18B.

ADVANCES IN BOTANICAL METHODS OF PROSPECTING FOR MINERALS
PART II—ADVANCES IN BIOGEOCHEMICAL METHODS OF PROSPECTING

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Abstract

Biogeochemical methods involving chemical analysis of vegetation have been in use since the Second World War. In Australia some work has been carried out on ***Hybanthus floribundus****, a hyperaccumulator of nickel which can indicate nickel-rich rocks. Discriminant analysis of biogeochemical data on bark samples of* ***Eucalyptus lesouefii*** *at Spargoville was used to delineate the nature of the bedrock. A large amount of biogeochemical work has been carried out in Canada including work on silver at Cobalt, Ontario. Work in Central Africa has been centred mainly around the copper plant* ***Becium homblei*** *and the nickel plant* ***Pearsonia metallifera****. A number of recent developments in Fennoscandia are described, particularly on bog plants in Finland. A large number of nickel plants have been found over nickeliferous rocks in New Caledonia and many of these have a nickel content which correlates well with the nickel content of the soil. By far the greatest volume of biogeochemical work has been carried out in the Soviet Union. This work is summarized in tabular form. An interesting development in this work is the recognition by Alexander Kovalevsky that plant species and their organs may be classified according to their resistance to metal uptake. "Barrier-free" organs of selected species are clearly the best for biogeochemical prospecting. Most of the biogeochemical work in the United States has been centred around the Denver area and has involved a search for gold, zinc, copper and molybdenum.*

Important recent developments include the use of plant exudates for prospecting. Air sampling of these exudates has been suggested. Chemical analysis of herbarium specimens is another procedure which has been developed and which shows some promise for identification of plant species which may indicate mineral deposits or rocks potentially favourable for mineralization.

Résumé

Des méthodes biogéochimiques qui s'appuient sur une analyse chimique de la végétation, sont utilisées depuis la seconde guerre mondiale. En Australie, on a effectué des travaux sur l'espèce ***Hybanthus floribundus****, plante hyperaccumulatrice de nickel, qui indique la présence de roches nickelifères. On a fait une analyse approfondie des données biogéochimiques sur des échantillons d'écorce d'* ***Eucalyptus lesouefii*** *à Spargoville pour définir la nature du socle. Au Canada, il y a eu de nombreuses recherches biogéochimiques en particulier sur l'argent à Cobalt en Ontario. En Afrique Centrale, on s'est plutôt concentré sur la plante concentratrice de cuivre* ***Becium homblei*** *et la plante concentratrice de nickel* ***Pearsonia metallifera****. On a décrit un certain nombre de découvertes récentes en Fenno-Scandie, concernant surtout les plantes de tourbières de Finlande. On a signalé la présence d'un grand nombre de plantes concentratrices à nickel sur des roches nickelifères de Nouvelle-Calédonie; leur teneur en nickel concorde bien avec celle du sol. C'est un URSS qu'a été effectué le plus grand nombre de travaux de biogéochimie et ceux-ci sont présentés sous forme de tableau. Un point intéressant de cette recherche, est la constatation faite par Alexander Kovalevski, que les espèces végétales et leurs organes peuvent être classifiés selon leur résistance à l'absorption de métal. Il est clair que les organes de certaines espèces, où rien ne s'oppose à l'absorption des éléments métalliques conviennent le mieux à la prospection biogéochimique. En général, aux États-Unis, la prospection biogéochimique était concentrée dans la région de Denver et portait sur l'or, le zinc, le cuivre et la molybdène.*

Comme innovation récente d'importance, citons l'analyse des sécrétions végétales parmi les méthodes biogéochimiques. On a suggéré de prélever des échantillons d'air pouvant contenir ces sécrétions. On a mis au point un autre procédé consistant à faire l'analyse chimique de spécimens botaniques, et qui pourrait aider à identifier des espèces végétales indicatrices de gîtes minéraux ou de roches favorables à la minéralisation.

INTRODUCTION

In contrast to geobotanical methods of prospecting which involve visual observations, biogeochemical methods involve chemical analysis of vegetation. The methods were first used just before World War II when Tkalich (1938) found that vegetation could be used to delineate a Siberian iron orebody. Since then, much biogeochemical work has been carried out in the Soviet Union, Canada, the United States, Australasia and Scandinavia.

Analysis of the accumulation of elements in vegetation and the upper humic layer of soils is the basis of biogeochemical prospecting. The mechanisms whereby plants accumulate trace elements are extremely complicated but in essence involve uptake via the root system, the passage of the elements through the aerial parts of the plants into organs such as the leaves and flowers, and finally a return of these elements to the upper layers of the soil when the leaves or flowers wither and fall. The elements are then leached through the various soil horizons and are reaccumulated by vegetation in a series of steps known as the biogeochemical cycle.

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Trees and shrubs with long root systems can effectively sample beneath a nonmineralized overburden and under favourable conditions can indicate the existence of minerals at depth. This possibility is the greatest advantage of the biogeochemical method, but this advantage is worthless unless accumulation of trace elements from depth is achieved in a reproducible manner and to a degree which is proportional to the concentration of the element or elements which are sought. Although there are a large number of factors which can affect reliability of the biogeochemical method, it is still possible to apply the technique successfully, and the purpose of this review is to discuss approaches adopted in various countries under varying field conditions and to highlight the course of probable future developments. As far as possible, only fairly recent references (mainly after 1970) will be given. The reader is referred to Malyuga (1964) and Brooks (1972) for fuller listing of earlier references.

