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GEOCHEMICAL PROSPECTING FOR TIN AND MOLYBDENUM

(Third Report)

by

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CONTENTS

SUMMARY

Background

This Report is intended to bring Amdel Reports No.708 and 871 up to date.

Objective

The purpose of the present study was to monitor papers on geochemical prospecting techniques to determine whether improvements have been devised in the methods of prospecting for tin and molybdenum.

Summary of Work Done

A search has been made of the available relevant literature. The principal sources have been Chemical Abstracts and the Bibliography and Index of Geology published by the Geological Society of America. Where possible, papers cited have been obtained and studied in detail.

Conclusions

The additional papers reviewed in this Report do not materially affect the conclusions presented in Amdel Reports No.708 and 871. It is clear, however, that it is hoped that techniques will be generated which will enable single samples taken from primary dispersion zones of (unidentified) orebodies to be recognised as anomalous, and related to ore. Sheetwash sampling is a possible alternative to stream sediment sampling.

1. INTRODUCTION

This Report represents a continuation of Amdel Reports No.708 and 871 which were issued, under the same title as the present Report, in July 1970 and July 1972 respectively. Search has continued through Chemical Abstracts (to the end of Volume 77) and through the Bibliography and Index of Geology issued by the Geological Society of America (up to and including Volume 36 No.10). Where it has proved possible, the original papers have been obtained and examined. For other papers only an abstract is available. A number of papers listed in name only in the Bibliography and Index of Geology have been included in the bibliography at the end of this Report, as their titles appear to be relevant. Such papers are not normally mentioned in the body of the Report.

2. GENERAL PAPERS AND TECHNIQUES

The most important paper published during the period under survey has been the bibliography completed by Hawkes (1972) and published by the Association of Exploration Geochemists. This lists the major papers on exploration geochemistry from the period 1965-1971. However, to a large degree this bibliography omits those papers which discuss soil chemistry and the mobility (or otherwise) of ions through the soils. A paper by Shima (1972) reviews recent developments in geochemical prospecting, in the form of a literature survey, and contains 43 references to general geochemical exploration techniques and case histories and a further 25 references to analytical methods.

State-of-the-art papers have been produced by Dall'aglio (1970), Chakravarty (1971), Gallon (1969), and Punwasee (1970) for Italy, India, North West Zambia, and Guyana respectively. Each of these papers, except that of Dall'aglio, reviews all current exploration techniques and geochemistry is considered as a part of the total exploration programme. Dutt (1970) has also written on the standardisation of prospecting techniques for mineral exploration.

The series of papers referred to in Report No.871 by Bradshaw *et al.* and published in 'Mining in Canada' in 1969 and 1970 were continued in the Canadian Mining Journal (Bradshaw *et al.* 1971).

There has been a major upsurge of interest in geochemistry in relation to the environment and to health. Examples of such papers, which commonly consider molybdenum as one element among many, include Miesch (ed. 1970), Kubota (1972) and Thomson *et al.* (1972). Such papers are not immediately relevant to exploration, though it is possible that mineralisation may be discovered as a result of such studies.

Other papers of a general nature, but devoted mainly (or largely) to geochemical prospecting are those of Dokrovskiy and Rakitskiy (1971), Pozharisky (1971), and Yanishevskii and Resnikov (1971). Dokrovskiy and Rakitskiy's main interest is in supergene haloes, Pozharisky considers the methods of exploration for porphyry copper deposits and Yanishevskii and Resnikov review geochemical methods in combination as an exploration tool. The view of Yanishevskii and Resnikov is that an area suitable for prospecting should be mapped on a scale of 1:1 000 000. Mapping should be followed by geochemical investigations of source rocks, sediments and waters, in that order. Last should come a study of 'porous formations' and soils.

There are no startlingly new developments on the analytical scene but research continues, particularly in neutron activation analysis (Evans and Herage, 1971). This paper concerns the field assay of cores and down-drill-hole assaying and includes discussion of a technique for assaying rocks in water filled holes.

