples were collected in the area, representing the full range of volcanic rock types present, and were analysed for 20 selected major and trace elements.

The deposits from the cycle containing the Zn–Cu–Ag orebody are characterized by their relative enrichment in Zn, Pb and Sn and relative depletion in Co and Ni as compared with deposits from the other cycle. The bedrock data were classified into basic, intermediate and acid volcanic groups on the basis of their silica content. For each group the distributions of the elements from one cycle were compared statistically with the distributions of the corresponding elements from the other cycle by use of the non-parametric Mann–Whitney *U* test. The compositions of the basic volcanic rocks in both cycles are fairly similar. Despite considerable overlap in ranges of metal concentration in similar rocks from different cycles, a number of statistically significant differences are apparent between the distributions of certain elements in both the acid and intermediate groups of the two cycles. Of particular interest in relation to the differences in the relative metal content between the deposits of the two cycles is the fact that the acid and intermediate rocks of the volcanic cycle containing the orebody and other zinc-rich deposits are significantly higher in zinc and lower in cobalt and nickel than the corresponding rock types of the other cycle. Lead and tin in all the volcanic rocks were below the detection limits of the analytical methods used. Thus, it appears that the differences observed between the relative metal content of the two types of deposit are associated with similar differences between the contents of certain trace elements in the volcanic host rocks.

In view of the close similarities which exist between many Archaean volcano-sedimentary belts it is suggested that by examination of the trace-element distributions present in the constituent volcanic cycles of a similar belt it may be possible to determine which of the cycles is likely to contain zinc deposits.

A statistical approach to the classification of geochemical anomalies

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Many anomalies discovered as a result of geochemical exploration are subsequently shown to be indirectly connected with non-commercial material. The classification of anomalies and the selection of those worthy of further treatment, and the search for their origin, are still based to a great extent on subjective reasoning. Classification and interpretation are especially hampered when contradictory features are present.

Quantitative comparisons of these features by use of mathematics have met with some success, but examples abound of the failure of mathematical techniques to yield economic results. Geochemical exploration experience suggests that two paths should be followed with regard to the classification and interpretation of anomalies.

(1) Current methods of classification tend to be based on purely statistical propositions as estimates of the probability of association with the objects sought. The risk of correct and incorrect conclusions is expressed also in terms of estimates of probability. Many mathematical methods do limit themselves to considerations of a small number of anomalous features in

view of the calculation difficulties associated with large numbers of features.

It is proposed that the anomalies should be separated into classes such that the expectation of profit is at a maximum. If the cost of proving holes is small, and the expected profit in the event of ore being discovered is great, then the anomaly must be taken into the ore class even if the probability of such an association is relatively small.

The algorithm based on the well known formulae of bias is worked out for such a classification: it offers the possibility of considering economic conditions in addition to many other aspects.

(2) Exposure of the objects sought with the help of geochemical anomalies is possible in many instances only by consideration of the physical nature of processes which form the anomalies. Algorithms for the calculation of positions and parameters of objects from anomalies caused by these objects are solutions of so-called 'inverse' problems. Such problems have already been fully considered in geophysics, but in the field of geochemistry their discussion has begun only recently.

By computation of displacements it is possible to discover the initial positions of the substances which form anomalies, i.e. to expose the positions of the sources and the main mineralizing zones in plan form. The method has been tested in zones of diamond kimberlites. Solution of the 'inverse' problem for the diffusion process enabled the position and parameters of orebodies to be estimated by secondary diffusion aureoles. The solution is already being put to practical use with the aid of computer techniques.

Gaseous surveys in prospecting for sulphide ore deposits

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The survey technique proposed as a gas geochemical method for prospecting for oil deposits has been used in an attempt to discover blind orebodies, which are believed to enrich the underground atmosphere with sulphur-bearing gases.

Study of the composition of the underground atmosphere at a depth of 1·5–2 m in a semi-desert area of sulphide ore deposits showed that more than 0·005% of hydrogen sulphide was present in the composition of the underground atmosphere above the exposed orebodies and in those occurring at a depth of 30 m. The thickness of the overburden varied from 1 to 10 m: H_2S content was not dependent on the composition of the overburden.

The presence of H_2S in the underground atmosphere appears to be connected with chemical and biochemical oxidation–reduction processes of sulphides and sulphates. Hydrogen sulphide seems to be quite stable in reduced or weakly acid environments characteristic of secondary enriched sulphide orebodies in the zone of oxidation of sulphide ore deposits.

Results of gaseous surveys in central Kazakhstan and Middle Asia are presented.

Application of helium surveying to structural mapping and ore deposit forecasting

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A survey is based on the investigation of the natural field of free-filtering helium in the saturation zone, samples being taken at a depth of 20–30 m. At such a depth the effect of atmospheric factors is eliminated and the high sensitivity of the method is assured. Direct analysis of the helium concentration is done by use of mass spectrometry (sensitivity above 5.10^{-5} equivalent %) or ion pump-type detectors (sensitivity above 5.10^{-4} equivalent %). The results of the analyses of samples from different depths are attributed to the most informative horizon by interpolation.

The number of sampling points required for the first stage of the study varies from 1 to 4 per 100 km^2 (survey scale, 1: 1000000). Investigations to date have mainly been carried out in areas where the basement is exposed or lies not far from the surface (less than 500 m). A helium field determined by this method is characterized by high contrast relative to geological background. It varies in the order of from 4 to 6 at a horizon 30 m below surface. Helium flow rate observations carried out over a number of years show that the helium field is stable in time: significant variations arise only as a result of seismic activity.

It appears that only rock permeability affects the helium field, and no influence arises from factors related to geological structure near the surface. Permeability zones through which the helium flow is transported to the surface extend to significant depths, and they are of tectonic origin. Helium migration is mainly effected by means of filtration with other gases and fluids.

The intensity of helium anomalies depends directly on the depth at which the fracture zone is located. The main helium source would appear to be below a granitic sedimentary layer.

The earth's crustal structure in the helium field resembles a combination of impervious solid blocks, separated by permeable zones. Granitic masses usually occur inside these solid blocks, and the helium field within the blocks has the minimum intensity. Junctions and intersections of the zones between the blocks are regarded as maximum permeability areas. The helium-bearing zones are in agreement with the grid lines of high horizontal gradients and seismic zones. In general terms, the earth's helium field reflects the position of small, vertical-amplitude, diagonal and orthogonal fractures and consolidated blocks separating them.

Helium-bearing anomalies occur in geological formations directly or indirectly associated with mobile diagenetic fractures. They are revealed in association with diamond-bearing kimberlite pipes, carbonatites, hydrothermal gold, lead–zinc, iron and mercury deposits.

Further development and the application of helium surveying in conjunction with geophysical and geochemical studies offer considerable promise in structural mapping, prospecting for ore deposits and earthquake forecasting.

Flameless atomic absorption and ion-sensitive electrodes as analytical tools in copper exploration

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A brief description of the instrumentation of both sets of apparatus is given. Sensitivity, detection limits and precision of replicate copper analysis are investigated. Determination of copper in natural waters can be carried out with a 'heated graphite atomizer' as well as with 'copper-sensitive electrodes'. This has definite advantages in that tedious methods which involve preconcentration and extraction are avoided.

The determination of copper in soils, stream sediments and rocks always requires an initial preparation, but with the flameless atomic absorption technique a direct analysis of such samples is possible.

The applicability of the technique is discussed.

Regional geochemical study of Cretaceous acidic rocks in the northern Canadian Cordillera as a tool for broad mineral reconnaissance

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Except for work carried out in the U.S.S.R., the use of primary geochemistry as an exploration tool has not been widespread in the western world. The reasons for this would appear to be twofold: first, it is not simple to satisfactorily sample rocks, and, second, the interpretation of the resulting data requires that close attention be paid to the mineralogy and major-element chemistry of the rocks sampled. With respect to the first point, some rocks are far simpler to sample than others; for instance, large, relatively homogeneous masses of plutonic rocks present less of a problem to the sampler than a series of sediments whose composition may vary from shale to sandstone to limestone both across and along strike.

The sampling and interpretative phases of a regional bedrock geochemical study of acidic plutonic rocks of Cretaceous age in the northern Cordillera of Canada (Yukon and Northwest Territories) are described, the aim of the study being to develop broad regional exploration tools which can be used to focus in on areas of increased potential within the intial reconnaissance area. The field area extends over some 20 000 square miles and contains a variety of types of mineralization, some genetically associated with intrusions and others which have no observable genetic relationship with the plutons. The most important deposit directly associated with intrusion activity in the region is the tungsten skarn orebody at Canada Tungsten.

A practical compromise plan for sampling the plutons has been developed, the compromise being necessary to attract exploration companies to the technique. Ideally, a carefully designed hierachical sampling plan should be used, with sufficient sample sites to outline any predefined scale of zoning within the body. The compromise consists of collecting two chip samples some 20–30 ft apart at each of a number of sites, depending on the size of the pluton. The two samples are analysed separately and the resulting data allow an estimate of the local variability to be made. By use of this estimate a simple statistical test will indicate whether or not there is evidence of significant zoning in the body. A further simplification of the sampling programme has been introduced by some exploration companies during the 1971 field season. The two chip samples are increased to several, which are used to make up a local composite for analysis. In all these modifications, however, the same number of sites are visited.

Each sample has been analysed for 22 elements, including major, minor and trace elements, by a variety of spectrochemical, colorimetric and fluorimetric techniques. All field data and analytical data are stored in a computer-processible form, which allows tasks from report generation to sophisticated statistical analysis to be carried out rapidly and efficiently.

The interpretation of data can be divided into two stages. In the first stage elements such as molybdenum, tin, tungsten and beryllium are considered. These elements occur essentially in characteristic minerals, e.g. molybdenum in molybdenite, tin in cassiterite; some tin is present in the biotites of the igneous rocks. From these features it follows that high levels of these elements in any of the calc-alkaline plutonic rocks can be considered favourable as a regional indicator of mineral potential. The present study has shown that increased mean values between intrusives is not the only criterion for discrimination between barren and potentially mineral-associated rocks. A far more sensitive indicator is the nature of the frequency distribution of the elements in each pluton, the distributions of elements being more positively skewed in plutons associated with mineralization.

The second stage of interpretation involves elements of economic importance which occur both in discrete minerals or as a persistent minor and/or trace constituent in major rock-forming minerals and accessories, e.g. lead in potash feldspars, and copper and zinc in hornblende, biotite and magnetite. Because the amounts of these major minerals fluctuate throughout the calc-alkaline plutonic series, the backgrounds and, hence, the thresholds vary continuously. The problem of the interpretation of these data has been greatly simplified by the use of a combination of two well established statistical methods. The major element data are subjected to an *R*-mode principal components analysis, and the scores for each sample are computed on the Varimax-rotated components. In effect, the first component is a differentiation index for the calc-alkaline rocks under study; the remaining components reflect other features of the major element development of the rocks. At this point the major-element data are interpreted in terms of the general petrochemical development. The trace elements of interest are then used as independent variables in a multiple regression in which the dependent variables are the component scores. Confidence bounds, similar to the arbitrary selection of the two standard deviation limit in common use as a threshold, are set up above and below the regression, and samples with either anomalously high or low residuals are further investigated. Anomalously high values may indicate the presence of ore minerals, or corresponding low values may indicate areas of alteration leading to a search for channelways and a possible locus of ore mineral deposition.

Data and examples are presented to illustrate the techniques and to substantiate the methods of sampling and interpretation as viable regional exploration tools.

Zoning of major and minor metals in the Coeur d'Alene district, Idaho, U.S.A.

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The principal ore deposits in the Coeur d'Alene district are lead–zinc–silver replacement veins in Precambrian rocks of the Belt Supergroup that are intruded by Cretaceous quartz monzonites. The host rocks are mainly quartzites and argillites. The most important ore minerals are galena, sphalerite and tetrahedrite. The district is the most important silver producer in the United States.

During the U.S. Geological Survey's recent geochemical study of the district approximately 8000 soil samples and 3000 rock samples were collected along roads and ridges (sample spacing, about 1 sample per 500 ft of traverse line). The area sampled covers about 200 square miles. A review of computer-generated geochemical maps shows that the surface dispersion patterns of selected metals in soils are areally equal to or greater than the dispersion patterns of these metals in rocks.