BIOGEOCHEMISTRY IN SELECTED REGIONS

Australia

The earliest biogeochemical work carried out in Australia was that of Debnam (1955) who examined vegetation in Northern Territory for uranium indicators, but found no species as reliable as soil in indicating ore deposits.

A great deal of work has been carried out throughout Australia by Cole and her co-workers (Cole, 1965; Nicolls et al., 1965; Cole et al., 1968; Elkington, 1969; Cole, 1971). Most of this work was geobotanical in nature and is described elsewhere (see report 18A, this publication).

Other biogeochemical investigations have been reported by Nielsen (1972). Severne (1972), Severne and Brooks (1972) and Cole (1973), indicated the unusually high nickel-accumulating ability of **Hybanthus floribundus** which can contain up to 23% nickel in the ash (i.e. over 1% on a dry-mass basis). The plant chemistry of **H. floribundus** has been studied by Severne (1972), Kelly et al. (1975) and Farago et al. (1975). Although it is now well established that **H. floribundus** is an accumulator of nickel, its role in mineral exploration is less clear. Severne (1972) concluded that **H. floribundus** appeared to be useful as an indicator plant for soils containing more than 0.04% nickel and Cole (1973) deduced that although this species indicates a nickeliferous environment it does not necessarily delineate a nickel sulphide orebody. The same author concluded that the nickel content of this species is related to the concentration of this element in soils and that the plant has some significance for biogeochemical prospecting.

Studies by Nielsen (1972) and Nielsen et al. (1973) have shown the possibility of using discriminant analysis of multielement data to deduce the nature of bedrock from chemical analysis of bark samples of **Eucalyptus lesouefii** from the Spargoville area of Western Australia. Samples were collected from 63 sites of known geology and analyzed for calcium, chromium, cobalt, copper, lead, magnesium, manganese, nickel and zinc. The computer was used to formulate a regression equation of the form:

$$Y = a_1\,(Ca) + a_2\,(Cr) + a_3\,(Co) + a_4\,(Cu) + a_5\,(Pb) + a_6\,(Mg) + a_7\,(Mn) + a_8\,(Ni) + a_9\,(Zn) + C$$

The coefficients a_1-a_9 were chosen to maximize the difference in scores for samples derived from two geological units (ultrabasics and amphibolites). Using the regression equation, it was possible to predict the nature of the bedrock with a certainty of 71%, from the analysis of any one sample. The method has obvious potential for areas where the bedrock is not easily available for analysis.

Other biogeochemical work in Australia includes the studies of Groves et al. (1972) at Herberton, North Queensland who showed that analysis of copper, lead, tin and zinc in **Scleria brownei** and **Coelospermum reticulatum** could be used to delineate an orebody.

Hall et al. (1973) investigated the use of **Melaleuca sheathiana** to delineate nickel mineralization at Norsewood, Western Australia and concluded that analysis of leaf material did indeed indicate mineralization in the bedrock.

To summarize, a number of biogeochemical investigations have been carried out by researchers in Australia during the past 20 years. Most large exploration companies have their own geobotanical/biogeochemical programs, though most of the published work has been done by outside experts working in collaboration with exploration companies.

Canada

A survey of biogeochemistry in Canada cannot fail to give credit to H.V. Warren and his associates from the University of British Columbia, for pioneering work on the method in that country. In the period 1947-1975 nearly 30 scientific papers on this subject were published. Much of this work has been summarized by Warren (1972) but because many of this author's publications predate 1970, and because of the emphasis on later references in this review, the reader is referred to Brooks (1972) for more complete bibliography. Warren's latest work has been concerned with analysis of vegetation for gold (Warren and Hajek, 1973) and with the use of barium/strontium ratios in geochemical prospecting (Warren et al., 1974). Warren must also be given credit for having trained a number of biogeochemists who have carried on this work elsewhere in Canada.

Apart from Warren's group at British Columbia, an appreciable amount of biogeochemical work has been carried out during the past decade by workers at the Geological Survey of Canada. The earliest of these publications are due to Fortescue and Hornbrook (1967a, 1967b, 1969) who reviewed the progress of biogeochemical research at the Geological Survey during the period 1963-1966. Perhaps one of the most interesting developments of this period was the establishment of a mobile biogeochemical laboratory (Fortescue and Hornbrook, 1967a) which was used for the routine analysis of plant material using emission spectrography. These authors have also been responsible for a number of orientation surveys in which the efficacy of the biogeochemical method was tested at various locations in Canada such as: Timmins, Ont., and Gaspé Park, Quebec (Fortescue and Hornbrook, 1969); west-central British Columbia (Hornbrook, 1969a, 1970a); Chalk River, Ont. (Hornbrook, 1970b); Cobalt, Ont. (Hornbrook, 1971, Hornbrook and Hobson, 1972); Coppermine River, N.W.T. (Hornbrook and Allan, 1970).

