

GEOCHEMISTRY OVERVIEW

R.W. Boyle

Geological Survey of Canada

Boyle, R.W., *Geochemistry overview; in Geophysics and Geochemistry in the Search for Metallic Ores; Peter J. Hood, editor; Geological Survey of Canada, Economic Geology Report 31, p. 25-31, 1979.*

Abstract

In retrospect, geochemical prospecting has made major advances in the last 40 years as a result of the development of rapid and accurate analytical methods for the determination of most of the elements of the Periodic Table, a circumstance that has facilitated the elucidation of the nature of primary and secondary dispersion halos associated with most mineral deposits and accumulations of hydrocarbons. Application of this knowledge has resulted in the accelerated discovery of numerous large mineral deposits.

In prospect, it is certain that geochemical prospecting will offer an efficient and economical way of prospecting both for mineral deposits and accumulations of hydrocarbons. Future research should be focused on techniques for discovering deeply buried deposits and on aspects such as heavy mineral surveys, specific elemental and mineral indicators of mineralization, the use of isotopes, mathematical interpretative procedures, and the fundamental factors controlling the migration of the elements in endogene and exogene environments.

Résumé

La prospection géochimique a effectué des progrès considérables ces 40 dernières années, par suite du développement de méthodes analytiques rapides et précises, permettant d'identifier la plupart des éléments du Tableau périodique; ceci nous a permis de mieux comprendre la nature des auréoles de dispersion primaires et secondaires associées à la plupart des gîtes minéraux et d'hydrocarbures. La mise en application de ces connaissances explique l'intensification des découvertes de gîtes d'importance.

La prospection géochimique représentera sans aucun doute à l'avenir une méthode efficace et rentable d'exploration des gîtes minéraux et d'hydrocarbures. Désormais, les recherches devraient surtout porter sur la mise au point de techniques d'investigation des gîtes profonds, les relevés géochimiques des concentrations en minéraux lourds, les minéraux ou éléments indicateurs des minéralisations, l'utilisation des isotopes, les procédés d'interprétation mathématique et les facteurs fondamentaux qui régissent la migration des éléments dans les milieux endogènes et exogènes.

INTRODUCTION

Briefly stated "geochemical prospecting" is the application of geochemical and biogeochemical principles and data in the search for economic deposits of minerals, petroleum, and natural gases. In this paper a review of some general concepts is given followed by a summary of advances that have been made in recent years; the paper concludes with some thoughts for the future.

Some of the techniques used in geochemical prospecting have been employed for centuries in the search for mineral deposits. One is reminded of the descriptions in ancient Greek and Roman treatises of the search for gold deposits by panning the streams of an area and of the detailed instructions in Georgius Agricola's *De re metallica* of the best methods for discovering mineral veins by analyzing the water of springs and observing the deleterious or toxic effects wrought on vegetation by the presence of metallic deposits. One is also reminded of the first successful geochemical prospector, Giovanni de Castro, a Genoese gentleman of the mid-fifteenth century. It is recorded that he was engaged in manufacturing alum from alunite at the mines near Edessa in Syria. While there he observed a particular type of holly plant that characteristically grew near the veins. On returning to Italy he found similar plants growing in the hills at Tolfa, near Rome. Prospecting in this area he soon found alunite float and later the veins from which it came. This led to an important alum industry at Tolfa, and for his efforts Pope Pius II granted Castro an annuity for life and erected a statue in his honour.

In the present century the techniques of geochemical prospecting had their origin mainly in the Soviet Union and in

the Scandinavian countries, where much research on methods was carried out in the late 1930s. After World War II, the various methods were introduced into the United States, Canada, Great Britain, and other countries where they have since been used extensively in mineral- and petroleum-exploration programs by both mining companies and government agencies.

RETROSPECT AND PROSPECT

The Earth is characterized by five distinct spheres – lithosphere, pedosphere, hydrosphere, atmosphere, and biosphere – the various materials of which provide sampling media for geochemical surveys carried out in the search for mineral deposits, coal, oil, and natural gas. Geochemical surveys are, therefore, commonly classified as lithogeochemical, pedogeochemical, hydrogeochemical, atmogeochemical, and biogeochemical.

Within a specific geological terrane a general background or abundance for the various individual elements of the Periodic Table prevails in the five geospheres. Near mineral deposits or accumulations of hydrocarbons the abundance of their constituent elements generally exhibits an increase in the materials of the various spheres producing anomalies. These anomalies are manifest by primary and/or secondary elemental dispersion halos, trains, or fans in the rocks, soils, glacial deposits, hydrologic system, stream and lake sediments, atmosphere, plants and animals; also under certain conditions by the presence of indicator plants (and animals) or by elemental stimulative or deleterious (chlorotic) effects on the plants (and animals). The nature of the halos, trains, and fans are complex: in most cases there is a

consistent increase in the content of a specific element or elements toward a mineral deposit or hydrocarbon accumulation (positive or addition halos); in other cases the reverse may be true (negative or subtraction halos). These various halos, trains, and fans provide a means of tracing and locating the focal point or source from which the ore elements, gangue elements, or hydrocarbons were dispersed. They constitute the fundamental basis for all geochemical surveys.