The metal distribution found in the district shows the effects of different mobilities of the metals during primary mineralization and of remobilization of some metals during subsequent intrusion of the monzonites.

Many of the metals are zoned both vertically and laterally with respect to local centres of mineralization as well as to major geologic features of the entire district. Patterns of trace silver, derived from tetrahedrite and argentiferous galena, clearly define the various mineral belts in which the silver-bearing deposits are shallow or of only moderate depth. The presence of tetrahedrite is indicated by anomalous silver and antimony in the surficial materials, whereas argentiferous galena is indicated by anomalous silver and lead.

In contrast, tellurium seems to have been driven beyond the ore metals at the time the ore deposits were emplaced and it forms haloes far out from the centres of mineralization. It would seem, therefore, to be a useful pathfinder element for deeply buried deposits. Manganese, like tellurium, forms haloes far above the ore metals.

Cadmium is more temperature-sensitive than zinc, and both metals tend to be fractionated around monzonite intrusives. Sphalerite in or near the intrusives is depleted in cadmium. Because of the high temperature of the intrusion, the cadmium has moved down the temperature gradient (away from the centre of the intrusion) and formed a cadmium-rich halo around the stocks. Preliminary data indicate that cadmium, relative to zinc, is depleted in vein material and enriched in the wallrock of the ore deposits.

Lead isotope analyses indicate that the lead in the ore deposits is older than the monzonite intrusives that are in the district. Limited data pertaining to the distribution of total sulphur now in the oxidized or partly oxidized surficial materials also indicate that the vein deposits are older than the monzonite intrusives. Anomalously high concentrations of sulphur are coextensive with the mineral belts, except that the high-sulphur zones cross the monzonite stocks and the mineral belts do not. The most abundant iron mineral in the monzonite is normally magnetite, but most of the iron in the high-sulphur belts within the monzonite has been used in the formation of pyrite. It is postulated that the monzonite stocks intruded some of the mineral belts, destroyed the original sulphide deposits, reused the sulphur to form pyrite and froze before any significant mixing could be accomplished. Metals such as silver, lead and zinc were remobilized and redeposited within a concentric belt peripheral to the stocks.

One of the major faults within the district is a post-mineralization right-lateral fault that has shifted the northern part of the district 16 miles eastward relative to the southern part. On the basis of district geology and geochemical fabric this part of the district can be restored to approximately its original position. Several potentially large exploration targets are then apparent. The distribution patterns of silver, antimony, tellurium and manganese suggest other targets.

Visualization of the zoning relations of elements was enhanced by the use of computer-contoured geochemical maps of not only individual elements themselves but also the combinations of elements as ratios, sulphur equivalents and mathematical enrichment vectors. For each variable a contour was generated from both 'right' and 'left' perspectives, and the resulting three-dimensional stereo pair greatly facilitated the interpretation.

Differential secondary dispersion in transported soils and post-mineralization rocks: an electrochemical interpretation

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Multi-element analysis of various residual soils, transported soils and post-mineralization rocks has shown antipathetic dispersion of some ore elements near mineralization. This is of particular interest with respect to measurable dispersion in soils derived from transported overburden and in post-mineralization rocks; it is suggested that the mechanism of such dispersion is strongly influenced by electrochemical processes.

Soils derived from glacial till overlie a sulphide orebody in northern New Brunswick, Canada; the sulphides consist of more than 80% pyrite, the other sulphides being galena, sphalerite, chalcopyrite and arsenopyrite. The average grade of the sulphide body is 2·0–3·0% Zn, 0·6% Pb and 0·2% Cu. The distribution of Pb shows a pronounced peak immediately over mineralization, with an abrupt decrease to background values each side; Zn and Mn are very low over mineralization, with very high and broad peaks each side, and Cu shows a similar although much subdued pattern. The ratio of Ni: Co is about 0·25 over mineralization and 2·0–4·0 either side of the orebody.

Some Ni–Co–Cu sulphide orebodies in mafic intrusions in southern New Brunswick are covered by a variety of transported overburden, including marine clay, beach sands, alluvium and glacial till; the sulphides are dominantly pyrrhotite, with lesser amounts of chalcopyrite, pentlandite and niccolite. Anomalous concentrations of Ni and Co (and, rarely, Cu) have been detected in these transported materials up to the surface. Even minor mineralization in bedrock is reflected by anomalous concentrations of Ni and Co in a 5-ft section consisting of beach sand, marine clay and glacial till in upward succession.

In Cyprus both pre- and post-mineralization pillow lavas adjacent to sulphide bodies are characterized by abnormally high concentrations of Zn and abnormally low concentrations of Cu. These abnormalities persist, in places, for more than a mile from the orebody.

The complex metal distribution related to these three sulphide deposits is clearly due to secondary processes; simple solution and movement in groundwater is not an entirely adequate explanation.

Preliminary laboratory tank experiments with an artificial mixed-sulphide 'orebody' set in a crushed basalt matrix covered with artificial sea water gave electrical potential differences consistent with normal self-potential anomalies, both laterally away from the 'orebody' and vertically through it. After a period of two months, analysis of the crushed basalt showed that the Zn concentration in the basalt had increased from 1·2 to 2·0 times throughout, the maximum increase being close to the base of the 'orebody'. Pb showed a similar behaviour, but there was no increase in concentration at the farthest point from the 'orebody'. The behaviour of Cu was essentially the reverse of Zn and Pb; Cu concentration in the basalt generally showed a decrease by a factor of about 0·75, except adjacent to the top of the 'orebody', where it had increased by a factor of about 1·5.

These preliminary studies suggest that there can be significant differential secondary rearrangement of metals in soils and rocks related to sulphide orebodies under the influence of electrical potentials. The possible use of geochemical techniques to prospect for deep deposits covered by transported overburden or post-mineralization cap rocks is therefore indicated. Inasmuch as absolute changes in concentration of metals will decrease in magnitude with increasing distance from a sulphide orebody, differences in the behaviour of metals which have widely differing electrochemical characteristics should be sought. To be fully effective on deeply buried deposits this approach demands greater analytical precision than is presently accepted for metal determinations in geochemical exploration.

Application of sulphur and nickel analyses to geochemical prospecting

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Specimens of basic and ultrabasic rocks from mineralized prospects in eastern Canada and Western Australia have been analysed for sulphur and nickel, and compared for different rock types. Log–log plots of nickel against sulphur values suggest a method for evaluating the mineralization potential of specific rock types. Assay data group together characteristically for different rock types – indicating a geochemical method for correlating lithology and possibly identifying rock types from a given area.

A comparison of serpentinites from mineralized and unmineralized localities suggests that concentrations and ratios of sulphur and nickel (near 1 to 1) may be used as a guide to more favourably mineralized districts. Sulphur–nickel plots are presented for serpentinites from several known producers and prospects, including the Thompson belt, Texmont mine, Mount Keith and Kambalda.

A method is proposed for screening favourable prospects, based on the comparison of nickel and sulphur analyses with rock types.

Cluster analysis of rocks in the New England igneous complex, New South Wales, Australia

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The geological mapping of the New England igneous complex (total area, about 20 000 km^2) over the past few decades has led to the description of more than one hundred intrusive bodies, including a wide range of granites, adamellites, granodiorites and porphyrites. The classification of the rocks has been based on chemical analysis of major elements and mineralogical composition. The task of delineating the various intrusive bodies and of establishing genetic relations between the rock types has been extremely difficult owing to the variability of the complex. The present paper is the first attempt to use the technique of quantitative numerical analysis for comparing various rocks which constitute the intrusions and for establishing their degree of similarity or dissimilarity with regard to both their major- and trace-element content.

The work forms part of a wider programme concerning mineralization (mostly tin and molybdenum) in the granitoid rocks of New England. This programme was initiated in the CSIRO Division of Mineralogy in 1969 and is aimed at finding criteria for the association of mineral deposits with the type of rock in which they occur. 72 of the 134 samples collected have been analysed. These samples provided data for the present calculations.

The statistical method of calculation involved the selection of orthogonal (i.e. unrelated) variables by *R*-mode analysis with correlation coefficients. A hierarchical dendrogram was obtained for the variables and, subsequently, four major (Si, Al, Na, Ti) and 14 trace elements (Ba, Co, Cr, Cu, Ga, Li, Mo, Pb, Sc, Sn, Sr, V, Y and Zr) were selected as good discriminators for the rocks. The MULTCLAS program was used to obtain criteria of similarity by *Q*-mode analysis of the samples on a CDC 3600 computer. The calculations were carried out in two parts, major-element oxides being used in the first instance, and both major and trace elements in the second case. From the original similarity matrix, containing squared Euclidean distances, a similarity dendrogram was derived by use of the 'group-average' sorting technique.

The classification of rocks on the basis of *major-element* oxide content resulted in two main groups, the first containing 24 samples of granites and leuco-adamellites, and the second group consisting of 46 samples of adamellites, granodiorites and porphyrites – showing that the frequency of the latter type of rocks in the New England area is higher than that of the granites. Within the two major groups it was possible to distinguish between sub-groups, and this distinction is reflected in the above classification. Two samples, a gabbro and a tonalite, did not fit into either of the two main groups.

There was a good general agreement between the previous geological mapping and the present statistical grouping of the rocks. Some differences were noted, however, within some outcrops – which indicates the necessity of taking further samples from certain locations and will eventually lead to modifications of the existing nomenclature and boundaries of intrusions.

When both *major and trace elements* were used for classification the pattern of rock associations was found to be distinctly different – suggesting that the factors which determined trace-element concentrations were different from those responsible for major-element contents in the formative stages of rock solidification. The processes (presumably postmagmatic alteration) which determine trace-element distribution appear to have had a regional character and affected most rocks in a similar manner. On the other hand, in certain intrusives uniform major-element distribution is associated with significant variations in trace-element content, which may be a sign of localized alteration events.

In the course of cluster analysis useful information was also obtained on the distribution of major and trace elements in the rocks, ranges, mean values standard deviation, coefficient of variation and the number of samples required to obtain mean values at a required level of confidence.

Work in progress includes the use of data for a larger number of samples. In addition to chemical composition, mineralogical and petrological information will be used for a statistical comparison of the rocks and to establish the relative importance of processes relevant in ore genesis.

Dispersion from a submarine exhalative orebody

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Along the length of the median valley of the Red Sea layered metalliferous deposits have been observed which vary in thickness from a few centimetres to several metres or tens of metres. The best documented occurrence is that in the Atlantis II Deep off Jeddah, Saudi Arabia, where layered manganese and iron oxides and sulphides contain variable quantities of copper and zinc.

Occurrences of metalliferous precipitates compositionally similar to certain layers in the Atlantis II Deep have been recorded in the first 1 or 2 m of sediment in other deeps elsewhere in the median valley. Whether these deposits persist at depth and whether they are layered in a similar manner to those in the Atlantis II Deep has yet to be determined. Analytical data on these deposits obtained following a recent (1971) cruise are presented.

Thin (few cm) metalliferous layers observed at numerous localities in the median valley are commonly highly manganiferous, but with lower concentrations of copper and zinc than were observed in the major deposits referred to above. The variations in the composition of these thin bands relative to major deposits are described.

Apart from the Atlantis II Deep occurrence off Jeddah, the existence of brines at other widely separated localities has recently been established – off Suakin, Sudan, and the Brothers Lighthouse, Egypt. The composition of these brines and the associated sediments is considerably different from that in the Atlantis II Deep. This is consistent with the brines being meteoric water whose compositions are closely related to the temperature of reaction with rocks through which they have passed.

Evidence of the existence of the exhalative deposits in the median valley is widespread in the sediments of the Red Sea. The ore metal content of the calcareous sediment varies with depth, being greatest within the median valley and lowest near the coast. There is also a variation in ratios of the ore metals with distance from the median valley.

Analysis of suspended particulate matter has revealed variations in composition and metal ratios, which can be related, at least in part, to the occurrence of the brines and to metal-rich precipitates now not associated with brines. Preliminary (continuing) studies of the filtered Red Sea waters, collected both within and outside the median valley, have revealed variations which are considered to be also related to the deposits in the median valley.

The results obtained have important implications to prospecting for present and past submarine exhalative deposits.

