

New Perspectives on Biogeochemical Exploration

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ABSTRACT

Significant refinements of biogeochemical methods applied to mineral exploration have been made over the past quarter century, with advances on all continents. Databases from surveys around the world provide enhanced information on which species and tissues to collect from all major climatic environments, and how, why and when to sample. Recent commercialization of sophisticated new ICP-MS analytical technology and the information emerging from studies involving the Synchrotron are permitting immensely more insight into the multi-element composition of plants. From determinations of precise ultra-trace levels in dry tissues of mineral 'pathfinder' elements, and the recognition of element distribution patterns with respect to concealed mineralization a steady understanding of relationships is unfurling. Data are now readily available on the biogeochemistry of almost all elements of the Periodic Table. Surveys conducted in undisturbed areas over the past 30 years can now be put into context of results from subsequent exploration activities, some of which have been developed as mines. Examples are presented from surveys for Au, PGEs, U, and kimberlites by reference to a wealth of previously unpublished data that until recently has been classified as confidential.

INTRODUCTION

At the 1997 decennial meeting of this series there was no paper that presented the progress in biogeochemical methods applied to mineral exploration. Hence, the last update was twenty years ago, and so this paper also includes developments over the period 1988-2007 but with the emphasis on the last decade. 1988-1997

From 1988-1997 there was steady accrual of new information as studies continued to examine the relationship of plant chemistry with respect to concealed zones of mineralization at various locations around the world. At the beginning of this period some of these studies were summarized in Kovalevskii (1987) and Brooks (1987) with later compilations by Brooks (1992) and Brooks et al. (1995). Whereas many papers were disseminated amongst the world literature, the majority of the biogeochemical studies related to mineral exploration were published in the Journal of Geochemical Exploration. The Association of Exploration Geochemists offered several short courses and published short course notes that included many 'case history' studies (Parduhn and Smith, 1991; Dunn et al., 1992, 1993, 1995). During this same period there was an increase in the application of plant chemistry to reconnaissance-level geochemical mapping (e.g., Dunn et al., 1989, 1992a,b, 1994a,b,c, 1996a,b; Dunn and Balma, 1997; Selinus, 1988), with much of the data obtained from INAA of dry and ashed material, and ICP-ES analysis of ash for those elements for which INAA is not an appropriate method. On the analytical scene method development included

improvements in the analysis of precious metals (Hall et al., 1990a,b, 1991; Hall, 1995).

In the early 1990s Markert and his co-workers further developed the concept of a 'standard reference plant', building on the attempts made by several researchers to define the average composition of plants e.g., Salisbury and Ross (1969), Lisk (1972), Bollard (1983), Marschner (1988, 1995), Mengell and Kirkby (1987), Kabata-Pendias and Pendias (1992), Markert (1992). Markert (1994) reviewed a large amount of data and published a table listing element concentrations in a world 'Reference Plant' (Table 1).

Markert's useful guide was an ambitious and difficult task because there are such wide variations in composition of the many plant species from around the globe. It has largely stood the test of time for more than a decade of new data, but the values should be considered for what the table represents - a broad guide to the world average composition of all parts of all plants, because each plant species has its own distinct chemical composition and ability to accumulate the chemical elements. Since Markert's compilation was published, the subsequent wealth of new data obtained from low-cost multi-element ICP-MS analyses has provided much lower detection limits than could previously be readily obtained for some elements, and improved estimates can be made for some elements (notably Au, Ag, Hg, PGEs, Re, Te, Tl) from many tens of thousands of new analyses. These modifications are shown in Table 1 in bold font and marked with an asterisk. It is of importance to realise, too, that element concentrations among individual tissues from a single plant are substantially different. Just as the various components of a plant - wood, bark, twigs, foliage, flowers/cones, etc. - bear no physical resemblance to each other, nor do the chemical

Table 1: Element abundances in plants (dry weight) – summary of estimates of worldwide averages of all tissues from all plants (after Markert, 1994; * indicates modifications by Dunn, 2007).

Element	Units	Conc.	Element	Units	Conc.
Major Elements (>0.1%)			Trace Elements (<1000 ppm)-cont.		
C	%	44.5	La	ppm	0.2
O	%	42.5	Li	ppm	0.2
H	%	6.5	Lu	ppb	3
N	%	2.5	Mn	ppm	200
K	%	1.9	Mo	ppm	0.5
Ca	%	1	Na	ppm	150
S	%	0.3	Nb	ppb	50
P	%	0.2	Nd	ppm	0.2
Mg	%	0.2	Ni	ppm	1.5
Cl	%	0.2	Os	ppb	0.0015
Si	%	0.1	Pa	ppb	?
Trace Elements (<1000 ppm)			Pb	ppm	1
Ag*	ppb	20	Pd*	ppb	0.1
Al	ppm	80	Po	ppb	?
As	ppm	0.1	Pr	ppb	50
Au*	ppb	0.2	Pt	ppb	0.005
B	ppm	40	Ra	ppb	?
Ba	ppm	40	Rb	ppm	50
Be	ppb	1	Re*	ppb	0.1
Bi	ppb	10	Rh*	ppb	0.01
Br	ppm	4	Ru	ppb	0.1
Cd	ppb	50	Sb	ppm	0.1
Ce	ppm	0.5	Sc	ppb	20
Co	ppm	0.2	Se	ppb	20
Cr	ppm	1.5	Sm	ppb	40
Cs	ppm	0.2	Sn	ppm	0.2
Cu	ppm	10	Sr	ppm	50
Dy	ppb	30	Ta	ppb	1
Er	ppb	20	Tb	ppb	8
Eu	ppb	8	Te*	ppb	20
F	ppm	2	Th	ppb	5
Fe	ppm	150	Ti	ppm	5
Ga	ppm	0.1	Tl*	ppb	20
Gd	ppb	40	Tm	ppb	4
Ge	ppb	10	U	ppb	10
Hf	ppb	50	V	ppm	0.5
Hg*	ppb	20	W	ppm	0.2
Ho	ppb	8	Y	ppm	0.2
I	ppm	3	Yb	ppb	20
In	ppb	1	Zn	ppm	50
Ir*	ppb	0.01	Zr	ppm	0.1

compositions of each type of tissue. Furthermore, there are chemical barriers to element translocations between tissues (Kovalevskii, 1987)

Textbooks produced during this period that contain significant amounts of biogeochemical information of use to the explorationist include those by Brooks (1992); Kabata-Pendias and Pendias (1992); Brooks et al. (1995); and a book with some fundamental new data that remains only available in Russian (БИОГЕОХИМИЯ РАСТЕНИЙ - 'The Biogeochemistry of Plants' by Kovalevsky, 1991).