Elements investigated, included cobalt, copper, lead, manganese, molybdenum, nickel, silver and zinc. The same authors have also been responsible for two other reviews of biogeochemical methods (Hornbrook, 1969a, b; Fortescue, 1970).

It is impossible to review in detail all the work carried out by the above authors, but as a case history, we may briefly consider the work of Hornbrook (1971). Geochemical and biogeochemical exploration methods for silver were compared at Cobalt, Ontario. Plant samples and soils were collected from 452 stations at 25 foot intervals over six traverse lines 100 feet apart and orientated perpendicular to the strike of the silver veins. The most suitable plant organs were spurs of white birch (**Betula papyrifera**) followed by twigs of trembling aspen (**Populus tremuloides**). Anomaly

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maps for silver, cobalt, copper, nickel, lead, zinc and manganese were compared for birch spurs and soils from the $A_0 + A_1$ horizons.

The principal findings of the survey were that:

1. Silver in soils was the most effective in delineating the silver veins. Individual leakage halos from sub-outcrop fractures were detected and could be related to the projected path of principal ore veins at depth.
2. Other effective anomaly maps were: lead, manganese and zinc in soils and birch spurs, and cobalt and nickel in soils.
3. Copper anomaly maps were not effective.
4. The cobalt anomaly map for birch spurs showed preferential enrichment of cobalt in the western portion of the region. This was delineated by the soil map. The enrichment of cobalt in the western part has been established by drilling and is due to zoning of the silver veins.
5. On many anomaly maps, and most obviously on the map of silver in birch spurs, the most interesting anomalies were associated with surface contamination and not the principal ore veins.

It is clear from this survey that biogeochemistry is not an end in itself, but if combined with other methods can furnish additional useful information.

Other workers in the field of biogeochemistry in Canada include Lily Usik who has reviewed geochemical and biogeochemical prospecting methods in peatlands (Usik, 1969). This excellent review (178 references) gives a good coverage of the field, and is of particular importance because the location of ore deposits beneath organic swamp soil is one of the principal prospecting problems in Canada since water-saturated organic terrain occupies at least 1 250 000 square km (one sixth) of this country.

Further recent biogeochemical investigations are due to staff of the University of British Columbia. Doyle et al. (1973a) studied plant-soil relationships for molybdenum, copper, zinc and manganese in the Yukon. The molybdenum content of several species correlated well with the content of this element in soils. Further investigations on the molybdenum content of plants, soils and bedrock in the same area are reported by Doyle et al. (1973b). Fletcher et al. (1973) investigated the selenium content of Yukon plants and showed a correlation with selenium in soils.

Wolfe (1971, 1974) carried out biogeochemical investigations in eastern Canada. A study of molybdenum mineralization at Setting Net Lake in northwestern Ontario showed that only molybdenum distribution patterns in black spruce needles (**Picea mariana**) showed a reasonable correlation with levels of this element in soils. Copper anomalies in vegetation were extremely shallow in comparison.

Despite the very considerable amount of biogeochemical work carried out in Canada (probably greater than in any other country outside the Soviet Union), there is little evidence that the art has left the hands of the experts and has been taken over by exploration companies on anything approaching a widespread basis.

Central and Southern Africa

By far the greatest proportion of botanical prospecting in central and southern Africa has involved geobotany rather than biogeochemistry (see report 18A, this publication). The pioneering work of Duvigneaud (1958) in Katanga (Zaïre) was later followed by other work in central Africa, mainly centred around the copper indicator **Becium homblei** (Reilly, 1967; Howard-Williams, 1970). Other geobotanical work was carried out by Cole (1971) in South-West Africa and Botswana.

Certainly the most active centre of this type of research is at the University of Rhodesia where Professor Wild and his associates have carried out extensive work, mainly of a geobotanical nature (see report 18a, this publication).

The chromium, nickel, copper and cobalt content of several indigenous species has been investigated by Wild (1974) who found (all on an ash mass basis), 48 000 µg/g chromium in **Sutera fodina**, and 153 000 µg/g nickel and 3300 µg/g cobalt in **Pearsonia metallifera.** The same author Wild (1970) studied the relationship between the nickel content of eight species of plants and the nickel content of the substrate. Some of the species such as **Becium obovatum** (which is also an indicator of copper) and **Securidaca longepedunculata** showed some potential for biogeochemical prospecting.

As far as known, none of the biogeochemical work in central and southern Africa has progressed beyond the stage of looking at elemental levels in vegetation. This is in sharp contrast with geobotany which is very highly developed in central Africa.

Czechoslovakia

The first biogeochemical work in Czechoslovakia was a study by Nemec et al. (1936) on the alleged gold accumulation by **Equisetum arvense** (see also Cannon et al., 1968). Recently, a paper by Matula (1973) has shown that pine needles could be used in the Spissko-Gemersky region to prospect for chalcophile elements over sulphide deposits. The deposit was delineated by an increase of copper levels from 32 µg/g to 340 µg/g (ash mass basis). Similar results for tin and tungsten were obtained over a greisen zone.