Pattern recognition problem in applied geochemistry

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The aim in an applied geochemical survey is basically to interpret multi-element data with a view to the location either of specific exploration targets or patterns of element distribution indicative of particular geological or environmental phenomena. The pattern recognition problem begins with the choice of which features are to be measured. These may be chemical analyses for major or trace elements, and may include additional non-geochemical features. The choice of what observations to make will depend on the nature of the exploration goal, the cost of taking the measurements and the noise associated with these measurements. Given a specific feature set, there are various approaches, both statistical and empirical, to the extraction of an optimum feature set. These will be discussed in an exploration context. The pattern recognition problem will often become a pattern analysis problem with geochemical data when the classes of interest are *a priori* unknown to the investigator. If we are faced with a pattern classification problem, knowledge of the classes will help in the definition of the feature set, and a wide variety of parametric and non-parametric multi-class classification methods are at our disposal (unconditional maximum likelihood, sequential, discriminant function, potential function and nearest neighbour classifiers).

In the pattern analysis problem, however, we have a set of multi-dimensional features which we must analyse to determine the natural or inherent classes contained in the data. For example, we may use a system of three-component colour mapping as a display tool for visual pattern analysis of spatially distributed data. This will be demonstrated with maps produced by an LGP 2703 laser plotter system. Examples of the digital approach will be given by use of Sammon's non-linear mapping algorithm as applied to multi-element stream-sediment geochemistry. This appears to be an intuitively appealing technique, projecting *n*-space on to 2-space in such a way that inter-sample *n*-space distances are preserved with minimum distortion. The human eye is ideal for detecting clusters in the resultant display, and, hence, the algorithm is suitable for interactive use. Comparison will be made with trained non-parametric partitioning procedures such as the empirical discriminant function. The pattern recognition problem will be discussed with examples from the United Kingdom and elsewhere.

Atomic absorption determination of thallium and indium in geologic materials

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Crustal abundance is estimated to be 0·3–1·3 ppm for thallium and 0·1–0·25 ppm for indium. The usual semi-quantitative emission spectrographic detection limit is 50 ppm for thallium and 10 ppm for indium; consequently, these elements are rarely detected by spectrographic analysis and their geochemistry is poorly known.

The atomic absorption method described here provides a sensitivity of 0·2 ppm for thallium and indium in geologic materials. The more detailed geochemical study made possible by this method may prove useful in geochemical exploration. The procedure is indicated below.

An oxidized sample is covered with hydrofluoric acid. The acid is slowly evaporated to dryness. The sample residue is dissolved in a solution of bromine in hydrobromic acid, heated to dispel the excess bromine, and diluted with water. The cool solution is shaken with methyl isobutyl ketone to extract thallium and indium. Interference of iron is minimized by extracting the ketone with 1·5 N hydrobromic acid. Thallium and indium are then measured by aspiration into an air–acetylene flame by use of appropriate cathode lamps and a Perkin Elmer 403 atomic absorption instrument. Fifty samples can be analysed per man-day for the two elements.

Organic-rich samples are ashed in a porcelain dish over a Bunsen flame before the hydrofluoric acid attack.

Sulphides are oxidized with a carbon tetrachloride–bromine–nitric acid mixture, evaporated to dryness and dissolved in a bromine–hydrobromic acid solution.

Preliminary data obtained by this atomic absorption procedure indicate an association of thallium with the gold ores from the Getchell, Carlin and Cortez mines in north-central Nevada. Indium was not detected by this method in these ores. Examination of sulphides – principally sphalerite from the Montezuma district in Colorado – showed an inverse relationship of thallium and indium. Samples of high indium content (1000 ppm) contained only a few (5–7) ppm thallium. Similar samples of high thallium content (50–75 ppm) from the same district contained only 1–2 ppm indium. We are currently analysing suites of samples from several geologic environments to determine the relationships of these elements to ore deposits of various types.

Snow – a sampling medium in hydrogeochemical prospecting

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Recent work on the geochemistry of soil gases above hidden sulphide ore deposits has provided much information on the migration patterns of mercury from such orebodies. It has been shown that mercury in soil gases can be used as an effective prospecting tool in arid zones with sparse vegetation cover.

Current interest in mercury is not confined to its usefulness or otherwise in exploration geochemistry. Considerable attention is now being focused on mercury, the environmental contaminator. A number of comprehensive review articles document these aspects of mercury geochemistry. Volatile organic compounds, such as dimethyl mercury, have been shown to be present in lake muds and sediments and are thought to be generated in humic soils as well. But, whatever the chemical form of volatile mercury in soils may be, there becomes a definite possibility that mercury may also move into winter snows from underlying base-metal mineralization.

There is limited information only on metal contents of fresh snow and practically none at all on the chemistry of fallen snow overlying mineral deposits. A summary of relevant literature is given.

A preliminary snow sampling programme was devised for the winter of 1970. The test site chosen was a known mercury prospect near Clyde Forks, eastern Ontario. There the mineralization consists of narrow veinlets and blebs of disseminated tetrahedrite, chalcopyrite and pyrite in a barite–calcite gangue. Traces of cinnabar are visible in association with each of the sulphides. Tetrahedrite contains up to 4% w/w mercury. The occurrence lies in Precambrian sediments of Grenville age and appears to be associated with a number of northeast-striking parallel faults.

First results of the study are presented. Snow samples were taken from two locations carefully selected to represent a typical unmineralized background site and a site close to some narrow tetrahedrite veinlets. Data are presented for trace-element contents of soils from each site.

An adit has been driven beneath some surface-exposed tetrahedrite veins that strike northeast. Groundwaters leaching into the adit through the mineralized carbonate rocks formed icicles and ice stalagmites on the roof and floor, respectively. Frost crystals covering the roof and walls were probably formed from evaporation of the same groundwaters. For comparative purposes samples of each of these were taken in order to determine the influences dissolved carbonates would have on the hydrochemical migration of the trace metals of interest – Cu, Hg, Zn, Pb, Ag, Mn and Cd.

From the data presented it is apparent that carbonate ions have a severe restrictive effect on trace-metal migration, most of the metals being precipitated with calcium carbonate as the ice forms.

The maximum metal contents attained by the snows were generally greater than those measured for the adit ice samples. One interpretation is that the mechanisms of transport in each case are quite different, the transfer of metals from soil to snow probably being achieved by gaseous emanations and ionic diffusion, whereas that from rock to water (ice) is controlled by purely solution processes.

It is shown for both background and anomalous snow samples that a definite concentration gradient exists from ground-level snow up to surface snow. Two deductions appear probable: that the source of the metals, Hg, Cu and Zn, is from below the snow and not from atmospheric particulates; and that these metals are derived from the weathered mineralization beneath the soils rather than from the soils proper or plant mull.

One further point of interest is that the trace metals Mn, Pb and perhaps Zn are present in the background snows and the anomalous snows at about the same concentrations. This is because they are not of significance in the ores or the mineralized soils of the deposit and therefore do not produce measurable dispersion aureoles in the soils around the sulphides. These data are also recorded. The contents of Ag and Cd in the snows are very low and are therefore of little use as indicators of mineralization.

It may be argued that metals find their respective ways into the fallen snows by two possible processes – gaseous diffusion of organometallics or solution migration by capillary movement of water across interlocked ice crystal faces. At present there is no simple way to distinguish between the mechanisms. It is hoped, however, that further studies by means of gas chromatography–mass spectrometry techniques on the soil gases may lead to the detection and characterization of traces of organometallic vapours which may be present.

Nevertheless, the data indicate that snow may be used as a sampling medium to detect the presence of buried mineralization, although, obviously, much more work needs to be done to check on the practicality of this technique. The present work also describes snow aureoles over other types of base-metal deposits and over nickel–copper deposits in both temperate and arctic regions. The usefulness of spring thaw hydrogeochemical techniques is also discussed.

Analysis of water-extractable chloride in rocks by use of a selective ion electrode

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Previous studies have indicated that chlorine abundances can be useful in distinguishing intrusive rocks genetically associated with hydrothermal mineralization. Because of the difficulty of determining total chlorine in rocks, this potential exploration tool has not been widely utilized. An attempt has been made to render the technique more amenable to inexpensive routine exploration by use of a chloride selective ion electrode to determine the water-soluble chloride in rock powders such as are commonly used for trace-metal analysis.

There has been a recent upsurge in the development and utilization of selective ion electrodes as analytical tools. A largely overlooked field of application is that of geochemical exploration. In contrast with many traditional chemical techniques, electrodes can be readily used with portable equipment (the Orion 401 expanded scale pH/mV meter was used in this study), which makes mobile field operations possible.

Average granitic rocks contain 100–250 ppm chlorine, of which a significant, but variable, proportion is present as dissolved NaCl in fluid inclusions of *primary* and *secondary* origin. In the case of hydrothermal ore deposits associated with intrusive rocks, this fluid inclusion chlorine should be the most effective indicator of favourable intrusive rocks. Furthermore, when a fluid inclusion is broken during sample preparation, the dissolved chlorine will precipitate on the surface of the fragments, rendering it easily recoverable with cold water leaching.

Analyses made by stirring 1 g of rock powder in distilled water for 2 or 3 min give a range of values of from 10 to 150 ppm chloride (rock) on the suite of granodioritic rocks tested so far. Optimum grain size for the powder is 200 mesh. Further grinding gives no significant increase in chloride values. Replicate analyses of 10 different powder samples from the same rock indicate a repeatability of ±2% at the 95% confidence level. In 90% of the cases solutions could be left in contact with the powders for up to one month without appreciable changes in chloride content.

Selective ion electrodes do *not* respond specifically to the ion of interest. In the case of the chloride electrode, however, only sulphide, bromide and iodide (none of which is important in this application) are likely to interfere in geochemical sample solutions. It must be kept in mind that electrodes measure ion activity, and, hence, corrections in some instances of high salt content solutions may be necessary to give proper concentration values.

Linear electrode response to chloride is obtained over the range 4–40 000 mg/ml, with response times of 10–30 sec, depending on concentration. Chloride in the range 0·1–4 mg/ml can also be determined, but response times are much slower (30 sec–5 min).

The electrode used for this study was constructed for $3.00 from silver chloride precipitate embedded in dental acrylic. When the membrane surface is coated with a thin layer of silicone oil and the electrode used in conjunction with a sleeve-type double-junction reference electrode, work can be done in highly turbid solutions containing abrasive particles with good reproducibility.

The method was used on a suite of granodioritic intrusive rocks from Puerto Rico. Some of these rocks are from the Utuado batholith and its younger satellites, which have generated two (known) medium-size porphyry copper deposits. Others are from the La Torrecilla and San Lorenzo plutonic complexes, which are not known to be associated with commercial mineralization. The most interesting result of these tests is that whereas total copper in these rocks is highest in samples from the Utuado batholithic complex, the water-soluble chloride is not. Instead, the highest chloride content occurs in unmineralized or weakly mineralized rocks. No significant difference has been detected so far between porphyritic and equigranular rocks. This too is a surprise because it would be expected that porphyritic intrusions would have crystallized in a shallow environment in equilibrium with a more abundant chloride-rich vapour phase. At present the results obtained suggest that within individual pluton complexes high copper values are associated with high chloride values in cases of (presently) marginal or sub-ore grade mineralization. But high copper values are associated with low chloride values in rocks that are host to ore grade mineralization. If this relation is found to be generally applicable, it could be possible to distinguish economic from weak mineralization by using part of the rock powder (used for copper analysis) to obtain a chloride value.

Evaluation of this technique is continuing on other rock suites in both fresh and weathered conditions. Attention is also being given to the possible use of other ion-selective electrodes (e.g. fluoride, cupric and sulphide) for related determinations. The results of these tests are reported.

Non-destructive determination of metals in rocks by radioisotope X-ray fluorescence instrumentation

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Rapid and non-destructive analytical techniques are of great value in geochemical exploration and mineral prospecting. In this respect radioisotope X-ray fluorescence, with both balanced X-ray filter and

X-ray spectrometry techniques, can greatly reduce the number of samples necessary to establish ore tonnage and grade.

Radioisotope X-ray fluorescence instrumentation is proposed for the following situations in geochemical exploration: (*a*) semi-quantitative analysis of stream-bed samples collected upstream; (*b*) rapid qualitative determinations of elements in the heavy fraction of stream-bed sediments; (*c*) qualitative and semi-quantitative analysis of samples from loose boulders, moraines and quaternary deposits; (*d*) *in situ* analysis of rock outcrops for the estimation of orebody boundaries and ore grade, and for rapid analyses of surrounding rocks; (*e*) multi-element analysis of stream-bed samples and drill cores in the laboratory.