1998-2007

During this period the world lost most of the leading proponents of biogeochemical methods of exploration – e.g., Professor Harry Warren in 1998; Professors Robert Brooks and Alexander Kovalevsky in 2001. These researchers provided many of the building blocks for the science, and armed with subsequent new instrumentation and ideas others are now moving forward to expand upon the concepts that they developed.

The development of ICP-MS as a commercially viable method of plant analysis over the past decade or so has resulted in a rapidly expanding database of element concentrations in dry plant tissues. ICP-MS has the advantage over other analytical methods that accurate and precise determinations can be made on dry tissue at ultra-trace levels for more than 60 elements for remarkably low cost. The method is steadily providing data for many elements that were previously difficult to determine in dry vegetation because of their very low concentrations. Some elements are present in such small quantities (e.g., Be, Bi, In, Pd, Pt, Re, Te, Tl, W) that plant tissues must still usually be reduced to ash before their concentrations can be determined by ICP-MS. High resolution (HR) ICP-MS instrumentation is required to determine their concentrations in dry vegetation.

On several fronts experimentation on sample digestion has helped to elucidate the complexities of plant chemistry, such that the explorationist now has available improved knowledge on the appropriate method to employ for optimizing the data quality for a particular element. For example, Hall et al. (2001) provided data on determination of the high field strength elements (HFSE) in vegetation. Partial leaches of vegetation have been shown to provide further insight to the labile phases of elements in plant structures, notably the halogens (Dunn et al., 2006). Details of these developments are given in Hall (1995) and Dunn (2007).

New analytical instrumentation that has high potential for providing new insight to the chemistry of plant tissues and the distribution of elements within them include Synchrotron X-ray Fluorescence (SXRF) and Proton Induced X-ray Emission (PIXE). Whereas the synchrotron is not readily available to the mineral explorationist, results from research studies are providing intriguing new information. Pickering et al. (2000, 2003) used a Synchrotron to study the distribution and chemical speciation of Se in leaves of the Se hyperaccumulator plant *Astragalus bisulcatus* (milk vetch). This fundamental investigation on Se speciation in *Astragalus* clearly demonstrated that organoselenium is concentrated in young leaf tissue whereas it is preserved as a selenate in mature leaves, and there is very little Se in stems. Similar studies have been undertaken on Tl (Scheckel et al., 2004), using one of the

hyperaccumulator species identified by Leblanc et al., 1999. In Australia, studies at CSIRO (Commonwealth Scientific and Industry Research Organization) under the AMIRA (Australian Mineral Industry Research Association) are currently making use of the Geo-Pixe instrumentation attached to a synchrotron, that involve the mapping of elements within individual plant tissues (Rob Hough and Ravi Anand, personal communication, April 2007). This information can assist the field geologist in collecting the most suitable sample medium, and the chemist in optimizing an appropriate extraction procedure.

Isotopes in plant tissues are being examined at several institutes, but their role in biogeochemical exploration for minerals is poorly established and remains at the research stage. Over the past decade more reconnaissance biogeochemical surveys were undertaken (Dunn and Hastings, 1998, 1999, 2000; Fedikow et al., 1997a,b, 1998, 1999, 2000, 2002; Lax and Selinus, 2005; Leybourne et al., 1999), and the overall biogeochemical database has been augmented from detailed studies over mineral deposits scattered around the world (e.g., McInnes, 1996 [Papua New Guinea]; Dunn et al., 1996 [Morocco]; Lintern et al., 1997 [Australia]; Lima e Cunha et al., 1997 [Brazil]; Ackay et al., 1998 [Turkey]; Arne et al., 1999 [Australia]; Cohen et al., 1998, 1999 [Australia]; Kovalevsky, 2001 [Siberia]; Nkoane et al., 2005 [Botswana]; Dunn et al., 2006 [Canada]; Anand et al., 2007 [Australia]; Batista et al., 2007 [Portugal]; Cornelius et al., 2007 [Brazil]; Ghaderian and Baker, 2007 [Iran]; and Lintern, 2007 [Australia].

New books with information of relevance to biogeochemical exploration for minerals include those covering:

- Plant analysis (Kalra, 1998)
- Hyperaccumulation of metals by plants (Brooks, 1998)
- Selected trace and ultratrace metals in plants (Shtangeeva, 2005)
- Biogeochemical processes in general (primarily those elements that are fundamental to plant structures and metabolism – C, O, H, N, S, P, Fe, Mg, Mn (Schlesinger, 2005)).
- The ninth book in the series 'Handbook of Exploration and Environmental Geochemistry', dealing specifically with Biogeochemistry in Mineral Exploration (Dunn, 2007).

SYNOPSIS OF WORLD-WIDE DEVELOPMENTS

North America

In North America the research biogeochemical activities of the United States Geological Survey have been somewhat diminished over the past twenty years, such that the incisive studies by Cannon, Shacklette, Erdman and their co-workers have not advanced significantly during this period. Meanwhile, systematic studies at the Geological Survey of Canada (summarized in Dunn, 2007), at the Manitoba Geological Survey by Fedikow et al. (1997a,b, 1998, 1999, 2000, 2002) and at various institutions across Canada have augmented the databases on the chemistry of tissues from common species of the boreal and temperate forests.