Fennoscandia

Finland, Norway and Sweden tend to be grouped together for prospecting methods because of a similarity of terrain and geological conditions. The main problems are associated with glaciation, where the original soil cover has been removed and where the glacial till does not represent bedrock. Under such conditions, vegetation, with its ability to penetrate to bedrock, would seem to be a natural material for sampling. It is not surprising therefore that biogeochemical prospecting began in Scandinavia at about the same time as in the Soviet Union. The earliest work was that of Brundin (1939) who took out a patent for the method. This work was then followed by pioneering investigations by Vogt (1939) in the same year. One of the most useful works on biogeochemical prospecting in Fennoscandia is by Kvalheim (1967) who summarized work carried out in Norway, Sweden and Finland.

Most of the biogeochemical work in Norway has been centred around Trondheim, both at the University and at the Norwegian Geological Survey. Recent publications include a study of vegetation in lead-rich areas (Låg et al., 1969) where lead-tolerance of many species was investigated. In a later paper (Låg and Bølviken, 1974) this work was extended to encompass implications in the fields of soil chemistry and epidemiology.

Though Sweden was the home of much of the original biogeochemical work in the late 1930s, most of the subsequent biogeochemical work has been concerned with pollution studies from heavy metals and in particular with the use of mosses for measuring industrial pollution.

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Nevertheless, during the past decade there has been an upsurge of interest in biogeochemical prospecting. For example, Fredriksson and Lindgren (1967) used leaves of **Betula nana** and **Salix polaris** to investigate a sulphide orebody at Västerbotten in northern Sweden. Plants growing over the Levi orebody gave a definite anomaly (3 to 5 times background). Elsewhere the results were unreliable and uptake of copper appeared to be influenced by the degree of drainage.

In investigations over a uraniferous bog at Masugnsbyn, northern Sweden, Armands (1967) measured the alpha activity of leaves and twigs of birch (**Betula nana** and **B. alba**), willow (**Salix**) and alder (**Alnus**). Willow twigs contained up to 860 µg/g uranium in the ash. The fruit and leaves contained up to 450 µg/g. In general there was good agreement between uranium levels in plants and in the peat substrate.

The relationship between heavy metal uptake of spruce (**Picea abies**) needles and variable edaphic factors of the soil was studied by Nilsson (1972) in southern Sweden. Though not specifically oriented towards biogeochemical prospecting, the work nevertheless has important implication for this field. A similar project (Tyler, 1970) involved studying the distribution of lead in a coniferous woodland ecosystem.

Perhaps one of the most extensive Swedish biogeochemical studies in recent years was carried out by Ek (1974) over a sulphide deposit in northern Sweden. Various organs of common trees (birch, pine and spruce) were analyzed for Zn, Cu, Pb, Ni, Co, Cr, Fe, Mg, Ba and Ca. The only material giving anomalously-high values of Cu, Pb and Zn was birch bark. Most of the orebody could be delineated by levels of these three elements in the plant material.

After a long absence from biogeochemical work, Brundin reinvestigated this field by studying the use of organic material (stream peat) in stream sediments as an alternative to inorganic matter (Brundin and Nairis, 1972). This method was found to be superior to conventional methods for regions covered with glacial till. This work was later extended still further by Brundin (1975) using living roots of trees growing on stream banks. He considered that **Carex** roots were a suitable alternative to organic material in streams.

There can be no doubt that most of the biogeochemical work in Fennoscandia has been carried out in Finland in the vicinity of mineral bogs which are so common in that country. Salmi (1956) studied vegetation and peat in the vicinity of the Vihanti mining camp and showed that vegetation could be used to pinpoint anomalous parts of the bog. In a later review (Salmi, 1967), the same author summarized the "state of the art" as regards mineral bogs. Erämetsä et al. (1969) have studied the vertical distribution of uranium and other metals in peat bogs and have shown that distribution is controlled by solid humic acids and results in a concentration of elements at about one quarter of the distance from the bottom of the bog.

Lounamaa (1956) published a monumental paper on elemental abundances in various plants growing on different substrates in Finland. This work which was later extended (Lounamaa, 1967), has provided useful information on expected elemental abundances in various plants growing over specific substrates in Finland.

Kontas has studied molybdenum in till and birch leaves at Sarvisoavi (Kontas, 1976a) and Lahnanen (Kontas, 1976b) but found little response to anomalies present in the till or bedrock.

Yliruokanen (1975a, 1975b) has been responsible for determining uranium, thorium, lead, yttrium and rare earths in Finnish plants.

In the course of analyzing 172 plants (Yliruokanen, 1975a), the author determined normal background levels of these elements. Anomalously high values were only obtained for specimens growing directly over mineralization. Nevertheless (Yliruokanen, 1976b) the rare earth content of the plants appeared to reflect the rare earth content of the associated soils and rocks.

The selenium content of Finnish plants, peats, soils and rocks has been studied by Koljonen (1974, 1975) who reported up to 2.3 µg/g selenium in forest humus overlying sulphide-rich rocks. An investigation of the selenium content of 25 plant species (Koljonen, 1974) gave values ranging from 0.010 µg/g in **Picea excelsa** to 0.420 µg/g in **Alnus incana.** Higher uptakes were unusual because of the low mobility of selenium in Finnish soils.

A thorough investigation of the biogeochemical method was carried out by Bjørklund (1971) who sampled over 4000 birch twigs and soils over the Korsnäs lead deposit in western Finland. Statistical methods were used to improve the biogeochemical data and to give a better plant-soil correlation for Zn, Pb, Co and Cu. This was achieved by standardization of such variables as vegetation type, height of sampled trees and length of sampled shoots.