Work with a simple laboratory set-up (comprising a proportional counter as the X-ray detector, a 1-mCi ^{109}Cd excitation source and balanced X-ray filters for Zr, Nb and Ti) was started in 1968. Regression analysis of difference count rates of irradiated areas of cut alkali syenite rocks versus chemical analysis of a 2-mm thick removed surface layer of this area yielded linear calibration curves for the three elements. Estimated detection limits were 0·44% Zr, 0·14% Nb and 0·13% Ti. Precision calculated from repeated measurements on plane surfaces was generally better than 6% for coarse-grained and 3% for medium- to coarse-grained rock surfaces. A set of calibration slabs for field work was made from these rocks.

A commercially manufactured radioisotope X-ray probe (Nuclear Enterprises, Ltd., England), connected to a portable single-channel analyser (25 kg in weight) developed at Risö, Denmark, was employed for two field seasons in the Ilímaussaq intrusion, south Greenland. It was possible to make more than one hundred measurements per day. A systematic comparison of outcrop chip samples with chemical analysis provided calibration curves for Zr, Nb and La plus Ce, whose distributions were measured in the surfaces of layered and homogeneous rock bodies. The calibration data yielded estimates of detection limits: 0·44% Zr, 0·15% Nb and 0·17% La plus Ce; the mean of their accuracies was 0·15%. Simple rock volume calculations, together with the results of X-ray assays, permitted an estimate of the approximate size of a Zr orebody.

Similar assays were carried out recently with a lightweight (8 kg) portable instrument (EKCO Electronics, Ltd., England) in the Jameson Land area of east Greenland. The radioisotopes used were ^{238}Pu for determination of Cr, Ni, Cu and Zn, ^{109}Cd for Zr, Nb and Mo, ^{241}Am for La plus Ce, and ^{57}Co for Pb. Measurements on outcrops of Jurassic sediments showed the distribution of the elements Pb, Zn, Zr and La plus Ce in the surface of the different horizons of the sediment.

Dried stream-bed samples indicated by their La plus Ce count rate the presence of a rare-earth mineralization nearby, which was also confirmed by airborne gamma spectrometry. In two days more than four hundred measurements of outcrops of a molybdenite deposit in this area provided information about the grade of the orebody and the Mo content of the transition zone to the surrounding sediments.

For multi-element analysis of cut rock hand specimens in the laboratory a non-dispersive Ge (Li) spectrometer, constructed at Risö, connected with a multi-channel analyser, and a small computer were used. X-ray spectra were excited with a 10-mCi ^{241}Am source. La and Nd calibration curves were constructed, relating X-ray intensities determined by least-squares fitting of the X-ray spectrum to mass-spectrometric analyses of the thin surface layer of the samples. Regression analysis yielded detection limits of 400 ppm Ce and 180 ppm Nd. Longitudinally cut drill cores were scanned manually along the exposed surface. A Si (Li) X-ray spectrometer (ORTEC, U.S.A.) was applied for quick multi-element assay of stream-bed samples. An apparatus for drill core scanning incorporating this spectrometer is under construction.

Geochemical mapping and prospecting by use of rapid automatic X-ray fluorescence analysis of panned concentrates

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Geochemical mapping by use of X-ray fluorescence analysis (X.R.F.) of panned concentrates has been successfully related to regional rock geochemistry in the Cheviot area of northern England and the Scottish Highlands. Multivariate statistical methods have been applied to the absolute data and element ratios and populations have been correlated with the observed geology.

The X.R.F. analysis of panned concentrates is considered to be particularly useful in assisting geological mapping in areas with little contrast between the major rock types. The high precision of the analyses enables interpretation and comparison of sample sites to be based primarily on elemental ratios and interrelationships rather than absolute quantities, so reducing the effect of environmental factors which produce geochemical noise. The influence of secondary precipitation on trace-element distribution is considerably less in panned concentrates than in fine sediment fractions.

Dried concentrates are split into two fractions, one of which is used for analysis and the other for mineralogical examination. The analysis fraction is mixed with an acrylic resin binder, elvacite 2013, in the ratio 4 parts concentrate to 1 part elvacite, and ground in a tungsten carbide pot Tema swing mill for 3 min. The resultant powder is pressed into a 32-mm diameter disc at 15 ton/in^2 pressure for a few seconds. The discs are analysed for Si, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ag, Sn, Sb, Ba, Ce, Pb, Th and U and ratioed against a synthetic mineral matrix standard, spiked with 1000 ppm of each of the trace elements, by use of a Philips 1220C automatic X-ray spectrometer. Raw count data are output on paper tape and corrections for mass absorption differences between standard and unknown are completed on an IBM 1130 computer with an 8K store.

In the Cheviot area of the north of England it has been possible to distinguish between different phases of granite, Old Red Sandstone lavas and various sedimentary rocks by use of Zn/Fe, Ni/Fe, Mn/Fe and Nb/Ti together with absolute Cu, Sn, Zr and Th values. With similar ratios in the Scottish Highlands it has been possible to differentiate between basic rocks of Moinian and Lewisian age, Old Red Sandstone sediments, Caledonian granites and different types of siliceous gneiss.

Mineralization has also been recognized either in terms of absolute contents of elements such as Pb or by significant departures of ratios such as Zn/Fe from the norm. In the Cheviots vein Pb, Zn, Ba, Cu and disseminated Cu mineralization has been indicated, and in Wester Ross the presence of disseminated celestite and pyrite and vein pyrite, galena and sphalerite has been demonstrated.

Gold – a useful pathfinder element for porphyry copper exploration in Puerto Rico

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Geochemical studies of residual soils in selected areas of the copper belt of west-central Puerto Rico indicate that porphyry copper deposits, enriched by supergene processes, may easily be missed in soil surveys which utilize as indicators copper or other acid-leachable elements. Gold in soils, however, serves as a reliable indicator of primary and enriched deposits alike. Gold and copper data, evaluated together, may serve to distinguish soils overlying primary deposits from soils overlying enriched deposits.

Within the copper belt of Puerto Rico the soils overlying the five known major deposits and several additional minor deposits contain strongly anomalous amounts of gold. Furthermore, the gold content of these soils is remarkably uniform from deposit to deposit. The silver and base-metal contents of soils show much less consistent relations to the deposits than does the gold content. A comparison of copper and gold contents of soils overlying two adjacent deposits illustrates the relations.

Cala Abajo deposit			*Piedra Hueca deposit*		
Gold content of soils, ppm					
Range	*Median*	*Background*	*Range*	*Median*	*Background*
0·02–0·79	0·19	<0·02	0·02–0·52	0·27	<0·02
Copper content of soils, ppm					
70–5000	150	200 (approx).	300–20000	2000	200 (approx.)

The Cala Abajo deposit is an enriched deposit overlain by a thick leached capping, whereas the Piedra Hueca deposit is a primary deposit. The much lower copper content of the soils over the Cala Abajo deposit, as well as lower amounts of lead, zinc, silver and manganese in these soils, is attributed to acid leaching.

The foregoing relations are based on the −0·25-mm fraction of samples from the *B* soil horizon, but, in fact, the parameters of soil horizon and grain size are not critical.

Automated colour-mapping of three-component systems and its application to regional geochemical reconnaissance

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The mapping of simultaneous concentration variations of three elements is achieved by use of colour-mixing. Additive and subtractive colour schemes, each containing 27 visually distinguishable colours, have been derived for maps in which three elements are each present at any of three concentration levels. These enable unique identification of the element concentrations in any particular colour field.

Examples are presented of subtractive colour maps obtained directly by the superimposition of magenta, cyan and yellow diazo transparencies derived from single-element grey-tone maps produced automatically by use of an LGP 2703 Lasergraphic plotter. This is a high-speed computer-controlled plotting device which uses a laser optics system to produce visual representations of information taken directly from a computer's core memory. It is capable of plotting to any scale data which can be expressed in x, y coordinates and enables the rapid production of high-quality originals on black and white film from which colour transparencies can be produced.

The colour maps to be illustrated have from three to six concentration classes per element and are of geochemical data smoothed by moving-average filtering. The use of more than three classes per colour component produces a wide range of colour fields which reveal the maximum detail in the data and are most helpful for the identification of broad-scale patterns. For the practical *retrieval* of the element concentration values present at any point on the map three concentration classes per element have been used. A theoretical study has shown that additive colour-mapping can be directly implemented by use of colour television display.

Mapping of multi-element stream-sediment reconnaissance data by these techniques has shown that there is a considerable information gain over conventional single-element maps. It has been highly successful in distinguishing between bedrock lithologies, as well as delineating areas of mineral exploration potential and regions of agricultural trace-element deficiency.

The generality of the method makes it of use in the mapping of any three-component system.

Some aspects of geochemical dispersion from base-metal mineralization within glaciated terrain in Norway, North Wales and British Columbia, Canada

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Some results are presented of geochemical research and exploration within glaciated terrain over and in the vicinity of base-metal mineralization in Norway, North Wales and British Columbia, Canada. These study areas are all characterized by siliceous overburden and a topography of rolling hills and broad U-shaped valleys. The climates of the regions, however, are somewhat dissimilar, varying from cold and dry to temperate and wet.

The results of the investigations show that ore elements are dispersed from their bedrock source beneath glacial till dominantly by solution in shallow groundwaters and to a lesser extent by mechanical (ice) transport and biochemical processes.

It is concluded that secondary metal dispersion patterns related to sulphide mineralization in these and similar environments may be readily detected on a broad regional scale by sampling groundwater seepage sites. Where seepages occur in lakes, as, for example, in the central interior of British Columbia, the existence of bedrock mineralization in the general vicinity of the lakes can be detected by sampling the organic-rich bottom lake sediments in the central, deeper parts of these lakes. Interpretation of these seepage anomalies, as well as of anomalies which may occur as a result of seepage in streams or rivers, is dependent on an assessment of groundwater dispersion trains.

Microwave-induced argon plasma emission system for geochemical trace analysis

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A microwave-induced argon plasma emission system has been developed for geochemical trace analysis. This system provides improved sensitivity, particularly for volatile elements, and can be used for the analysis of inorganic or organic powders and solutions. The main advantage of microwave-induced plasmas in emission analysis are the high electronic temperatures (as high as 10 000°K) and the presence of an inert gas atmosphere which prevents the formation of stable forms such as metal oxides and hydroxides.

The system described makes use of a variety of techniques for introducing metal vapours to the plasma, including radio-frequency heating, volatilization by an RF plasma and controlled heating for the study of mineral decomposition products. The combination of sensitivity and fractional thermal separation of volatile species has provided an exploration technique for the identification of anomalies which cannot normally be distinguished from background. Examples of the geochemical applications of this technique in a variety of exploration situations are provided.

Detection of concealed mineralization in northern Scotland

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In the search for uranium and other mineralization in Caithness, Orkney and eastern Sutherland geochemical sampling of stream sediments, waters, peats and soils, supplemented by radiometric and radon probe surveys, has led to the identification of mineralization in bedrock. In the region, except for stream and coast sections, there are large areas where peat, glacial drift and 'head' exceed 3 m in thickness. Large-scale mapping of radioactive 'float' detectable by scintillation counter surveys either at surface or at peat–drift interfaces provides a valuable guide to subsequent trenching and drilling operations. In northern Scotland, because of the association of uranium with lead, molybdenum, fluorite and, in places, copper mineralization, the radiometric surveys have led indirectly to the detection of a wide range of mineral occurrences.

Geochemical patterns in peaty soils overlying uranium and other mineralization can be profoundly modified by the secondary environment – for example, by the concentration of metals in 'bog iron ore' horizons in peat and by local surface drainage. Sampling of peat bogs fed by waters draining metalliferous ground may, nevertheless, provide a useful mineralization guide – for example, at the margin of Caledonian granite in the Lairg district of Sutherland. Here concentrations of up to 200 ppm U, 100 ppm Mo and 2000 ppm Pb are present in peat formed some hundreds of metres downslope from metalliferous sources in the Grudie granite and in the adjoining Moine Schists. High concentrations of uranium in stream waters and sediments and of lead in stream sediments and peaty soils have also outlined possible mineralized districts within Caledonian granite near Helmsdale.