Australia

In Australia biogeochemical studies are enjoying renewed investigation. A perceived problem in the past has been the complexities that arise in dealing with the multitude of species comprising Australia's two main genera of plant - the eucalypts and the acacias. In Australia alone, there are about 850 species of eucalyptus and more than 1000 species of acacia. As yet, it has not been established if there are significant differences in metal uptake and accumulation among all the species of each of these genera. If there are, then there are problems in establishing the baseline information that is desirable for determining which might be the preferred species for sampling. However, if differences are quite minor among members of a genus or perhaps other grouping of species, then it should prove possible to mix data from similar species without compromising a survey. Furthermore, if an area has a particular species that is dominant (e.g., red river gum, *Eucalyptus camaldulensis* - a species investigated by Karen Hulme at the University of Adelaide), then that species can be used since it is the spatial relationships of element concentrations, rather than the absolute concentrations, that are the over-riding dominant factors of value to biogeochemical exploration.

In Western Australia, Nigel Brand (personal communication, with information released courtesy of Jubilee Mines NL) has reported that following the successful application of biogeochemistry over the Prospero deposit (Ni), properties owned by Jubilee Mines have been tested to assess the value of biogeochemical methods to assist in delineating the Sinclair-Skye nickel sulphide deposits. These deposits are hosted in the komatiite sequence of the Agnew-Wiluna greenstone belts, one of the world's great komatiite-hosted nickel sulphide provinces. Over the Tapinos-Prospero deposits, samples of soil, and foliage of turpentine bush (*Eremophila fraseri*) and mulga (*Acacia aneura*) were collected to assess their respective values in delineating concealed PGE-rich komatiites. From a multi-element analysis by ICP-MS it was demonstrated that the underlying ultramafic lithologies (Ni-rich komatiites) were more clearly defined by the Ni signature from the vegetation (both species tested) than the soils; Pd was not detected in the soils, yet strongly evident in the vegetation growing over the surface-projected occurrence of concealed metal-enriched bedrock. Both plants and soils were analyzed by a similar aqua regia leach. It is noteworthy that mulga is unusual among the acacias in that it is long-lived and has a deep taproot; seedlings of only 10 cm height have been found to have taproots reaching 3 m deep into the ground (ref. <http://farrer.riv.csu.edu.au>).

The Cosmos Ultramafic Belt is developing into a major nickel "Camp" where multiple deposits are clustered in close proximity. Biogeochemistry could prove to be an expedient and sensitive exploration tool for this environment.

Similarly, Cullen Resources Ltd. has recently confirmed positive but subtle indications of Ni and PGE mineralization in litter (mostly eucalypt bark) from a traverse over subcropping to thinly covered ultramafic rocks in Western Australia (Matthias Cornelius, personal communication).

Other studies pertaining to biogeochemical processes in Australia are currently under way at the University of New South Wales (Cohen et al., 1998, 1999); University of Melbourne (Arne et al., 1999); University of Adelaide (under the direction of Steve Hill); and at CSIRO in Perth. Ravi Anand at CSIRO is spear-heading an impressive range of

biogeochemical studies under the umbrella of the AMIRA project P778 'Predictive Geochemistry of Transported Overburden'. Results from these studies remain confidential at this time, because a considerable level of funding comes from participating private companies. Preliminary data from hydroponic studies and the use of the Geo-Pixie and synchrotron instrumentation clearly demonstrate uptake and location of a number of elements within the structures of common Australian plants (Mel Lintern, personal communication, 2007). This cutting-edge research will be of considerable value to understanding processes and refining the application of biogeochemical methods to assist in mineral exploration.

South America

Baccharis spp. (Thola bush of the Andean highlands, or Carqueja of southern Brazil), is one of the most common plants from the drier areas of South America. This genus is probably the most studied from a biogeochemical exploration perspective, and, because of its widespread occurrence and proven ability to accumulate metals it is a high priority biogeochemical sample medium. In southern Brazil some local studies have examined a number of species, including *Baccharis trimera* from an area of ultramafic rocks (Lima e Cunha et al., 1997). In Bolivia and Argentina Viladevall (1994) has reported on the use of *Baccharis* species in the exploration for Au and Sb, and results of several studies by Viladevall and Queralt are summarized in Dunn (2007).

Unpublished data on tree ferns (*Cyathea*) from the western Amazon have provided good responses to Au mineralization and Mo porphyries, whereas other species, such as the liana *Clusia* spp., were less informative. Surveys using bamboo-like plants (*Chusquea* spp.) from the same general area have met with limited success in that they proved to be the least sensitive of several plants collected at the same sample stations. In a study that included another bamboo-like plant, *Ischnosiphon*, collected near the Igarapé Bahia deposit in Pará State results were mixed (Machesky et al., 1993). In the Tapajos area of the Amazon jungle (Pará State) common species that have proved of value for Au exploration and environmental monitoring of Hg include *Imbauba* (*Cecropia* spp.) and *Vassoura de Botão* (*Borreria verticillata*) (Dunn and Angelica, 2000).

Indonesia

In the tropics there are many trees that have distinctive shapes or vein patterns to their leaves, assisting the non-botanist in identifying the frequency of plants in a given survey area. In Papua New Guinea and throughout Melanesia there is the tree *Astronidium paluense* that has a very distinctive leaf and has been of use in delineating Au/As mineralization at Lihir (McInnes et al., 1996).

Asia

The spectrum of climatic regimes across China ranges from desert in the northwest, through several steppe zones extending from Tibet to Mongolia, and southward into a forest zone. At the 16th International Geochemical Exploration Symposium held in Beijing in 1993, it was reported in a workshop that in China systematic biogeochemical studies began in the 1970s and in recent years the focus has been mainly on the search for deeply buried mineralization in arid regions. Researchers claim that from the analysis of willow twigs they can delineate Pb-Zn stratabound deposits beneath more than 100 m of loess and over 100 m of redbeds. Few publications on biogeochemistry applied to mineral exploration in China are in English, and when last consulted a few years ago the Chinese considered that their biogeochemical studies are still in the experimental stage.