Because of the nature of the vegetation cover in Finland, particularly in northern latitudes, it is not surprising that a good deal of work has been carried out on the elemental content of mosses and lichens (Lounamaa, 1956). Several other surveys have been carried out and include recent work by Erämetsä and Yliruokanen (1971a, 1971b). Up to 4900 µg/g uranium was found in samples from an abandoned uranium mine, and extensive data are recorded for background (normal) levels of the rare earths and other elements in 90 lichens and 142 mosses from all over Finland.

The overall position of biogeochemistry in prospecting in Fennoscandia is dictated by the overriding problem of exploration in these glaciated areas as summarized by Brotzen et al. (1967). Because of the ubiquitous presence of glacial till, many geochemical methods (such as soil sampling) tend to be unreliable. In such cases, other methods such as biogeochemistry can play a useful role in reinforcing geochemical techniques in the search for elusive anomalies in bedrock.

Germany

A large amount of biogeochemical work has been carried out by W. Ernst in Germany. A useful reference is his 1967 summary of work on plant communities growing over heavy metal deposits (Ernst, 1967). This bibliography comprises references numbering 82 from Europe, 2 from Asia, 6 from Africa, and 6 from North America. Professor Ernst's recent work has been oriented towards plant tolerances to heavy metals, with obvious significance for the fields of geobotany and biogeochemistry in mineral exploration. He is author of a useful book on the subject (Ernst, 1974).

India

Some biogeochemical work has been carried out in India. Chowdhury and Bose (1971) examined humic complexes of several metals and discussed mechanisms whereby these could be removed from the soil. Gandhi and Aswathanarayana (1975) studied a possible base-metal indicator in south India. The plant, **Waltheria indica** appeared to be confined to mineralized ground and contained anomalously high values of Cu, K, Mn, Na, Rb, Sr, and Zn.

Italy

Biogeochemical investigations in Italy have been confined almost entirely to the work of Vergnano Gambi who was instrumental in discovering the first hyperaccumulator of nickel (**Alyssum bertolonii**) in 1947 (Minguzzi and Vergnano, 1948). This was followed by several other papers on the ecology and plant chemistry of this and other serpentine plants (see Brooks, 1972 for a fuller list of papers up to 1970). The same author (Vergnano Gambi et al., 1971) studied manganese uptake by various plants of the Appennines. **Vaccinium myrtillus** showed a remarkable accumulation (nearly 300 µg/g on a dry mass basis). The metabolism of this and other accumulators of manganese seemed to be characterized by a lower uptake of iron and consequently high Mn/Fe ratio.

Middle East

Because of arid conditions and the presence of many deep-rooted plant species, the Middle East would seem to be a good locality for successful use of the biogeochemical method. In Egypt, El Shazly et al. (1971) used **Acacia raddiana** and **A. ehrenbergiana** for prospecting for chalcophile elements such as Co, Cu, Ni, Pb and Zn. Vegetation was superior to alluvia or water in delineating anomalies in bedrock. An investigation of uptake of B, Be and Li by **A. raddiana** showed that the biogeochemical method was superior to alluvium sampling for Li but inferior for the other two elements.

Biogeochemical work has also been carried out by Allcott (1970) in Saudi Arabia.

New Caledonia

Some biogeochemical work and an appreciable amount of geobotanical work has been carried out in New Caledonia by French scientists at O.R.S.T.O.M. (Organisation de la Recherche Scientifique et Technique Outre-Mer) and by New Zealand scientists working in collaboration with them. The geobotanical work is described in Paper 18A of this review. New Caledonia is unusual in having one of the largest ultrabasic areas in the world with a serpentine flora containing a large proportion of endemic species. This flora is noteworthy in that it contains a high proportion of hyperaccumulators of nickel. So far about 15 of these hyperaccumulators (containing >1000 µg/g Ni on a dry-mass basis) have been discovered (Jaffré et al., 1971; Brooks et al., 1974; Jaffré and Schmid, 1974; Brooks et al., 1974; Jaffré et al., 1976). These hyperaccumulating plant species are always found over nickeliferous ultrabasic substrates though they do not necessarily indicate the presence of economic mineralization in the bedrock. Plant-soil relationships have been studied by Lee et al. (1977) for the hyperaccumulators **Homalium kanaliense** and **Hybanthus austrocaledonicus.** They concluded that although the nickel content of **H. austrocaledonicus** was correlated with the nickel content of the soil (i.e. this species was suitable for biogeochemical prospecting), the paucity of statistically-significant plant-soil relationships for nickel and other metals, indicated that organic constituents may have a role in controlling nickel levels in the plant.

New Zealand

Biogeochemical work in New Zealand began in 1965 when Brooks and Lyon (1966) prospected for molybdenum using **Olearia rani.** A molybdenum anomaly was delineated in combination with a soil sampling study. This work was followed by numerous investigations during the succeeding decade involving work on nickel (Timperley et al., 1970a), uranium (Whitehead and Brooks, 1969), tungsten (Quin et al., 1974), copper (Yates et al., 1974a), and zinc and lead (Nicolas and Brooks, 1969).