During geochemical prospecting surveys sampling is conducted on the grid principle, on the directed walk principle, or on the random walk principle. In the first, samples are obtained at standard intervals in two or three dimensions; in the second, samples are obtained at standard intervals along some topographic or geologic feature, e.g. along a stream net or along a specific stratum; in the third samples are selected here and there with no particular pattern. The last method is not generally employed except where the geochemical survey is ancillary to other types of surveys, and the geologist observes something that excites his interest. Surveys may be shoeborne, muleborne, camelborne, shipborne, carborne, or airborne, depending on the facilities available, the elements sought in the surveys, the terrain, economics, and other factors. When the samples from the various surveys are analyzed and the results plotted, anomalies are revealed by contouring or by an inspection of increases or decreases in metal or hydrocarbon content toward some point, hopefully an economic mineral deposit or concentration of hydrocarbons.

The modern methods of geochemical exploration owe their rapid development in the 20th century to a number of circumstances which can be briefly stated as follows:

1. Elucidation of the nature of primary and secondary dispersion halos and trains that are associated with all mineral deposits and accumulations of hydrocarbons. Halos and trains have been recognized by geologists for centuries. Their importance, however, in a geochemical sense was first emphasized by A.E. Fersman and his co-workers in U.S.S.R. in the early 1930s.

2. Development of accurate and rapid analytical methods utilizing the spectrograph and the various specific sensitive colorimetric reagents, especially dithizone. G.R. Kirchhoff and R.W. von Bunsen founded the science of optical spectroscopic analysis in 1859, and Assar Hadding first employed X-ray spectrography in chemical analysis in 1922. Both methods have given immeasurable service in geochemical prospecting. Dithizone was first prepared in 1878 by Emil Fischer, who noted that its reactions with heavy metals gave brilliantly coloured products. No analytical use, however, was made of it until 1925, when Hellmut Fischer demonstrated its particular use in estimating the amounts of various trace metals in substances. Since then, dithizone and many other similar organic compounds have been widely used in geochemistry and geochemical prospecting. Actually, dithizone methods approach the limits obtainable by spectrography and in some cases they surpass them.

3. Development of polyethylene laboratory ware of all types. This permitted greater freedom in sampling and field analysis and reduced the incidence of contamination. The introduction of resins for the production of metal-free water for use in trace analysis requires no comment.

4. Development of atomic absorption spectroscopy, a particularly rapid and accurate method of determining many of the elements in earth materials in the parts per million range. For this advance we owe a great debt to the sustained research in instrumentation and methods by A. Walsh at C.S.I.R.O. in Australia. One can say without exaggeration that atomic absorption has been the most significant development in analytical geochemistry in recent years.

5. Development of fluorimetric methods of uranium analysis in the early 1950s. These methods are based on the discovery by E. Nichols and M.K. Slattery in 1926 that a trace of uranium fused in a sodium fluoride bead gives an intense yellow-green fluorescence, the magnitude of which is proportional to the amount of uranium present. More recent developments by Scintrex Ltd. of Concord, Ontario include a laser-induced fluorescence method for uranium in solution which is said to have a sensitivity of 0.05 ppb uranium in natural waters.

6. Development of sensitive methods utilizing specific ion electrodes particularly for elements such as fluorine and chlorine.

7. Development of gas, partition, paper, adsorption, and ion exchange chromatography and other precise methods of trace analysis of hydrocarbon compounds and various gaseous inorganic substances. These are probably the most significant developments as regards the rapid analysis of traces of hydrocarbons and associated gaseous inorganic compounds in petroleum prospecting surveys utilizing rocks, soils, waters, and lake and marine sediments.

8. Development of radioactive methods of detection of the radioelements, particularly uranium and thorium and their daughter elements. Following the discovery of the phenomenon of radioactivity by A.H. Becquerel in 1896, Marie Skłodowska Curie, the first radiochemist, began an extended study of natural radioactivity resulting in the discovery of polonium and radium in pitchblende from Jáchymov, Czechoslovakia. This was followed by extensive studies of the natural radioactivity of rocks, minerals, natural waters, and the atmosphere by many chemists, geologists, and physicists. The instruments used in the early work were the photographic plate, electroscope, electrometer, ionization chamber, and spinthariscopes, the last a most valuable instrument developed for nuclear research by W. Crookes. In 1908 the Geiger tube was developed and modified in 1928 as the Geiger-Müller tube; the latter was adapted to field use by G.M. Shrum and R. Smith (1934) at the University of British Columbia in 1932. Prior to this (about 1930) H.V. Ellsworth (1932) of the Geological Survey of Canada used an improved version of the electroscope in the field surveying of uranium- and thorium-bearing pegmatites and other radioactive bodies. Electronic scintillation counters based on the principal of the spinthariscopes, but employing sensitive photomultiplier tubes, were developed by S.C. Curran and W.R. Baker in 1944. This was followed in succeeding years by much research on large volume crystals for counting beta-particles and gamma radiation, culminating in the development by R. Hofstadter in 1948 of thallium-activated sodium-iodide crystals for the detection of gamma radiation. These crystals have remained for many years the most important detector medium for gamma-ray scintillation spectrometry. Scintillation counters were first adapted to field use in 1949 by G.M. Brownell (1950) of the University of Manitoba. Today many of the airborne spectrometers have reached a high degree of sophistication employing as many as 1024 channels for total gamma counting and specific quantitative analyses of elements such as potassium (^{40}K), uranium (as ^{214}Bi), and thorium (as ^{208}Tl). Early radiometric surveys were mainly shoeborne; today many of the surveys are carborne, airborne, or shipborne.