The Japanese archipelago encompasses a wide range of vegetation zones. In the south of Japan the Japanese beautyberry (*Callicarpa mollis*) was found to be an effective indicator of Au mineralization (Yoshiyuki Kita et al., 1992). Other species of use were the fern *Arachnioides aristata*, the fig (*Ficus erecta*) and the artichoke (*Gleichenia japonica*). The leaves of pepperbush (*Clethra barbinervis*) are known to accumulate certain heavy metals, and bulk samples of this species have been collected by the Japanese National Institute of Environmental Sciences for use as a Standard Reference Material (SRM-NIES-1).

In India after a flurry of studies in the 1980s and 1990s under the direction of the late E.A.V. Prasad (Tirupati University), over the past decade there have been a few studies directed toward mineral exploration that have been reported, but much work remains to be done. The primary sources of information have been the *Journal of Exploration Geochemistry* and publications by the Indian Academy of Sciences.

Africa

Results of some biogeochemical investigations made during a National Geographic-sponsored expedition to Morocco were reported in Dunn et al. (1996), and common species that are suitable for assisting the mineral explorationist were listed. Farther south in Central Africa, results from extensive surveys undertaken by private companies are proprietary at this time. Unpublished results of surveys in the North Mara region of Tanzania by Placer Dome (P. Taufen, personal communication, 2005) demonstrated the value of several acacia species, particularly the foliage, in delineating Au mineralization from the multi-element signature that included Ag, Au, Ga, REE and U.

Europe

Many studies on biogeochemical processes are in progress throughout Europe. Most are related to environmental geochemistry, but results are pertinent to the exploration community (e.g., Reimann, 1997). A wealth of information emerges every two years from ICOBTE (International

Conference on the Biogeochemistry of Trace Elements) and ISEB (International Symposia of Environmental Biogeochemistry).

RESULTS FROM OLD SURVEYS IN CONTEXT OF SUBSEQUENT DEVELOPMENTS

In 1995 Robert Brooks noted that with respect to biogeochemical surveys: "potential pitfalls are now better understood, and methods have been streamlined. Biogeochemical prospecting for minerals is not difficult provided a number of simple steps and precautions are followed. It is a young science requiring a great deal more knowledge before its enormous potential can be fulfilled" (Brooks et al., 1995, p.239).

Since that pronouncement an abundance of new data has been acquired in order to address this 'enormous potential'. Of importance, data acquired over the past thirty years from biogeochemical surveys in undisturbed areas can now be put into context of results from subsequent exploration activities, of which some have been developed as mines. The following accounts represent a sampling of some 'case histories'.

Gold: Bisbee, Cochise County, Arizona (Summarized from Smith, 2003)

In 2003 Shea Clark Smith summarized the results of a biogeochemical survey undertaken in 1991 that resulted in the discovery of Au and Ag mineralization (Smith, 2003). Approximately 30 km south of the Bisbee porphyry copper mine, a structurally complex assemblage of Cretaceous siliciclastic rocks is covered by Quaternary pediment gravel. The latter is up to 60 m in thickness and covers what appeared to be the most structurally favourable areas. The water table was known to be at a depth of 150 m, yet mineralization was presumed to be from 30 – 60 m below the surface.

Orientation work indicated that mesquite (*Prosopis juliflora*) and white thorn acacia (*Acacia constricta*) accumulate comparable levels of metals in their tissues so that these species could be mixed without compromising the integrity of the biogeochemical response. Tests of this sort are critical before data from different species are mixed, because most plant species have unique element uptake characteristics.

Samples of dry plant tissues (the plant organs were not reported) were analyzed by INAA and ICP-ES. The data disclosed several structural trends, and drill targets were defined from zones of Au, Ag, As and Sb enrichment, accompanied by depletion of Zn and anomalous haloes of Br. Anomalous concentrations of As, Ba, Pb and Sb characterized a significant 'Fault Zone'.

The biogeochemical results were used to target 10 drill holes. The drilling confirmed mineralization beneath the biogeochemical anomalies, and found no mineralization in areas where the biogeochemical data predicted the bedrock to be barren.

Gold: Jolu Gold Mine – Saskatchewan (Summarized from Dunn, 2007)

Located in a northeast-trending linear belt of greenstones of the La Ronge Domain (Central Metavolcanic Belt) in the Star Lake area 120 km north of the town of La Ronge, Au deposits are underlain by an Aphebian (1875 Ma) metasedimentary-volcanic assemblage intruded by the Hudsonian Star Lake Pluton. Metamorphism is lower amphibolite facies resulting in chlorite-biotite-hornblende schists, locally rich in tourmaline. Gold occurrences are located within a system of regional shear zones in the metavolcanic-sedimentary succession or with shear zones in the diorite-monzonite members of the Star Lake Pluton. Shears form mylonitic zones trending 060°. The surrounding metasediments have been fractured to form a system of intersecting fractures trending 060° and 035° into which quartz veins have been emplaced. Tourmalinization and chloritization of the wall rocks to the veins are well developed.

In 1985 the Rod Zone was a trenched occurrence of a quartz vein containing visible Au and molybdenite. Field observations indicated that the quartz veining was likely to follow the regional trend of the shears, extending north-eastward beneath glacial material covered by black spruce forest rooted in boggy ground. The challenge was to discern where along this trend the quartz might be Au-bearing. It had been ascertained that the glacial till comprising the overburden was variable in thickness with a maximum of ~3 m.

Samples of outer bark scales (about 50 g) were scraped from black spruce (*Picea mariana*) at 20 sites spaced at 50 m intervals along the projected strike of the quartz vein. Samples were dried, reduced to ash by controlled ignition at 475°C and 0.5 g portions analyzed by INAA. In the following account concentrations are shown in ash with dry weight (DW) equivalents in parentheses.