The theoretical basis of biogeochemical prospecting has been investigated by Brooks (1973) and Timperley et al. (1970b) who showed that the biogeochemical method is less effective for elements which are essential in plant nutrition. This is particularly true for copper and zinc. Unessential elements such as nickel and uranium tend to give much more satisfactory results.

The New Zealand workers have been instrumental in attempting to quantify biogeochemical prospecting by statistical procedures. Timperley et al. (1972a) used multiple regression analysis to reduce the variance of plant/soil ratios for copper and nickel by correcting for a number of chemical and physical variables in plants, soils and the environment. The same workers (Timperley et al., 1972b) applied trend surface analysis to biogeochemical data. Factor analysis of biogeochemical data was used by Yates et al. (1974b) in order to delineate copper anomalies at Coppermine Island, New Zealand.

The New Zealand workers have also investigated edaphic factors controlling a serpentine flora in Nelson Province. Lee et al. (1975) showed that an endemic nickel-accumulating species (**Pimelea suteri**) had a distribution controlled mainly by excess magnesium levels in the soil. Much of the New Zealand work has been reviewed by Brooks (1972).

Soviet Union

The volume of biogeochemical exploration work carried out in the Soviet Union far exceeds that of any other country. The volume is so great, that it is hardly feasible to detail it within the confines of the present review. There are several standard textbooks on biogeochemistry in mineral exploration (i.e. as distinct from geobotany). The most important of these is a work by Malyuga (1964). This book was the first to appear on the subject and has a useful bibliography of nearly 400 references. This was followed by a book by Talipov (1966) which lists 98 Russian references. Other standard texts include Nesvetaylova (1970), Tkalich (1970), Safronov (1971) and more recently, Kovalevsky (1974a). The latter work has 104 references. Kovalevsky is perhaps the most prolific of the Russian biogeochemists. He has also edited (Kovalevsky and Perel'man, 1969) a series of essays on biogeochemical prospecting. This work lists several hundred references. Kovalevsky (1975) is also author of another more specialized text (350 references) on biogeochemical aureoles. Another useful general work (mainly epidemiological but including biogeochemical prospecting) listing over 600 references is a collection of essays by Koval'sky (1974).

Study of the literature shows that a large part of the biogeochemical prospecting research is centred at the Vernadsky Institute (Moscow), Institute of Geology and Geophysics (Tashkent) and at the Buriat Interscience Research Institute (Ulan Ude). Leading biogeochemists include I.K. Khamrabaev and R.M. Talipov (Tashkent), V.V. Koval'sky (Moscow) and A.L. Kovalevsky (Ulan Ude). Because of the difficulty of covering in detail the large volume of Soviet biogeochemical literature, a selection of later references (mainly after 1970) is given in Table 18B.1.

The reader is referred to Brooks (1972) and Malyuga (1964) for Russian references before 1970.

United Kingdom

Although the volume of biogeochemical work carried out by researchers in the United Kingdom is not great, this

Table 18B.1

A summary of recent Soviet literature on Biogeochemistry in Mineral Exploration

Author	Date	Topic or elements investigated
Alekseyeva – Popova	1970	Various
Do Van Ai	1972	B, Ba, Cu, Mn, Ni, Sr
Dvornikov and Ovsyannikova	1972	Chalcophile elements
Grabovskaya and Kuzmina	1971	Be, Li, Mo, Nb, Pb, Sn
Gruzdev and Rubtsov	1972	Ra, Th, V
Ivashov and Bardyuk	1971	Zr
Kovalevsky	1969	Zn
Kovalevsky	1971	Theoretical review
Kovalevsky	1972	V
Kovalevsky	1974a	Standard text
Kovalevsky	1974b	Be
Kovalevsky	1974c	Various
Kovalevsky	1975	Standard text
Kovalevsky and Perel'man (eds.)	1969	Series of essays
Koval'sky	1974	Series of essays
Koval'sky et al.	1973	B
Letova	1970	Various
Malyuga	1964	Standard text
Malyuga and Aivazyan	1970	Various
Melikyan	1972	B
Mitskevich	1971	Various
Molchanova and Kulikov	1972	Radioactive isotopes
Nesvetaylova	1970	Standard text
Ovchinikov and Baranov	1970	Chalcophile elements
Panin and Panina	1971a	Co
Panin and Panina	1971b	Zn
Panin and Schetinina	1974	B
Prozumenshchikova	1972	Mo
Safronov	1971	Standard text
Skarlina-Ufimtseva and Berezkina	1971	Chalcophile elements
Shchulzhenko et al.	1970	Chalcophile elements
Sudnitskaya	1971	Be
Talipov	1966	Standard text
Talipov and Glushchenko	1974	Au
Talipov, Glushchenko et al.	1973	Au
Talipov, Glushchenko et al.	1974	Au and related elements
Talipov, Glushchenko et al.	1975	Au
Talipov, Glushchenko et al.	1976	Au and Sb
Talipov, Karabaev and Akhunkhodzhaeva	1971	Various
Talipov and Khatamov	1973	Various
Talipov and Khatamov	1974	Various
Talipov, Musin et al.	1974	Various
Talipov, Tverskaya et al.	1976	U and Au
Talipov, Yussupov and Khatamov	1970	Au
Yussupov, Talipov, Khatamov et al.	1970	Lichens in prospecting
Yussupov, Talipov, Yussupova et al.	1970	Various
Yussupova et al.	1970	Various

work is nevertheless of considerable historical interest because it was in England that the earliest work was carried out (Brundin, 1939). This work was continued just after World War II by J.S. Webb and his collaborators at Imperial College (e.g. Millman, 1957), again in southwest England. The same workers based at Imperial College have also carried out several other biogeochemical studies overseas (e.g. Nicolls et al., 1965).