9. Development of methods of radioactivation analysis: In a modern sense these methods, utilizing certain nuclear properties of the isotopes of the elements sought in the sample, were developed after the Second World War. Most methods utilize thermal neutrons as the bombarding particles (neutron activation analysis). Such methods have an extremely high sensitivity in the parts per billion range for elements such as gold, platinoids, uranium, and so on. They have been used extensively in basic geochemical research for many years and are now finding increasing use in geochemical prospecting.

10. Development of methods for estimating radioactive elements such as uranium, thorium, and radon by fission and alpha-track analyses. These methods have had a long history in nuclear research. Within the last five years a number of variations of the method have been adapted for the field and laboratory analysis of radon by consulting geochemical companies. A novel in-field method for the determination of radon by alpha-sensitive dielectric film under the trade name "Track Etch" has been developed by Terradex Corporation of Walnut Creek, California. This method utilizes cups that are placed in a shallow hole in the ground and left for a period of 3 weeks or more; they are then recovered and the film returned to a central laboratory for analysis. Another novel radon gas detector developed by Alpha Nuclear of Caledon East, Ontario utilizes a solid state detector (silicon diffused junction) coupled to an electronic integrating readout metering device. This reusable instrument is placed in a hole in the ground and left for one or two days, after which the radon concentration and the number of hours of integration can be read from a visual numeric display.

11. Development of rapid and precise methods of analyses of various volatile elements such as mercury, sulphur compounds, helium, and radon in rocks, soil gases, waters, and in the atmosphere. The instruments adapted for such work include the gas chromatograph, atomic absorption spectrometer, mass spectrometer, and a number of variations of alpha counters.

12. Utilization of mass spectrometric methods, originally developed by F.W. Aston in 1919, for the determination of the isotopic abundances of lead, sulphur, hydrogen, and so on. Some of the abundance data may indicate the presence of certain deposits (e.g. radiogenic lead derived from thorium and uranium deposits); other systematic abundance data may be the basis for vectoring in on mineral deposits or accumulations of hydrocarbons.

13. Development of rapid and precise methods of analysis of various types of both organic and inorganic particulates in the atmosphere. O. Weiss (1971) in South Africa and A.R. Barringer (1977) in Canada have pioneered these techniques utilizing aircraft as sampling vehicles. The methods provide a broad scanning technique of a terrane and under favourable circumstances may indicate the location of mineral deposits and oil fields.

14. Refinement of field techniques in carrying out reconnaissance and detailed surface geochemical surveys of all types but especially those based on stream sediments, lake-bottom sediments, heavy minerals, stream and lake waters, groundwaters, springs and their precipitates, and biological materials. In recent years the use of helicopters has revolutionized sample collection in reconnaissance surveys in practically all terrains.

15. Development and refinement of methods of detailed geochemical prospecting using overburden drilling techniques in permafrost terranes, glacial terranes, and in deeply weathered and lateritized terranes.

16. Development of methods for discovering ore shoots or their extensions based on primary halos and leakage halos.

17. Development and refinement of methods using ore boulder, gangue boulder, and heavy mineral trains and fans for prospecting in glacial terranes and in deeply weathered and lateritized terranes.

18. Research and development of efficient methods in the processing and assessment of geochemical prospecting data by statistical and computer techniques.

19. Improved understanding of the geochemistry of mineral deposits and concentrations of hydrocarbons, particularly the chemistry of their genesis.

