RB 72/40
DM 365/72

1/1/131 February 1972

SOUTH AUSTRALIAN DEPARTMENT OF MINES

Amdel Report

No.826

GEOCHEMICAL PROSPECTING FOR NICKEL COPPER, ZINC AND LEAD A REVIEW

by

R. Davy and B. Steveson

Investigated by: Mineralogy and Petrology Section
Officer in Charge: K.J. Henley

F.R. Hartley. Director

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
Adelaide South Australia

CONTENTS

CONTENTS

CONTENTS

SUMMARY

Background

The South Australian Department of Mines has for several years undertaken geochemical surveys in different parts of the State. Arid areas present particular problems for this kind of prospecting. Consequently, Amdel proposed undertaking a literature survey on copper, nickel, lead and zinc with particular reference to arid areas.

Objective

The objective of this study was to ascertain which, if any, geochemical techniques had been used successfully in prospecting for copper, nickel, lead and zinc in arid regions. If no obviously suitable techniques were available, Amdel was asked to discuss the advantages and disadvantages of different methods and to indicate fields in which further development work might be undertaken.

Summary of Work Done

Chemical Abstracts were systematically searched back from the current issues. References to early work were obtained from Hawkes and Webb (1962) and from bibliographies in other books and review papers. Several papers were obtained from the CSIRO, Division of Soils, the Bureau of Mineral Resources, the Botany Department, University of Adelaide and from the authors' own collections of papers.

Conclusions

a. General

1. In no circumstances are water surveys recommended.

2. Wherever possible orientation surveys should be carried out.

3. Biogeochemical surveys show such variability of analysis that values obtained should be regarded as effectively semiquantitative. Once an area of interest is located, auger drilling or some other more positive method of approach is recommended in locating a target.

4. When carrying out stream sediment surveys more consideration than has been shown in the past should be given to the choice of size fractions and sample intervals.

5. As an alternative to conventional stream sediment surveys,

sampling of iron-stained or iron-enriched float (or laterite) may lead more directly to mineralisation.

6. There is no positive evidence that the cold extractable heavy-metal survey techniques work in arid regions.

7. Despite differences in leaching properties all four elements tend to collect on/with iron and manganese oxides/hydroxides. In any geochemical survey iron-enriched material should be tested for its trace element content.

b. Copper

1. Copper is relatively easily oxidised from its primary occurrence in sulphide ores. It is capable of migrating in acid solutions, and after precipitation or adsorption it travels mechanically. It is an essential constituent of plants and is ubiquitous, at detectable levels, in plant ash.

2. Copper tends to be leached from the surface of residual soils but may be collected in a hard pan or calcareous 'B' horizon, or in calcrete. Soil geochemistry with samples collected from the appropriate part of the profile, is a suitable method of prospecting for copper.

3. Copper may be found in coarse or in very fine fractions in stream sediments. In the coarse fractions (+60 mesh) it is likely to be a component of partly broken down rock, in the fine fractions most of the copper is secondary and is a product of either precipitation or adsorption onto (secondary) minerals. Copper in solution is readily trapped by carbonates. Hence, in any stream sediment survey, prior consideration must be given to the optimum size fraction and to the optimum sample interval.

4. Indicator elements may be useful in the search for copper deposits. In particular molybdenum may be expected to be present in residual soils near the focus of porphyry copper mineralisation. Zinc and mercury are possible alternative indicator elements. However, zinc is so mobile that it tends to be dispersed too widely in arid conditions so that no anomaly is detectable. The case for mercury as an indicator of copper is not proven.

5. It appears to be possible to use either or both geobotany and biogeochemistry in the search for copper deposits. All plants contain copper and several are known which are accumulator plants. In any given biogeochemical survey thorough orientation work must be carried out.

6. There appears to be no great value to be obtained using cold extractable methods for determining copper.

7. The possibilities of either using calcrete (massive or in stream courses) or the calcite of calcite-cemented alluvium in the search for copper should not be ignored. Care is needed to obtain consistent samples.

8. The possibilities of using heavy minerals (eg. iron oxides) in placer deposits in creeks should be considered. In areas of generally low values, assay of these minerals may produce sharper contrasts.

9. Copper may be collected on iron/manganese oxides/hydroxides and in laterites.

c. Zinc

1. The behaviour of the zinc in the supergene environment is very similar to that of copper except that it is more mobile. Zinc is more readily leached from rock and less easily precipitated.

2. Dispersion trains of zinc tend to show a wide, low level distribution. Stream sediment surveys are therefore appropriate, subject to the correct choice of size fraction and sample interval. Zinc is also precipitated readily onto carbonate. This fact may be used to advantage or else taken into account when interpreting results.

3. Zinc is so mobile in soils that soil surveys using zinc are less effective for this element than others. If soil surveys are to be carried out samples need to be collected in hardpan or carbonate layers. Zinc soil anomalies are commonly offset, by the drainage, from mineralisation to which they are related.

4. Zinc may be collected in iron/manganese oxides/hydroxides. All iron-rich outcrops should be sampled. However, because of the mobility of zinc, iron-enriched outcrops, *per se*, are not likely to

lead directly to zinc mineralisation.

5. Biogeochemistry is a possible tool in the search for zinc deposits; however, because zinc is an essential element at trace to minor levels in plants, care should be taken in interpreting assay values obtained.

6. Mercury appears to be a possible indicator element for low temperature, hydrothermal, lead-zinc deposits. Mercury is sold as a by-product of Rosebery ore (Argall, 1971) and as a by-product of lead-zinc deposits elsewhere in the world.

7. There appears to be no value in using cold extractable zinc survey methods in arid regions.

8. As for copper, the possibilities of using heavy minerals in placer-type deposits should be considered. However, zinc is more likely to be leached than copper from iron oxides, etc.

d. Lead

1. Lead is less easily oxidised from its ores than other metals under discussion. This is not because galena is less reactive but because a lump of ore is quickly coated with either cerussite or anglesite. Both of these are almost insoluble and impede further reaction. Lead does not travel in solution to any large extent but does travel mechanically.

2. Lead is less susceptible to leaching than either copper or zinc. This makes it a suitable element to be sought in residual soil surveys. Because of its relative lack of mobility there is little tendency to concentrate in certain parts of the profile.

3. Lead is present with iron and manganese oxides, possibly because of its lack of mobility rather than an inherent concentration effect. Values recorded tend to be rather erratic; however, all ironstone/laterite should be sampled for lead.

4. Lead is not a particularly suitable element for stream sediment surveys. Reconnaissance is better with zinc or copper, and lead used in the follow-up work on soils. Because of its lack of mobility little lead gets into streams. When in streams lead minerals tend to travel mechanically. The three main lead minerals

galena, cerussite and anglesite all have good/excellent cleavage and grains are quickly broken down. Consequently lead in streams tends to be found as a wide, very low level anomaly. Lead in the coarse fractions can be used to locate a source.

5. Lead is a suitable element for consideration using heavy minerals from 'placer' deposits in streams. This may be a suitable technique for enhancing the contrast in stream sediment surveys.

6. Zinc and mercury are potentially useful indicators of lead mineralisation. If any showing is present a test survey of the values of these elements can be made.

7. There appears to be no merit in using hydrogeochemistry or cold extractable methods in the search for lead.

8. The usefulness of biogeochemistry in the search for lead is of questionable value. However, because of lead's highly toxic nature to many plants, there are likely to be variations in ecological patterns in the vicinity of lead deposits.

e. Nickel

1. Though nickel can be leached from its ores it is not one of the most mobile elements. It is capable of migrating in acid solutions, or of travelling mechanically after precipitation or adsorption. It is also capable of being adsorbed into plants.

2. A first approach to the search for nickel is the search for ultrabasic rocks. Because nickel can be leached at the surface, when there is no outcrop high chromium values are considered to be a good indicator of the presence of ultrabasic rocks.

3. Nickel is commonly leached from the upper parts of residual soils, but it is collected by hardpan or calcareous layers in the lower parts of the profile. Sampling for nickel in well stratified soils in arid/semi-arid regions should be restricted to the 'B' or even 'C' horizons.

4. Though nickel may show a relative displacement in the profile compared with iron, it tends to remain concentrated in laterite, and ironstone soil profiles. All outcrops of this material should be sampled and assayed for nickel. If nickel is present in concen-

trations greater than 1,000 ppm at the surface, trial drill holes should be made to test whether there has been any concentration at depth.

5. Most nickel in stream sediments is related to outcropping ultrabasic or basic rocks. Relatively unaltered rock may be found in the coarser fractions. These may show reasonable nickel values. Secondary nickel is concentrated in the finer fractions.

6. No direct way is known for prospecting for nickel. The current technique appears to be to find a magnesium-rich ultrabasic/basic rock, preferably with high sulphur values, and then to drill the rock systematically paying particular attention to any basal contact zone.

7. Apart from chromium - copper, selenium, sulphur and arsenic have all been used as indicators of nickel mineralisation. Whether these are suitable needs to be determined by trial and error in any given area. Primary nickel deposits are believed to be emplaced at high temperature, therefore it is not likely that mercury will be a suitable indicator element.

8. Biogeochemical and geobotanical prospecting have been used with success in some areas, and so these techniques should be considered as possible tools.

1. INTRODUCTION

This project has arisen out of a need for a workable method or methods of geochemical prospecting in South Australia, particularly in the more arid regions. The project consists of a review of geochemical prospecting literature, not restricting the review to those papers which deal specifically with geochemistry in arid regions, but including much of the available literature published in English on non-arid regions. It is clearly recognised that there are two fundamental problems; the first concerns the genetic character of the ore deposits with their associated geochemical patterns; the second concerns the varying geochemical behaviour of the elements under different climatic conditions. It may therefore be as relevant to consider the aureoles of minor mineralisation around a deposit in Alaska as it is in South Australia. However, it cannot be expected that there will be an identical pattern of dispersion behaviour away from the deposits in the two areas.

The chief source of information has been Chemical Abstracts, which has been examined in detail back to 1960. Other sources extensively consulted include Mineralogical Abstracts, Hawkes and Webb (1962) and members of the CSIRO, Division of Soils, and publications suggested by them. Information on primary biochemical behaviour has been obtained from Dr A. Smith of the University of Adelaide Botany Department. For material published earlier than 1960 the bibliographies of more recent papers have been extensively used.

It is believed that the bibliography given (Section 12) contains most of the important papers relevant to geochemical prospecting. Where several papers have been written about the same area and cover essentially the same topics, only the most important or the most detailed paper has been included.

Papers which deal primarily with the mathematical or statistical interpretation of geochemical data have been omitted.

2. GENERAL GEOCHEMISTRY OF THE ELEMENTS

2.1 Nickel

2.1.1 General Chemistry

Nickel, together with cobalt, is closely related to iron in its properties. All three metals occur in the fourth period of the Periodic Table and they are referred to as the ferrous metals (Moeller, 1952). Since nickel is a transition element its chemistry might be expected to be rather complex, but in fact the divalent state is so dominant that this is not the case. The ionic radius of Ni^{++} is 0.69 Å (Krauskopf, 1967) and this dimension influences the geochemistry of nickel since ionic bonding can be assumed to occur in most geological environments. When nickel is bonded with oxygen a 60% ionic bond occurs and this has a length of 0.91 Å (Green, 1959). Because the properties of Ni^{++} are similar to those of other divalent ions, much more abundant in the earth's crust, nickel usually occurs in minor amounts in common minerals, rather than in rare, nickel minerals.

As might be expected, nickel is a siderophile element, always concentrated in metallic phases in meteorites (84,900 ppm Ni; Krauskopf, 1967). However, in the lithosphere nickel shows marked chalcophile tendencies and the low abundance of nickel in troilite (1,000 ppm; Krauskopf 1967) is due solely to the peculiarities of the Fe-Ni-S system.

The average abundance of nickel in the earth's crust is 75 ppm (Krauskopf 1967); presumably this is lower than the abundance in the earth as a whole, since nickel is likely to be relatively concentrated in the mantle and core. The crustal abundance is similar to those of copper and zinc, but is six times that of lead.

2.1.2 Distribution in Rocks

The most outstanding feature of the distribution of nickel is the concentration in ultrabasic igneous rocks. Turekian and Wedepohl (1961), Vinogradov (1962), and derived references quote the concentration of nickel as 2,000 ppm in such rocks. Values summarised by these authors for abundances in the rock types are listed below:

Author		Rock Type, ppm				
		Ultrabasic	Basaltic	Intermediate	Granitic	Syenites
Turekian & Wedepohl,	1961	2000	130	-	10	4
Vinogradov,	1962	2000	160	55	8	-
Goldschmidt,	1954	3600	160	40	2.5	2.4
Nockolds & Mitchell,	1948	650	230	80	20	-
Sahama,*	1945	>800	47	-	2.5	8
Wager & Mitchell,	1951	1000	150	<2	-	-
Sandell & Goldich,	1943	-	160	15	10	6

Author		Rock Type, ppm				
		Ultrabasic	Basaltic	Intermediate	Granitic	Syenites
Rankama & Sahama,	1950	3160	158	40	2.4	2.4

* Quoted - Goldschmidt (1954).

The significance of these data will be discussed below (Section 2.1.4). In normal sediments nickel occurs mostly in iron and manganese oxide/hydroxide grains and the abundance rarely exceeds 100 ppm; only sulphide-bearing muds (formed in reducing environments) tend to give somewhat higher values. In certain lateritic sediments it may be present in silicates or in the oxides. In limestones nickel is usually present only to the extent of a few ppm - there seems to be no relationship between magnesium and nickel in dolomite. Turekian and Wedepohl (1961) give the concentrations in shales, sandstones and clays as 68, 2 and 20 ppm, respectively. Slightly higher values in deep-sea carbonate and clay (30 and 225 ppm, respectively) may reflect the presence of meteoritic dust.

2.1.3 Nickel Minerals and Ore Deposits

Nickel forms a considerable number of primary and secondary sulphide, arsenide, telluride, etc. minerals. In many of these minerals, diadochic relationships occur between arsenic, sulphur, and tellurium on the one hand, and nickel, cobalt and iron on the other, and consequently nickel contents are variable. Bravoite and penroseite have structures similar to that of pyrite whereas rammelsbergite is related to the polymorph, marcasite. A most important group of minerals is that with the nickel arsenide hexagonal structure: pyrrhotite, niccolite, breithauptite, millerite and pentlandite. Pentlandite, nickeliferous pyrrhotite and millerite are among the most important nickel minerals found in magmatic ore deposits. Trevorite is a nickeliferous spinel. A large number of secondary or supergene nickel minerals are known; violarite is particularly well-known in supergene zones in Western Australia. Gaspeite, garnierite and other brightly coloured minerals occur in weathered zones.

Nickel ore deposits are of two kinds: magmatic sulphide ores and lateritic silicate/oxide ores.

Whether or not nickel in a magma is disseminated in silicates (olivine, pyroxene, etc), or concentrated in sulphide, probably depends primarily on the sulphur content of the magma (Townend and Turner, 1968). Nickel is partitioned between sulphide and silicate phases and most crystallises in early-forming sulphide minerals of which pentlandite (32 to 37% nickel) is the most important. Over this primary disseminated ore, lower temperature veins can be found containing violarite, millerite and bravoite (Melent'ev 1961).