A promising development in biogeochemical exploration is the potential of neutron activation analysis when applied to this work. Such studies are now underway at Westfield College, London under the direction of P.J. Peterson. Elements investigated include gold and arsenic (Minski et al., 1977).

United States

Despite the tremendous impetus given to biogeochemical prospecting by the well-known work of the U.S. Geological Survey in the 1950s and 1960s (e.g. Cannon, 1960; Cannon, 1964), the amount of direct research in this field has declined in the past decade. This is partly due to a shift of emphasis into the related fields of pollution, epidemiology and general environmental chemistry. Insofar as such studies involve a study of natural levels of trace elements in vegetation, they may legitimately be classified as investigations of use for biogeochemical prospecting and are therefore included in this review. References are in the main confined to publications since 1970. The reader is referred to Brooks (1972) for a listing of earlier work.

Contents

Virtually all biogeochemical prospecting work in the United States has been carried out at the U.S. Geological Survey where pioneering work was carried out by H.T. Shacklette, H.L. Cannon and many others. The investigations of each worker will be considered separately.

Natural levels of eighteen elements in vegetation of Georgia were determined by Shacklette, Sauer et al. (1970) as part of an epidemiological study. Vegetation sampled, included vegetables and eight species of common trees. The absorption of gold by plants was studied by Shacklette, Lakin et al. (1970), Lakin et al. (1974), and has been reviewed by Jones (1970). Laboratory experiments showed that gold uptake was largely a function of the complexing agent used in the test solutions. Natural levels of gold in lodgepole pines and aspens near a gold-bearing vein in Colorado were up to 1.96 µg/g (ash mass) in pine wood and up to 1.0 µg/g (ash mass) in aspen wood. Shacklette (1970) reported mercury levels in 196 native trees and shrubs of Missouri. All specimens contained <0.50 µg/g mercury. However species growing over a cinnabar deposit in the lower Yukon contained up to 3.5 µg/g (**Ledum palustre**) and there was a minimum of 0.5 µg/g in **Betula papyrifera.** The biogeochemical method has been reviewed along with other techniques by Dorr et al. (1971). The same review proposed priorities for future research in tropical regions. A comprehensive survey of trace element levels in vegetation of Missouri has been published in six open-file reports (e.g. Shacklette, 1972a) and by Erdman and Shacklette (1973). The work involved analysis of 19 elements in a large number of smooth sumac (**Rhus glabra**) stems taken from six different vegetational areas of the state. The cadmium content of plants has also been investigated (Shacklette, 1972b). Numerous values are presented for many plant species obtained from different environments in the United States some of the highest values were up to 40 µg/g in the ash of willow (**Salix** sp.) from mineralized areas in Colorado. Much of Shacklette's work on elemental levels in natural vegetation has been summarized in a recent paper (Connor and Shacklette, 1975). Values are given for 48 elements in several hundred specimens of 18 native plant species taken from 147 landscape units in the United States. Perhaps one of the most significant advances in biogeochemical exploration is the use of this technique for on-site inspections of suspected underground nuclear explosions (Shacklette et al., 1970).

Most of H.L. Cannon's publications are listed in Paper 18A of this review because of the preponderance of geobotanical papers in her bibliography. However, mention should be made of an extensive survey carried out by Cannon et al. (1968) on 21 trace elements in the horsetail (**Equisetum**). This investigation showed that the earlier reputation of this species as a gold-accumulator (Nemec et al., 1938) was completely unfounded and that the earlier high values were probably due to analytical error. In recent years Cannon and her co-workers have been increasingly involved in studies of elemental concentration in vegetation as a part of epidemiological work (Cannon, 1970, 1974). The geochemist's involvement with the pollution problem has been discussed by Cannon and Anderson (1971) and by Cannon and Hopps (1971, 1972). The same authors have published a useful paper on problems of sampling and analysis in trace element investigation of vegetation (Cannon et al., 1972).

Another active worker in the field of biogeochemical prospecting is M.A. Chaffee who has analyzed specimens of **Olneya tesota** (ironwood), **Cercidium microphyllum** (foothill palo-verde) and **Larrea tridentata** (creosote bush) for copper, manganese, molybdenum and zinc in the vicinity of porphyry copper deposits in Arizona (Chaffee and Hessin, 1971). Zinc, copper and molybdenum plots in the ash of all three species gave anomalies above a concealed deposit whereas no anomalies were evident in the soil. It was concluded that biogeochemical prospecting would be a useful tool for this particular area. In a review of geochemical techniques applicable in the search for copper deposits, Chaffee (1975) concluded that use of deep-rooted phreatophytes such as **Prosopis juliflora** (mesquite) renders biogeochemical prospecting an effective tool in the search for copper in arid environments.