Geochemical prospecting is now being employed with increasing emphasis in all terrains of the world from tundra to tropical belts. Among its successes can be claimed the discovery of a considerable number of large, low grade deposits that yield gold, copper, uranium, nickel, lead, and zinc. Here we may mention a few of these with brief comments: Carlin-type gold orebodies (Cortez deposit) in Nevada related to anomalies discovered by the United States Geological Survey using gold, arsenic, and other indicators in oxidized bedrock and residual soil surveys (U.S.G.S., 1968); the enormous auriferous Muruntau deposit in Uzbek S.S.R., discovered by a U.S.S.R. prospecting syndicate using arsenic as an indicator in soils and weathered residuum (Khamrabaev, 1969); the great Panguna (Bougainville) copper porphyry in the Solomons chain located by stream sediments and soil sampling (Baumer and Fraser, 1975); the extensive Beltana and Aroona willemite deposits in South Australia discovered by stream sediment sampling (Muller and Donovan, 1971); the McArthur River lead-zinc deposits, Northern Territory, Australia by soil sampling (Murray, 1975); the large Lady Loretta lead-zinc deposit in Queensland by grid soil sampling (Cox and Curtis, 1977); the large Woodlawn copper-lead-zinc deposit in New South Wales by roadside reconnaissance stream sediment and soil sampling (Malone et al., 1975); the Casino porphyry-copper-molybdenum deposit in Yukon by stream sediment, water, bedrock, and soil sampling (Archer and Main, 1971); a number of prospects and deposits, particularly the Husky lead-zinc-silver deposit in the Keno Hill area, Yukon by overburden drilling and geochemical sampling methods (Van Tassell, 1969); the Howards Pass zinc-lead belt in Yukon by stream sediment and soil surveys; the Island Copper porphyry deposit in Vancouver Island, British Columbia by soil sampling (Young and Rugg, 1971); the Sam Goosly copper-silver-molybdenum deposit in central British Columbia by stream sediment and soil sampling (Ney et al., 1972); the Brandywine gold-silver-copper-lead-zinc deposit in western British Columbia by stream sediment and soil sampling (Anon, 1974); the Coed-y-Brenin porphyry copper deposit in North Wales by soil surveys (Mehrtens et al., 1973; Rice and Sharp, 1976); and the Tynagh and a number of other lead-zinc-copper-silver deposits in Eire mainly by soil sampling (Schultz, 1971). This by no means exhausts the recent successes by geochemical methods. In a recent paper Glukhov (1974) estimates that some 80 000 surface (metallic) halos and anomalies have been identified by geochemical prospecting methods in U.S.S.R. in the last 20 years. Investigation of these has led to the discovery of some 220 deposits (now being mined or at the development stage) of a variety of elements and some 900 prospects. The percentage ratio of deposits to anomalies is, therefore, a not very impressive, 0.3 per cent. The percentage is no better in other countries. The present writer estimates that of some 100 000 anomalies located in Africa, Europe, Asia, North America, South America, and Australia in the last twenty years by geochemical methods, some 150 orebodies (now being mined or at the development stage) have been found associated with these anomalies, giving about the same order of magnitude for the ratio. In both U.S.S.R. and other countries many of these anomalies have not been adequately tested, and more discoveries of orebodies associated with perhaps about 500 anomalies may be expected in each case.

It is interesting to note which methods have been most successful. Glukhov (1974) attributes nearly all of the successes in U.S.S.R. to surface lithochemical methods (soils, stream sediments, heavy minerals, and rocks). Only a few discoveries have been made by hydrogeochemical (water) methods, and none by biogeochemical (plants, animals) and atmogeochemical (gases) methods. Glukhov (op. cit.) also mentions that the discovery rate and the potential for discovery of near-surface deposits is declining rapidly in U.S.S.R. and advocates greater attention to depth methods

of geochemical prospecting. In other countries the story is about the same. Nearly all discoveries are attributable to stream sediment, pedogeochemical, and lithogeochemical work and very few to hydrogeochemical (water), biogeochemical (plants), and atmogeochemical work. With respect to airborne radioactivity surveys for thorium and uranium the recent report by the International Atomic Energy Agency, Vienna (1973) on uranium exploration methods is of interest if considered with caution because of different definitions of deposits, prospects, etc. Of some 11 284 anomalies outlined by all means in 21 countries (excluding Australia, Canada, France, South Africa, U.S.A. and U.S.S.R.) some 256 deposits were discovered. Of the total anomalies 3402 were outlined by aerial surveys resulting in 37 deposits. In the 17 conterminous Western States of U.S.A. some 100 000 radioactive anomalies were outlined resulting in some 700 deposits. Of the total anomalies some 4000 were discovered by aerial surveys resulting in 120 deposits. Again it is apparent that surface methods are the most effective. Without going into details it is also apparent from the data that airborne methods are most effective in arid, low vegetation, and desert terrains.

There is little public information available on the discovery of oil and gas fields by geochemical methods and one cannot draw any logical conclusions. In recent years some oil fields have been located by detailed studies of hydrocarbons in groundwaters and overlying soils and glacial deposits (Heroy, 1969). Even the hydrocarbon content of the sediments of the sea and of the overlying seawater has been employed in searching for submarine oil pools (Hitchon, 1977), but no case histories on the success or failure of this type of work appears to have been published.

The writer would now like to turn the reader's attention to desirable future research in geochemical prospecting and discuss some aspects of the subject that should receive immediate attention. Some of these are general whereas others are of a detailed nature and demand action if sufficient minerals and energy materials are to be available to maintain our industrial society as it now exists let alone possible future expansion in the world community.

The first general problem concerns the delineation of geochemical provinces and their relationship to metallogenic provinces. Many metallogenic provinces are known and were clearly outlined in many parts of the world long before geochemistry came into vogue. Others remain to be discovered and defined not only in remote and inaccessible regions but also in those that have been extensively explored. Numerous extensions of known metallogenic provinces under extensive drift or younger rocks, likewise, remain to be delineated. It is now clear that surficial and biological materials such as soils, stream sediments, lake sediments, groundwaters, and vegetation reflect the presence of certain types of exposed metallogenic provinces, particularly those mineralized with copper, lead, zinc, nickel, and uranium. But what about the other 50 or more important elements of the Periodic Table? Here we have very little precise knowledge. Furthermore, we do not yet know for certain whether or not fresh (unmineralized) rock samples (or lithogeochemistry) reflect the presence and type of metallogenic provinces in a region. It would appear that the cases for uranium (e.g. Bear Province in Canada's Northwest Territories; Lake Athabasca region, Saskatchewan; Bancroft area, Ontario) and copper (e.g. Kupferschiefer; Michigan copper belt, Seal Lake copper belt, Labrador) are positive, but in the writer's experience the cases for gold, silver, lead, zinc, and many other elements are equivocal in most regions. We need to know much more about the trace and major element chemistry of rocks and their geochemical relationship to metallogenic belts especially when drilling through deep overburden or younger overlying rocks. The targets in such types of mineral exploration are

small, even the primary halos, and enlargement of the target utilizing favourable indicator rocks is highly desirable.