The silicate types of ore deposits are associated with zones of weathering of ultrabasic or basic rocks and these deposits supply about 10 to 15% of the world's production of nickel. Garnierite and pimelite (nickeliferous montmorillonite) are the principal ore minerals and these silicate/arsenate ores commonly contain 1 to 1.5% nickel.

2.1.4 Igneous Trends

The nickel content of the silicate phase of igneous rocks depends largely on the extent of partitioning between silicate melt and early sulphide crystals. Certainly the high values for nickel in ultrabasic rocks reflect the presence of these early sulphides rather than indicate that nickel concentrated in early-formed silicates. Rankama and Sahama (1950) assert that, in fact, the proportion of nickel held in sulphides is unimportant compared with that "camouflaged" in silicates.

The distribution of nickel in silicate minerals follows that of magnesium very closely and the fact that, in minerals of variable composition, magnesium-rich members crystallise first during the cooling of magma means that nickel, too, is concentrated in early differentiates. Therefore, the high concentration of nickel in ultrabasic rocks is due to two factors: the presence of discrete sulphide minerals and the "capture" of nickel by magnesium-rich silicates. This latter factor is shown by data from the Stillwater complex (Turekian and Carr, 1960) from which the following table is extracted:

Nickel Content (in ppm) of Minerals from the Stillwater Complex, Montana

	Plagioclase	Orthopyroxene	Clinopyroxene
Upper Gabbro	34	310	-
	26	650	460
	36	650	480
Anorthosite	17	490	380
	25	-	-
Lower Gabbro	-	890	590
	26	-	590
	67	1400	630
	54	1100	1400
	44	1350	660
	74	830	970

	Plagioclase	Orthopyroxene	Clinopyroxene
Lower Gabbro	66	1,300	640
	135	2,000	1,300
Norite	34	1,150	610
	42	10,000	650

In igneous rocks in which olivine and pyroxene occur, most nickel occurs in the former:

Nickel Content (in ppm) in Minerals from Skaergaard, South-West Greenland (Wager and Mitchell, 1951)

Ni in Olivine	Ni in Orthopyroxene	Ni in Plagioclase	
325	140	<2	Gabbro 4077
10	<2	<2	Hortonolite ferrogabbro
250	200	2	Chilled margin

In granitic rocks nickel presumably replaces magnesium in biotite or hornblende.

2.1.5 Sedimentary Cycle and Weathering Behaviour

It has already been stated that nickel occurs in only small quantities in sedimentary material. Nickel occurs in the lattice of montmorillonite (pimelite is nickeliferous montmorillonite) and chlorite and is adsorbed on the surface of clay minerals. Le Riche (1959) found that nickel in lower Lias shales (35 - 260 ppm nickel) of the UK occurred with organic matter.

The weathering behaviour of nickel is most important since it sometimes leads to the development of ore deposits. The special features of laterite profile will be discussed below; it is sufficient to point out here that the concentration of nickel in sheet silicate minerals as observed in New Caledonia, for example, is not necessarily typical of all laterite profiles; for instance, Zeissink (1969), has indicated that in the Greenvale Deposit, Queensland, nickel occurs mainly in goethite.

During normal weathering nickel is leached by acid solutions but most of it is quickly precipitated in hydrolysate sediments. Some nickel may remain effectively undisturbed in hydrolysates in the residuum.

From calculations based on the composition of seawater, Rankama and Sahama (1950) have shown that nickel is more stable in the solid state in compound form, and is rapidly extracted from seawater. The following tabulation

(Rankama and Sahama, 1950) clearly shows the preference of nickel for the clay minerals:

Content of Nickel (in ppm) in Various Sediments and Sedimentary Rocks

Mississippi silt	134
Terrigenous clays	498
Red clay	253
Sandstone, Sweden	2
Shale, Sweden	150
Bituminous schist	70
Limestone, Sweden	3-10
Quartzites, Lapland	2-8

The abundance of nickel in soil is about 40 ppm, but this can vary from 5 to 500 ppm (Hawkes and Webb, 1962). Mitchell (1964),in a study of Scottish soils, found that soluble nickel (0.5 N acetic acid) was very low (less than 100 ppm, generally less than 20 ppm) even when total nickel reached 870 ppm.

2.1.6 Nickel in Water

The nickel content of seawater has been measured by several authors:

	Ni in Seawater, ppb
Krauskopf, 1967	2
Ernst and Hormann, 1936 (Goldschmidt)	0.1-0.25 *
Noddack, 1939 (Goldschmidt)	500
Wattenberg, 1943 (Goldschmidt)	0.1*

* These low values are recorded because nickel is removed from the sea by adsorption onto or into clay minerals.

In fresh water a value of 0.02 to 10 ppb nickel has been estimated by Hawkes and Webb (1962).

2.1.7 Biogeochemistry

Soluble salts of nickel are poisonous and reduce the fertility of soils. However, nickel is not an important element in agriculture. Nickel occurs in the organic matter of sediments (probably in porphyrins, replacing magnesium) and also in petroleum. Wells (1946) reports a nickel content of 3,000 ppm in liquid asphalt and Malyuga (1964) has measured values of 1 to 250 ppm nickel in oil.

Both marine and land plants carry about 3 ppm nickel (Bowen, 1966) and

Alyssum bertolinii accumulates the metal. Some woody plants may be prevented from growing on particularly nickel-rich soils, but apart from this the toxicity of nickel is not documented.

2.1.8 Metamorphic Behaviour

Little is known of the effect of metamorphism on nickel. Shales have a mean nickel content of 71 ppm, whereas for schists the figure is 114 ppm nickel (Turekian and Carr, 1960). These authors examined a shale/dolerite contact zone but except for local metasomatism near the contact, no enrichment or depletion of nickel was recognised.

Figures given by Shaw (1954) for the progressive metamorphism of a pelitic sediment suggest that the mean nickel content decreases with grade (low grade - 79 ppm; medium grade - 74 ppm; and high grade - 59 ppm nickel). However, the spread about these means is so great that the results can be regarded as tentative at best.

2.2 Copper

2.2.1 General Chemistry

Copper is one of the so-called coinage metals of Group I of the Periodic Table, having affinities with silver and gold. The metals have rather differing properties, characterised, in the case of copper, by the stability of the divalent state. In solutions at equilibrium:

$$K_{298} = (Cu^{++})/(Cu^{+})^2 = 1.2 \times 10^6 \text{ (Moeller, 1952)}$$

and cuprous compounds occur only when stabilised by insolubility or the formation of complexes.

The cupric ion radius is 0.72 Å (Krauskopf, 1967); consequently the metal ought readily to enter the six-co-ordinate sites in ferromagnesian silicate minerals. However, copper is typical of sulphide ore deposits and the marked chalcophile nature of the metal dominates its geochemistry. This can be judged from the abundance of copper in metal, troilite and silicate phases of meteorites; 200, 500 and 2 ppm, respectively (Krauskopf, 1967).

Copper, then, forms a large number of sulphide minerals and only two silicates, chysocolla and dioptase are at all common.

These latter do not occur in igneous rocks, but rather in hydrothermal veins. The status of copper in the silicate minerals of igneous rocks is not fully understood; cupric copper is unlikely to co-exist with ferrous iron of basic magmas unless shielded by complexing with OH^- ions. Truly ionic cupric ions probably do not occur in olivine, pyroxene, etc.

However, copper can substitute for iron in ferromagnesion minerals. At least two porphyry copper deposits are situated in intermediate to acid igneous rocks which have biotite or hornblende with up to 1% copper in the lattice and biotite containing up to 1.5% copper in the lattice is known from South Australia. Copper-rich vermiculite is also known from the Rhodesian Copper Belt.

The abundance of copper in the earth's crust is 55 ppm (Krauskopf, 1967) and it is the twenty-sixth most abundant element.

2.2.2 Distribution in Rocks

The tabulation below indicates some average values for copper in igneous rocks (the behaviour of copper in differentiation trends is discussed below - Section 2.2.4):

		Copper, ppm				
		Ultrabasic Rocks	Basic Rocks	Intermediate Rocks	Acid Rocks	Syenite Rocks
Sandell & Goldich	(1943)	-	149	38	16	-
Vinogradov*	(1962)	20	100	35	20	-
Turekian & Wedepohl	(1961)	10	87	-	20	5
Hawkes & Webb	(1962)	80	140	-	30	-

* World averages.

Griffiths and Nakagawa (1960) analysed monzonites from the western USA; their mean values for each intrusion vary widely and there is also a great scatter of values from each intrusion. The means vary from less than 1 to 110 ppm for 36 monzonites; the overall mean value is 24 ppm copper.

The values in the table do not indicate how much copper is found in silicates as opposed to sulphide minerals and this is an unresolved question. It seems likely that apparently erratic behaviour of copper in igneous rocks is really a reflection of the relative age and quantities of sulphide and silicate phases. Chalcopyrite and bornite tend to be late differentiates of igneous rocks, whereas the pentlandite - pyrrhotite paragenesis, being early-stage minerals, probably 'capture' much copper.

2.2.3 Copper Minerals and Ore Deposits

The sulphide minerals of copper are most characteristic, and some of these minerals are very rich in copper. Most important, economically, are chalcocite, chalcopyrite, covellite and bornite. Arsenides and tellurides are known but are insignificant from an economic point of view. Copper ore deposits are particularly susceptible to supergene enrichment and chalcocite (79 - 80% Cu), cuprite (89% Cu) and tenorite (80% Cu) are important in such supergene environments. Secondary copper minerals are interesting since they show the difficulty of forming anhydrous, ionic compounds; for example, cupric carbonate, $CuCO_3$ is unknown as a mineral but the hydroxy-carbonates, malachite and azurite, are common. Similarly the chloride, atacamite, is $CuCl_2.3Cu(OH)_2$. Native copper is known to occur naturally.

Most large ore deposits are formed by hydrothermal replacement and the largest deposits are the so-called "porphyry copper" type. These are generally associated with intrusions of monzonitic rocks which are usually fissured and sericitized. Chalcopyrite is the major ore mineral, disseminated throughout the igneous rock.

The ore grade is usually 0.5 to 1.5% copper and reserves commonly reach many millions of tons. Supergene enrichment, in many cases, is widespread and helps to make some "porphyry coppers" viable economically.

Other types of copper ores are stratiform, cupriferous sandstones — the origin of the copper in such ores is the subject of dispute. These may contain chrysocolla in addition to, or instead of, copper sulphides, oxides or carbonates.

The Mansfeld (Germany) sandstone is only 2 ft thick and it averages 3% Cu. Apparently the bed formed at a very low rate of sedimentation and clastic fragments are rare. Presumably base metals were precipitated rather quickly compared to the rate at which barren material was deposited. The host rock of stratiform ores is most commonly a shale, often occurring in a stratigraphic sequence suggesting that a period of relative stability occurred within a period of earth movements.

High temperature, hydrothermal deposits and copper-rich skarns are also mined.

2.2.4 Igneous Trends

It has been mentioned already that the distribution of copper in igneous rock is erratic, partly because an unknown proportion is contained in sulphide minerals and also because of the inherent problems of including copper in non-hydrated silicate lattices.

Sandell and Goldich (1943) found that the copper content is proportional to that of sulphur and inversely proportional to the silica concentration. This indicates that most copper is contained in a primary sulphide mineral. Wager and Mitchell (1951) working on the Skaergaard intrusion found that copper in silicates is rather evenly distributed amongst the phases:

Copper (ppm) in Co-existing Minerals in Skaergaard Intrusion

	Plagioclase	Pyroxene	Olivine	Ilmenite	Magnetite
Gabbro 4077	35	35	20	-	-
Ferrogabbro 1907	250	300	300	300	500
Chilled margin 1724	40	40	100	-	-
Ferrogabbro 4194-5	700	1000	400	400	300

These writers generally find that copper increases in the minerals of the differentiates until a separate sulphide phase crystallises. However, anomalous results were obtained for some rocks which may be explicable in terms of sampling problems.

2.2.5 Sedimentary Cycle and Weathering of Copper

The concentration of copper in sedimentary rocks is given in the tabulation below:

	Shales	Sandstones	Limestones
Turekian & Wedepohl, 1961	45	1-10	4
Hawkes & Webb, 1962	30-150	10-40	5-20

As in the case of other heavy metals, the high value in argillaceous sediments probably reflects the influence of adsorption on clays or reactions with organic phases. Older data, quoted by Goldschmidt (1954) give the values below:

	ppm Cu
Mississippi silt, average	34
Terrigenous clays, average	128
Red clay, average	160
Italian argillaceous sediments	192
Manganese nodule	3000
Limestones, average	20
Dolomites, average	13

Krauskopf (1967) gives the average value for shale as 57 ppm copper. Values for deep-sea carbonate and clay are, respectively, 30 and 250 ppm copper according to Turekian and Wedepohl (1961). The Lias shale examined by Le Riche (1963) gave a copper concentration of 7 to 95 ppm, with an average of 46 ppm copper.

Hawkes and Webb (1962) estimate the average copper content of soils to be about 20 ppm, probably ranging up to 100 ppm. In soils the copper occurs in limonitic material, manganese oxides or in organic phases. Where the pH is low (and the above materials are usually absent in these conditions) copper is mobile in percolating solutions. Malachite and azurite are known as detrital minerals in neutral to alkaline soils (as at Montacute, South Australia).

Re-deposition of copper from groundwater as sulphides is relatively common and this may lead to supergene enrichment. Copper is also removed from solution by adsorption on clays, etc, and by inclusion in manganese nodules. As a consequence of these processes very little copper remains in the ocean, and its residence time there is only 50 years (Bowen, 1966).

2.2.6 Copper in Water

The following tabulation presents data on the concentration of copper in both seawater and freshwater. The data of Van Price and Ragland (1968) may be derived from an anomalous area. The solubility of copper in seawater is kept low by the extraction processes mentioned above.

		Cu in Seawater ppb	Cu in Freshwater ppb
Sverdrup et al.,	1942	1 -10	-
Wattenberg,	1943	0.2- 1	-
Noddack,	1939	4	-
Picotti & Baldassi,	1942	-	5.7- 47
Riley,	1937-8	-	1 - 15
Krauskopf,	1967	3	-
Hawkes & Webb,	1962	-	0.2- 3
Bowen,	1966	3	-
Van Price & Ragland,	1968	-	40 -1100

2.2.7 Biogeochemistry

Copper is present in plants and animals as an essential microconstituent. Bowen (1966) quotes values of 11 ppm in marine plants, 14 ppm in land plants and notes the accumulation of copper in some sponges (up to 50 ppm copper).

Some plants tolerate very high concentrations of copper, up to 6,500 ppm, according to Vogt and Braadlie (1942). Species of *polycarpaea* are known to tolerate higher than average abundancies of copper in soil, even though, for many plants, large amounts of copper are toxic. Copper is probably a constituent of most plants and animals in the form of proteins.