Interest has remained high in prospecting alluvium. Cossais and Parfenoff (1971) discuss the techniques of examination of concentrates from alluvium (heavy mineral separations, X-ray fluorescence (XRF) and microscopy) and Krook (1970) discusses the same general techniques but particularly applied to prospecting in tropical areas.

A number of other papers are pertinent to exploration but are not specific for any particular element. They primarily provide fundamental geochemical backgrounds on which to discuss the behaviour of specific elements. Langmuir (1971) discusses the measurement of Eh and pH in sedimentary environments. Mitchell (1972) and Moore (1972) both discuss trace elements in soils from a philosophical point of view, the factors that affect their availability and the mechanism of uptake of these elements into plants.

A paper of general relevance is that by Thomson and Bankston (1971) who investigated the contamination of samples by grinding and sieving, using emission spectroscopy.

In addition to routine soil and sediment geochemical surveys, investigations have been made of wall rock alteration (Khan, 1971), primary dispersion haloes (Zavorotnykh, 1971) and the use of gas surveys. Netreba *et al.* (1971) report on large-scale mapping of regions of buried ore potential in the northern Caucasus using gas survey geochemistry.

Bugrov (1971) discusses the distribution of, among others, molybdenum in vertical profiles of residual dispersion haloes. Enrichment occurs in surface layers (0.2 m) compared with deeper zones (0.4 to 1m) but, overall, the haloes generated are weaker in the soil than in the scarcely weathered rock at depth. Allochthonous (transported) clays blanket out residual haloes.

The US Water Resources Science Information Centre has published a bibliography on the trace element contents of water in the USA (and includes some information on elemental values). This is most useful for providing general data on the metal content of waters. Shimkova (1971) discusses how to evaluate hydrogeochemical anomalies in general.

3. GENERAL RECONNAISSANCE CASE HISTORIES

The number of papers published which report the results of regional geochemical surveys is growing. Tin and molybdenum are usually considered where emission spectrography or XRF is used as the means of analysis. The Alaskan Division of Mines continues to publish such reports (e.g. Herreid, 1971), while there is a constant stream of papers from Korea (Lee, 1969; Yup *et al.*, 1971; Park *et al.*, 1971a, 1971b). Many of these papers report anomalies which require follow-up investigation. Mosquera and Carlos (1970) report a programme similar to that in Korea from Ecuador and Fletcher and Doyle (1971) and Biancon and Saager (1971) report case histories from the Yukon.

4. TIN

Papers which are involved with the applied geochemistry of tin fall into four well-defined groups:

(a) papers which discuss the tin concentration of suites of rocks and the behaviour of tin as igneous rock series are differentiated,

(b) papers which discuss tin in specific minerals,

(c) papers which discuss the primary dispersion haloes around orebodies, and

(d) papers which discuss secondary dispersion haloes around orebodies

In addition, one paper gives assay data on the concentration of tin in sediments and shells or skeletons, particularly in marine environments. Smith and Burton (1972) report the following ranges of tin concentrations (the number of samples assayed is indicated in brackets):

Rock	Range of Sn values, in ppm	
Ultrabasic	0.74 - 0.88	(3)
Basic and intermediate	0.70 - 3.5	(14)
Silicic igneous	1.0 - 4.3	(6)
Carbonate sediments	<0.05 - 4.6	(10)
Phosphorites	0.11 - 0.25	(2)
Mudstones	0.11 - 8.8	(17)
Algae	0.1 - 0.65	(4)
Molluscs	0.33 - 0.71	(2)
Pelecypods	0.23 - 0.67	(2)
Iron-manganese concentrations	0.21 - 5.8	(14)
Carbonate rocks (total tin)	0.23 - 1.66	(5)
Carbonate rocks (acid soluble tin)	0.03 - 0.44	(5)

A paper by Moreno (1972) is alleged to discuss geochemical exploration characteristics of Mexican tin deposits, but this paper is not available in Australia.