In Canada's northern forests background levels of Au in spruce bark are typically 5-10 ppb in ash (0.1-0.2 ppb Au DW). In sharp contrast, at the trench the bark ash yielded 230 ppb Au (3.7 ppb Au DW), and levels greater than 100 ppb Au (2 ppb Au DW) were recorded in bark from four additional sites reaching a maximum of 690 ppb Au (14 ppb Au DW). Subsequent drilling at these sites yielded Au in each drill hole (Table 2).

After a decline was excavated at the Rod Zone, sufficient reserves were identified to establish the underground Jolu Au

mine that went into production in 1988. Reserves were exhausted by 1991 at which time the mill had processed 520,000 tons of ore and recovered 205,000 ounces of Au at an average grade of 0.42 oz/t (14.4 g/t).

Gold: Waddy Lake – Komis Deposit (Saskatchewan)

The Komis property is located in the La Ronge Domain, comprising relatively low-grade metamorphic rocks of the Central Metavolcanic Belt. Gold mineralization at Komis occurs primarily in andesite and granodiorite/tonalite dikes related to the Round Lake granodiorite stock (and locally in rhyolite), as fine disseminations of native gold (<1.0 mm) and as coarse flakes (up to 5.0 mm) in quartz veins and as fine disseminations associated with pyrite in hydrothermal alteration halos.

In 1984 Placer Development Ltd. completed a pre-feasibility study on Komis using an open pit model and concluded that the drill indicated and probable geological reserves of 1.45 million tonnes (grading 5.14 grams per tonne Au [0.15 oz/ton Au], containing 241,500 oz Au) were sub-economic at the time. Subsequently, the Komis gold mine was operated as a test mine from November, 1993 to April, 1994 and as a producing mine from 1996 to 1997.

Biogeochemical surveys were conducted in the area in 1983 and 1985, using twigs of mountain alder (*Alnus crispa*) and outer bark from black spruce (*Picea mariana*) (Dunn, 1985, 1986). In sharp contrast to background levels of < 5 ppb Au in ash, concentrations (with dry equivalents indicated as DW in parentheses) were up to 280 ppb (6 ppb DW) Au in alder twigs and 1800 ppb (36 ppb DW) Au in spruce bark. The latter value, from close to the then undeveloped Komis pit, may be partially attributed to some of the drilling activities; however, some bark samples from close to drill sites showed no Au enrichment, whereas others from apparently undisturbed forest yielded anomalous concentrations, with by far the highest concentrations occurring in samples from close to the projected contact between andesite and rhyolite. Other elements that yielded a strong response to mineralization were Mo in alder twigs and locally W in spruce bark. Zinc, REE and Ba were mostly depleted at sites of Au enrichment in the vegetation, with zones of enrichment peripheral to the Au.

Table 2: Gold in the outer bark of black spruce (*Picea mariana*) and results of a subsequent drilling programme (courtesy of G. Burrill, Mahogany Minerals). Rod Zone (subsequently the Jolu Mine), Saskatchewan. Modified after Dunn (1986).

Gold (ppb) in Outer Bark from Black Spruce		Overburden Thickness	Drill Results
In ash	Dry weight		
230	3.7	1 m	Near main trench.
120	2.4	1 m	Erratic mineralization: 1 m of 0.85 oz/t (29 ppm) Au at depth of 50 m.
690	14	2.5 m	Subcropping mineralization: 0.11 oz/t (3.8 ppm) Au over 60 cm.
450	11.3	1 m	Well mineralized shear zone: 0.3 to 0.7 oz/t (10-24 ppm) Au over 4 m.
200	3.5	3 m	Mineralization, locally over 1 oz/t (35 ppm), at shallow depth.

The latest published information states that “the bulk of the ‘minable resource’ sits within a modelled open pit at Komis with a measured and indicated resource of 601,000 tonnes grading 4.16 grams gold per tonne, about 80,500 contained ounces. A modelled pit at EP contains 24,000 measured and indicated tonnes at 6.4 grams gold, about 4,900 contained ounces” (Northern Miner, p.B2, April 30-May 6, 2007).

Gold: QR Deposit, central British Columbia (Summarized from Dunn, 2007)

The QR deposit is located in central British Columbia 140 km southeast of Prince George, adjacent to the steep banks of the Quesnel River. Outcrop is mostly masked by glacial tills of variable thickness (up to several metres), and the extensive forest cover is dominated by interior Douglas-fir and lodgepole pine.

Propylitic gold skarns are contained within a 300 m-wide hornfelsed aureole around a diorite stock. Gold occurs in and along the contact between a calcareous basalt and overlying siltstones and argillites. Gold occurs in five known zones in association with pyrite and pyrrhotite. There is minor chalcopyrite, sphalerite and galena. A detailed account of the geology and soil geochemistry of the area is given by Fox et al., 1987.

In 1988 a helicopter-borne sampling programme was undertaken by the Geological Survey of Canada to collect 103 samples from the tops of Douglas-fir (*Pseudotsuga menziesii*) trees. At the time of sampling there was little ground disturbance. Sampling was mostly at intervals of approximately 200 m along 12 lines spaced 200 m apart, with lines varying in length from 500 to 2300 m. After drying and separation of needles from stems, the stems were reduced to ash and the ash analyzed by INA.

A substantial and intense Au anomaly in the treetops was outlined (Dunn and Scagel, 1989). Subsequently, the Main and West Zones were mined by Kinross Gold Corporation between 1994 and 1998. During that period the mine produced 118,000 ounces of Au (approximately 30,000 ounces per year) from 1,060,000 tonnes of ore milled at an average grade of 4.1 grams Au/tonne.

In 2005 Douglas-fir needles from the samples that were collected in 1988 were retrieved from archive storage. Dry needles were milled and analyzed by ICP-MS (Dunn et al., 2006). Results confirmed and refined the original anomalies identified from analysis of stems validating the robustness of the geochemical signature (Figure 1).

In 2006 Cross Lake Minerals announced that they were restarting the mine after significant new reserves were discovered at the North Zone (possibly 200,000 oz Au). The North Zone is a broad area of propylitically altered basalt located below the Main Zone in the footwall of Wally's Fault. This is the largest zone of gold mineralization on the property with a drill indicated strike length of at least 1 km. Average grade for this deposit is estimated at approximately 6 g Au/tonne.