2.2.8 Metamorphic Behaviour

As is the case with most base metals, little is known of their behaviour during metamorphism, but it is thought that only minor changes in concentration (if any) occur during metamorphic processes. Shaw (1954) has measured copper concentrations in pelitic schists as: 23 ppm in low, 22 ppm in medium and 17 ppm in high-grade rocks.

2.3 Zinc

2.3.1 General Chemistry

Zinc has a fundamentally simple chemical character since it exhibits only one valency, the +2 oxidation state. The Zn^{++} ion has the same radius as Fe^{++} (0.74 Å; Krauskopf, 1967); however, because of the electronic configuration of zinc, it has a tendency to form tetrahedral complexes, as well as the commoner octahedral complexes. In meteorites zinc is strongly chalcophile and this tendency may also be observed in the lithosphere. Some lithophile character is also shown.

Zinc has been particularly important in geochemical prospecting because of its great mobility in the weathering zone. This is due principally to the solubility of Zn^{++} which is usually precipitated only by limonitic material and organic compounds.

The crustal abundance of zinc is about 70 ppm (Krauskopf, 1967) and a great deal is known of the geochemistry of the metal, with respect to secondary zinc minerals and weathering behaviour.

2.3.2 Distribution in Rocks

Except in special circumstances under which sphalerite (or one of its weathering products) forms, zinc occurs in rocks as a trace element in the lattice, or on the surface, of nominally zinc-free minerals. Consequently, the mean concentration of zinc in most rock types rarely exceed 100 ppm. Basalts and shales have zinc values of about 80 to 100 ppm and sandstones have values of only 10 to 20 ppm.

Concentrations of zinc (in ppm) in major crustal units are shown below:

		Ultrabasics	Basics	Intermediate	Acid	Syenites
Krauskopf,	1967	-	100	-	40	-
Rankama & Sahama,	1950	-	90	120	30-200	-
Turekian & Wedepohl,	1961	50	105	-	50	130
Vinogradov,	1962	30	130	72	60	-
Hawkes & Webb,	1962	50	130	-	60	-

In igneous rocks zinc is not involved in the early-formed sulphides (pentlandite-pyrrhotite paragenesis), but has affinities with late sulphide segregations. Zinc occurs in diadochic replacement of iron in magnetite and of magnesium and iron in silicates, but the zinc spinels, gahnite and franklinite, are rare. Apart from sulphides and oxides most zinc is carried in igneous rocks in biotite (especially), amphiboles and pyroxenes.

Zinc is concentrated in hydrolysate sediments and those rich in sulphur; its concentration in sandstones is less than 20 ppm. The concentration of zinc is rather high in phosphorite deposits and can be several thousand parts per million (Rankama and Sahama, 1950). The following values for zinc concentrations in sedimentary rocks and sediments are taken from various authors:

		Shales	Sandstones	Limestones	Deep-sea Sediments	
					Carbonate	Clay
Turekian & Wedepohl,	1961	95	16	20	35	165
Vinogradov,	1962	80	-	-	-	-
Hawkes & Webb,	1962	50-300	5-20	4-20	-	-
Rankama & Sahama,	1950	200-1000	<20	⩽50	-	-

High values for argillaceous sedimentary rocks probably represent sulphur-rich samples containing sphalerite or, possibly, may be organic-rich sediments.

2.3.3 Zinc Minerals and Ore Deposits

The most significant zinc minerals are:

Sphalerite	ZnS
Zincite	ZnO
Smithsonite	$ZnCO_3$
Willemite	$Zn_2(SiO_4)$
Hemimorphite	$Zn_4(OH)_2Si_2O_7.H_2O$

Sphalerite has the tetrahedral structure mentioned above as being a characteristic feature of Zn^{++} (where an octahedral arrangement might be expected), whereas wurtzite (ZnS) and zincite have hexagonal, polar forms. Sphalerite is by far the commonest of these three minerals. Smithsonite and hemimorphite are well-known secondary zinc minerals, often found in the weathering zone of zinc deposits.

In describing ore deposits, lead and zinc can be considered together. Sphalerite and galena occur in limestone terranes either as disseminated deposits, cave fillings, etc. Replacement ores can be massive or lode-like. Often the structure of original sediments is preserved in the replacement process (Sullivan, Mount Isa).

The tenor of zinc ores is about 2 to 3% Zn in the Tri State district of the USA, and 4 to 12% Zn elsewhere. Lead ores are usually somewhat richer, but the economics of mining are affected by the trace silver which can be obtained from the lead ore. Deposits containing as much as 20% Pb are known.

Lead and zinc also occur in primary hydrothermal vein deposits (eg. Northampton area, WA), but these represent a minor proportion of the total lead-zinc ore mined.

Most modern economic geologists regard the major lead-zinc ores as being ultimately derived from hydrothermal solutions of igneous derivation.

2.3.4 Igneous Trends

Although the general knowledge of zinc distribution is comprehensive, the details of the behaviour of zinc in differentiation of igneous rocks is meagre. This is probably due to the fact that emission spectrographic methods of analysis are not so satisfactory for zinc as for many other base metals. Neither Wager and Mitchell (1951) nor Sen et al. (1959) consider zinc in their papers. In the monzonitic intrusion of the western USA Griffiths and Nakagawa (1960) found an average concentration of 63 ppm zinc. The suggestion of Rankama and Sahama (1950) that zinc is concentrated in late sulphides, appears to be a valid generalisation; however, the zinc content of silicate minerals can be high in rare instances and values of 4.7% ZnO have been reported in amphibole and 0.24% in biotite (Rankama and Sahama, 1950). That zinc's affinity in these silicates and others is with ferrous iron rather than magnesium, is suggested by the fact that ilmenite from igneous rocks contains as much as 3,000 ppm Zn and magnetite up to 1,000 ppm Zn (Goldschmidt, 1958). (This is confirmed by the common substitution of zinc for ferrous iron in staurolite from metamorphic rocks.)

2.3.5 Sedimentary Cycle and Weathering Behaviour

Sulphate and chloride ions do not precipitate zinc from solution and consequently Zn^{++} is a relatively mobile ion in many weathering environments. It is also possible that zincate ions could be responsible for the solubility of zinc. Smithsonite ($ZnCO_3$) is a common secondary mineral precipitated in alkaline conditions associated with limestones. Zinc also has affinities with the hydrolysate sediments and, in soil, is weakly attached to clay mineral grains by adsorption. Some studies on zinc deficiencies in soils indicated that much zinc was in the form of ilmenite and silicates (not extractable in cold, dilute acid) and "available zinc" was commonly only 6 to 10 ppm (Goldschmidt, 1958). Hawkes and Webb (1962) suggest that the average content of zinc in soils is 50 ppm and the range of values, 10 to 300 ppm. White's (1957) work on zinc in soils suggests that much zinc is included in the lattice of clay minerals.

2.3.6 Zinc in Water

The concentration of zinc in the ocean was measured as 0.5 ppb by Wattenberg (1943); however, higher values appear to be accepted generally, Krauskopf (1956) gives a range of values of 5 to 21 ppb and in his book (Krauskopf, 1967) a value of 10 ppm Zn is given. That zinc which exists in true solution is probably in the form of Zn^{++} and $ZnCl^{+}$ ions.

In fresh water, zinc occurs in concentrations between 1 and 200 ppb, according to Hawkes and Webb (1962). Measurements of concentrations in both fresh water and seawater probably include some colloidal material or ions absorbed on colloids and the actual amount of the element in true solution might be significantly less than the quoted concentrations suggest.

2.3.7 Biogeochemistry

Zinc is one of the more important trace elements in both plants and animals. High concentrations of the metal are toxic but on the other hand, zinc is essential to the health of the plants. Some plants accumulate zinc and Rankama and Sahama (1950) quote a concentration of 16% Zn in the ash of *Zhlaspi calaminate*. Bowen (1966) gives *Zhlaspi alpestre van calaminore* as an accumulator along with *Viola tricolor van calaminore* and others. The average abundance of zinc in land plants is about 100 ppm (Bowen, 1966).

Zinc in the biosphere occurs in enzymes and proteins, the metal being bonded in the centre of these structures.

Zinc is an important pollutant in both the atmosphere and in some rivers.

2.3.8 Metamorphic Behaviour

Data on the distribution of zinc during metamorphism are not readily available; however, it is unlikely that the concentration of zinc in a metamorphic rock would differ from that in the igneous or sedimentary precursor.

2.4 Lead

2.4.1 General Chemistry

Lead occurs in the fourth group of the Periodic Table with germanium and tin. Silicon and carbon (also in Group IV) have special properties setting them apart, geochemically, from the other elements in the group.

Stable inert gas configurations affect the chemistry of lead only slightly since, having a low electronegativity, the Pb^{4-} or Pb^{4+} states (which have stable electron configurations) are impossible to attain. The Pb^{++} state is stable and involves an "inert pair" of 6s^2 electrons — it is the stability of these two electrons which renders the Pb^{4+} state rare in nature. A corollary is that co-valent bonding is relatively common, usually in a tetrahedral arrangement.

Pb^{++} has an ionic radius of 1.32 Å (Rankama and Sahama, 1950) and consequently occurs in silicates in a diadochic relationship with potassium. Pb^{4+} (radius 0.89 Å) has a similar radius to magnesium, copper, ferrous iron, etc., but the charge discrepancy makes diadochy with these metals rather unusual.

Lead is one of the rarer elements in the crust, its abundance being only 12.5 ppm (Krauskopf, 1967); less than that of gallium, niobium, scandium, lanthanum and yttrium, for example.

Although, from an economic point of view, lead sulphide, galena, is most important, lead does show considerable lithophile character as well as this most obvious chalcophile tendency.

2.4.2 Distribution in Rocks

The following tabulation gives the data collected on the distribution of lead in various rock types:

		Igneous Rocks (Pb ppm)				
		Ultrabasic	Basic	Intermediate	Acid	Syenite
Hevesy et al.,	1931	-	5	-	30	-
Sandell & Goldich,	1943	-	9	-	19	-
Sahama,	1945	-	-	-	9-27	-

		Igneous Rocks (Pb ppm)				
		Ultrabasic	Basic	Intermediate	Acid	Syenite
Krauskopf,	1967	-	5	-	20	-
Vinogradov,	1962	<1	8	15	20	-
Turekian & Wedepohl,	1961	1	6	-	17	12
Hawkes & Webb,	1962	-	12	-	48	-

		Sedimentary Rocks (Pb ppm)					
		Limestones	Resistates	Hydrolysates	Evaporates	Carbonate*	Clay*
Goldschmidt,	1937	5-10	20	-	-	-	-
Boury,	1938	-	-	-	1.1	-	-
Hawkes & Webb,	1962	5-10	10-40	20	-	-	-
Turekian & Wedepohl,	1961	9	7	20	-	9	80

* Deep sea sedimentary rocks.

It can be seen that lead is not concentrated markedly in any particular rock type and presumably occurs only as a trace constituent in common minerals. Lead occurs mainly in a diadochic relationship with potassium in alkali-feldspar and micas; consequently most lead occurs in acid rocks rich in these minerals. Clearly there is no association of Pb^{4+} with magnesium or iron.

Lead in limestones probably occurs in the lattice of the carbonates, in a diadochic relationship with calcium, barium or strontium.

The high concentration of lead in marine clays may reflect the influence of meteoritic dust, or, possibly pollution.

From the similarity of the lead concentrations in sedimentary and igneous rocks, it is clear that the geochemical cycle of this metal is rather "flat" and the metal is widely spread throughout the crust.

2.4.3 Lead Minerals and Ore Deposits

As has been indicated above, lead occurs mainly in the felsic silicate minerals, rather than ferromagnesian types. Augite contains about 3 to 10 ppm lead, probably replacing some calcium; however, in their work on the Skaergaard intrusion Wager and Mitchell (1951) found less than 10 ppm lead in minerals (plagioclase, olivine, pyroxene) separated from different members of the differentiation series. Rankama and Sahama (1950) report that apatite is a common host for lead, but that early-crystallised potash feldspar can contain most lead (up to 100 ppm). Little is known of the relationship between lead and potassium in micas, but some concentration of lead would be expected in these minerals.

The major ore mineral of lead is galena, the monosulphide with a halite type of structure. Other sulphides of lead are exceedingly rare. Anglesite ($PbSO_4$) and cerussite ($PbCO_3$) are the major oxidised ore minerals; in these lead acts as a cation as it does in most other lead minerals, of which the chloro-phosphate, pyromorphite, is the most important.

Lead deposits have been considered with those of zinc and will not be discussed further here.

2.4.4 Igneous Trends

The distribution of lead in different igneous rocks contrasts strongly with that of copper, zinc and nickel; whereas these last three metals are concentrated in basic or ultrasbasic rocks (sometimes as sulphides), lead occurs in late differentiates. This is mainly due to the capturing of lead by potassium or, more rarely, by selenium. Patterson's (1952) data on Irish lavas exemplify the distribution:

	Pb ppm
Olivine basalt	<20
Tholeitic basalt	25
Quartz trachyte	43
Rhyolite	43

Sandell and Goldich (1943) found that lead increased from 8 to 20 ppm from olivine basalt to rhyolitic obsidian in volcanics from the Clear Lake area of California. However, the possibility that some of this lead is present in sulphide phases should always be considered with respect to these figures.

2.4.5 Sedimentary Cycle and Weathering Behaviour

On the weathering and oxidation of galena, lead forms a range of secondary minerals with many different anions — sulphate, carbonate, molybdate, phosphate, etc. — and, because of the insolubility of these compounds, lead tends to be immobile in the weathering environment. According to Rankama and Sahama (1950) lead is most soluble in bicaronate-rich environments. The metal may also be mobile in unusually acid environments (see Section 2.4.6) where cerussite, anglesite and other secondary minerals have appreciable solubility.

Lead in soils reaches a concentration of only 10 ppm on average (Bowen,

1966) but this figure can be exceeded in soils derived from limestones. Under reducing conditions in badly drained soils precipitation of lead as PbS can occur and the extent to which lead is "fixed" by humus or iron oxides is not known. Only little is known of the distribution of lead in sediments, but many authors assert that lead is included on iron hydroxides or on clay minerals. Except in rare instances where PbS is precipitated, lead concentrations do not exceed 100 ppm. In the Mansfeld copper-shale of Germany, concentrations of 5,000 ppm lead have been reported (Goldschmidt, 1958).

2.4.6 Lead in Water

Early measurements of lead in seawater of 4 and 5 ppb Pb were made by Boury (1938) and Noddack and Noddack (1939), respectively. Krauskopf (1956) gives a range of values from 3 to 8 ppb, but in his later book (1967) quotes the value obtained by Riley and Skirrow (1965) of only 0.03 ppb. Much of this lead is in the form of $PbCl^+$ ions according to Gucker and Garrels (1949). The metal is extracted from seawater principally by absorption on iron and manganese oxides, by absorption on clays and by involvement in organic processes.

Hawkes and Webb (1962) give a range of 0.3 to 3 ppb lead in fresh water — a low value which might be expected from discussion in previous sections. Livingstone (1963) mentions several analyses and concludes that the mean lead content of lakes and rivers is between 1 and 10 ppb.

Lead, therefore, is not a metal associated with aqueous environments since it forms too many insoluble compounds with common anions and is probably readily absorbed in ion-exchange reactions with clays, etc.