The interrelationship between the metal content of peaty soils, the gamma radiation at surface and at depth and the radon content of soil air can provide a coherent picture of the distribution of metals from underlying mineralization. A detailed study is presented of the location of uranium mineralization in Old Red Sandstone arkose generally covered by at least 2 m of peat, drift, 'head' and, in places, soil occurring in an area of incised topography in southern Caithness. The distribution of gamma radiation at surface is dispersed 100 m or more downslope from uraniferous bedrock and head, and a similar dispersion pattern is illustrated by the distribution of uranium, copper, lead and zinc in the peaty soils. The distribution pattern of radon in soil air is somewhat different, but it appears to be displaced downslope from bedrock mineralization by some tens of metres. Most effective in this environment has been the use of scintillation probes to measure radioactivity at peat (or soil–drift (or 'head') interfaces, leading directly to the exposure of bedrock uranium mineralization. The measurement intervals are necessarily small (2–3 m), however, and the technique is best employed after the much more rapid measurement of surface gamma radiation.

In a flat-lying area of thin soil cover overlying uraniferous structures in the Old Red Sandstone of north-central Caithness, the radon and gamma-probe patterns are broadly coincidental and delineate the sub-outcropping mineralization more sharply than the surface pattern of gamma radiation. The distribution of radon in soil air is, however, modified locally by water movement in the soil and in the underlying drift and weathered rock. The distribution of radon in thin soil and drift overlying a sandstone member of the Old Red Sandstone of Orkney has also proved effective in extending bedrock uranium mineralization having a limited gamma expression at surface.

Comparison of multivariate techniques in the interpretation of geochemical data

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Multi-element drainage sediment data have frequently been found to yield significant information in regional geochemical reconnaissance surveys for focusing attention on areas where more detailed exploration methods can be applied. In exploration the general requirement of interpretation of geochemical data is to distinguish metal patterns derived from mineralization from those related to other causes. In some cases the recognition of these anomalous patterns may be relatively straightforward. Elsewhere, as in regions of transported overburden, the contrast between anomalous and background metal contents may be small and the overlap of metal populations of differing provenance considerable. In these cases the confidence level at which anomalous metal contents may be identified is thereby reduced. In recent years a number of electronic data processing techniques have been applied, with differing degrees of success, to a variety of interpretational problems. In the present investigation attention has been given to carrying out an evaluation of the usefulness of a number of multivariate techniques in the interpretation of multi-element geochemical data.

The data used as a basis for the investigation relate to a drainage reconnaissance survey over some 700 square miles in New Brunswick previously carried out by the Geological Survey of Canada. This area is underlain by a number of bedrock types and contains a variety of mineralization types. Distinct single-element and metal association patterns are apparent from a consideration of the metal distributions. These metal associations are undoubtedly related to particular types of bedrock, mineralization or dispersion environment. In part, the metal associations occur as distinct patterns, but, elsewhere, considerable overlap is apparent, in which case it is frequently difficult to establish with any degree of confidence the extent to which particular associations are represented in certain samples.

Cluster and factor, both *R*- and *Q*-mode, and multiple regression analyses were carried out on data relating to twelve variables for some 700 samples. These techniques variously achieved a grouping and redistribution of the data in terms of metal associations on the basis of correlations between the variables. The results of the different data treatments are presented for comparison. Attention was drawn to certain anomalous areas. These had not been recognized in a visual examination of the reconnaissance data – due largely to the camouflaging effect of metals from other sources. Field investigations confirmed the validity of a selection of these anomalies.

These results indicate that selected computerized procedures may in certain cases be of assistance in data interpretation as sources of unique information or as methods for clarifying features already apparent. The economic justification for their use needs to be assessed in the light of particular problems. The selection of a particular interpretational procedure should be conditioned by the character of the interpretational problem and personal experience.

Successful application of mathematical procedures to the interpretation of geochemical data requires liaison between geochemists, statisticians and computer programmers. It must be realized that all statistical procedures will provide solutions of varying significance. The final analysis of the usefulness of any interpretation lies with the geochemist, whose responsibility it must remain to evaluate, frequently by field examination, the significance of results provided by mathematical interpretations.

Use of cluster analysis in geochemical prospecting, with particular reference to southern Derbyshire, England

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Cluster analysis was applied to a multi-element geochemical stream-sediment survey south of the Derbyshire Limestone Dome. The −80-mesh fraction of 170 samples was analysed by a direct-reading spectrometer for Al, Ca, Mg, K, Fe, Ti, Mn, Ba, Co, Cr, Cu, Ca, Li, Ni, Pb, Sr, Zn and Zr. Cold-extractable Zn, analysed colorimetrically, was included in the data matrix. Both *R*- and *Q*-mode analyses were performed on the data matrix.

The *R*-mode analysis delineated three main groups of elements, from which the following associations are deduced: (1) elements associated with clay minerals and resistates; (2) elements associated with Mn and Fe oxides; and (3) elements associated with the dominant type of mineralization in the area.

When all 20 elements were considered in *Q*-mode cluster analysis, an areal grouping of similar samples was shown, depicting mainly the lithology of the area and the most intense anomalies. Various combinations of elements were tried for *Q*-mode analysis, each time elaborating on the areal similarities and dissimilarities of samples on the basis of the elements considered.

By the selection of suitable combinations of elements areas of mineralization could be distinguished. It appears that the technique may also be capable of distinguishing anomalies related to virgin mineralization from those associated with old mine workings or other contaminating influences.

Gaseous geochemical methods of structural mapping and search for ore deposits

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There is a continuous, but localized, release from the earth's crust of significant amounts of various gases to the atmosphere. Zones of abyssal fractures and associated cracks are particularly significant in this respect, the gas stream increasing sharply with metalliferous deposits in such zones. The gaseous phase plays an integral part in the formation of endogenic ore deposits, and is also preserved in the post-ore phase. Gaseous products of ore oxidation occur in hypergene conditions in near-surface areas of ore deposits. Thus, gases of different genesis and composition accompany ore deposits throughout their existence and evolution. They are either preserved in gaseous and gas–liquid micro-inclusions in rocks and ores or they migrate along gas-permeable fractures, entering the systems of ore-controlling fractures.

Hence, gases can be used as sensitive indicators both for structural mapping, to reveal fractures of different age, origin and depth, and in the search for hidden deposits.

Gaseous haloes of ore deposits usually have a multi-component composition: these include CO_2, H_2, CH_4, O_2, N_2, He, Rn, A, H_2S and others – in particular, SO_2 – as well as F, C, I and Br.

Mobile gases are of both near-surface and abyssal origin. The former include products of the oxidation of sulphide ore (H_2S, SO_2, CO_2) and vaporous mercury and radon. Gases of abyssal origin are much more varied, e.g. H_2, CH_4, N_2, He and A. They also include CO_2, Hg and Rn. They are always associated with systems of ancient mobile fractures.

Practical aspects of the use of these techniques include work undertaken in various Russian ore provinces.

Application of neutron activation analysis to the evaluation of placer gold concentrations

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A method of neutron activation analysis for gold is described in relation to the economic assessment of the valley deposits in the Strath of Kildonan, Sutherland. The material investigated comprises alluvium and fluvioglacial detritus infilling a glacially overdeepened section of the Helmsdale River Valley. Orientation studies in the tributary drainage of the area indicated that native gold occurs in particles up to 3 mm in diameter; the concentration of gold in panning concentrates varies between 5 and 300 ppm. The fineness determined by electron-microprobe analysis of the core of grains varies between 573 and 911, and gold-enriched rims are present on most grains.

The gold content of samples is conveniently measured by neutron activation analysis employing the reaction $^{197}Au\,(n,\gamma)\,^{198}Au$. Access to the reactor core is by means of a simple air-cooled hand-loaded hole. Known weights of sample are irradiated for 20 min in sealed polyethylene containers, to which a small gold foil disc is attached to monitor the neutron flux. After irradiation, the samples are stored for six days. They are then divided into portions not exceeding 130 g in weight and are transferred to 8-cm diameter polythene containers. The area under the 0·41 MeV ^{198}Au photo peak on the resulting gamma spectrum is compared with that of a standard sample over a counting time of 10 min. All results are corrected for variations in neutron flux.

This neutron activation technique is considered to have widespread application in the evaluation of geologic materials. The principal characteristics of the method are (*a*) high productivity (it is possible to analyse 20 samples per man-day) and (*b*) the capability of analysing large samples (up to 500 g of material) non-destructively.

The combined sampling and analytical reproducibility compares favourably with that attained by atomic absorption spectrophotometry or fire assay analysis. No systematic bias occurs in relation to fire assay analysis, and self-absorption of neutrons by gold grains is insignificant for individual particles less than 40 mg in weight. An advantage of the method compared with classical techniques is the elimination of errors associated with the estimation of a fineness correction.

The limit of detection is 0·01 ppm on 500 g of samples, irrespective of small variations in weight. In the Helmsdale Valley investigation determinations were carried out on heavy mineral concentrates obtained from the beneficiation of samples of 360 kg in initial weight. Thus, a limit of detection better than 0·0005 ppm was obtained. The incorporation of the analytical techniques into a general procedure, which permitted calculation of the local gold content and classification of the type and source of the unconsolidated sediments, is described.

Determination of total and cold-extractable fluoride in soils and stream sediments with an ion-sensitive fluoride electrode

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An ion-sensitive fluoride electrode shows a Nernst-type response to fluoride ion activity over more than five orders of magnitude. The feasibility of this type of electrode in geochemical analytical work is demonstrated. Interference by other ions involved in the analysis and the technique by which it is eliminated are discussed.

Depending on time, electrolyte and the nature of the clay mineral, the fluoride adsorption capacity has been experimentally proved on soils in general, and for clay minerals in particular.

Based on these studies, a method has been developed for the determination of the cold-extractable fluoride content of soils and stream sediments. This method has been successfully applied in determining the secondary dispersion patterns of various fluorite deposits. A further method and its application for the determination of the total fluoride content of soils and stream sediments, by sintering with NaOH, are also discussed.

Geochemical zoning of copper–nickel mineralization and its endogenous haloes, with reference to the ore deposits of the Norilsk Group

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All the copper–nickel deposits of the Norilsk region are connected with differentiated basalt intrusions, but not all the intrusions are ore-bearing. Investigations on the main ore deposits of the Norilsk region have led to the following conclusions.

(1) Ore-bearing intrusions with a complex structure are surrounded by endogenous haloes of considerable dimensions which carry both the main and accessory elements, Ni, Cu, Ag, Pb, etc., and elements typomorphic of rocks that form traps, Ti, V, Mn, Cr, etc.

(2) A feature of the endogenous haloes is their close relationship to tectonic disturbances, which determine their configuration to a considerable extent.

(3) A distinct zoning can be established in the structure of the endogenous

haloes – expressed in the relative concentration of some elements in parts of the haloes above the intrusions (Cu, Pb, Ag, etc.) and of others below the ore-bearing intrusions (Ti, Co, etc.).

(4) A lateral zoning of the distribution of the elements, established in the ore-bearing intrusions, clearly determines the direction of movement of the magmatic melt: a relative concentration of Ba and Sn is observed in the upper portions, whereas Co, Ni, Cr, etc., are concentrated in the lower portions.

(5) A comparative study of the ore-bearing and barren intrusions revealed criteria for their recognition – for example, the elementary composition of the haloes and the nature of zoning.

Features of the distribution of elements in intrusions and accompanying endogenous haloes can be used successfully in prospecting for copper–nickel deposits. Endogenous haloes above intrusions having a considerable vertical extent (the first 100 m) can be used to trace concealed deposits, and the lateral zoning of the haloes and of the ore-bearing intrusions themselves can be used to correct the direction of the exploration work.

Data from lithogeochemical ore sampling will help to solve genetic problems associated with the deposits – for example, determination of the direction of movement of the magmatic melt and the role of disturbances in localizing mineralization.

Zeeman spectrometer for the measurement of atmospheric mercury vapour

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There has been considerable recent interest in the use of mercury vapour as a tracer for various classes of mineral deposits. As a very volatile toxic metal, mercury and its components are also receiving attention as an environmental pollutant. In the past the accurate determination of the vapour by atomic absorption has been notoriously unreliable – due mainly to the many possible interferences.