4.1 Tin in Rocks

Most of the work in this area is being carried out in the USSR. Papers of a very general nature which either compare tin in different types of granitoid in the one area, or follow tin through a differentiation series, include those by Tolok *et al.* (1971) (differentiation in sodic granitoids), Tischendorf *et al.* (1971) (the Erzegebirge), Mogarovskii (1972) (the Pamir-Shugnan complex), Mahfouz (1969) (Kirchburg granite), Grebennikov *et al.* (1971) (Transbaikalia), Gerasimovskiy and Borisenok (1971) (East Africa Rift Valley) and Onikhimovskiy (1972). The last paper is a review of the development of tin ores in igneous rocks.

Tolok *et al.* (1971) note that tin concentrations increase regularly during differentiation of hypabyssal sodic gabbroids increasing in concentration from teschenites to monzonites and syenites. They note that alkaline olivine basalt magmas appear to be enriched in tin compared with tholeiitic basalt magmas. Tischendorf *et al.* (1971) report that tin leached from biotite is reprecipitated as cassiterite. At Shugnan, Mogarovskii (1972) found a direct correlation between tin and fluorine, and tin and boron, whereas in the Pamirs tin does not correlate with fluorine (though there is still a direct correlation with boron) and there is an inverse relationship with titanium.

Levashev *et al.* (1972) use not only bulk rock tin determinations but also the tin contents of biotite to distinguish granitoids of different tectonic zones of the maritime province.

On the more theoretical side Kurilchikova and Barsukov (1971) have investigated the effects of carbon dioxide and of sodium and potassium bicarbonates and carbonates on the formation of Sn (IV) complexes in solution. They found that hydroxycarbonate tin complexes can be found in hydrothermal solution containing adequate concentrations of carbonate ions and virtually no fluorine ions, and consider that these complexes can be a mode of transport of tin in hydrothermal solutions and can assist in the formation of primary dispersion haloes. Aktanov (1971) is more conventional and ascribes high concentrations of tin, boron and fluorine in greisenised granites to redistribution by post-magmatic solutions. Though he does not discuss the mechanism, he says that in the course of albitization and muscovitisation tin is released from biotites, incorporated into hydrothermal solution and later precipitated as SnO_2.

4.2 Tin in Mica

Rub *et al.* (1971) measured tin and lithium in biotites and protolithionites to determine granitic rock ore-bearing potentials. Micro-inclusions of zircon, rutile and cassiterite occur in the biotite and are the main concentrators of tin, though the biotite itself does contain elevated amounts of tin in the lattice.

4.3 Primary Dispersion Haloes

Of the five papers in this group, four are based on Russian work. The fifth, Flinter *et al.* (1972), discusses Australian granitoids. Though this last paper is not strictly on primary dispersion haloes, it attempts, by judicious rock analysis, to establish diagnostic links between tin (copper and molybdenum) mineralisation and selected features of the major granitoid types. Examination of 121 plutonic rocks from the New England igneous complex has been made. Tin, copper and molybdenum mineralisation was detected in 53 of these. There was no correlation between mineralisation and the geochemical concentration of the elements in the rock and a purely geochemical approach to prospecting the rocks of this area seems to be inadequate. The tin and molybdenum occur in two different distinct environments, (a) in lodes or veins in high silica leucogranitoids, and (b) disseminated (with copper) in low silica mesogranitoids. Flinter *et al.* found, using cluster analysis, that the colour index (or ferromagnesian content) of the granitoids is the most important petrological feature. They believe that their approach can successfully indicate the host or carrier petrological units within a granitoid complex.

Vorontsov *et al.* (1969) found primary tin and copper dispersion haloes to be more prominent than those of other elements. Tin values ranged from 5 to 200 ppm. Sisykh *et al.* (1971) examined the primary haloes at a Transbaikalia 'rare metal' deposit. Haloes of W, Bi, Mo, Sn, Co, Pb and Zn, were commonly thirty to fifty times larger than the width of the orebody (unspecified). The haloes have a hyperbolic shape, and are believed to be of an infiltrational nature with a minor rôle played by diffusion.