2.4.7 Biogeochemistry

Lead is toxic to most plants and much of the lead absorbed through roots is precipitated therein. However, enough lead reaches other organs of the plant, for this to be measurable. Hawkes and Webb (1962) give average values of lead (in ppm) in ash of plants as follows:

Pb ppm	
33	Grasses (excluding roots)
44	Other herbs (excluding roots)
85	Shrubs, leaves
54	Deciduous trees, leaves
75	Conifers, needles

Various tree species from Nigeria gave lead values in oven-dried twigs of 0.3 to 0.8 ppm (Webb and Millman, 1951). These values may not be indicative of the total lead absorption by the plant, since Hammett (1928) has found that lead is precipitated in the roots (see above).

2.4.8 Metamorphic Behaviour

Little information is available on the behaviour of lead during metamorphism, although Shaw's (1956) data indicate that schists and their unmetamorphosed equivalents have similar lead contents.

3. BEHAVIOUR OF ELEMENTS IN AQUEOUS ENVIRONMENT

3.1 General

The major advantage of geochemical prospecting techniques is that weathering makes available an anomalous, detectable amount of metal, derived from a hidden orebody. However, reliance is placed on the efficiency of weathering and transport, both processes depending largely on the behaviour of the elements in water.

Two basic steps are involved: the dissolution of ore minerals and the redeposition of metals from the water onto soils or stream sediments (the take-up by plants is considered elsewhere).

The weathering and breakdown of ore minerals has been researched extensively and the papers of Anderson (1955), Ellis et al. (1967), Sveshnikov and Dobychin (1956), Shcherbina (1956), Hansuld (1966), Habashi (1966), Sato (1960a, 1960b) and the book by Garrels and Christ (1965) are all relevant. Much attention has been devoted to this subject because of its connection with supergene enrichment. All the papers proceed from one of two approaches: from experiments which try to simulate the natural weathering environment (occasionally measurements have actually been made in natural conditions) and from thermodynamic calculations. Both procedures rest on simplifications of the chemical and, more rarely the physical, environment.

The question of the redeposition of metal ions from water onto soil phases or stream sediment is more difficult to solve because not only are solubilities in complex solutions involved but absorption and reactions with organic and clay phases must be considered. This has been done only by experimental methods so far, by Bondarenko (1968), Richardson and Hawkes (1958) and Newberg (1967). Much of the basic information below is obtained from standard chemical texts and Garrels and Christ (1965).

Primary sulphide ores on reaching the weathering zone suffer processes of oxidation during which sulphur changes from the reduced $S^{=}$ state to the oxidised, $SO_4^{=}$ state. Sato (1960a) has measured the redox potential (Eh) and acidity (pH) of mine waters near oxidising sulphides and has found that environments with and without free oxygen fall in two fields about on line with the equation:

$$Eh = 0.68 - 0.059\,pH$$

which corresponds to the hydrogen peroxide-oxygen gas couple:

$$H_2O_2 = O_2 + 2H^+ + 2e.$$

Sato suggests that the mechanism of oxidation of common sulphides is the reduction of oxygen to yield hydrogen peroxide and the decomposition of the latter to oxygen and water by the catalytic activity of common metals. This reversible equilibrium controls (acts as a buffer) Eh-pH conditions in the oxidising environment. Sato (1960a) presents an Eh-pH diagram indicating the probable ranges of conditions near surface and at depth. In a later paper Sato (1960b) uses experimental methods to arrive at actual mechanisms of oxidation of particular sulphides.

Habashi (1966) and Sveshnikov and Dobychin (1956) have tried to show that electrochemical factors are also involved in dissolution of sulphides: briefly, when two or more sulphides occur together the differences in electrode potential set up a small galvanic cell and the dissolution of ore sulphide is hastened. Hence if galena and sphalerite occur together more galena and less sphalerite dissolve in a given time than would dissolve if they existed singly.

In order to study the stability of sulphides, secondary minerals and ions of metals, Eh-pH diagrams have been widely employed. The method allows one to include not only Eh and pH, but also factors such as chemical composition. The stability relations amongst some copper minerals will be considered briefly as one example (Figure 1).

In Figure 1 the solid line between tenorite and Cu^{++} represents the position at which the dissolution of tenorite contributes a Cu^{++} concentration of 10^{-6} M (0.06 ppm Cu), ie. for normal purposes tenorite is insoluble and copper is not going into solution. In a system containing total dissolved sulphur concentration of 10^{-1} molar and with a partial pressure of CO_2 of $10^{-3.5}$ then the stability relations are as shown in Figure 2. The prevalence of malachite and cuprite amongst the secondary minerals is clearly shown; also, copper moves in solution as Cu^{++} at a pH of less than about 0.5. The positions of the lines are independent of the total concentration of copper in the system and unless compounds or ionic complexes of copper and another metal, say zinc, occur, the relations will be independent of the other metal in the system.

With respect to lead, anglesite and cerussite, the major secondary minerals, are very stable over a great range of pH values and, in more reducing conditions, galena is completely unreactive. In normal conditions lead's mobility would be caused by:

a. formation of soluble complexes not accounted for in Figure 2;

b. absorption on or reaction with suspended organic matter or manganese iron hydroxides; or

c. movement as Pb^{++} in sulphur-free environments, where anglesite will not form. Cerussite then begins to dissolve at a pH of about 6.

Nickel should be mobile in moderately oxidising and neutral or acid conditions since the stability field of Ni^{++} is quite large.

Diagrams published in Garrels and Christ (1965) do not include those for the zinc compounds; however, since smithsonite, $ZnCO_3$, is the commonest secondary mineral, a simple calculation shows the relation between Zn^{++} ions and this mineral. The reaction, with the standard free energies of formation of the compounds, is -

$$\begin{array}{ccccccccc} ZnCO_3 & + & 2H^+ & = & Zn^{++} & + & CO_2 & + & H_2O \\ -174.8 & & 0 & & -35.2 & & -92.3 & & -56.7 \text{ kcal.} \end{array}$$

Therefore

$$\Delta Fr = -9.4 \text{ kcal and } \log K = +6.9 = \frac{(Zn^{++})}{(H^+)^2}$$

where K is the equilibrium constant. Substituting -log (H^+) for pH: $\log(Zn^{++}) = 6.9 - 2\text{ pH}$. A Zn^{++} concentration of 10 ppm (1.5×10^{-4} M) is obtained at a pH of 5.2.

It is assumed that natural conditions will always be more complex than those that can be incorporated in thermodynamic calculations and the presence of complex ions is possible — in fact, many such ions are known (for example

$HNiO_2^-$, ZnO_2^{2-}, $PbCl^+$) but their free energies have not yet been measured so that they cannot be included in calculations. It is important to realise that the presence of complexes (and of absorbed ions on organic or hydroxide phases) always decreases the stability fields of solid phases on the Eh-pH diagrams. Shcherbina (1956) considers the formation of silver and gold complexes, but his Figure 1 (page 488) shows that Ni, Pb, Zn and Cu are unlikely to form complex ions in normal conditions.

Listova (1966) studied the solubility of galena in acidified water and found that after 490 days all solutions had a pH between 5.5 and 5.9. Anglesite formed first (sulphuric acid was used to lower the pH) but carbon dioxide in the atmosphere changed this to cerussite. Figure 3 can be interpreted to suggest that at low pH little lead goes into solution because the solubility of $PbSO_4$ is reduced by high concentrations of sulphate ions. A "plateau" at pH 4 is caused by the normal solubility of $PbSO_4$ (27 mg/litre of Pb). Listova asserts that the maximum in the solubility curve is caused by the formation of relatively soluble complexes $(Pb(S_2O_3)_2)^{=}$ and $(Pb(S_2O_3)_2)^{4-}$. Low solubilities at high pH are caused by the limited solubility of lead hydroxide. After equilibrium was reached in these experiments most lead (85 to 90%) remained as galena and very little of the remaining 10 to 15% stayed in solution. There are discrepancies between the work of Listova and Shcherbina.

It is interesting that Listova obtained a maximum lead concentration of 40 ppm lead, whereas the solubility calculated from the solubility product of galena quoted in Krauskopf (1967) leads to a lead concentration of about 2×10^{-9} ppm. The solubility of 20 ppm lead obtained at low pH agrees well with the solubility calculated from Krauskopf's (1967) data on the solubility of anglesite.

In the light of Listova's work, Bondarenko's (1968) results on the solubility of organic complexes of lead (fulvates) do not seem very conclusive since maximum solubility of galena in acidified fulvic acid solutions is only 50 ppm lead. Values of this order were only reached at very low pH. At moderate pHs concentrations of 30 ppm were reached, whereas in the same conditions galena in pure acidified water yielded solubilities of 40 ppm lead (Listova).

No papers on a third aspect of lead movement — adsorption — were found, but Richardson and Hawkes (1958) studied the adsorption of copper on crushed quartz. Figure 4 is taken from their paper and shows the weight of copper adsorbed (in mg) per gram of quartz. To the left of the isoelectric line the quartz surface has a positive charge and adsorbs no copper. As the authors state,

> "In a stream containing 0.01 ppm copper and with a pH of 6, quartz particles 41 microns in size adsorb only 0.1 μg of copper per gramme of quartz. In the usual geochemical prospecting field test using a 0.1 g sample .... this concentration of copper would be undetectable."

The above discussion summarises that part of the literature in which experiment and thermodynamic calculations have yielded satisfactory data on solubilities of metals. One of the most important aspects has not received so much attention; this is the adsorption of metals on iron or manganese hydroxides. The latter form precipitates — and possibly gels — in stream sediments and are thought to co-precipitate or adsorb metal ions. Antropova (1968) and Horsnail et al. (1969) present some pertinent results. Antropova analysed two stream sediments and found that the weight percentage lead in each fraction was (average of two):

	%
organic fraction	0.8
hydrogoethite fraction	0.9
magnetic fraction	1.0
quartz, etc.	0.01
ferruginised quartz	0.1

The greater concentration of lead in organic and iron-manganese hydroxide phases is clear. Horsnail et al. examined stream sediments from North Wales and found that about half the copper, lead, zinc and nickel occurred with secondary manganese oxides which made up 15% by weight of the drainage sediment. This means that, in considering stream sediment data, some allowance has to be made, when setting background and threshold levels, for the manganese oxide content. Apparently anomalous results may more properly be related to a relatively reducing environment rather than to the presence of ore. Figure 5 shows how some anomalous values are in fact misleading when compared with the manganese content of the sediment.

Finally, Ellis et al. (1967) have compared the rates of extraction of copper, iron and manganese from stream sediments with a variety of reagents. They assumed that equal rates of extraction implied that the three elements were similarly bonded in the sediment — ie. copper was in the same phase as iron and manganese — the oxide/hydroxide phase. Prosser, in the discussion of Ellis et al. (1967), points out some of the hazards in interpreting rate data and it appears that far more work is required on rate-of-extraction experiments before satisfactory conclusions can be reached.

Newberg (1967) has postulated that chrysocolla is formed from waters derived from weathering ore deposits, by reaction between silicon and copper, both derived from weathering:

$$Cu_2S + 2O_2\ (aq) = 2Cu^{+} + SO_4^{=}$$

$$2NaAlSi_3O_8 + 2H^{+}\ \text{(from oxidation of sulphides)} + 9H_2O$$
$$= H_4Al_2Si_2O_9 + 2Na^{+} + 4Si(OH)_4$$

then $$Cu^{++} + Si(OH)_4 = CuSiO_3.H_2O + 2H^{+}.$$

The overall reaction is that copper ions and albite (representative of many possible silicate sources of silicon) react to form kaolinite and chrysocolla.

An essential part of a geochemical prospecting survey must be an understanding of the behaviour of elements in water and a knowledge of the conditions in the waters of the survey area. Baas Becking et al. (1960) summarise the Eh-pH conditions met in many different environments and in general a range of Eh values from plus 0.8 to minus 0.4 volts is encountered, with a pH range of 1 to 10. Fresh water sediments range in Eh from plus 0.6 to minus 0.15 volts and in pH from 4 to 9.5. The value of determining the position of relevant sediments within these ranges cannot be exaggerated.

3.2 Summary

Copper sulphides dissolve in waters having a pH of less than about 6 (Cu in solution then 6 ppm) and a redox potential in excess of approximately plus 0.2 volts. The normal precipitates when conditions subsequently change are malachite, azurite or copper oxides. As for the other three elements (Pb, Zn and Ni), any adsorption on clays or co-precipitation with manganese oxides/ hydroxides, will alter this behaviour markedly. Such an alteration is always in the direction of reducing the apparent solubility of the metal.

Zinc is soluble in sulphate-rich waters and is usually precipitated as the carbonate, smithsonite. This occurs at a pH of approximately 5.2, where the equilibrium zinc concentration is 10 ppm. At extremely high pH values the soluble complex ion $ZnO_2^=$ forms.

Lead is extremely insoluble in most circumstances because of the low solubility of anglesite, even in acid solutions of moderate to high redox potential. Cerussite begins to dissolve at a pH of 6.5 (approximately), whereas anglesite is effectively insoluble (Pb^{++} concentration of 27 ppm) until a pH of 1 is achieved. This very different character in different waters probably accounts for some discrepancies reported in the literature.

Nickel should travel in solution in waters having redox potentials greater than plus 0.2 and pH less than about 8. Consequently nickel is apparently a most mobile element and secondary minerals are not well known except for the silicate, garnierite. Precipitation on goethite or manganese hydroxides reduces the mobility of nickel considerably.

Where these metals are not soluble, transportation is mechanical, ie. minerals are broken down in the stream bed until the particles are small enough to become part of the suspended or sediment load of the stream.

4. PAPERS WRITTEN ON PROSPECTING USING SOIL AND ROCKS

This part of the review is rather complex in its format. The following subsections are used:

Section 4.1 discusses general papers which deal with natural soil metal contents, the position of these metals in the soils and the general philosophy of using soil and rock geochemistry for prospecting.

Section 4.2 discusses papers on the use of rock and soil geochemistry for prospecting for copper, lead and zinc. A further subdivision has been made rather arbitrarily in that Subsection 4.2.2 deals with papers which were published before the publication of Hawkes and Webb's (1962) "Geochemistry in Mineral Exploration". Since this book is used as the standard source book for practising geochemistry and its material is well known, early papers of general interest which apply to non-arid areas have been discussed very briefly, though more attention has been paid to those papers which discuss prospecting in arid climates. Papers published after the publication of Hawkes and Webb have been considered in more detail and have been split, for the purposes of convenience, into papers about arid areas, and papers about non-arid areas. The latter group are considered by continents. A separate subsection (4.2.4) reviews all papers which have been obtained which discuss the use of soil and rock geochemistry in prospecting for copper, lead and zinc in Australia.

Papers which discuss the use of soil and rock geochemical prospecting for nickel are reviewed in Section 4.3.

Section 4.4 reviews papers where the prospecting technique used has involved the assay of float or colluvium.