A dual-beam dual-wavelength spectrometer has been developed by use of the 2536-Å resonance line. The dual or reference wavelength is generated by Zeeman-splitting the emission line by repetitively pulsing a magnetic field around the discharge lamp. Differential measurements of the absorption during the periods of 'field' and 'no field' yield a direct value of mercury vapour concentration.

A more advanced technique makes use of the different planes of polarization of the centre and split emission components. With an electro-optical modulator and analyser the two components may be sequentially routed through the spectrometer. The extension of the technique to other elements and its application to the chemical analysis of airborne particulates are discussed. The possibility of isotopic measurements is also mentioned.

The mercury spectrometer has been extensively field tested, both in geological and pollution applications. Limitations of the technique as well as rejection figures for various ultraviolet-absorbing gases are presented. Data from both atmospheric and soil gas tests are put forward, and their geological significance is discussed.

New system of geologic mapping and geochemical sampling by light aircraft

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Reconnaissance geologic mapping and sampling for geochemical analyses from a light aircraft have been proved to be feasible. In areas of fair to good exposures in the Seward Peninsula, Alaska, reconnaissance geologic maps suitable for publication at 1:250 000 scale were prepared at a rate of one 15-min × 30-min quadrangle per day at a direct cost of approximately $100 per quadrangle. Several maps so prepared were checked by an impartial observer by use of a helicopter and were found to be sufficiently accurate as reconnaissance maps. From the air, mineralized structural features, gossans and potentially mineralized areas were easily seen, plotted and sampled. Devices were developed by which samples of soil, sands, stream sediments, rock fragments and humus could be collected by light aircraft. These devices are used to verify the identification of the mapped rock units and to sample the potentially mineralized areas indicated by the geologic maps made by light-aircraft traverses.

Geochemical samples can be obtained at a rate of about one sample in 2–3 min. Sampling devices were developed also for use with the helicopter. Their use enables collection of geologic and geochemical data from covered areas, steep slopes and timbered streams which, formerly, could not be sampled without long foot traverses; collection of all types of samples is materially speeded up by helicopter.

Nature of mercury anomalies at the New Calumet Mines area, Quebec, Canada

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In an effort to study the association of mercury with copper, zinc, iron, sulphur, magnesium and manganese in rock and ore, the concentrations of these elements were determined in 233 samples from the New Calumet Mine property, Quebec (a zinc–lead deposit), and from a mineralized copper prospect in the Labrador Trough.

Correlations and associations between mercury and the other elements were determined by multiple regression and factor analysis techniques.

Samples from New Calumet Mines consisted of 78 underground and 78 surface samples. Of the surface samples, in addition to fresh rock, specimens were taken from along the fractures in each outcrop. Mercury showed a significant positive correlation with sulphur at New Calumet in fresh rock samples and with zinc in samples along fractures. In the underground samples at New Calumet mercury was significantly correlated with copper and sulphur. The mercury content of samples from the copper prospect in the Labrador Trough showed a significant correlation with sulphur and copper. Mercury showed significant negative correlations with manganese at New Calumet and at the copper prospect, and with magnesium in New Calumet fresh rock samples.

Mercury and sulphur occur in higher concentrations in fracture samples at

New Calumet than in fresh rock samples. Factor analysis of both the fracture and fresh rock samples shows a factor with associated Hg, S, Cu and Zn. Ratios of Hg concentration in fracture samples with mercury in fresh samples show significant regression coefficients for analogous ratios for S and Zn. Thus, the introduction of Hg, S and Zn is probably a related phenomenon as opposed to a separate introduction of vaporous mercury.

Mercury and zinc anomalies from surface samples occur over the New Calumet orebody. Mercury anomalies occur with no coincident copper or zinc anomalies and, thus, give additional information. 51 % of the samples at New Calumet were located above underground ore and the percentages of anomalous samples located over ore were 92, 83 and 46, respectively, for Hg, Zn and Cu. Of those samples situated over ore, the percentages which were anomalous were 31, 38 and 16, respectively, for Hg, Zn and Cu.

Distribution and ratios of trace-element concentrations as a means of estimating the ore potential of granitic intrusions

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Average metal contents (ppm) in a number of eastern Siberian granitic intrusions (Table 1) show that the main ore manifestation of the region is mostly with Mesozoic granitoids, where the ore concentration does not differ from those of the Proterozoic and is only slightly higher than in the Palaeozoic (for Pb, Sn and Be).

Table 1

Age of intrusion	*Pb*	*Zn*	*Mo*	*Sn*	*Be*
Proterozoic	22	66	1·8	5·6	4·3
Palaeozoic	16	57	1·6	3·9	2·3
Mesozoic	26	44	2·0	5·4	4·7

In granitic complexes with potential tin, tungsten and other rare elements a considerably higher concentration of volatiles, and, first, of fluorine, is normally apparent. An average fluorine concentration of 0·08 % in granitic intrusions increases in tin-bearing granites to 0·3–0·4 % and in greisen to 0·8–1·0 %. Magmatic complexes with other potential ore elements differ by higher concentrations with regard to Cl, S and CO_2. In all cases the concentration level of H_2O is of great importance.

Potential ore-bearing granitoids usually show a considerable increase in the content of rare elements. This is particularly true of hypabyssal intrusions, where, in the apical parts, there may be a three- to fourfold increase in the concentration of rare elements able to migrate with the volatiles at the time of consolidation. Sometimes this enrichment is further increased by autometasomatic processes, which effect redistribution of the elements in the late stage of magmatic crustallization.

Potential ore-bearing rare metallic granitoids are characterized not only by their high concentrations but also by a high coefficient of variation, i.e. although in the apical parts of the hypabyssal intrusions of such granitoids the average content of some rare elements may increase by three or four times, the range of concentrations may increase by 10–15 times. A considerable increase of this latter parameter is one of the strongest criteria of the ore potential of granitoids for Sn, W, Be and other rare elements.

The concentration ratios of the elements also help to identify potential ore-bearing granitoids. This is particularly shown by the evolution ratios of those elements which have tended to differentiate during magmatic evolution. The Ba:Rb ratio is of greatest interest in this connexion. Thus, Ba tends to accumulate in the early potassic minerals of granite magmas, whereas Rb, which is bound up with volatile components, particularly with F, tends to concentrate in the residual melts. This is especially intensive in granitoids associated with potential Sn, W, Be and Li deposits. Differences in the Ba:Rb ratio for ore-bearing and non ore-bearing granitoids is illustrated by the Hertsinsky, Horsky and Rudohorsky granitoids of Czechoslovakia (Table 2).

Table 2

	Average content, ppm *Ba*	*Rb*	*Ba:Rb*
Non-mineralized Horsky granites	2200	150	15
Mineralized Rudohorsky granites	150	580	0·26
Average granite (after A.P. Vinogradov)	830	200	4·10

The Ba:Rb ratio in the mineralized Rudohorsky granites is seen to be 50 times less than in the non ore-bearing Horsky granitoids and 15 times less than in the average granite of Vinogradov. For this type of ore-bearing granitoids the K:Rb ratio is also of interest, especially if we compare the ratio in the later ore-bearing granitoids with that of earlier (pre-mineralization) granitoids of the same complex (Table 3).

Table 3

	Southeastern Transbaikalia K:Rb ratio	*Rudnie Gori (ore mountains), Czechoslovakia*
Granitoids preceding the ore-bearing intrusions	230	280
Ore-bearing granitoids	100	65

In the ore-bearing granitoids the K:Rb ratio does not exceed 100, whereas in the earlier granitoids it is greater than 200. The ratios for F:Li and Li:Zn are also discussed.

The importance of these trace-element features in estimating the ore potential of granitoids has been demonstrated for tin, tungsten and beryllium. Granitoids associated with Mo, Au, Pb, Zn and Hg mineralization have yet to be studied in detail from this point of view.

Identification of trace mercury compounds in rocks as a guide to sulphide mineralization at Keel, Eire

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In view of the geochemical significance of mercury as a pathfinder element for potential areas of sulphide mineralization, an investigation into the bedrock geochemistry of the Keel zinc–cadmium prospect, County Longford, Eire, is being undertaken at the Royal School of Mines, London, to study the relationship of mercury to the known areas of sulphide mineralization in the vicinity of this prospect.

Initial studies of total mercury in sieved −80-mesh (B.S.S.) fractions from crushed rock material, with a double-beam sensitive mercury vapour analyser, confirmed the existence of a regional mercury anomaly in this area. Correspondence between total zinc and mercury in the rocks, however, was very erratic and little relationship between these two elements was found. In view of the possible masking of this mercury–base-metal relationship by loss of mercury during sample preparation, extreme care was taken with the collection, handling, storage and preparation of samples.

Initial analyses of underground and drill core material in different size fractions of the jaw-crushed rock indicated that in underground samples in the mineralized zone there was an apparent gradual increase in the mercury content with decreasing grain size. Drill core material, however, at some distance from known mineralization showed, first, an increase in total mercury with increasing grain size, and then a sharp decrease. It was decided that the samples of drill core must contain more volatile or fracture-held mercury than samples in the vicinity of mineralization. As a result, the distribution of mercury and mercury compounds in these rocks was studied in preference to total mercury analyses.

It was concluded that mercuric sulphide, mercuric and mercurous chloride, mercuric oxide and mercuric sulphate, together with elemental mercury, would be the most likely forms in which mercury would occur in rocks. Standards containing 2, 1, 0·5, 0·25 and 0·125 ppm mercury in the form of these above-mentioned compounds were made up in each of five rock bases. It was necessary to use five synthetic rock bases in order to study the effect that different natural rock matrices might induce on the thermal dissociation of mercury from its compounds. The use of elemental mercury in standards of this type was not feasible; nonetheless, it was possible to establish the dissociation characteristics of the pure metal on a semi-quantitative basis.

The analytical apparatus used for these mercury determinations was a sensitive mercury vapour meter, which worked on the atomic absorption principle, measuring the absorbance of light of wavelength 2537 Å by mercury vapour. A thermostatically controlled tube furnace was used instead of the usual RF heater to heat the samples, and a current of clean, dry air was continually passed over the samples during the course of their 45-min heating programme to 700°C. The readout from the analytical equipment was on a variable-scale, multi-speed chart recorder, which enabled a continuous trace of mercury release with respect to temperature to be obtained.

Differential thermal release curves from the standards indicated that both a qualitative and semi-quantitative analytical technique could be developed for mercury and its compounds. The integrated area under the release curves of the different mercury compounds indicates that there is considerable recombination of the nascent mercury with the gases that transport it through the apparatus, and that this amount of recombination is specific for each compound. Total release analyses for mercury take no account of this recombination effect and are therefore subject to inaccuracies.

A programme of differential thermal release of mercury from prepared rock samples indicated that the mercury at Keel was basically in two forms: mercuric chloride and mercuric sulphide. Examination of samples closely associated with mineralization has identified a zone in which mercury is present as mercuric sulphide, whereas in samples farther from mineralization mercuric chloride is the dominant mercury species. A transitional zone of mercuric chloride–mercuric sulphide is also present in some cases.

In conjunction with these analyses hot wire X-ray analyses of galena, sphalerite and pyrite have given information as to the temperature of lattice breakdown of these minerals, and have enabled other mercury release peaks on the differential thermal release graphs to be identified as due to release of mercury from the lattices of these minerals.

Preliminary indications are that a total mercury analysis is primarily important in outlining a broad exploration area, whereas specific areas of potential sulphide mineralization are better delimited by the ability to identify the area of host rock in which mercuric sulphide is the dominant mercury compound.

Fission-track radiography of uranium and thorium in radioactive minerals

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The fission-track method is a quick, relatively simple and inexpensive technique to determine the location and abundance of uranium and, in some cases, thorium in thin or polished sections of rocks. Thermal neutrons induce fission in ^{235}U, and ^{232}Th and ^{238}U fission with fast-neutron bombardment. Therefore, sections with appropriate track detectors are exposed first to thermal neutrons to induce only U, then to fast neutrons for U plus Th. The detectors are etched to reveal the damaged areas (tracks) caused by passage of massively charged fission fragments. High-quality muscovite mica is the preferable track detector for minerals with U contents greater than 10–15 ppm, mainly because tracks in mica are easy to recognize.