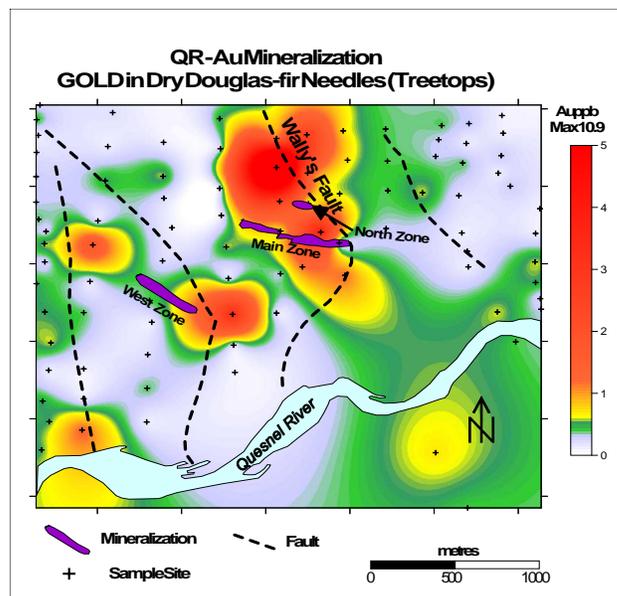


Figure 1: Gold in dry Douglas-fir needles from QR Deposit, central British Columbia

Uranium: Athabasca Basin, Northern Saskatchewan

World-class U deposits occur at the unconformity between Helikian (mid-Proterozoic) clastic deposits of the Athabasca Group and underlying crystalline basement rocks. The primary minerals are uraninite (UO₂) as massive pods, veins and disseminated aggregates; the massive variety of uraninite, pitchblende (UO₂) fills extensional features in reactivated fault zones and locally replaces the clay-mineral matrix of the Athabasca Sandstone. Associated elements include all or some of Ni (notably gersdorffite – NiAsS), Co, Cu, As, B and REE. Outcrop of Athabasca Sandstone is extremely sparse (<2 %) because of the extensive blanket of sandy glacial tills that are commonly about 1 m thick. Peat bogs and lakes fill depressions, and soils are thin podzol.

From 1979-1982 extensive biogeochemical surveys were conducted over and marginal to the Athabasca Basin. At the time that these surveys commenced in 1979 an open pit comprising the Rabbit Lake U mine was the only operating mine within a radius of several hundred kilometres from Wollaston Lake, and zones of mineralization in that area had been identified from drilling at McClean Lake, Midwest Lake and Dawn Lake. Grades of up to 27% U₃O₈ had recently been discovered at the basal unconformity beneath 150 m of unmineralized sandstone at McClean Lake (Dunn, 1981, 1983a, b).

The first surveys found that samples of black spruce twigs contained unusually high concentrations of U at McClean Lake and elevated levels at Midwest Lake. Background concentrations of U in plant ash (with dry weight equivalents in parentheses) are typically less than 1 ppm U (20 ppb DW), whereas these first samples locally yielded over 100 ppm U (2 ppm DW), and adjacent to the Rabbit Lake open pit operation a maximum of 2270 ppm U (45 ppm DW) was recorded in spruce twig ash, with nearby sites locally yielding in excess of 1000

ppm U (20 ppm DW). Subsequently, both detailed and regional surveys were conducted over the eastern part of the Athabasca Basin, which included the Athabasca Test Area (Cameron, 1983), and the ‘Wollaston Uranium Biogeochemical Anomaly’ was delineated. This anomaly comprises an area of approximately 10,000 km² within which all black spruce twigs contain >10 ppm U (0.2 ppm DW). Within this immense area the 50 ppm U (1 ppm DW) contour encompasses 3,000 km² and within a central core of 1000 km² almost all spruce trees sampled (more than 1000) contained in excess of 100 ppm U (2 ppm DW) – Figure 2. The ‘Wollaston Uranium Biogeochemical Anomaly’ remains the world’s largest known U biogeochemical anomaly.

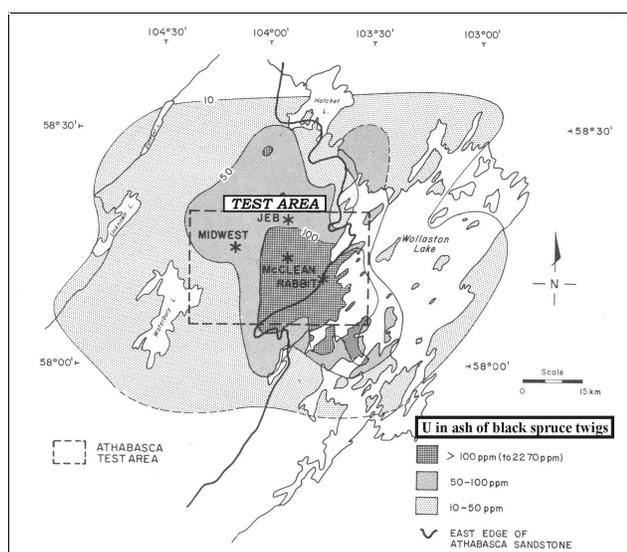


Figure 2: “Wollaston Biogeochemical Uranium Anomaly”, with U deposits referred to in the text and outline of Athabasca Test Area (Dunn, 1983a).

Within the large, zoned Wollaston anomaly there are several areas where intense local U in twig anomalies were delineated. Some of these local anomalies were sampled in sufficient detail to determine their relationships to locations of U deposits discovered since the 1979-1981 surveys. Others were too regional in their spacing to provide more than a general ‘signature’ to buried mineralization. The following observations are pertinent.