This division of material is not ideal but is considered to be useful in dividing the techniques. Many papers, however, report combined soil and stream sediment geochemical programmes or soil-biogeochemical programmes. Papers which deal mainly with biogeochemistry are discussed in a separate section (Sec.6). Papers which discuss both soil and stream sediment geochemistry are, for the most part, discussed under appropriate headings in separate sections.

Standard texts which discuss in detail prospecting using soil and rock geochemistry include Hawkes (1957), Ginzburg (1957, English 1960), Saukov (1963) and Hawkes and Webb (1962). Papers themselves of a review nature which include substantial sections on soil and rock geochemistry include Hawkes (1949), Webb (1953), Webb et.al. (1968), and Boyle and Garrett (1970).

4.1 General Behaviour of Copper, Lead, Zinc and Nickel in Soils and Laterites

4.1.1 General Discussion

Trace element concentrations in soils are dependent on the composition of the parent rocks, on whether the soil is residual or transported, and on the various weathering and erosional processes which have been active during the formation of the soil.

The formation of a soil involves solution processes, subsequent precipitation, pH, Eh, ionic potentials, ionic sizes, the formation and behaviour of colloids and biological activity. The degree of maturity of a soil depends on all these factors, together with the length of time avilable for creating a mature profile and also on the erosional (or gravitational) processes which tend to destroy the profile.

In igneous rocks nickel, zinc and copper all tend to occur in ferromagnesian minerals. Early formed minerals — olivines, pyroxene and amphiboles — are all unstable under normal weathering conditions and break down releasing their trace element cations. Lead normally follows potassium in igneous rocks and, except where it occurs as the sulphide, tends to remain longer in the more stable (at ordinary temperatures) micas and potash feldspar.

The general behaviour of trace elements is reported to be controlled by the ionic potential (Goldschmidt, 1954). Elements with values of ionic potential below 2 tend to be fully ionised and stay in solution; elements with ionic potentials between 2 and 12 precipitate as oxides or hydroxides and those with ionic potentials above 12 form soluble anions. Copper, zinc and nickel, therefore, should precipitate as hydroxy compounds or as oxides. Lead, by this theory, remains strongly ionic and should be readily soluble; however, it is trapped by many common anions to form insoluble compounds. Lead has demonstrably little tendency to form hydroxy compounds but its known oxidation products are all effectively insoluble (Krauskopf, 1967). A discussion of the breakdown of sulphide minerals is given in Section 3.1.

Soil material is composed of fresh rock fragments, altered or leached rock fragments, secondarily precipitated material and organic compounds, and the trace element composition is a function of the proportion and properties of the these components. A chart showing typical ranges, and extreme values of trace elements in soils is shown in Bear (1955; p 332) and is reproduced in Hawkes and Webb (1962; p 24). Assay information, however, depends on the method of attack on the soils and the degree of resistance to solution provided by the soil. Thus the assay data from an HF or a bisulphate fusion attack can generally be assumed to represent the total amount of the given trace elements present. On the other hand, a cold hydrochloric acid attack may liberate only those cations adsorbed on clays or trapped in oxides or hydroxides. Effective comparison of assays is possible only when the degree of extraction is known.

4.1.2 Location of Trace Elements in Soil

Distribution in Different Fractions and Soil Components. Much of the information in this section is taken from Mitchell (1965), Le Riche and Weir (1963) and White (1951).

Mitchell (1965) separated a number of Scottish soils into different size fractions and then related the trace elements found to each fraction obtained. The soils were developed over boulder clay and typically contained 75 to 90% sand fraction (0.02 to 2.0 mm), 10 to 15% silt (0.002 to 0.02 mm) and 5 to 10% clay (<0.002 mm) with only slight variations depending on whether the boulder clay was derived from basic or acid igneous rocks. The sand fraction, because of its dominating weight proportion, contains a high proportion of the total trace elements. However, the clay fraction contains a larger concentration (on a weight for weight basis) of the base metals. This phenomenon has been confirmed by many workers - *viz.* Hawkes and Webb (1962, Chapter 9). Though the total amount of a given trace element in a soil is considered to be relatable to the concentration of the same element in the parent rock, Mitchell (1965; p 335) considers that differences in the ratio of easily extractable to total values are a function of the degree of drainage of the soil and such ratios are independent of the nature of the parent rock.

On weathering, cations of copper, zinc and nickel may be admitted into the lattice of clay minerals, from which they are not easily extractable, or be adsorbed on the surface of clays whence they may be relatively easily removed. These elements may also be co-precipitated with iron or manganese oxides or hydroxides and probably also with aluminium oxides/hydroxides. Organic compounds absorb part of the freely available cations and many organo-metallic compounds are formed from which it is difficult to release the cations.

Lead is believed to be immobilised as the sulphate or carbonate except for traces which may be taken into organic complexes.

Free cations of all four elements are readily adsorbed by exchange-active clay minerals, possibly (Mitchell, 1965; p 336) because these elements form bases or basic salts on reaction with the clay. The mechanism for lead adsorption is not certainly known.

Le Riche and Weir (1960) have carried out tests on sesquioxides and clays in brown earths from southern England. They found that copper and lead were appreciably richer in surface clays than in subsurface clays. (A similar report for lead has been given by Swaine and Mitchell, 1960.) The greatest proportions, however, of copper, lead and nickel are concentrated in the sesquioxide-rich soil layers. Le Riche and Weir confirmed that these three elements tend to be enriched in the B horizon, although lead is more variable and may be more concentrated in the surface (A) horizons.

These writers note that for many soils the total trace element content is a function of the sum of the sesquioxides and clay minerals present and is not relatable directly to the soil's parent rock.

Mitchell (1965; p 337-338) suggests that reported accumulations of trace elements in the clay fraction may be related, not to adsorption or absorption, but to a film of oxide coating the clay minerals. He bases this on the proportions of trace elements extracted by oxalate solutions compared with those extracted by acetic acid.

Mitchell (1965; p 338) has also found that the extent of sorption of copper, zinc and nickel, released from fermenting and decaying plant material, on to previously precipitated iron oxide is greater than the amount which can be co-precipitated with ferric oxide from extracts of decaying plants. Experiments on co-precipitation showed that precipitation of lead occurred simultaneously with precipitation of iron oxide but over 90% of the total copper, zinc and nickel remained in solution.

In a further test Mitchell (1965; p 339) discovered that nickel, zinc and lead could be mobilised from iron sesquioxides on anaerobic incubation with plant material. Copper could be mobilised on anaerobic incubation but was removed again if plant material was added.

Nickel forms organic complexes with humic acids at pH greater than 8. The complexing of copper has been studied in some detail and the optimum acidity for complex formation is pH 2.5 to 3.5 with humic acid and pH 6 with fulvic acid. A large number of organic copper complexes are known. Nickel forms organic complexes with humic acids at pH greater than 8.

White (1951) has published details on the distribution of zinc within some Tennessee soil composites and has given figures of the proportions of total zinc in the soil held by the various components. Thus, he asserts that 43% of the total zinc content of the soil is associated with iron oxides/hydroxides, 35% of the total zinc is held within the lattice of clays, and 2.6% of the zinc occurs in base exchangeable form attached to clays. The remainder is postulated to be held in a mixture of organic zinc compounds and in resistate minerals such as magnetite. The figures quoted are mean (averaged) values following zinc determinations on fourteen soil composites. Absolute levels of zinc present ranged from 123 to 1015 ppm.

<u>The Distribution of Elements in Soil Profiles</u>. Elements are rarely distributed evenly through the soil profile. Features which contribute to profile zonation include:

1. Surface enrichment of trace elements, derived from decaying plant material (the so-called "Goldschmidt effect").
2. The leaching (eluviation) of mobile elements, either completely out of the soil or to lower zones of accumulation.
3. Absorption, adsorption and precipitation (illuviation) onto and with oxides and hydroxides, particularly those of iron, aluminium and manganese (the so-called sesqui-oxides).
4. The varying mobilisation of elements in soils subject to seasonal fluctuations of the water table.
5. Mechanical movement of particles, particularly on slopes or in ground water (with, commonly, some segregation of clay, sand and silt fractions).
6. Accumulation of salts by evaporation in "arid" regions.
7. Changes accomplished by soil bacteria.

Indications of the patterns of such changes are given by Vinogradov (1959), who gives details of the behaviour known for each element in "Russian" soils and by Mitchell (1965), who discusses the behaviour of elements in podsols from various parts of the world, in soils with impeded drainage and, in less detail, in soils of other types. Mitchell lists many references. Other papers with a geological emphasis are those of Le Riche (1958) and Swaine and Mitchell (1960).

From the data presented by these authors it is clear that no universal rules can apply. In one area there may be surface enrichment, in another enrichment in B horizons, and elsewhere no enrichment at all. In the last case the parent rock normally contains the highest local concentration of trace elements.

It is this variation in behaviour and a lack of understanding of it by the authors, which led to some controversy between Boyle and Dass (1967) who favoured the A horizon for prospecting purposes (in Canada) and Roy and Paul (1967) who favoured the B or C horizons (India).

Australian information has been generated mainly by the CSIRO Division of Soils. Information relevant to South Australia is given by Tiller (1957), McKenzie (1958), Giles (1960 and 1968) and Blackburn and Giles (1963). Additional pertinent papers, with data for other Australian states, are those by McKenzie (1956, 1960 and 1966), Tiller (1959) and Turton et al. (1961).

These authors have been mainly concerned with soil assays from areas used for agricultural purposes. Details of values given in these papers are presented in Tables 1 to 9. In most cases the authors' tables have been compressed but, where few profiles are given or the number of soil types is high, all relevant data are given. Minor rearrangements of figures have been carried out so that values may be compared at standard depths.

These papers show that, for the Australian soils examined, values are generally low, with concentrations below the average world values (Clarke values given by Vinogradov, 1959). Only over basalt does the soil trace element concentration reach the Clarke value. These papers give no assay figures for lead except for the paper by Turton et al. (1961), where a few figures are given for lead in laterite profiles in Western Australia.

Blackburn and Giles (1963) compared the properties at the surface of terra rossa and rendzina soils in the south-east of South Australia with similar properties reported in profiles of similar soils by Tiller (1957), McKenzie (1958) and Giles (1960). They concluded that, in these types of soil copper and zinc were preferentially concentrated in top soils. They considered and discounted fertilisers as possible causes of this phenomenon. In other types of soil, surface and subsurface soil layers showed similar values with no marked preference for any horizon. Blackburn and Giles draw no conclusions from the behaviour of nickel, but examination of the values quoted in the paper shows that the metal has no significant variation in the profile. McKenzie's (1958) conclusions differed slightly in that he found that zinc concentrations were fairly constant through the profile. Absolute concentrations of copper, zinc and nickel reported in all these papers are low, commonly below 10 ppm.

Giles (1968) gives further assay figures for surface samples (1 to 6 inches) from the south-east of South Australia and from parts of western Victoria.

Tiller (1957) made an examination of soils over basalt and tuff in the Mount Burr area of South Australia. In this area modified aeolian sands cover residual soils. As expected the parent rocks have contributed to the residual soils but there is very little sign of basaltic influence in the upper "aeolian" soils. Copper, nickel and zinc are all of low concentration in the surface soils: they increase in depth through the (fossil) profile of residual soils. Tiller (1959) carried out a similar study on residual soils over various Tasmanian dolerites and reached similar conclusions for the behaviour of copper and nickel. In the wetter climate of Tasmania, however, zinc did not appear to concentrate in the lower parts of the profile.

McKenzie (1956) discussed trace element distributions in South Australian red-brown earths from county Victoria, the Martindale estate and the Barossa Valley. The soils are derived from alluvial material which is, in turn, derived from siliceous sedimentary (or metasedimentary) rocks. The only element studied relevant to the present discussion, copper, increased in concentration down the profile to the B horizon then decreased. As with other similar studies the total copper concentration is very low.

McKenzie (1966a and 1966b) reported values for copper and zinc in Victorian soils. Overall values were low and no profile studies were carried out.

Of interest, because of the arid regions on which it is based, and because of the similarity of climate with many parts of northern South Australia, is the paper by McKenzie (1960) on the soils of the Todd River area. In these desert soils, with rudimentary profiles, the concentrations of copper and zinc generally increase with depth. No assays for nickel are given.

Lead, because it is non-essential to plant life, appears rarely in these papers concerning assays of soils. However, Turton et al. (1961) and Turton et al. (1962) do include some values for lead, with a greater number of values of copper and zinc, in a laterite covered area of south-western Western Australia. Lead is in some cases high (over acid igneous rocks) but the concentration of copper is very low indeed. Zinc is more variable and high values are recorded in some profiles. No major trends of concentration are shown, down the profile, for any of the three elements. In non-lateritic soils, used by Turton et al. (1962) for comparison, copper increases with depth in the profile.

Two papers have been written examining regional variations to determine whether a pattern diagnostic of mineralisation can be identified. Presant (1967) has made a study of podsols in New Brunswick, Canada. Values for copper, lead and zinc, in soil (the mesh size is not stated, but is probably -80 mesh) increase by an order of magnitude over sulphides. Over both mineralised and unmineralised ground, copper values generally increase with depth towards the C horizon. Lead and zinc behave more erratically, the humus layer containing more metal than the layer immediately below, but are most concentrated in the C horizon.

Whitten (1969 - for 1967) carried out a regional investigation of an area near Clare, South Australia. Line traverses were made across the regional strike of the underlying rocks (sediments) at 2 to 4-mile traverse separations and ¼-mile sampling intervals. Assays of minus 80-mesh material were made;

soil was sampled at 12-inch depth; rocks, if outcropping appropriately, were chip sampled. In areas of deep soil with no outcrop the soil was sampled at 3 feet in lieu of rock (both soil and rocks were collected where possible).

This survey showed essential similarities of composition of soil and rocks on four different traverses with only slight tendencies to leaching in the soil. In detail, there was some variation between values obtained for soil and rocks, but both indicated one rock sequence of interest. Absolute values were low, mean values being as follows:

	Soil ppm	Rock ppm
Cu	16	17
Ni	23	20
Pb	16	14
Zn	55	55

Note: Values obtained by AAS assay.

Variations of values were obtained when two analytical techniques were compared. In the following tabulation of spectrographic assays the mean values obtained for rock assays appear to be higher for each of the trace elements than are the similar values for the soils:

	Soil ppm	Rock ppm
Cu	16	30
Ni	8	21
Pb	7	18
Zn	22	33

All the papers discussed to this point present analyses with little discussion of sampling procedures, steps taken to avoid contamination and with little consideration of the causes of variation. Two papers which help in understanding these problems are those of Hosking (1959) and of McPhar Geophysics (1956). Hosking, in a general paper about techniques of prospecting in Cornwall, lists many of the ways in which samples can become contaminated. He illustrates the contamination in a number of line profiles of metal concentrations over ore veins of various types related to the southwest England batholith. The paper by McPhar Geophysics discusses sampling problems and variations of assay data caused by inadequate sampling. No specific paper has been found which discusses the possible effects of systematic analytical errors though the problems are illustrated in Hawkes and Webb (1962).