Polycarbonate plastic (Lexan or Makrofol) is preferred as a track detector for low contents of U and Th because this material contains essentially no inherent U; therefore, it has no background track density. Thorium is determined successfully if the Th/U ratio of the mineral is sufficiently large. Relative errors (from counting statistics) in Th are less than 25% if Th:U is greater than 3; for ratios less than 3 the errors increase rapidly and exceed 40–50% if Th:U is less than 1.

The method was applied to the study of U and Th in granitic rocks of the Sierra Nevada batholith, California, and in strongly contrasting mineralized terrains in south and east Greenland. In the Sierran granitic rocks radioelements are concentrated primarily in the accessory minerals sphene, zircon and allanite. U and Th contents, generally in the hundreds of ppm range, vary by as much as factors of 2–3 between nearby grains of accessory minerals within a single thin section.

The intense U and Th mineralizations of south Greenland are associated with lujavrites, peralkaline rocks wherein the mineral steenstrupine controls whole-rock radioactivity. Mean values of Th and U in steenstrupine are 23 000 and 6200 ppm, respectively. Adjacent grains show less radioelement variation than in the granitic rocks. Lower-radioactivity lujavrites are characterized by eudialyte, whose U and Th contents are at least an order of magnitude less than those of steenstrupine. The distribution and abundance of radioelements were also investigated in monazite, thorite and pigmentary material of the lujavrites.

Fission-track examinations of thin sections of mineralized fault zone breccia from east Greenland indicated that U is strongly associated with limonitic material in thin fluoritized veinlets, and is occasionally found concentrated near the edges of reddish opaque grains.

By combining fission-track results with an electron-microprobe study of the minerals, it may be possible to correlate the abundance of U and Th with other elements.

ADDITIONAL SYNOPSES

Given below are synopses of papers which cannot be included in the Symposium proceedings. Requests for further information on the work described should be sent to the author(s) concerned.

Geochemical prospecting for uraniferous blind orebodies

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Geochemical prospecting for shallow uraniferous orebodies has achieved some success in spite of competition from radiometric prospecting techniques. In cases where radiometry cannot be used (for example, to detect hidden deposits), geochemical exploration has an important role to play – in three particular areas.

(1) In rocks – to discover primary anomalies, which generally accompany orebodies. Investigations undertaken in France in granites could not confirm satisfactorily the existence of these aureoles. There were also sampling difficulties because of emanations from near-surface rocks. Thus, it is necessary to sample below the phreatic level either by drilling or by underground development.

(2) *In vegetation* – deep roots pass through barren subsoils to seek nourishment underground. Blocking of uranium at root level has been noted – a fact which has an important bearing on anomalies revealed in the parts of the plants above ground.

(3) *In water* – water penetrates deep underground and can yield information on the types of formation met during its passage there.

In crystalline areas, waters are generally poorly mineralized, and if the orebody is not in the zone of oxidation, there are but minor changes in their composition. If there are abnormal amounts of uranium, it is difficult to determine if these anomalies are caused by an orebody or by formations high in U. The chances are slight of being able to determine, even approximately, the origin of the anomaly because of the difficulty of discovering how waters circulate in crystalline formations.

In sedimentary areas waters are generally more extensively mineralized and reflect better the character of the geological formations encountered. Moreover, water circulation conforms to better known behaviour and it is therefore easier to localize the origin of the anomalies.

It seems that geochemical propsecting in waters, even if they are collected on surface, may be better suited than other methods to yield valuable information on subsurface uraniferous orebodies. It is necessary to be able to interpret correctly the results of the complete analyses of waters and to determine their underground course from full geological knowledge of the region under investigation. Recent examples (Ribeauvillé, Haut-Rhin, and Montmorillon, Vienne) illustrate the possibilities opened up by the procedure outlined.

Geochemical peculiarities of hydrocarbon gases in recent and ancient sediments

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A comparison is made of the compositions of oil-field gases formed in sedimentary rocks as a result of organic matter thermocatalytic transformations and marine sediment gases of biochemical origin. Investigations into the composition of gases in recent sediments show that methane is present with an admixture of heavier hydrocarbons, the content of which was many times less than methane. Also present in the gases were carbon dioxide, hydrogen sulphide, nitrogen, hydrogen, ammonia and others.

Ethane, ethylene, propane and propylene constitute the greatest part of the heavy hydrocarbon gases. Gases in recent marine sediments are of biochemical origin: typically, there is a very small amount of heavy hydrocarbons in comparison with methane, and unsaturated hydrocarbons are present. The concentration of unsaturated hydrocarbons in recent sediments of the Black Sea is 35–40% of that of heavy hydrocarbons.

Investigations of the gas background of recent marine sediments showed a considerable fluctuation of values. With increase in depth the value of the gas background in sediments also increases. A reducing environment is favourable for the increase of hydrocarbon background. The content of hydrocarbons in shallow sediments is much less than that in deep-sea sediments.

The gases in recent sediments caused by biochemical transformation of organic matter are subjected to continuous scattering, as a result of dissolution in water, diffusion and other types of migration. The most intensive scattering takes place from the upper layers of sediments: therefore, methane concentrations usually increase with depth.

Unlike the biochemical gases of recent marine sediments, the hydrocarbon gases of oil and gas pools – the formation of which is connected with thermocatalytic processes of organic matter transformations and with peculiarities of chemical reaction – contain a considerable amount of heavy saturated hydrocarbons. They do not contain significant quantities of unsaturated hydrocarbons.

Owing to the vertical migration of hydrocarbons from oil and gas pools, the gas anomalies are formed through the section up to recent sediments. From gas surveys of shelf sediments the presence of oil and gas can be determined from methane anomalies, total concentrations of the heavier gaseous saturated hydrocarbons, concentrations of individual saturated hydrocarbons and correlation of methane with other hydrocarbons and saturated and unsaturated hydrocarbons.

Portable emission spectrograph for geochemical exploration

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A new technique has been applied to geochemical exploration in the Pinchi Fault area of British Columbia, Canada, and the results obtained have proved to be extremely satisfactory. The property reported here is located approximately six miles north and west of Fort Saint James, B.C. Ajax Mercury Mines, Ltd., has a group of claims which lie in a low relatively flat basin. Mercury is only exposed in one small area, where altered limestone crops out. Near-ore-grade cinnabar in these few outcrops is closely associated with rocks which were faulted and fractured prior to fumarole mineralization.

This exposed orebody is believed to be on or close to the huge Pinchi Fault, locally referred to as Canada's mercury fault. In the vicinity of the exposed orebody the bedrock is covered by 1–8 (or more) ft of overburden, and overburden has prohibited prospecting elsewhere along the length of the fault. In fact, the strike and location of the fault structure are not known outside the immediate area where the few outcrops are located, and there are no more outcrops. Limited drilling and trenching attempts proved expensive and failed to expand the known deposit or find new ones. A programme more likely to produce an exploration target was therefore begun.

A geochemical soil and plant sampling programme was selected. It was fully realized that they were in an area where the Pinchi Fault disappears under overburden for many miles and that it had to be located before more drilling was attempted. The possible location beneath overburden of suitable structure and host rock had to be found before exploration for mercury could continue.

The methods discussed proved to be very satisfactory for this property, but the same techniques would be suitable for other prospects and for almost any mineral.

The prime purpose of the programme was to find soil along the traverse routes similar in content to the soil around the exposed orebody. First, the rocks of the exposed orebody were resampled and carefully analysed and assayed. All minerals and elements associated with the cinnabar, and their relative amounts, were noted. Soil and plants on, near or otherwise associated with the orebody were carefully sampled.

Widely spaced north–south and east–west traverse lines were run in all directions from the exposed orebody. Soil and plant samples were taken at 100- and 200-ft intervals along each line. Thus, more than 500 samples were taken not close to any known mercury occurrence. All samples were assayed for copper, zinc and, possibly, other elements. These elements were chosen for the internal standards for quantitative spectrographic analyses. Many of the samples were analysed for all or some of the same key elements mentioned above. A photograph of the spectrum of each sample was taken and compared with the spectrum of the soils from the exposed orebody, content similarities and differences being noted. If a soil appeared to contain the same elements as the soil from the orebody, a complete quantitative spectrographic analysis was run to determine the similarity of the element amounts. Thus, *complete* soil comparisons were made.

Basically, a small portable spectrograph (weight, 35 lb) was used to analyse the mineral samples. The instrument has several unique features. (1) It operates on alternate rather than direct current and can therefore be connected to any 220-V outlet or ac generator. (2) The electrodes used to excite the sample are horizontal. The specimen is fed vertically into the arc and can be raised and lowered independently of the arc: this facilitates the sequential vaporization of the various elements in the sample according to melting point. Thus, such low metling elements as lead, zinc and tin can be identified before the more complex spectrum of iron appears. (3) The spectrum from the sample is viewed directly by eye, which removes the need for elaborate photographic plates or delicate photomultiplier tubes. (4) Standard spectrograms of all the elements are built into the instrument so that they can be viewed side by side with the sample spectrum. Sample analysis consists of simply matching up the line patterns on the master spectrogram films with those in the sample spectrum. This can be done rapidly and with considerable precision. (5) Any standard 35-mm camera or Polaroid camera can be fitted on to the wide-field eyepiece to provide permanent records – and increase sensitivity. (6) A 'multi-spectra' attachment facilitates the taking of a series of photographs of various standards and unknown spectra, side by side, on the same photographic plate. (7) A 'Quantrex' attachment can be added to record the spectral lines on polaroid film in such a manner that the line lengths are proportional to the percentages of the elements generating them.

Soil in several locations was found to be similar to the soil from the exposed orebody, and high mercury and mercury associates were found. If the geochemical programme had consisted of analysis for mercury and one or two other elements only, at least three of the anomalies would have been missed. The average cost per sample was $16.00.

Geochemical criteria for oil and gas in the South Caspian Basin

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Oil and gas content in the Tertiary deposits of the South Caspian Basin is universally recognized. Drilling, however, requires the use of all possible research techniques, and geochemical criteria are of particular significance.

One of the surface indications of oil and gas in the South Caspian Basin is mud (gas-oil) volcanism, which is widespread over its continental and marine area. Given the presence of positive structural form and dislocation, geochemical investigations of solid, wet and gaseous products of the eruptive activity of volcanoes throw light on the geochemical peculiarities of the interior of the earth and enable separate stratigraphic intervals and structures to be ascertained in the context of oil and gas.

The other important criterion used in prospecting in the South Caspian Basin is the geochemistry of stratal water. Within the territory investigated most oil fields are characterized by being confined to warm zones. These zones are characterized by anomalously high stratal pressures. Hydrochemical investigations of stratal water, in combination with the study of the chemical composition of water-solved gas, have been undertaken.

Problems of searching for ore deposits beneath defluctuated formations on and at the foot of slopes

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The form and depth of secondary dispersion haloes associated with ore deposits, which are of considerable importance in geochemical prospecting, depend very much on the type of unconsolidated formations on hill slopes and the processes by which these formations developed. In the forest-covered territory of Siberia the main process of transportation of products of weathering on hill slopes is the downhill movement of unconsolidated material. In this environment, even if the cover is rather thin, lithogeochemical sampling at or near surface does not provide fine samples over the lower one-half or two-thirds of the slope. Here, the upper part of the unconsolidated formations is composed of defluctuated material, that is to say, displaced from the upper parts of the slope. [Colluvium – Ed.]

A quantitative theory of defluctuated dispersion haloes has been derived from mathematical models. It is based on an equation of material balance of unconsolidated masses undergoing slow spontaneous movement downslope:

$$\frac{\partial(\bar{u}h)}{\partial x} + \frac{\partial h}{\partial t} + K_{\rho}\frac{\partial Z_{\kappa}}{\partial t} = 0$$

where h is the thickness of the unconsolidated formations, $\bar{u}$ is the average speed of movement, $K\rho$ is the coefficient of loosening up of rocks during weathering, $\frac{\partial t_{\kappa}}{\partial t}$ is the rate of weathering x is the distance from topographical divide and t is time. Simplification of the equation for stationary processes permits a solution yielding formulae from which contours of the defluctuated haloes can be constructed. This halo type is characteristic with a sharp stretch down the slope (up to 500–700 m or more); their bedding depth depends on the disposition of orebodies on the slope.