The second most important field of research in geochemical methods involves the development of methods for discovering mineral deposits and concentrations of hydrocarbons deeply buried in the rocks. We tend to think and work within a two-dimensional framework and generally have the mentality of areal explorers, paying practically no attention to the third or depth dimension. Mining geologists are forced to think in three dimensions if their respective mines are to remain in business, and they have developed a number of sophisticated methods in their search for ore. If these techniques were combined with those of geochemistry, basing the search for ore on the principles of primary halos, leakage halos, and favourable primary and secondary ore localizing features, it is certain that many orebodies would be discovered within the confines of known mineral belts at minimal cost. We need to know much more about the three-dimensional morphology of primary halos, particularly leakage halos, and their relationship to orebodies, subjects that have received very little attention in the last few years. In this respect it is well worth mentioning that lithogeochemical techniques are potentially powerful exploration tools which offer depth penetration well beyond the limits of any foreseeable conventional geophysical method. The nature of the groundwater systems in mineral belts has also received only cursory attention, yet sampling of this medium can be profitable in ore search as outlined by Boyle et al. (1971). Concerning concentrations of hydrocarbons it can be said without exaggeration that we have little precise knowledge about the nature, morphology, and chemistry of the rock and ground (stratal) water halos associated with accumulations of hydrocarbons, a circumstance that is ludicrous considering the enormous amount of drilling done for oil and gas in the last 75 years. Until we know the exact characteristics of both the elemental, salt, and hydrocarbon halos associated with oil and gas fields we cannot use geochemical prospecting to discover such fields. The writer predicts that when we seriously begin to use geochemical prospecting in petroleum and natural gas exploration we shall find throughout the world as many oil and gas pools as are now known. The writer made a similar prediction with respect to mineral deposits in a talk in 1960; that prediction is rapidly proving true.

Large sections of metalliferous regions in many countries containing potential orebodies are covered by deep surficial deposits; in countries like Canada and U.S.S.R. these deposits constitute various glacial materials; in Australia and parts of United States, Central America, South America, and Africa the deposits are laterites; and in various countries the surficial materials are recent sediments or volcanoclastics. After considerable research in many countries it is now evident that the only viable geochemical approach to mineral exploration in these deeply covered terrains is the overburden drill and chemical analyses of materials from favourable horizons, commonly the basal horizon. Some research has been done on defining the character (hydromorphic and/or mechanical), morphology, and relationship to mineralization of dispersion fans, trains, and halos buried deeply in or by surficial deposits. Much more research, however, must be done on the mechanical and chemical dispersion characteristics of the elements in glaciated, lateritized, and sediment-volcanoclastic covered terranes to provide a sound basis for the interpretation of the dispersion patterns found in such terranes.

During geochemical surveys it is common to find numerous anomalies that vary in elemental nature, size and intensity. At our present state of knowledge it is not generally possible to differentiate anomalies related to mineralization and mineral deposits from those that represent enrichments from the country rocks due to an infinite variety

of geochemical factors. In other words we lack definitive screening techniques. In this respect much more work is required on specific indicators of particular types of mineralization and mineral deposits, on the relationship of the ratios between elements to mineralization, and on the intensity relationship of elemental dispersion with distance from the focus of mineralization. Concerning the same subject we should concentrate considerable research on the elucidation and formulation of interpretative techniques to relate the size and intensity of trace element halos and dispersion trains to the estimated size and grade of mineral deposits.

Biogeochemical, geobotanical, and atmogeochemical methods have received considerable research in recent years but have not as yet found extensive use in mineral and hydrocarbon exploration. The reason for this is not clear. Despite the fact that anomalies found during biogeochemical and atmogeochemical surveys are of a second-order nature and thus twice removed from primary mineralization, the dispersion patterns are commonly more distinct and often possess greater contrast than those in associated soils, weathered residuum, stream sediments, and waters. There is also the added factor in biogeochemical surveys that trees and shrubs draw metals from depth, in some cases a hundred feet or more in arid regions. This should be a great advantage in Australia and in many countries in Africa, Asia, and South America. A novel approach is the use of sap analysis where the appropriate tree coverage is present. This method has already proved of interest in defining auriferous zones and those enriched in elements such as copper, zinc, niobium, uranium, etc. Another novel method, the use of dogs as "ore sniffers" deserves much more attention than it has so far received.

Increased research in the use of geochemistry in locating viable thermal zones in the earth for harnessing geothermal power should be assiduously pursued. Much research of this kind has been conducted in the North Island of New Zealand and in the Larderello Valley of Italy where much electric power is generated from thermal waters (steam). Work in these and other countries has shown that thermal areas are indicated by elevated contents of elements such as mercury, arsenic, antimony, thallium, boron, and silica in spring and groundwaters. In addition there is considerable evidence that the thermal zones are indicated by increased amounts of the alkalis, including Na, K, and Rb, and by increases in the Na/K and other ratios in the waters.