It seems clear to the present authors that insufficient study has been made of sampling and of problems associated with it. It appears that optimum size fractions for analysis and the optimum depth of profile for sampling purposes is very different in different areas. In our personal experience there have been considerable changes in both the fractions and depths considered as most useful over quite small areas. These are believed to be functions of microclimatic effects. We have noted that in many South Australian soils there is a large, fine-grained, wind-blown component which has the effect of diluting trace element concentrations — even in what appear to be residual soils. In many such soils a coarser grained size fraction gives better results for the purposes of identifying possible mineralisation. In general, because of the existence of wide variations in metal content in the different fractions, at different depths, in different areas, the authors believe that it is imperative to carry out an orientation survey in each new area proposed for survey by soil geochemistry.

4.1.3 Laterites

Laterite is an important type of soil in tropical and subtropical areas although its extent is not as great as was once thought. Laterite is forming in present day tropical areas subject to monsoonal influence, but it occurs as "fossil" in many parts of Australia, having formed in Tertiary (Miocene) times when conditions were wetter than they are today. There is still contention about whether lateritic soils are forming in Australia at the present time.

The A horizon of laterites has a light, eluvial texture and sometimes a darker brown (organic-rich) A_o horizon is preserved. The B horizon of laterites is dominated by sesquioxides which are the residual fraction of the parent material remaining after the leaching of other components. This horizon commonly shows nodular textures and in places the nodules (or pisolites) have a cement of oxide material causing them to become hard and non-permeable. Wind or other erosion may later strip the A horizon leaving the B horizon as a hard cap or duricrust, standing above the general erosional level. The lateritic hard-cap zone occurs in the zone of a fluctuating water table. It is succeeded by a mottled or pallid zone relatively poor in sesquioxides and richer in clays. The C horizon, well below the level of the permanent water table, is typically rich in kaolinitic clays and in both silica and ferrous iron.

Lateritisation is characterised by several factors:

a net loss of silica from the profile;

the possible upward migration and certain concentration of large quantities of iron, aluminium and manganese in indurated horizons;

a depletion of bases;

the breakdown of clays to oxides and sesquioxides.

Factors causing the development of laterite are high temperatures throughout the year combined with marked wet and dry seasons. Under these high-energy conditions leaching and weathering are extreme. Laterite develops on any parent rock but tends to be thinner over acid rocks and to be thicker, with well developed mottled and pallid zones, over basic rocks.

Historically there has been a relationship between laterites and peneplains. The peneplains must have suitable conditions to allow a fluctuating water table to be present. However, lateritisation is not confined only to peneplains but also occurs on gentle hill slopes and upland areas.

As indicated, remnants of old lateritised land surfaces occur within Australia. Mulcahy (1960) and Jessup (1960) have discussed the geomorphological significance of laterites in Western Australia and in South Australia, respectively. Papers by Turton et al. (1961), Turton et al. (1962) and Zeissink (1969, 1971) present data on the chemistry and mineralogy of some of the laterites within Australia. The papers by Zeissink are particularly interesting because they discuss nickel-bearing laterites developed over serpentinite.

A good discussion of the behaviour of elements in a lateritic profile is provided by Bonifas (1959) — for the Conakry area, Dahomey.

DeVletter (1955) has discussed the behaviour of various elements in a nickeliferous laterite profile from Cuba.

In general, however, there are few papers which adequately investigate the geochemistry of laterites and lateritic soils.

4.2 The Use of Soil and Rock Geochemistry in Prospecting for Copper, Lead and Zinc

4.2.1 General

Of all the techniques which are available for geochemical prospecting for these metals, the technique of assaying soil has been the most common and most widely reported in geochemical literature. In many cases soil assay values have been compared with rock analyses to determine whether there has been leaching, or enrichment in the soil with respect to the rock, or whether there is any real advantage in sampling the soil at all. These techniques were initiated in the USSR and were introduced to the western world, following the second world war by workers in Canada, the USA and, later still, by workers in England. Data on soil and rock geochemistry in Australia are relatively scanty and most papers on work in Australia have been published since 1965.

The books published by Ginzburg (1957 in Russian, 1960 in English) and by Hawkes and Webb (1962) have provided most of the impetus for later geochemical work. Both books carry summaries of the most important papers which were in print before the books were published. Because of the importance of these books, particularly that of Hawkes and Webb, and because of the large number of papers to be considered, as indicated previously, the subsequent discussion has been split into three major groups:

a. papers published before the publication of Hawkes and Webb (1962);

b. papers published after the publication of Hawkes and Webb (1962); and

c. all papers concerned with soil and rock geochemical prospecting in Australia (and Papua-New Guinea).

Because this report is concerned in particular with techniques of prospecting in arid climates such as South Australia, the first two groups are subdivided further into:

i. papers concerned with prospecting in arid climates;
ii. papers concerned with prospecting in non-arid climates.

In general, papers published after the completion of Hawkes and Webb (1962) and papers concerned with prospecting in Australia have been discussed more fully than those which are included in Hawkes and Webb.

Nickel is only mentioned in this section where the main search targets are copper, lead or zinc.

Summaries of the more important papers are given in Tables 10 to 12.

4.2.2 Papers Published Before the Publication of Hawkes and Webb (1962)

Papers Concerned with Prospecting in Arid Climates. The earliest paper is that of Lovering et al. (1948) who investigated total heavy metals (not differentiated but believed to be mainly zinc) in the East Tintic district of Utah, USA. Altered rocks (lavas) which overly sphalerite orebodies within dolomites were crushed and ground to minus 80 mesh and assayed. No definite evidence of the mineralisation below was obtained. A follow-up paper by Almond and Morris (1951), who worked in the same general area, contains assays of separate elements (together with details of the sampling and assaying procedures). They found, using partial extraction techniques, zinc and lead anomalies in altered lavas 350 to 400 ft above mineralised limestones. The anomalies were found adjacent to fractures in the lavas. No anomalies were found in altered but unbrecciated rocks. The alteration of the lavas occurred before mineralisation and negative anomalies (that is, troughs) were found in altered lavas compared with unaltered lavas. The maximum (anomalous) values found were 400 ppm lead, 70 ppm zinc and 160 ppm copper.

In a third paper on the same area, Morris and Lovering (1952) discuss the mechanisms of dispersion of the elements from the ore. Solutions were considered and it was noted that of gold, silver, lead, copper and zinc, only zinc would travel more than 50 ft within carbonate rocks. All these elements are mobile in the oxidised zone of pyritic shales. Zinc (and silver) may travel several hundred feet but copper travels a shorter distance before being fixed by adsorption on clays. In quartzitic rocks both copper and zinc travel considerable distances. In both rock types primary dispersion is restricted to a few feet. Lead shows no evidence of lateral secondary dispersion in either rock type.

Also in Utah, USA, Huff (1955) measured copper, lead, zinc in the Chinle formation of the Capitol Reef area. Adjacent to the Oyler mines the bleached zone of the lower Chinle formation contains "several hundred" ppm zinc and about 100 ppm copper. Unbleached beds adjacent, have values of the order of 10 to 50 ppm for both metals. Huff suggests that assays for zinc and copper could be used as a prospecting tool for copper-uranium deposits.

In the Rocky Range, Utah, Erickson and Marranzino (1960) assayed for copper in alluvium over known bedrock copper deposits. Assays of minus 80-mesh samples, using a total extraction technique, showed no apparent spatial relationship to mineralised rock, but assays of locally deposited calcrete/calcite showed that the largest highs occurred near the known, but concealed, deposits. The authors concluded that the calcrete reflects the bedrock chemistry.

In Arizona, Lovering et al. (1960) investigated the dispersion pattern away from a large, low-grade porphyry copper deposit, by analysing soil, alluvium, ground water and vegetation. Sampling of sediments was restricted to the silt and clay fractions. They found little copper in the ground water/ run off and little in vegetation (though they noted that certain plants appeared to grow preferentially on the ore, and were possibly indicators of copper). Tests showed copper to be concentrated in the minus 80-mesh fraction of the soil. Copper is believed to be dispersed in acid, sulphur-bearing solutions. The present day environment is alkaline and semi-arid, with 10 inches of rain per annum, and copper is no longer moving chemically. Soil, derived directly from underlying rock, has a copper content similar to that of the parent rock (0.1 to 0.5%) more or less diluted by additional unmineralised material. The effects of dilution bring values down to 100 - 3,000 ppm. The ore outcrop is 70,000 sq ft in area in a basin of 42 million square feet. The dispersion train in this basin is traceable for 1.4 miles below the outcrop. The copper is concentrated in the finer fractions. Present day transport of copper is mechanical with a modest contribution by chemical weathering. No zinc anomaly (background - 100 ppm) was detectable.

At Johnson, Arizona, copper-zinc ore is present 400 feet below the surface (Cooper and Huff, 1951). The host rock is limestone partly metamorphosed to calc-silicate rocks. The surface expression of ore is copper staining and a larger number of faults than elsewhere. Analysis of rock chips and of soils over the orebody showed there to be quite large, medium level anomalies with high values adjacent to the faults. A few of the anomalous zones are displaced and are not vertically above the ore (presumably controlled by the fracture pattern). Local background values are of the order of 10 to 25 ppm for each of copper, lead and zinc. The fault zones contain up to 2,300 ppm heavy metal. Cooper and Huff showed that dispersion by soil creep, amounting to several hundred feet of movement, had occurred. In general, soil contains more metal than does the underlying unmineralised rock, a concentration effect apparently caused by dissolution of carbonate leaving a residue of enriched silicates and ?sesquioxides.

Clarke (1953) found increased concentrations of copper in plants and soils over an orebody at Ray, Arizona, but also found that soil and plant (oak and mesquite leaves) assays were affected by the type of rock, the drainage and leaching within the soil. Clarke found soil sampling more useful than biogeochemical sampling.

Huff (1955) investigated a fossil geochemical anomaly near Jerome, Arizona. Precambrian copper deposits are overlain by Palaeozoic sandstones. Huff assayed the basal part of the sandstone, where exposed, and showed that, adjacent to the ore, and for 2 miles distant, the copper content was 100 ppm, compared with 20 ppm elsewhere. Zinc has similar values and distribution but lead only shows high values in the sandstone when it overlies ore. The copper and zinc are believed to have been transported from the ore by the then existing ground water. Huff recommends prospecting the base of unconformities for anomalous zones such as are indicated here.

Also in Arizona, Huff and Marranzino (1961) have prospected for porphyry copper deposits buried beneath recent alluvium. A carbonate-cemented zone at the base of the alluvium in the Pima district contained 200 to 1,000 ppm copper for 2 to 3 miles downslope from known orebodies.

In a further paper Huff (1952) examined copper, lead and zinc values in soils adjacent to mineralised veins and the dispersion of residual soils downhill under gravity. The localities quoted are largely in arid to semi-arid parts of Colorado, Arizona and Idaho, but examples are also given from Wisconsin and North Carolina. In this paper Huff compared values in soil with values in weathered and in fresh rock and he also compared values obtained in the field with those obtained by more accurate methods in the laboratory.

Huff's conclusions may be summarised as follows:

1. Soil anomalies may be derived both from ore veins/lodes and from mineralised wall rocks. The shape of the anomaly depends on whether the wall rock effects are large and wide. A clean contact of ore with unmineralised wall rock will give a sharp, clear cut anomaly.

2. Soil anomaly shapes can be influenced by gravity dispersion and by solution and reprecipitation effects.

3. Anomalies uphill from a vein indicate primary dispersion into wall rocks.

4. Where the soil cover is thick, anomalies are apt to be extensively diluted.

5. Transported soils obscure or modify anomalous behaviour.

Robertson (1956) has found that in part of Montana metals from ore shoots are not present for any considerable distance downhill. The maximum detectable distance downslope is of the order of 100 to 250 feet.

Papers on prospecting in arid parts of the USSR are quoted in Ginzburg (1957). Discussion is rendered difficult because of the lack of information on climatic conditions. USSR arid climates tend to have hot or mild summers with long, cool to very cold, winters. Geochemical behaviour may therefore differ markedly from that in Australia.

One paper on soils (with a misleading title) is by Malyuga and Makarova (1956). Assays of soils in part of Tuva for copper, cobalt and nickel delineated a zone of mineralisation. Anomalous soil values were over 100 ppm for each element. These authors established to their satisfaction that these elements were preferentially concentrated in two horizons — in the upper humus layer and in the lower carbonate-calcrete layer (equivalent to the lower B horizon).

Little work was published in the pre-Hawkes and Webb period from arid regions in other parts of the world; however, Eakins (1956) used soil geochemistry with some success in southern Peru in the search for copper, and Matheron (1956) assayed residual soils in Algeria for copper, lead and zinc. The anomalies Matheron found indicated the extent of the mineralised vein system and located new mineralisation. He found zinc to be more widely dispersed than copper and lead to show little or no dispersion at all.

<u>Papers Concerned with Prospecting in Non-arid Climates</u>. The main areas in which geochemical prospecting was practised prior to 1960 were the USSR, the USA and Canada, equatorial Africa and Scandinavia.

Most Soviet papers are not available in English, although translations of Sergeyev (1941) and Krasnikov (1957) are available. A translation of the lecture-textbook by Saukov (1963) — "Geochemical Methods of Prospecting for Useful Mineral Deposits" — is also available. Krasnikov (1957) edited the proceedings of a symposium on geochemistry. Summaries of the main Soviet papers are available through Chemical Abstracts, Ginzburg (1957) and Hawkes and Webb (1962). Soil and rock prospecting papers worthy of brief mention include Fersman (1939) and Karayeva and Chesnokov (1958).

The literature on North American work is moderately abundant. Key papers are discussed here; other titles are listed in the bibliography.

Hawkes and Lakin (1949) measured zinc in residual soils in east Tennessee and found that 500 ppm zinc in the (clay) soil was indicative of zinc mineralisation in the underlying carbonate rocks. Samples were collected from the lower part of the B horizon at 4-ft depth.

White and Allen (1954), in south central British Columbia, have shown that soil copper anomalies relate to known orebodies, but do not delineate the relationships exactly. Mean values of 27 ppm copper and anomalous values of greater than 100 ppm copper are quoted.

Agnew (1955) applied soil geochemistry to the search for lead-zinc deposits in Wisconsin-Illinois-Iowa. The orebodies occur in dolomite and Agnew used not only trace element contents, but also MgO/CaO ratios to locate orebodies.

Bradbury (1955) found soil geochemistry to be unhelpful when prospecting for buried lead-zinc orebodies in north-west Illinois. His conclusion was that there was not enough fracturing above the orebodies to allow the metal ions to reach the surface.

A symposium on geochemical prospecting, held at the twentieth International Geological Congress in Mexico (1956 - published 1960), produced a number of relevant papers. Kennedy found lead and zinc to be of use in the south-west of Wisconsin (this paper is also published in a US Geological Survey bulletin). Byers used the technique at Flin-Flon, Saskatchewan and Fulton; Hay and Kendall of the New Jersey Zinc Company measured copper, lead and zinc in soils of the eastern USA.