Calculations show that conventional metallometric surveys provide an effective search of only one-third of the territory: the lower and middle sections of hill slopes with a defluctuated cover of 2–3 m and more, the bottoms of hills having a loose cover of up to 5–10 m and more and sections of valleys with a thicker drift cover are left unsearched.

Effective methods of geochemical search in this environment would be (1) litho- or hydrogeochemical sampling of the drainage system; (2) investigation of slopes by pitting along profiles; (3) drilling holes at the foot of slopes with detailed vertical sampling in intervals of 5–10 cm; and (4) in certain circumstances, biogeochemical surveys are suitable for the detection of hidden defluctuated haloes.

From sampling by these methods, the position of orebodies on hill slopes may be defined and their productivity estimated by use of the mathematical model of a defluctuated halo:

$$l = \left[\frac{2h_1}{h} - \left(\frac{h_1}{h}\right)^2\right]x$$

$$M = \kappa M'\left(1 - \frac{h_1}{h}\right)^2 \frac{x}{h - h_1}$$

where l is the distance of the orebody from the topographical divide; h_1 is the depth of the halo of the orebody in a given section of the prospecting hole; h is the general thickness of the unconsolidated formations in the hole; x is the distance of the hole from the divide; M is the productivity of the orebody (element quantity for one unit of area of the vertical projection of the orebody); M' is the vertical halo productivity taken as a product of the mass by the average metal content (%); and κ is the factor of proportionality (when κ is unknown, the productivity of the orebody is calculated M/κ).

Hidden defluctuated haloes requiring this method of geochemical search are characteristic of areas undergoing little or no active surface erosion. They are also of significance in tropical and sub-tropical woodland and savanna environments. In steppe areas, where surface erosion is intense, the haloes become open, permitting conventional metallometric surveys based on shallow sampling. The second maximum of hidden defluctuated haloes is, apparently, with zones of tropical and sub-tropical woods and savannas.

Role of structural analysis in the planning of geochemical exploration in northern Venezuela

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The knowledge of regional structures – principally, faults – is one of the most important factors in the planning of geochemical exploration in northern Venezuela, especially in the areas covered by the thick sequence of volcanic and metamorphic rocks associated with the Villa de Cura Group. The Group, which covers an area of more than 9000 km^2, is characterized by meta-tuffs, green lavas, cherts, feldspar schists and chlorite schists with copper, zinc and lead mineralization. The deposits are associated with hydrothermalism and they constitute massive lenses within structurally altered rocks of the metavolcanic sequence. It is quite possible that the basic and ultrabasic plutonic rocks which intrude the volcanic unit are associated with metallogenetic processes.

The zone under preliminary study covered areas of the upper Santa Isabel Formation, composed of feldspar schists, green lavas and chloritic rocks with evidence of mineralization. The area is situated in the northern part of Guarico State, about 120 km southwest of Caracas and 80 km southwest of Valencia.

A regional study of the structural geology of the entire area was carried out so that investigations could be concentrated on areas of economic potential. The results obtained were very satisfactory. The soil collected in the field was analysed at the sample site by Bloom's ammonium citrate-soluble heavy metals (Zn+Cu+Pb) in soil test. Four anomalies have been outlined, and they follow the structural pattern of the region.

Following this preliminary investigation, a 1:2000 scale mapping programme will be carried out on specific areas, emphasis being placed on the relationship between local structure and metal content.

Distribution parameters of minor elements in feldspar and mica crystals

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During geochemical investigations of east Siberian muscovite pegmatites considerable attention was paid to the study of element distribution parameters in minerals and rocks. It was shown by chemical and spectrochemical analyses of 45–90 small parts of giant crystals sampled on the uniform set that there are differences between crystals which grow from the melt (absence of chemical equilibrium) and metasomatic crystals (growing under conditions of crystal-solution equilibrium). The distribution of Na, Li, Cs and Tl in the former corresponds (95% level) to the log normal distribution, but in the latter to the normal one. The distribution of Rb and Pb in either case corresponds (same level) to the normal one. However, some asymmetry of frequency curves, noticeable even for these two elements, is more distinct in magmatic crystals.

In large muscovite crystals formed at the postmagmatic stage of pegmatite formation the normal distribution of all the above elements is typical. The same is true of muscovite crystals of zonal colour due to an unequal quantity of Fe admixture.

Analogous results are obtained as a result of studying the Na distribution in feldspars and mica crystals by use of the electron probe MS-46. It was shown that the Na distribution in magmatic K-feldspar is near log normal and that in metasomatic K-feldspar it is near normal.

Dispersion studies of element concentrations in feldspars and mica crystals show that for the majority of elements the coefficient of variation of element concentrations is not significantly higher than that of analytical errors. The reliability of sampling large crystals with small specimens (50–100 g) is therefore proved. Nevertheless, an estimation of sampling for each element and for each mineral must be carried out.

The possible determination of altered minerals and rocks by comparison of their distribution parameters is very interesting. For instance, it is possible to fix several stages of reformation of pegmatite bodies by use of Rb and Cs distribution curves for K-feldspars of muscovite pegmatites. Under the influence of postmagmatic solutions of the early alkaline stage one finds displacement of the mode to the side of large Rb and Cs concentrations, increase of dispersion and pronounced left asymmetry of log normal distribution. The influence of solutions of the next stage of acidity causes the displacement of the mode to the side of smaller concentrations and a pronounced right asymmetric form of frequency curve.

Geochemical exploration in an area of thick transported and residual soils, Bahia, Brazil

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On the east coast of Brazil the Precambrian rocks of the Brazilian Shield are concealed in many places by marine Tertiary sediments, called, in the State of Bahia, the Barreiras Formation. The base of the Barreiras Formation in outcrops is commonly a compact or nodular ferruginous duricrust. An attempt to prospect through this cover in a search for copper deposits by geochemical exploration techniques was only partially successful.

An area of 630 km^2 between the towns of Nazaré and Muritiba, 50 km west of Salvador, was selected for investigation because of a number of small copper prospects in high-grade metamorphic rocks of the granulite and amphibolite facies. Exposures of these Precambrian rocks are few and are confined to the valley floors. Elevations range from sea level to 200 m. The drainage pattern is trellised on the higher ground where streams are eroding through a 15-m thick cover of Barreiras Formation which rests on an uplifted marine terrace floored by metamorphic rocks.

The climate is hot and moist without prolonged dry periods. The mean annual rainfall ranges from 1734 mm at Nazaré in the south to 1000 mm at Muritiba in the north. This large variation in rainfall over the small distance of 70 km causes an important difference in soil type.

In the northeast the soils are montmorillonite-rich azonal brown soils, from 10 to 1000 cm thick, whereas elsewhere in the area the soils are kaolinite-rich and ferallitic. The kaolinite soils are divided into residual soils, commonly 20 m in depth and developed over saprolitized metamorphic rocks at lower elevations in the south, and transported soils developed over, and grading imperceptibly into, the kaolinite-rich Barreiras Formation at higher elevations in the west and north. The kaolinitic soils have a range in pH from 4·5 to 6·0 and have a very low base-exchange capacity. Consequently, cxCu and 'total' Cu (by pyrosulphate fusion) contents are low even when samples are collected adjacent to visible copper mineralization.

In a 2-km^2 area containing a copper prospect, sampling of kaolinitic transported soil on a grid pattern showed that median values are less than 5 ppm for cxCu and 5 ppm for 'total' Cu, whereas the peak values are 40 ppm cxCu and 200 ppm 'total' Cu. Although the contrasts for cxCu and 'total' Cu are high, the anomalous dispersion patterns are inhomogeneous and lack pronounced focal points. In another area kaolinitic residual soils have background cxCu and 'total' Cu values at a distance of 5 m from a small adit excavated in malachite- and chrysocolla-encrusted Precambrian rocks.

Copper mineralization has not been observed, nor have copper anomalies been located in preliminary sampling of montmorillonitic soils. 'Total' Cu background values are higher in montmorillonitic soils than in kaolinitic soils and these values may be attributed to the higher base-exchange capacity and to the higher pH, from 6·0 to 7·0, of the montmorillonitic soils.

Approximately four hundred active stream-sediment samples were collected above and below stream intersections in the Nazaré–Muritiba area in order to determine if reconnaissance drainage surveys can aid in the location of copper mineralization. The pH of stream waters in the area is high, from 5·4 to 6·2 – sufficient to ensure that most cupric ions are precipitated and held in the sediment. The −80-mesh fractions of the samples were tested for cxCu and 'total' Cu (by pyrosulphate fusion).

For interpretation the sediment samples were divided into three populations on the basis of the soil type in the drainage basin upstream from the sample station. Rock lithologies were not used as a basis for this division because lithologic changes are numerous in the sporadic outcrops. Also, few outcrops, and evidence of much rain-wash of soil down steep valley sides because of a general absence of natural vegetation, indicate that soil type more than lithology influences the chemical composition of stream sediments. Calculation of mean, standard deviation, coefficient of variation and threshold values of cxCu and 'total' Cu for each population demonstrates that the 'total' Cu threshold of sediments collected from transported kaolinitic basins is higher (at 60 ppm) than thresholds from residual kaolinitic and montmorillonitic basins (both at 40 ppm). However, cxCu threshold of montmorillonitic basins is higher (at 10 ppm) than thresholds from transported kaolinitic and residual kaolinitic basins (8·5 and 7·0 ppm, respectively). Anomalous sediment trains from known areas of weak copper mineralization are short and have a maximum length of 300 m for 'total' Cu and 700 m for cxCu. Dilution by barren colluvium from stream banks and by background sediment from tributary streams combine to cause short anomalous trains.

The presence of thick transported and residual overburden in this area of Bahia does not diminish the utility of stream-sediment geochemical surveys at a reconnaissance or semi-detailed scale for the location of copper deposits. Conventional pedogeochemical surveys at a detailed scale for the definition of primary dispersion patterns of copper in interfluvial areas are limited in their usefulness because of the thick cover. This problem will have to be overcome by the application of geochemical techniques new to the area and, perhaps, as yet undeveloped.

Deep gas survey of the South Caspian Basin

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Gas geochemistry methods play an important role not only in little studied oil regions but also in areas which have been investigated thoroughly: in the latter case they provide an additional technique for the full evaluation of the possible oil and gas fields and of different parts of the structures.

A study has been made of geological profiles of Sangachaly in an attempt to discover the possibility of using gas geochemical methods in the search for oil and gas. Twelve wells were drilled to a depth of 100 m. Changes in gas composition in the rock samples were noted. The wells have exposed the Tertiary deposits of Apsheron and the Productive Series. Samples were selected every 10 m, starting from a depth of 30 m. Comparison of gas compositions in the samples with the distribution of oil and gas deposits in Sangachaly showed that oil and gas in the northeast part of the structure coincide with the increased percentage of gaseous components from rocks of the same part of the structure.

Geochemical criteria of super-ore primary haloes of blind orebodies

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In geochemical prospecting one of the most difficult problems is the evaluation of non-commercial ore traces to ascertain if the super-ore primary haloes of blind orebodies warrant further investigation and diamond drilling. The solution of this problem is possible by study of the primary zoning of ore deposits of the same genetic type, the ratios of elements which change considerably with depth and show significant differences at various ore levels being used.

A computerized study has been undertaken of the zonality of the main genetic types of ore deposits in the U.S.S.R., satisfactory results being obtained for mercury, lead–zinc, copper and tin, among others.

Pilleys Island: an illustration of the importance of petrochemical and tectonic setting in the search for deep base-metal deposits

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The base-metal orebodies of central Newfoundland have long been known to be confined to Lower Palaeozoic basic volcanic rocks. Recent interpretations of this area within the framework of plate tectonics have emphasized that these volcanics might be from two distinctly different tectonic environments, viz. the oceanic tholeiites formed at mid-ocean ridges and the calc-alkaline lavas formed in island arcs above subduction zones. It appears that the central Newfoundland orebodies of simple mineralogy (pyrite–pyrrhotite–chalcopyrite), such as Whalesback, Little Bay and Tilt Cove, are found in the oceanic tholeiites, and the polymetallic (Cu–Pb–Zn–Ag–Au) orebodies, such as at Buchans, are found in the calc-alkaline volcanics.

Pilleys Island, lying at the boundary between these two environments, contains both types of orebody and possibly both types of volcanic. Bulk rock geochemical data are presented to demonstrate the importance of such studies in base-metal exploration in such terrains.