The Lifudzin tin ore is localised in Cretaceous sandstone, mudstone and argillaceous schist. Anakhov and Nikolaev (1971) measured the extent and intensity of the primary haloes at this deposit and found that tin, lead and zinc haloes were all present, and that their width exceeded that of the ore by three to five times. Disseminated elements in the country rock have been transported to form a concentrated phase in orebodies localised along 'coarse' fractures. Vertical zoning is also present. Morozova and Bel'chanskaya (1971) found that haloes of tin were wider than those of other metals over cassiterite-silica ores, whereas, over complex tin-sulphide ores, copper haloes extended further than those of tin. These authors found that a direct correlation existed between the size of the orebody and the size of the halo.

4.4 Secondary Dispersion of Tin

A number of papers have been written on the secondary dispersion characteristics of elements adjacent to tin deposits. Bugaets *et al.* (1971) and Zagoskii and Shimanskii (1971) both discuss secondary dispersion in the vicinity of stanniferous pegmatites. Bugaets *et al.* used statistical methods to interpret the inter-elemental behaviour of lithium, cesium, beryllium and tin.

The main techniques used were correlation studies and principal component analysis (the abstract does not record whether any helpful conclusions could be drawn). Zagoskii and Shimanskii (1971) determined concentrations of the same elements, with the addition of rubidium, in soils and plants. The abstract of this paper indicates only that plants apparently absorb the elements in the following increasing order Cu-Rb-Li-Sn-Be.

Belyaeva (1971) found that tin, lead, zinc, copper and boron were the main indicators of tin mineralisation at the Verkhnee deposits but that silver and bismuth could be used as indicator elements to some extent. The elements forming distinct haloes in soil layers are spatially (and genetically) related to the primary dispersion haloes. Lead and tin were found to have the largest contrast characteristics, bismuth and copper the lowest. The 'B' soil horizon is the best for sampling purposes.

In one of the very few papers on geochemical prospecting in Australia, Groves *et al.* (1972) report their findings on soil and geobotanical studies in the Emuford district of the Herberton tin fields, North Queensland. In the vicinity of the Ivy mine, copper, lead, zinc and tin at both 5 cm (2 in.) and 15 cm (6 in.) depths in the soil all closely reflect the position of known mineralisation. Stream sediments show scarcely any anomaly except where the drainage either cuts, or is present adjacent to, the mineralisation. However, at Emma Creek there is a prominent stream sediment dispersion of tin with high values extending for 1.2 km ($^3/_4$ mile) downstream from the Siberia lodes. At the Ivy mine *Scleria brownei* and *Coelospermum reticulatum* tend to grow only on soils with high rare-metal values and can be used as local indicators of mineralisation.

5. MOLYBDENUM

Summary papers on the geochemical behaviour of molybdenum written by Billings and Sonderegger (1971) and Shcherbina (1971) add very little to our knowledge of the element.

Pilipchuk (1972) measured the content of molybdenum in the eastern part of the Mediterranean Sea and in the associated sediments. The concentration of molybdenum in the water varied between 10.9 and 17.7 μg molybdenum/litre (ppb) He demonstrates a selective reaction of molybdenum with manganese (IV) ions, and not with ferric ions, in the oxidising regime. Associations of iron and molybdenum are formed during diagenetic redistribution of elements. In sediments with reducing conditions there is a direct correlation of molybdenum with organic matter concentration.

Studenikova (1971) has reviewed the behaviour (and concentration) of molybdenum (and tungsten) in sedimentary and metamorphic rocks. In a paper which is an example of the major shift of emphasis to environmental geochemistry, Thomson *et al.* (1972) assayed black shales from various time sequences between the Ordovician and the Cretaceous in England, and stream sediments derived from them, and demonstrated that the pattern of molybdenum in the sediments is related to the bedrock. Pasture grasses contain more than 3 ppm molybdenum in some areas; this has produced zones in which animals (cows) contract bovine hypocuprosis.

On the more theoretical level Arutyunyan (1969) examined the possibilities of molybdenum migrating in the form of halogen compounds, concluding that it was most unlikely that molybdenum could migrate in natural processes in this manner.