Chibougamau, Quebec, was chosen as a test site for geochemical exploration in glaciated terrains. Ermengen (1957) collected residual soils over basalts, and sampled drumlins and other glacial deposits. The samples were subjected to both hot and cold extraction techniques and were assayed for copper, lead and zinc. He concluded that the A_o horizon (humus) and the lower B_1 and the C horizons of podsols contained similar amounts of copper and zinc, whereas intermediate layers are leached. Secondary haloes were discovered in glacial fill and were revealed in drill holes 30 to 40 ft deep, but no clearly defined anomalies were found in drumlins. The most reliable position for finding enhanced amounts of the metals was the top 2 feet of soil. Cold extraction procedures were not particularly useful in this area.

A number of papers have been written about the Keno Hill-Galena Hill area of the Yukon (*vid.* Harbaugh, 1953). One of the most important of these papers is by Boyle and Cragg (1957). They found that zinc is too widely dispersed to be an adequate indicator of lodes. Copper distribution in the area is erratic, and, as it is not universally present in the ore deposits (Pb/Zn), it was not found to be a suitable indicator of ore. Lead has a very limited dispersion and has been enriched in the soil near the lode deposits; it is a most useful indicator in soils related to orebodies. Boyle and Cragg suggest that, in circumstances such as these, a total heavy metal method is all that is needed.

Cannon (1957) investigated a peat and its soils in New York State. She reported that plants growing on the soil were potentially poisonous due to their unusually high lead and zinc contents.

Alaska has proved a fruitful ground for geochemists. Chapman (1958) explored the Kantishna area and found arsenic and/or lead in the C horizons of soils to be the best indicators of gold and silver-galena veins. Background and anomalous values are as follows:

	A1 Horizon, ppm		C Horizon, ppm	
	Background	Anomalous	Background	Anomalous
Pb	<10-100	>100-(2000)	<10-100	>100(-4000)
Zn	<10-150	>150	<10-140	150(-3000)
As	<10-200	>200(-1200)	<10-300?	>300(-4000)
Cu	<10- 80	?100	<10-100?	>100

Chapman and Shacklette (1960) have summarised all geochemical exploration in Alaska to 1960, comparing assay values from eight areas. Drainage sediments and biogeochemistry are also discussed in their paper.

Three papers written about prospecting in Canada were widely publicised in 1960. Aleva (1960) carried out soil geochemistry at the Nigadoo base metal deposit in New Brunswick, with only limited success. Hawkes and Salmon (1960), also worked in New Brunswick. They assayed swamp soils over peats, and assayed moss growing on the soil. A well defined copper anomaly was obtained; this was displaced from the ore zone by the action of water movement through the swamp. Dreimanis (1960) investigated glacial deposits and soils over them in New Brunswick, Quebec and Ontario. He found that trains of sulphide-bearing fragments were present in some deposits (*vid.* also Dreimanis, 1958). Most geochemical anomalies in glacial deposits are caused by groundwater movement. These anomalies are commonly displaced by the water and there may be a zone of background values between the anomaly and the ore. Plants, as elsewhere, have collected trace elements and, on the plant's death, the elements collect in the top soil and may cause anomalous values in the upper parts of the glacial overburden.

Prospecting in Africa was extensive in the 1950s. Hawkes (1954) made a geochemical study of residual and alluvial soils in the vicinity of lead mineralisation at Nyeba, southern Nigeria. Minus 80-mesh fractions of lateritic soil were collected at 6-inch depth and sampled at 50-ft intervals. Anomalous values of 100 to 200 ppm zinc, and 500 to 1,000 ppm lead were obtained over a background of 50 ppm zinc and 30 ppm lead. This technique located all known lead-zinc veins but no new veins were discovered. "Success" was not as apparent in alluvial soils.

Webb (1956) and his associates worked in a number of areas in tropical Africa (some of the work briefly mentioned by Webb is published in separate papers at a later time, eg. Govett, 1960). Webb reported on the geochemistry of freely drained and swamp (dambo) soils in Northern Rhodesia. In an area of seasonal rainfall (50 inches), copper mineralisation (2.5% copper in unweathered rock) has been weathered to a depth of up to 300 ft. Webb compared total copper against readily soluble copper. Absolute values for total copper were high, but the readily soluble copper (especially over argillaceous rocks) gave a better anomaly to background ratio (contrast). This paper is the first of many in which cold extractable techniques are advocated.

In part of Uganda, Webb demonstrated that the concentration of copper in the soil fractions increased as the size decreased. On hill slopes known, but unworked, mineralisation gave pronounced soil anomalies, displaced by creep and lateral subsurface drainage. The B horizon gave the most useful, highest contrast, values. Copper was found to increase with depth in lateritic overburden. Similar patterns were shown over argillaceous and arenaceous rocks, with copper concentrated in the B horizon over clays. In Bechuanaland (Botswana) a calcrete horizon may be present and calcareous soils are common. In background areas, values lie in the 20 to 50 ppm copper range with little change down the profile. Adjacent to mineralisation, lateral movement of copper is hindered or arrested by the calcareous soil, which has a pH of 8.0 to 9.2.

In South Africa, Webb showed lead to be concentrated in two size fractions, the minus 20 plus 35-mesh fraction and the minus 200-mesh fraction, with the latter being more consistently higher. In Tanganyika, Webb reported broad anomalies (greater than or equal to 300 ft) down gentle slopes away from low-grade copper-lead mineralisation. His work is confirmed elsewhere in

Tanganyika by Carter and King (1959) who also found that lead tended to be concentrated in lateritic profiles, though with too erratic a distribution for there to be an easy method of interpretation. On the whole lead concentrations increased with depth.

Nicolai (1956) sampled soils and stream sediments at Niari in French Equatorial Africa and assayed these for copper, lead and zinc, and delineated zones for further study.

Govett (1960) expanded Webb's work in Rhodesia. He showed that, on the whole, cold extractable copper (cx Cu) in non-organic soils increases with increasing total copper in the soils. The cold extractable copper content is related to the cation exchange capacity of illite, but not to the total content of clay sized material. Illite is more common in poorly drained soils and the amount of cx Cu in such soils may simply be a function of the proportion of illite present. Kaolinite is the most common clay mineral in the freely drained soils. Total copper tends to be high where there is a high organic content in the soils and the highest percentages of cx Cu also occur where organic matter is greatest. This fact may be fortuitous, and the cx Cu may be related to the illite content only, for the illite percentage and the organic content tend to move sympathetically. In freely drained soils copper shows maximum values in the B horizon (lateritic rich in sesquioxides), with lower values above and below, except that, adjacent to one, values increase below the B horizon. There is little cx Cu present in these soils.

Other relevant papers include Straczek et al. (1956), who found that high copper (and cobalt) in residual soils overlapped areas of high self potential (Rajasthan, India); Melcher (1956) who used lead in soils to "confirm" by this means, known orebodies and to indicate new anomalies (Rio Ribiera de Ignape, Brazil); Chowdbury (1956), who used soil copper to find extensions to known orebodies in Bihar, India; and Beaumont (1956) who failed to find geochemistry useful in the search for blind orebodies in western France.

In England, Hosking (1959) advocated the use of all forms of geochemical prospecting in Cornwall (but stressed the precautions necessary against contamination). Webb (1959) recommended soil geochemistry in the further search for lead-zinc orebodies, particularly in northern England. Success had been obtained during trial surveys at four localities in Derbyshire and Cumberland.

4.2.3 Papers Published after the Publication of Hawkes and Webb (1962)

Papers Concerned with Prospecting in Arid Climates. Few papers have been written since 1960 which contribute to an understanding of the problems of prospecting for copper, lead or zinc using soil (or rock) geochemistry in arid climates.

Huff (1963) reviewed and compared differing types of prospecting methods at the Malachite mine, Jefferson Company, Colorado, USA.

Roslyakov (1965) measured copper, lead and zinc in dispersion haloes of the sulphide deposits of the western Altai, a region of arid steppe. Copper and zinc have migrated in solution and precipitated or residual copper, lead and zinc have moved mechanically ("Salt dispersion haloes are much wider than mechanical haloes" - abstract).

Bloom (1966) summarised methods of prospecting for copper (and molybdenum) in arid regions, in particular, Arizona. Sahinen et al. (1967), in Montana, and Sharp and Gualtieri (1968), in Colorado found soil and stream sediment geochemistry useful. In both cases reconnaissance indicated areas for further investigation.

Watson (1970), in an interesting but inconclusive paper, discussed variations of soil geochemistry in the Kalahari desert caused by termite activity. His conclusion is that orthodox soil geochemistry is probably more effective than sampling termitaries as a prospecting technique. Brown (1971, personal communication), however, found that in Zambia, termitaries on the Kalahari sand series did give a better indication of ore than the minus 80-mesh fraction of the sand when ore was present at no greater depth than 30 to 50 feet.

In 1970 Huff returned to the problem of locating orebodies buried under alluvium. In Pima County, Arizona, he found that soil and alluvium samples contained 25 to 100 ppm copper, most of which is apparently derived from scattered orebodies several miles away. The alluvium showed little change with depth except that, just above bedrock, carbonate cemented alluvium contained approximately 4,000 ppm copper. Concentrations of this order of magnitude could be traced 1½ miles from known deposits. Despite the desert environment Huff recommends ground water analysis as the most promising technique for finding hidden deposits; together with the widely spaced deep drilling of alluvium and gravels with analysis of the basal zones of such material.

Chaffee and Hessim (1970) carried out similar work in Arizona. Copper, molybdenum and manganese did not correlate spatially with known ore, but zinc was observed to migrate downslope towards active drainage channels. Zinc concentrations did not define known ore but were interpreted as suggesting a favourable fringe zone environment. These authors favour biogeochemistry as a prospecting tool, and anomalous values of zinc, copper and molybdenum occur in plant ash up to 800 feet beyond mineralisation in places where there are no soil anomalies. Roots were shown to extend 100 ft into the overburden.

Beers et al. (1970) showed that mining districts in the Oquirrh Mountains of Utah, could be delineated by assay of soil for copper, lead, zinc, silver, gold and molybdenum.

Drewes (1970) used structural control interpretation to obtain the best use of geochemical anomalies south-east of Tucson, Arizona.

Papers Concerned with Prospecting in Non-arid Climates. Papers in this subsection are considered by continent for convenience.

North America. Many papers on geochemistry have originated from the Alaska Division of Mines (Geochemical Report 39 was issued in 1969). These papers mainly discuss soil and stream sediment geochemistry. They are factual about methods and assays. Anomalies are noted and areas for further work delineated. A few of the more important of these papers are listed in the bibliography.

In Canada, Scott and Byers (1965) found that copper and zinc were concentrated in the A_o horizon at the Coronation mine area. They were also concentrated, but to a lesser degree, in the C horizon. The values of the A_o horizon are very variable.

Riddell (1967) at Mount Pleasant, New Brunswick, examined soil patterns for copper, zinc, lead, tin and molybdenum. Linear anomalies were found for all elements with a moderate degree of overlap. Riddell interpreted the linearities of the anomalous distribution in terms of the preglacial, glacial and post glacial movements of the ions.

Warren, Delavault and Cross (1967) point to possible errors in soil sampling techniques illustrating their arguments from soils adjacent to mines in British Columbia.

Oja (1967) used zinc successfully in a search for zinc-silver mineralisation at Thunder Bay.

Van Tassell (1969) prospected successfully for silver-lead-zinc ore in the Yukon, by deep drilling of the overburden. By this deep drilling dispersion trains of mineralised float material were successfully traced back to their source.

In the USA, Pavlides and Canney (1964), in Maine, noted small seasonal variations of copper (and molybdenum) in residual and alluvial soils. Variations were of the order of 10 to 20 ppm. Thurlow (1965) noted that a lead-zinc ore occurrence (?Mississippi Valley area) was outlined by stream sediment and soil anomalies. Canney (1965) prospected part of the "Copper Belt" area of Vermont. He determined that anomalous chemical patterns of copper and zinc existed in glacial soils adjacent to pyrrhotitic copper deposits. Anomalous copper (greater than, or equal to, 500 ppm) is present, markedly so in the B soil horizon, and can be used as a prospecting guide. In one place 1,200 ppm copper was obtained from the B zone over sub-outcrop which assayed 1.1% copper. A highly skewed distribution was shown to be formed by mechanical dispersion by glacial ice of a pre-glacial copper-rich soil. Later modifications were caused by groundwater. Canney found that anomalies of cold extractable copper had a sharper contrast (anomaly: background ratio) than had anomalies of total copper, but either technique was adequate for prospecting in this area. Local conditions were strongly acid (pH 5.0 - 5.3) and there was little difference in copper values for the various size fractions. Tan (1968) examined soils and gossans in the southern Appalachians in searching for copper. Over amphibolite anomalous values for copper exceeded 1,500 ppm, but over quartzite or sericite schist they were only of the order of 100 ppm. Tan advocated molybdenum, bismuth, tin, lead and silver as indicator elements for similar ore zones in this area. Clarke (1970), searching for copper underlying laterite in Alabama, discovered that the B horizon preferentially concentrated copper. Even in unmineralised areas, over basic rocks, the lower B and upper C horizons contained 300 to 500 ppm copper. Over mineralised rocks, the B horizon on plateaus assayed 550 ppm copper, and on slopes, 1,600 ppm copper. The bleached zones above and below the main laterite commonly contained less than 100 ppm copper. Even over granite gneiss the B horizon of the laterite contained 200 ppm copper.

The USSR. Papers from the USSR which have been mainly concerned with the three trace elements in relation to soil geochemical prospecting have been written by Shirinyan (1961), Albul and Petersel (1961), Bozhko (1962), Makunina (1962), Polferov (1962), Kritsuk (1962), Kryatkovski and Kritsuk (1963), Lapp and Sudov (1963), Goleva (1963), Rakhimov (1966), Ivanov et al. (1966), Ruchkin and Sergeyeva (1967) and Novikov et al. (1969).

Shirinyan (1961), (in abstract), believes that in one area (unspecified) it is possible to prospect for orebodies beneath lavas by measuring copper, lead, zinc, silver and molybdenum in the extrusive rocks.

More detailed papers, available in English, are those of Bozhko (1962), and Makunina (1962). These papers report investigations on trace element behaviour adjacent to and in the immediate neighbourhood of copper ores in the semi arid lands of the southern Urals. Bozhko considered the general distribution of trace elements, in particular copper and nickel, in the soils; Makunina investigated dispersion away from a zone of chalcopyrite ore. Differences caused by variations in underlying rocks are noted in both papers.

Kritsuk (1962), in eastern Transbaikalia, confirmed American opinion by finding mechanical haloes of lead more useful than complex salt haloes of zinc in prospecting over a polymetallic (mainly lead-zinc) deposit. Lapp and Sudov (1963) were concerned with prospecting for deep-seated ores and assayed for eight elements (Pb, Zn, Cu, As, Ag, Sb, Mo and I). The halo of iodine was wider than that of the other elements. This was interpreted as being a feature of primary dispersion and the technique of using iodine dispersion haloes was recommended for hydrothermal deposits in general.

In the northern Caucasus, Goleva (1963) found enriched lead and zinc at the surface over blind orebodies. Mean (mineralised) values given were:

Surface	Pb, ppm	Zn, ppm
Sandstone	480	600
Siltstone	350	280
Argillaceous rocks	150-180	110-140

In a similar situation at the Kuvnsai lead-zinc deposits, Rakhimov (1966) noted that lead, zinc, copper and silver all formed distinct haloes round the orebody, detectable in all soil horizons. Wall rock analysis of ?drill cuttings showed that there was an inverted primary dispersion cone 100 to 150 m wide at the top, narrowing to 10 m at "depth".