The mesquite has also been used by Huff (1970) and Brown (1970) for biogeochemical prospecting. In the Pima district of Arizona, Huff (1970) detected anomalous molybdenum concentrations in the ash of mesquite stems collected 13 km away from a mineralized area. Brown (1970) discovered anomalous concentrations of copper in the stem ash of samples of mesquite collected over the Kalamazoo deposit at San Manuel, Arizona.

A brief mention will also be made of the work of Curtin et al. (1970, 1971), who studied the mobility of gold in forest humus and used it for prospecting in Colorado. The humus derived from pine and aspen proved to be a more reliable indication of gold in bedrock, than the soil, pebbles and cobbles beneath the humus. It was concluded that the technique shows promise for regions where bedrock is covered by a transported overburden.

FUTURE DEVELOPMENTS

It is clear that radically new biogeochemical techniques will need to be applied in the future if the method is to prosper. In the past, far too many biogeochemical procedures have merely involved measuring background elemental concentrations in vegetation or trying out the method over previously discovered ore deposits or anomalies. There are two fields in which the method may possibly show significant advances in the future. The first of these involves the use of multielement analysis of vegetation to detect subtle anomalies in the substrate. The data can be processed statistically, by some form of discriminant analysis (e.g. Nielsen et al., 1972) which compensates for the natural variability of the plant/substrate ratio for each element in each species. This sort of procedure will be particularly useful in environments with an overburden not representative of bedrock and particularly where phreatophytes with long root systems can be sampled (e.g. Huff, 1970; Chaffee, 1975).

A new development in biogeochemical prospecting involves the analysis of herbarium specimens. A geobotanical use of herbaria has already been made on a limited scale in the past. For example Persson (1956) noted the collection localities of Swedish herbarium specimens of the copper moss **Mielichhoferia mielichhoferi** and discovered three localities in Sweden with anomalous copper levels in the substrate (one turned out to be an existing copper mine). Later Cole (1971), carried out plant mapping of a mineralized area in southern Africa, identified characteristic plants of the region, and referred back to a herbarium for other collection localities of these species.

Until recently however, chemical analysis of herbarium material has not been feasible, because the size of sample needed for classical methods of analysis had been so great (5-10 g of plant material) that herbarium curators would hardly have tolerated such a disturbance of their collections. With the advent of atomic absorption spectrophotometry and particularly with the development of the ancilliary carbon-rod atomizer, it is now possible to analyze for several elements in tiny leaf samples less than 1 sq. cm in area (i.e. about 0.02 g). Brooks, Lee et al. (1977) used herbarium material to analyze over half of all species (nearly 2000 specimens) of the genera **Hybanthus** and **Homalium** and identified several new hyperaccumulators of nickel (>1000 µg/g in dried leaves) all of which were associated with nickeliferous substrates. The results showed that it was possible to identify most of the world's major ultrabasic areas within the tropical and warm-temperate zones by means of elevated nickel levels in the plants. This work has now been extended to a biogeochemical survey of eastern Indonesia (Celebes and Moluccas) using specimens supplied from several major herbaria. Several specimens of a species from a nickeliferous area in the Celebes were analyzed and resulted in the identification of a new hyper-accumulator of nickel (**Rinorea bengalensis**). Further herbarium specimens of this species collected from all over southeast Asia were then analyzed and resulted in the location of a previously unknown nickeliferous ultrabasic area in West Irian (Brooks and Wither, 1977). This latter specimen had been collected in 1940 by two Japanese botanists, but its significance had remained unknown for over 25 years.

Other herbarium work on species from central Africa (Brooks, 1977), has resulted in the identification of a new hyperaccumulator of cobalt (**Haumaniastrum robertii**) which is only the second known hyperaccumulator of this element (i.e. in addition to the previously known **Crotalaria cobalticola** discovered by Duvigneaud, 1958). It has also been shown that cobalt accumulation is a universal characteristic of the genus **Nyssa** (Brooks, McCleave and Schofield, 1977) and is not confined to **Nyssa sylvatica** var. **biflora** (Beeson et al., 1955).

There is however an inherent paradox in herbarium work of this nature. The more successful it becomes, the greater the demands that will be placed upon herbaria, and the greater will be the resistance of curators to furnishing further material. This reluctance to disturb specimens can be answered to some extent by use of small samples (e.g. 2-3 mg) but then the problem arises as to whether such a small sample is representative or not of the whole leaf.

An exciting new biogeochemical development is the use of plant exudates for mineral prospecting. Curtin et al. (1974) showed that condensed exudates from common conifers such as **Pinus contorta, Picea engelmannii** and **Pseudotsuga menziesii** showed the presence of a large number of trace elements transported from the substrate. The author suggested air sampling of these exudates as a tool in mineral exploration. Further work in this field was carried out by Beauford et al. (1975) who also suggested the possibilities of airborne sampling programs.

Because new ore deposits are becoming progressively more difficult to find, and because such deposits are likely to be found in the more inaccessible (often well vegetated) regions of the earth, it is clear that the biogeochemical method will continue to have a place in future prospecting operations. It is not likely that it will be used by itself, but if used judiciously in combination with other methods, should continue to be a useful component of the exploration geochemist's armoury of techniques.

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