For many years economic geologists have discussed the various mineralizers including B, CO₂, S, Se, Cl, Br, I, and F, elements and compounds that provide the ligands for the facile transport of the elements in both epigenetic and syngenetic processes. One or more of these elements are universal in practically all types of mineral deposits, yet we have not employed them to full advantage in geochemical prospecting methods. Two of these elements, B and F, are universal indicators of practically all types of epigenetic deposits; where one is not present the other is, and in many deposits both occur.

Many elements are specific indicators of certain types of deposits. Among these may be mentioned gold, beryllium, radium, antimony, bismuth, tellurium, and the platinoids. All have very low abundances in all geochemical spheres of the earth; when found in detectable concentrations (1 ppm or more for gold and 1.4×10^{-6} ppm or more for radium), one can be certain that deposits hosting these indicators (e.g. copper deposits, silver deposits, nickel deposits, uranium deposits, etc.) occur in the environment. Excepting gold and perhaps radium we have little precise knowledge of the distribution and geochemistry of these elements in mineral deposits and their dispersion halos, trains, and fans. This is a fertile field for research, and one that could prove most useful in various geochemical prospecting methods.

Much more attention should be paid to heavy mineral surveys in all terrains. The writer and his colleagues have observed that in the mountainous regions of Yukon Territory and in the Appalachians of Canada, elemental dispersion trains in the stream and river systems are caused as much by transport of particulate matter as by hydrologic processes. Traditionally, heavy mineral surveys have been used to define areas enriched in metals having a low degree of chemical mobility in the supergene cycle. Our studies indicate, however, that analyses of heavy mineral concentrates for the chemically more mobile elements can outline metalliferous zones. In this respect geochemical and mineralogical analyses of heavy mineral concentrates from the drainage net can complement normal stream sediment surveys and provide additional information that can aid in the interpretation of stream sediment data. Furthermore, particulate dispersion trains of hypogene and supergene minerals may be more extensive than hydromorphic trains especially in carbonate terranes where chemical mobility of a number of elements may be restricted due to the relatively high pH.

The writer would like to make a plea for the greater use of bogs (muskegs) as sampling media in northern terrains, especially those that have been glaciated. Many of these bogs represent ancient lakes infilled with gyttja and peat during the long interval since the last glaciation. Sampling of the bogs, particularly the lower horizons (which in actual fact represent ancient lake sediments), on a regional basis could be an effective method of locating mineralized belts and zones that are heavily drift-covered and not generally amenable to other methods of geochemical prospecting.

Studies of the isotopic distribution of a number of elements in mineral deposits and accumulations of hydrocarbons began in earnest some twenty-five years ago yet few of the results obtained have been utilized in geochemical prospecting. A number of papers have suggested the use of isotopes in geochemical prospecting, but the writer has seen no detailed accounts of case histories using the techniques available. The most suitable isotopes for prospecting purposes would appear to be sulphur, lead, uranium, carbon, and hydrogen although many others may eventually prove useful. Isotopes are a large subject, but a few simple examples of their possible use in prospecting may be given. High amounts of radiogenic lead isotopes in heavy minerals such as pyrite and galena in soils and stream sediments may indicate the presence of uranium and/or thorium deposits, and excess contents of ²³⁴U manifest in higher ²³⁴U/²³⁸U abundance ratios in natural waters may reflect the presence of concentrations of uranium minerals when compared with background abundances produced by disseminations of uraniumiferous minerals in a terrane. Systematic variations in the sulphur isotopic ratios in the metamorphic zones and alteration halos associated with sulphide deposits may indicate approach to orebodies. Similarly, systematic changes in the carbon and hydrogen isotopic ratios in sedimentary rocks and stratal waters may signal approach to petroleum and natural gas reservoirs.

Countries should now give thought to the production of standardized regional geochemical maps on a national grid based on analyses for the principal elements in the Periodic Table in materials of the lithosphere (rocks), pedosphere (soils), hydrosphere (waters, stream sediments, lake sediments), and biosphere (vegetation, bogs, etc.). One sample per square kilometre would appear advisable; in mineral belts a much higher density is desirable. For most countries such a program may require a concentrated effort lasting a century or more. Such maps will provide invaluable data for mineral exploration and a host of environmental studies concerned with forestry, fishing, agriculture, recreation, etc.

Considerable thought and research should be directed to the problem of the proper timing of the use of geochemical methods in the overall exploration program. Having carefully observed for more than 25 years the procedures of many companies and other organizations in many countries pursuing exploration, the writer is convinced that this subject is one that requires much more attention than it has up to now received. In my opinion the proper sequence of events in exploration is: (1) Geological assessment, (2) Geochemical reconnaissance utilizing one or more of hydrogeochemical and stream and lake sediment methods, pedogeochemical methods, lithogeochemical methods, biogeochemical methods, airborne radioactive methods, and atmospheric particulate methods, (3) Utilization of geophysical and/or detailed geochemical methods to obtain a sharp focus on the sites of mineralization indicated by the anomalous patterns revealed by the reconnaissance geochemical surveys. Only in terranes where geochemical prospecting is found unsuitable, and they are few in this writer's experience, should step 2 be omitted.