- The JEB deposit (announced in May, 1982) yielded ‘Rabbit’s Ears’ anomalies toward the eastern extent of concealed mineralization (Dunn, 1983b). Maximum concentration was 264 ppm U (5 ppm DW). The grade announced at the time was 9.72% U₃O₈ over 7 m at a depth of 90 m for a tested strike length of 190 m.
- Over the Dawn Lake deposits, spruce twigs collected by the Saskatchewan Mining and Development Corporation in 1983 yielded maximum concentrations of 80 ppm U (1.6 ppm DW).
- A linear trend of U enrichment, locally over 400 ppm U (8 ppm DW), was located 200 m west of the Sue deposits that were discovered in 1988. The Sue A, B, C, CQ and D deposits lie on a 2 km long north-trending segment of graphitic gneisses at the west contact with the Collins Bay dome.
- Intense U anomalies occur east and north of the Sue deposits. The strongest of these is 1360 ppm U (27 ppm DW) recorded from a site at the north end of Tut Lake, located 2 km northeast of the Sue and 5 km northeast of the McClean Lake deposits (Dunn, 1983b). To date the source of these anomalies has not been identified. Re-sampling of several of the same trees in 1990 confirmed that U enrichments persist.
- In 2005 Denison Mines Ltd. reported 0.53% U₃O₈ over 5 m south of Bena Lake.
- Drilling at the Mae Zone, 3 km north of the main Midwest mineralization, has recently intersected several extremely high-grade intersections over long intervals including 14.6 metres of 22.6% eU (26.7% eU₃O₈) between 189.8 and 204.4 m (Denison Mines press release, April 11, 2007).
- Since the biogeochemical sampling programme was completed in 1981, significant new discoveries (> 1 million pounds U₃O₈ and up to 70 million pounds) within the area outlined by the 100 ppm U in ash contour (Figure 2) include Collins Bay A-zone, Collins Bay B-zone, Collins Bay D-zone, Eagle Point, Raven-Horseshoe, Sue A, B, C, D and E and West Bear. Rabbit Lake and the Dawn Lake and McClean deposits had already been discovered, but only Rabbit Lake was being mined. Within the 50 ppm U in ash contour, where mineralization is mostly at greater depth, the Midwest Lake deposits were already known; subsequently, JEB was discovered and mined, and recently high grade mineralization has been reported at La Rocque (up to 31.9% U₃O₈ over 7 m reported) and Bell Lakes.
- The world-class Cigar Lake and McArthur River deposits are located to the south of the Wollaston Biogeochemical Anomaly. Any biogeochemical data that might have been acquired from over these deposits is not in the public record. However, both deposits occur at depths greater than 400 m and, unless there is considerable upward flow of groundwater from the basement unconformity (where the deposits are located) to the surface, it is considered unlikely that a significant biogeochemical response occurs. From the evidence accumulated to date, it appears that a cover of 250 m of Athabasca Sandstone is about the maximum through which a biogeochemical signature from basement-related U deposits can be detected.

These U biogeochemistry studies recount the results of survey programs completed more than 25 years ago. Extraordinarily high concentrations of U in vegetation were encountered, and the world’s largest U biogeochemical anomaly was delineated. During the intervening years there was a lull in the exploration activities because of the depressed prices for U. Over the past 2-3 years the pace of U exploration has picked up considerably and old results can start to be put in context of new activities and discoveries.

It can now be demonstrated that the Wollaston Uranium Biogeochemical Anomaly encompasses an area containing many significant zones of mineralization; more than 20 deposits have been discovered that each contain well in excess of one million pounds U₃O₈ and up to 70 million pounds.

Kimberlites

The biogeochemical signatures of several dozen kimberlites in Canada and South Africa have been examined, and details are summarized in Dunn, 2007. At this time it appears that the list of elements that most commonly are enriched in vegetation growing either over or marginal to kimberlites is, in alphabetical order, Au, Ba, Cs, Co, Hg, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, REE, Se, Sn, Sr, Ta, Te and Zn. The ultimate objective of discriminating barren from diamondiferous kimberlites remains a challenging goal.

THE NEXT DECADE

Fifty years ago Professor Harry Warren and his associates did much to raise the credibility of biogeochemistry in mineral exploration from a level of "general disbelief, through benevolent skepticism to general acceptance...and that, when used properly, biogeochemistry can be used as a viable exploration tool" (Warren and Delavault, 1950; Warren et al., 1968). Subsequently, the science has steadily progressed and a vast amount of new data has been acquired from thousands of locations around the world. However, the world of plants is complex and there remains that immense area of unknown and under-explored processes that present stimulating challenges to the next generation of researchers in this field. These include:

1. **Hyperspectral Imagery (HSI) in Relation to Biogeochemical Patterns.** In order to understand the signals and images obtained from HSI of the forests some 'ground-truthing' of the chemistry of the vegetation canopy is required. This aspect of trace element biogeochemistry is perceived as a future use of plant chemistry in recognizing signatures that might be related to concealed mineral deposits. In forested areas the ground surface signal from alteration zones may be completely obscured by the forest canopy. It follows, therefore, that if the more subtle signature from the chemistry of the forest canopy can be recognized from HSI there becomes the possibility of geochemically mapping the Earth using airborne sensors. At this time, it appears that hyperspectral data have insufficient resolution for individual element geochemical mapping of forested regions. Only major constituents (e.g., N, moisture and chlorophyll) can be mapped (Goodenough et al., 2003; McDonald et al., 2003). There is, however, potential for future development of remote geochemical mapping of the forests once sub-nanometre resolution is readily available. The integration of the hyperspectral data will require substantial ground-truthing by systematically collecting suitable plant tissues for analysis, and ultimately entering the signatures into reference databases of the type currently available for the reflectance characteristics of minerals.
2. **Exploration Geomicrobiology (Reith and McPhail, 2006; Reith and Rogers, 2007).** Microorganisms play a vital role in the cycling of elements in the environment, and many important steps in the nutrient cycle are catalyzed exclusively by microbes. They also play a key role in interfacing the inorganic world, comprising the geological substrate, and the organic world of higher order plants, by affecting the mobility, speciation and distribution of major and trace elements in the rhizosphere. There are estimates that a single gram of soil typically contains ten billion or more bacterial cells and that the bacterial population of the world is about 5×10^{30} . Consequently, this astronomical population plays a fundamental role in biogeochemical processes and an improved understanding of this part of the biogeochemical cycle can be used to advantage in refining biogeochemical exploration methods in general.
3. **Forensic Biogeochemistry.** The role of biogeochemistry in investigating past mining practices has come to the fore in recent years. There have been situations where mining companies, accused of improper practices by watchdog agencies, have required the expertise of the biogeochemist to resolve issues concerning possible environmental contamination. From chemical analysis of tree tissues it has proved possible to ascertain whether tree mortality is consistent with pollution or with death by drowning of roots that can occur following periods of natural water ponding. As more substantial biogeochemical databases are accumulated, the role of biogeochemistry in forensic investigations is likely to see an increase.
4. **Plant Mineralogy.** There remains much to be learnt about the mineral phases within plants. Proton microprobe analysis has been applied successfully to map the distribution of elements within plant tissues. Using this technique Morrison et al. (1981) were able to show the locations of Co, Mn and K in leaf tissue of the Co-hyperaccumulating species *Haumaniastrum robertii* from West Africa, and recent studies with state of the art analytical instrumentation have given greater insight into the distribution and speciation of trace elements in plants (Rob Hough, CSIRO, personal communication). Electron microscopy permits the examination of crystalline phases in plants, and there is scope for modern instruments to add substantially to the quite limited knowledge of the $<2 \mu\text{m}$ -sized discrete phases within which base and heavy metals in plant structures seem mostly to be concentrated.
5. **Chemical Analysis.** High-resolution ICP-MS is now available for determining extremely low levels of more than sixty elements. For some of the REE determinations routine detection levels are as low as 0.01 ppb using 1 g of dry vegetation dissolved in acids. For the exploration biogeochemist, ICP-MS and HR-ICP-MS are the analytical instruments that currently generate data for almost all practical requirements. However, sample dissolution requires additional research to establish the optimum methods for improving data quality at ultratrace levels. Closed vessel microwave digestion promises to be a useful technique that is not yet widely available from commercial laboratories that are generating biogeochemical data for the exploration and environmental industries. Development of these techniques should improve the precision on determinations for some elements – notably the precious metals. Partial leaches warrant further investigation to determine if they will generate biogeochemical data that better reflect the labile phases of elements, particularly the halogens, released from concealed mineralization. The synchrotron promises to provide important new insight into the location, migration and speciation of trace elements,

providing the biogeochemist with improved knowledge of when and what to collect. Isotopes in plant tissues are being examined at several institutes, but their role in biogeochemical exploration for minerals is poorly established and remains at the research stage.

CONCLUDING REMARKS

A basic premise to be remembered is that plants do not always provide the same geochemical information as soils. In an exploration programme for mineral deposits a soil sample collected for analysis is usually only a handful of a specific soil horizon. The usual procedure is for that soil sample to be sieved in order to obtain a few grams of a specific size fraction (e.g., -80 mesh ASTM aperture) for analysis. By contrast, a plant sample, because of its typically extensive root system, may represent an integrated signature of several cubic metres of all soil horizons and sometimes bedrock. Furthermore, roots may extract metals directly from migrating groundwater and accumulate them in their tissues, whereas little or none of that metal may be adsorbed by the soil.

There is an on-going need for multi-disciplinary collaborations, such as that established by Ravi Anand at CSIRO in Perth, Australia, for Project P-778 (AMIRA programme). Furthermore, close liaison between biogeochemists and geophysicists can assist in establishing whether certain geophysical signatures are from barren sulphides or from sulphides rich in valuable base and/or precious metals. Greater liaison with mathematicians and statisticians should help the biogeochemist to extract subtle structure in datasets that may prove to be of value in relating patterns to concealed mineralization. Judicious use of neural-net software might assist in revealing subtle trends in mobile pathfinder elements and their relationships to poorly defined signatures of the valuable, yet less mobile metals.

In his latter years Alexander Kovalevsky claimed to have succeeded in predicting from biogeochemical patterns both the depth to mineralization and an estimation of ore grade (personal communication, 1997). This quantification of depth to mineralization is an exciting concept, but it does not appear to have been tested outside of Siberia.

Biogeochemical methods comprise another tool that explorationists have at their disposal. Data should be interpreted in conjunction with all other available geological, geochemical and geophysical information, because the technique is not a panacea and in some environments there may be little or no biogeochemical response to mineralization and so it may not be the best tool to use. However, the 'case history' examples demonstrate that a number of mines have been developed long after the recognition of a biogeochemical signature, attesting to the value of the method.

The plant can be viewed as a sophisticated geochemical sampling device, as yet not fully understood. An extraordinary wealth of information on plant chemistry is scattered throughout the literature of botanists, plant chemists and geochemists. In spite of this, although past its infancy, the application of biogeochemical methods to mineral exploration must be considered to be only in the early stages of maturity. There is much that we have yet to establish. As research progresses on

conditions that control the accumulation of elements by plants, and as field studies continue to augment the data bases on plant chemistry, the role of the plant in mineral exploration programmes is becoming increasingly important.

As the science advances it is becoming apparent that biogeochemical data can exhibit subtle trends that assist in defining faults, structural trends, stratigraphic relationships and lithologies, all of which may combine to indicate a geological setting suitable for the emplacement of mineral deposits. Such trends, coupled with subtle enrichments of elements typically associated with specific styles of mineralization, can provide focus for further exploration activities. Pattern recognition of element distribution patterns and their spatial relationships is a significant factor in the successful application of biogeochemistry to mineral exploration. There is now sufficient knowledge of the application and usefulness of biogeochemical methods for the thoughtful explorationist to consider using biogeochemistry as an integral part of a comprehensive mineral exploration program. Vegetation chemistry frequently can provide information on the substrate that can not be obtained by other means.

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