Rekharskiy (1972) examined the behaviour of the principal ore elements which occur with molybdenum deposits during magnetic differentation. He arranged elements in order of increasing tendency towards accumulation in felsic differentiates as follows:

$$Cu \rightarrow Mo \rightarrow W \rightarrow U \text{ and } Bi$$

$$I \text{ and } Br \rightarrow Cl \longrightarrow F$$

$$Mg \rightarrow Fe \longrightarrow Ca \longrightarrow Na \longrightarrow K$$

The elements of the three series are placed in approximate corresponding positions under each other to indicate the more common associations observed by Rekharskiy.

The paper by Flinter *et al.* (1972) on the various geochemical, mineralogical and petrological features of New England granitoids has already been discussed under 'tin'. They believe that their approach is also of considerable help in the exploration for porphyry copper deposits.

Rossman *et al.* (1972) examined the content of bismuth, antimony, arsenic, thallium and mercury in ores and rocks which host uranium/molybdenum mineralisation. Anomalies of each were found peripheral to the orebodies and Rossman *et al.* say that the mapping of geochemical haloes of U, Mo, Bi, Pb, Cu, Sb, As, Ti and Hg can all lead to the detection of blind orebodies.

As noted in the discussion of papers on tin, Sisykh *et al.* (1971) determined primary dispersion haloes of W, Bi, Mo, Sn, Co, Pb and Zn at a rare-metal deposit in Transbaikalia. The haloes were shown to have widths 30 to 50 times greater than the width of the orebody.

Elinson *et al.* (1970) plotted the position of copper-molybdenum orebodies by logging and plotting concentrations of gas, in particular H_2S. The concentration of H_2S is greater over skarn-type deposits than over vein disseminations. Anomalies also occur in zones affected by tectonic movements. Elinson *et al.* discuss the effects of the climate on gas haloes for the area of interest (central Kazakhstan).

A few papers discuss secondary dispersion behaviour. Austria (1971) mentions molybdenum as one element among many. He notes that molybdenum tends to be concentrated in manganiferous sediments in his area of study (York County, New Brunswick).

According to the abstract, Pokrovskiy and Rakitskiy (1971) demonstrated a relationship existing between size fractions and ore metal content of secondary haloes round chalcopyrite, 'complex ores' (presumably mainly lead-zinc sulphide) and molybdenum mineralisation in central Karelia. Geomorphological, structural and climatic features all influence the deposition of secondary haloes. Kushnerenko and Rossman (1972) used γ anomalies over porous sediments to detect uranium/molybdenum mineralisation. The maximum distance between the centre of a γ anomaly and primary ore is of the order of 50 metres. γ anomalies also occur over unmineralised manganese hydroxide-rich sediments.

Maranzana (1972), carrying out a geochemical exploration programme in an arid part of the high Andes of Chile, used talus material instead of soil or stream sediment samples (because of a very limited development of these latter materials). Minus 80 mesh material was assayed and provided clear indication of the location of copper/molybdenum mineralisation. Maranzana believes this technique to be applicable in other parts of the world.

6. DISCUSSIONS

No new methods have been found which add materially to techniques of prospecting for tin and molybdenum.

Many papers reflect the interest in the bulk chemistry of rocks, and measure and discuss the extent and concentrations of trace elements in primary dispersion haloes.

The technique of sampling talus, although used by Maranzana (1972) in desert conditions in the mountains of Chile, may prove of relevance in

South Australia where the corresponding equivalent material is sheetwash. In view of the frequency of wind blown dust in surface materials in South Australia, it may be more effective in such situations to examine one of the coarser fractions of the wash.

7. CONCLUSIONS

The additional papers reviewed in this Report do not materially affect the conclusions presented in Amdel Reports No.708 and 871. It is clear, however, that it is hoped that techniques will be generated which will enable single samples taken from primary dispersion zones of (unidentified) orebodies to be recognised as anomalous, and related to ore. Sheetwash sampling is a possible alternative to stream-sediment sampling.

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