All aspects of mathematical interpretation of geochemical data require concerted research in the future. Particular attention should be paid to the methods of vector analysis in both two and three dimensions. The simplest vector is a stream with increasing concentration of elements in the water or stream sediments upstream to the site of a mineralized zone or deposit. It seems to this writer that considering the large amount of data now available one should now be able to quantify vectors obtained from surface surveys and also those obtained in three dimensions. In many cases we have at our disposal vectors with direction and magnitude (including concentrations or ratios between various elements) from which we should be able to predict precisely which kinds of vectors are likely to indicate orebodies.

Finally, the writer would urge that we devote more attention and research funds to a better understanding of the factors controlling the migration of the elements in endogene and exogene environments. In this respect the universities, and especially the geological faculties, have an obligation that in the writer's opinion has been neglected in many parts of the world. An examination of the curricula and research projects of many universities discloses a sad omission of what could be called "useful geochemistry", namely the study of the elements as we find them in nature. In the recent geological literature there is a plethora of erudite studies dealing with the great manifestations of the earth but few dealing with the fundamental geochemical factors that are useful in interpreting the results of geochemical surveys.

A number of recent textbooks and reviews are now available on the subject of Geochemical Prospecting; some of these are included in the Selected Bibliography.

SELECTED BIBLIOGRAPHY

Anon

- 1974: How geochemical prospecting found the Brandywine deposit in B.C.; *Western Miner*, v. 47, no. 9, p. 56-58.

Archer, A.R. and Main, C.A.

- 1971: Casino Yukon – A geochemical discovery of an unglaciated Arizona-type porphyry; p. 67-77, in *Geochemical Exploration*, Can. Inst. Min. Met., Spec. Vol. 11, Editors R.W. Boyle and J.I. McGerrigle.

Barringer, A.R.

- 1977: Airtrace – An airborne geochemical exploration technique; in *Proc. First William T. Pecora Mem. Symp.*, Oct. 1975, U.S. Geol. Surv., Prof. Paper 1015, p. 231-251.

Baumer, A. and Fraser, R.B.

- 1975: Panguna porphyry copper deposit, Bougainville; in *Economic geology of Australia and Papua, New Guinea*; Editor, C.L. Knight, Austr. Inst. Min. Met. Monogr. Ser. 5, p. 855-866.

Beus, A.A. and Grigorian, S.V.

- 1977: *Geochemical exploration methods for mineral deposits*; Editor A.A. Levinson, Translator R. Teteruk-Schneider, Applied Publishing Ltd., Wilmette, Illinois, 287 p.

Boyle, R.W.

- 1976: *Geochemical prospecting*; in *McGraw-Hill Encyclopedia of Science and Technology*, 4th ed., v. 6, p. 124-129.

Boyle, R.W. and Garrett, R.G.

- 1967: *Geochemical prospecting – a review of its status and future*; *Earth Sci. Rev.*, v. 6, p. 51-75.

Boyle, R.W., Hornbrook, E.H.W., Allan, R.J., Dyck, W., and Smith, A.Y.

- 1971: *Hydrogeochemical methods – Application in the Canadian Shield*; *Can. Inst. Min. Met. Bull.*, v. 64, no. 715, p. 60-71.

Boyle, R.W. and McGerrigle, J.I. (Editors)

- 1971: *Geochemical exploration*; *Can. Inst. Min. Met., Spec. Vol. 11*, 594 p.

Brooks, R.R.

- 1972: *Geobotany and biogeochemistry in mineral exploration*; Harper and Row, Publishers, New York, 290 p.

Brownell, G.M.

- 1950: *Radiation surveys with a scintillation counter*; *Econ. Geol.*, v. 45, p. 167-174.

Butt, C.R.M. and Wilding, I.G.P. (Editors)

- 1977: *Geochemical exploration 1976*; *J. Geochem. Explor.*, v. 8, no. 1/2, 494 p.

Cameron, E.M. (Editor)

- 1967: *Proceedings, Symposium on Geochemical Prospecting*, Ottawa, April, 1966; *Geol. Surv. Can.*, Paper 66-54, 282 p.

Canney, F.C. (Editor)

- 1969: *Proceedings Second International Geochemical Exploration Symposium*; *Colo. Sch. Mines Q.*, v. 64, no. 1, 520 p.

Cox, R. and Curtis, R.

- 1977: The discovery of the Lady Loretta zinc-lead-silver deposit, northwest Queensland, Australia – a geochemical exploration case history; *J. Geochem. Explor.*, v. 8, no. 1/2, p. 189-202.

Elliott, I.L. and Fletcher, W.K. (Editors)

- 1975: *Geochemical exploration 1974*; Elsevier Publishing Co., Amsterdam, 720 p.

Ellsworth, H.V.

- 1932: *Rare-element minerals of Canada*; *Geol. Surv. Can.*, *Econ. Geol. Series 11*, 272 p.

Ginzburg, I.I.

- 1960: *Principles of geochemical prospecting*; Pergamon Press, London, 311 p.

Glukhov, V.A.

- 1974: Effectiveness of geochemical methods of prospecting; in *Theoretical aspects of the migration of elemental indicators of ore deposits and mathematical methods of processing geochemical information, Part II, Examples of the discovery of mineralization and deposits by means of geochemical methods*; *Akad. Nauk. U.S.S.R. Ministry of Geology, Institute of Geology, Armenian S.S.R.*

- Hawkes, H.E. and Webb, J.S.
1962: Geochemistry in mineral exploration; Harper and Row, New York, 415 p.
- Heroy, W.B. (Editor)
1969: Unconventional methods in exploration for petroleum and natural gas; Southern Methodist University, Dallas, Texas.
- Hitchon, B. (Editor)
1977: Application of geochemistry to the search for crude oil and natural gas; J. Geoch. Explor., v. 7, no. 2, Special Issue.
- International Atomic Energy Agency
1973: Uranium exploration methods; Vienna, 320 p.
- Jones, M.J. (Editor)
1973: Geochemical exploration 1972; Inst. Min. Met. (London), 458 p.
1975: Prospecting in areas of glaciated terrain, 1975; Inst. Min. Met. (London), 154 p.
- Kartsev, A.A., Tabasaranskii, Z.A., Subbota, M.I., and Mogilevskii, G.A.
1959: Geochemical methods of prospecting and exploration for petroleum and natural gas; Univ. California Press, Berkeley and Los Angeles, 349 p.
- Khamrabaev, I. Kh. (Editor)
1969: The auriferous formations and principal features of the metallogeny of gold in Uzbekistan; Acad. Sci. Uzbek S.S.R., "Fan" Publishing House, Tashkent, 396 p. (in Russian)
- Kvalheim, A. (Editor)
1967: Geochemical prospecting in Fennoscandia; Interscience Publishers, New York, 350 p.
- Levinson, A.A.
1974: Introduction to exploration geochemistry; Applied Publishing Ltd., Calgary, Alberta, 612 p.
- Malone, E.J., Olgers, F., Cucchi, F.G., Nicholas, T., and McKay, W.J.
1975: Woodlawn copper-lead-zinc deposit; in Economic geology of Australia and Papua, New Guinea; Editor, C.L. Knight, Austr. Inst. Min. Met., Monogr. Ser. 5, p. 701-710.
- Malyuga, D.P.
1964: Biogeochemical methods of prospecting; Consultants Bureau, New York, N.Y., 205 p.
- Mehrtens, M.B., Tooms, J.S., and Troup, A.C.
1973: Some aspects of geochemical dispersion from base-metal mineralization within glaciated terrain in Norway, North Wales and British Columbia, Canada; p. 105-115, in Geochemical Exploration 1972, Editor, M.J. Jones, Inst. Min. Met. (London).
- Muller, D.W. and Donovan, P.R.
1971: Stream-sediment reconnaissance for zinc silicate (willemite) in the Flinders Ranges, South Australia; p. 231-234, in Geochemical Exploration, Can. Inst. Min. Met., Spec. Vol. 11, Editors R.W. Boyle and J.I. McGerrigle.
- Murray, W.T.
1975: McArthur River H.Y.C. lead-zinc and related deposits; N.T.; in Economic geology of Australia and Papua, New Guinea; Editor, C.L. Knight, Austr. Inst. Min. Met., Monogr. Ser. 5, p. 329-339.
- Ney, C.S., Anderson, J.M., and Panteleyev, A.
1972: Discovery, geologic setting and style of mineralization, Sam Goosly deposit, B.C.; Can. Inst. Min. Met. Bull., v. 65, no. 723, p. 53-64.
- Rice, R. and Sharp, G.J.
1976: Copper mineralization in the forest of Coed-y-Brenin, North Wales; Inst. Min. Met. Trans., Sec. B, v. 85, p. 1-13.
- Schultz, R.W.
1971: Mineral exploration practice in Ireland; Inst. Min. Met. Trans., v. 80, Sec. B, p. B238-B258.
- Shima, M.
1970: Geochemical prospecting methods (Chikyu Kagaku Tanko-ho); 2nd ed.; Kyoritsu Publishing Co. Ltd. Tokyo (in Japanese), 273 p.
- Shrum, G.M. and Smith, R.
1934: A portable Geiger-Müller tube counter as a detector for radioactive ores; Can. J. Res., v. 11, no. 5, p. 652-657.
- Siegel, F.R.
1974: Applied geochemistry; John Wiley and Sons, New York, 353 p.
- United States Geological Survey
1968: U.S. Geological Survey heavy metals program progress report, 1966 and 1967; U.S. Geol. Surv., Circ. 560, p. 1.
- Van Tassel, R.E.
1969: Exploration by overburden drilling at Keno Hill Mines Limited; Colo. Sch. Mines Q., v. 64, no. 1, p. 457-478.
- Weiss, O.
1971: Airborne geochemical prospecting; in Geochemical Exploration, Can. Inst. Min. Met., Spec. Vol. 11, Editors R.W. Boyle and J.I. McGerrigle, p. 502-514.
- Young, M.J. and Rugg, E.S.
1971: Geology and mineralization of the Island copper deposit; Western Miner, v. 44, no. 2, p. 31-40.