Ivanov (1966) found no profit in surface sampling but recommended drilling to bedrock rather than sampling the "loose" surface material. This was done at the Barystan orefield with considerable success. Elements investigated were copper, lead, zinc, tungsten and bismuth.

Novikov et al. (1969) found arsenic a useful surface indicator of copper ores at Kaibyn. The arsenic formed a wide (unspecified) dispersion halo over the ore.

South America. Papers of modest interest have been published by de Grys (1964), and da Silva (1969). De Grys studied soils (and stream sediments) from north-central and central Chile. In a paper in which she presents no adequate data for the reader's interpretation, she concludes that in soils, the nearer the source of the metal the more complex is the dispersion pattern, and vice versa. Da Silva carried out orientation work in the Pernambuco area of Brazil. Zinc was studied as a pathfinder for lead. The lead was immobile whereas the zinc dispersed but was precipitated near the mineralisation zone, mainly within carbonates.

Europe. In France, Aubague et al. (1964) described examples of geochemical anomalies overlying lead-zinc-silver orebodies buried as deep as 300 m at Vivarais. They found primary and ?leakage, ?fugitive (anomalies de fuite) anomalies controlled in the one case by fractures, and, in the other, by drainage within sediments. The leakage anomalies did not immediately relate to orebodies. Loup and Woodtli (1965) successfully delineated lead mineralisation at Valais using soil assays.

Cachau-Herreillat (1969) dealt with differences between syngenetic and epigenetic lead-zinc ores in the Lozere area in France. Two types of anomaly were discovered:

a. those related to tectonic disturbance (mainly lead anomalies); and

b. those correlateable with stratigraphic features (mainly zinc anomalies with minor lead).

Ledne and Barcetta (1970) studied the behaviour of lead and zinc in the weathered mantle of the Granite de Fougeres, Brittany. They found zinc to be more mobile than lead but are among the few authors who have found lead to be at all mobile. They separated components of the soils and found that iron and aluminium oxides contain approximately 50% of the total base metal (both lead and zinc). Clay minerals account for 16% of total zinc and 7% of the lead, while organic debris contains 20% of the lead. The authors are unable to account for the remaining metal.

A most interesting paper by Dijkstra and Bot (1968) deals with a geochemical investigation over an area of sub-economic mineralisation and low anomaly contrast in the Netherlands. The difficulties of interpretation in areas of low contrast subject to human (and other) contamination are discussed.

In England Bradshaw and Stoyel (1968) assayed stream sediments and soils in the south-west England tin province, and confirmed the applicability of these techniques for finding (sub-) economic mineralisation.

Kvalheim (1967) edited "Geochemical Prospecting in Fennoscandia". This book contains a number of case histories pertinent to exploration for copper, lead and zinc. The conclusion to be drawn from these papers, supported by Wennervirta (1968) is that geochemical prospecting is well worthwhile in the Scandinavian countries. This is an admirable text for those working in glaciated terrains.

A later paper by Padget et al. (1969) discusses soil prospecting in relation to the copper-lead-zinc ores in the Vargistrask area of north Sweden. The soil values revealed hydromorphic (ground water drainage) patterns but no new economic orebodies were found.

Africa. A paper by Tooms and Webb (1961) follows the earlier papers of workers at Imperial College, London, in their researches into African geochemistry. Tooms and Webb showed that the presence of copper/cobalt orebodies could be deduced by the analysis of near surface samples of local freely drained and swamp soils. Dispersion anomalies were found to be extensive downslope with geometries related to the groundwater pattern. Cations are fixed by "oxide" minerals, by exchange reactions with clay, wood and organic matter. Vegetation has contributed to anomalous metal concentrations in the upper parts of freely drained soils. In lateritic soils, anomalous values of cold extractable copper (cx Cu), where detected, are much less in magnitude and extent than comparable values of total copper. However, in swamp soils, cx Cu gave wider anomalies than did total copper. In the swamp soils the ratio cx Cu : total copper indicated the origins of the metal. This is an interesting paper which contains a serious attempt to come to terms with the relevant sedimentary geochemistry of copper.

Youssef and Elkahwagy (1963, published 1966) found that buried lead-zinc orebodies could be identified by soil sampling. Mineralisation was found to be in fault zones and anomalies were recorded above these.

Baldock (1969), in a paper of peripheral interest to this project, has used soil geochemistry to investigate chemical relationships at the Bukusu carbonatite complex. Soil copper anomalies are possible indicators of buried copper ores.

In Liberia Johnson et al. (1970) used stream sediments and soils to search for copper, lead and zinc. These metals are present in, and in association with, basic and ultrabasic rocks. These techniques were used for the better definition of target areas. In one particular area, stream sediments masked (ie. did not reveal) the presence of lead ore in granite gneiss and schist. Exploration of this body had to be carried out by trenching.

Asia. The most useful work on geochemical exploration in Asia is that published by the United Nations (1963). This is an account of the proceedings of a seminar on geochemical prospecting held at Bangkok in 1963. The case histories are mainly factual and do not lead to a better understanding of the fundamental chemistry of the elements under study.

Bosi (1964) summarised "recent" papers on the use of geochemical prospecting in India. Geochemical prospecting has evidently been useful. The paper is of most use for the background and anomalous values given for widely separated areas. Again, it is clear that no real interpretation of the (geo) chemical behaviour of the elements in Indian climatic conditions has been made up to this time.

A number of papers have discussed work carried out in the Phillipines. These include Brotzen and Obial (1964), Govett and Hale (1967), Miranda and Garcia (1968) and Govett and Brown (1968). Of these papers that of Govett and Hale is the most important. Stream sediment geochemistry defined mineralised areas and determination of cold extractable copper (cx Cu) in the minus 80-mesh fraction of soils defined the mineralised bedrock source. The cx Cu content increases abruptly from 0 - 10 ppm to 25 - 100 ppm over mineralisation. Hot extractable copper (hx Cu) rises from 25 - 100 ppm to 300 - 1,000 ppm. Samples were collected at 18-inch depth and at the surface with little apparent difference. Govett and Hale affirm that an association of high hx Cu and a low to intermediate cx Cu : hx Cu ratio should indicate proximity to primary mineralisation (in the tropical areas of which they are writing!). This paper should be compared with Cooper and Webb (1963) discussed elsewhere in this report.

Also in Asia Tan and Yu (1970) have published an account of prospecting at the Chimei copper deposit, Taiwan. Stream sediment and soil geochemistry were used to discover a small porphyry copper-type orebody previously completely unknown.

New Zealand. The only papers pertinent to prospecting using soil geochemistry, have been those of Williams (1967a, 1967c) and Williams and Wood (1967).

Williams (1967a) assayed for copper, nickel and zinc in waters, stream sediments and soils in Southland. Values were low but such concentrations as there were occurred in the B horizon. Williams (1967c) deals with the interpretation of a variety of geochemical data, in particular, data from the assay of soils from the Parakao area in Northland, from Shotover, Otago, and from Waitahuna, Otago. Williams and Wood (1967) describe the Shotover mineralisation in more detail. No economic mineralisation was found but the combination of methods used was reasonably successful in delineating areas of (sub-) economic interest.

4.2.4 The Use of Soil and Rock Geochemistry in Prospecting for Copper, Lead and Zinc in Australia

The following discussion deals with the majority of papers known to be published about geochemical prospecting using soils and rocks in Australia (and Papua-New Guinea). It is doubtful whether this list is complete though every effort has been made to obtain the relevant papers. Papers omitted are likely to be those which use geochemistry as an ancilliary, or minor tool, as part of a larger whole. In such papers geochemistry has not been referred to in either the title or the abstract of the paper. Papers referring to nickel in Australia are discussed at the end of Section 4.3.

Most of the papers listed in the bibliography have been examined; however, a number of Bureau of Mineral Resources' open file reports were unobtainable. Open file reports from the various Departments of Mines have not been examined although each Department of Mines has been approached for details of relevant reports or papers.

The majority of published papers on soil geochemical prospecting have been published by the Bureau of Mineral Resources and by the South Australian Department of Mines. Little published work from other states has been obtained.

Northern Territory. The main papers on prospecting in the Northern Territory have been written by Debnam (1956), Crohn and Oldershaw (1965), Ruxton (1963), Haldane (1963), Ivanac and Langren (1968) and Cole et al. (1968).

Debnam (1956) located two large residual lead anomalies at Namoona in residual overburden.

Tennant Creek has been subjected to intensive geochemical investigation and representative reports are those of McMillan and Debnam (1961), Dunnet (1965), and Dunnet and Harding (1965). Crohn and Oldershaw (1965) described the geology of the Tennant Creek 1-mile-sheet area and summarised the results of previous workers. Soil and bedrock were analysed for copper. Background values of 10 ppm in sediments and 30 ppm in ironstones were obtained. Anomalies greater than or equal to twice background were obtained and attributed to residual copper in the oxidised and leached bedrock or to secondary copper deposited from circulating ground water. Further samples taken from 20 to 40 feet by auger (Dunn, 1963) outlined several areas of abnormally high copper. To 1964 no new orebodies had been discovered geochemically in this area.

The Rum Jungle and Woodcutters area has also been extensively prospected for copper, lead and zinc additional to the search for uranium. The papers of Ruxton (1963) and of Ivanac and Langren (1968) summarise work in these areas. At Rum Jungle "surface" samples and samples taken from auger holes 20 to 60-ft deep were taken on a 200-ft square grid, and assayed for copper, lead and zinc. "Surface" samples were taken at 2-ft depth. Lead and copper both showed anomalous values with values of over 3,000 ppm lead and copper being recorded for both soil and weathered bedrock. Ruxton comments that lead contours in soil above 960 ppm are smaller in area than the equivalent contours in weathered bedrock, however the 240 ppm contour in soil has a greater areal extent than its equivalent in the bedrock. Copper is consistently proportionately lower in soil than in the bedrock. Threshold levels for soil were considered to be 960 ppm lead and 800 ppm copper, though as there was some displacement of anomalies from their source, it was difficult to obtain direct interpretations of the data. Later surveys in the area have been carried out by Shatwell (1966) and Semple (1967).

The discovery of silver-lead-zinc at Woodcutters, near Rum Jungle, is described in some detail by Ivanac and Langren (1968). Reconnaissance samples were gathered from weathered rock near the soil/weathered rock interface, and auger drills were used to achieve this. (Orientation had previously demonstrated the unsuitability of using the upper sediments/soils). Dodson and Shatwell (1965) showed that more than one population was present and that conventional calculations of background and anomalous values could not be made. The upper limits of "background" varied between 80 and 500 ppm for copper. Values at Rum Jungle East are presented in the following tabulation:

	Rum Jungle East (spectrographic values in ppm)					
	Cu	Pb	Zn	Cu	Mo	Ni
Background	100	30	100	40	10	50
Threshold	?	60	300	100	40	150
Typical limestone values	5- 20	5- 10	4- 20	0.2- 2	0.1- 0.5	3- 10
Typical shale values	30-150	20	50- 300	10 -50	1	30-100
Typical black shale values	20- 30	20-400	100-1000	5 -50	10 -30	20-300

Eight anomalous areas were detected (and subjected to geophysical follow-up work). Two anomalies were selected for more detailed testing: these included the Woodcutters deposit. Samples were taken at 200-ft intervals on traverse lines 400-ft apart and analysed for copper and lead by atomic absorption spectrometry. The following general values were obtained:

	Background ppm	Threshold ppm	% Values below Threshold
Cu	30-40	150	97
Pb	40-50	100	89

An elongate anomaly was found with lead values of greater than 1,000 ppm. A gossan was discovered in the anomaly area which assayed 2.9% lead and 180 to 4400 ppm copper. Geophysical surveys did not reveal any promise of sulphides. The deposit was proved by diamond drilling.

Cole et al. (1968) carried out extensive soil, biogeochemical and geobotanical investigations of the Bulman-Waimuna Springs area, NT. The biogeochemical and geobotanical aspects of this paper are discussed elsewhere (Section 6.4). Their treatment of soil geochemistry involves discussion of the soil type and pH as well as its trace element content. Their data are not presented in a manner suitable for extraction into tabular form and the interested reader should refer directly to the paper. Anomalies were recorded for lead and zinc in the skeletal soils at Waimuna Springs with values of about 150 ppm against background values of below 40 ppm. At Bulman surface zinc values in "soil" rose up to 10% and lead to over 1%. Low peaks of copper (to 800 ppm) were also obtained. Background levels appear to be below 1,000 ppm for zinc, below 500 ppm for lead and below 50 ppm for copper, but the figures given do not include enough background samples for these values to be representative.

Sample depth and size fractions assayed are not given. In heavy textured soils at Bulman the base metals appear to have been distributed mechanically and show a tapering profile from 380 ppm for zinc and 220 ppm for lead above bedrock down to values below 85 ppm for either element in the soil flats. The profile for zinc is concave (hyperbolic) and for lead more irregular. This lateral dispersion is measurable over 1200 ft. The authors found that any of soil, drainage or geobotanical/biogeochemical surveys would show the mineralisation in these areas. No mineralisation was located below the heavy textured soils and it is not known whether any mineralisation exists there.

Haldane (1963) wrote about prospecting over the lead-zinc mineralisation at the McArthur River, NT. The mineralisation occurs in the Barney's Creek member of the Amelia Dolomite in the McArthur Group and the host rock is a pyritic shale within this member. The soils are deep and consist of alluvial clays with bands of calcrete, gypsum or salt. Gravel and sand occur at depth in a number of places. There are small areas of ferricrete. Sediment sampling was effected by auger drilling to a maximum of 30 feet with cuttings sampled for every 2 feet of drilling depth. The minus 40-mesh fraction was assayed. At the HYC prospect, holes were drilled on a 100 by 400 ft basis. Zinc values were low (less than 50 ppm) at the surface, but values greater than 1% were recorded at depth over mineralisation. Lead values were rather higher at the surface (15 - 100 ppm) rising to approximately 1% at depth. Similarly, at the Mitchell Yard prospect and the Tenna prospect, the surface values were again low (unspecified) with values reaching 5,000 ppm zinc and 560 ppm lead at the Mitchell Yard prospect immediately above shale. Values of 4% lead were obtained in a shallow costean at the Tenna prospect.

> "With normal surface sampling methods, the geochemical results obtained over Tenna and other similar prospects in the area, would command more attention than prospects such as the HYC" (Haldane, 1963; p 131).

Work is continuing at the McArthur River and the Victoria River (Crohn, 1970).

Queensland. Papers of interest are those of Debnam, (1954), Ivanac and Branagan (1960), and Nicolls et al. (1965).

Debnam (1954) used field analytical techniques during prospecting in the Mount Isa area. Unfortunately the results were not quantitative and are expressed as "high", "some", "none", etc. Soil was assayed — to a depth of 8 feet in costeans, but at 9 to 15 inches elsewhere. Whole soil was assayed.

Rare irregularity of pattern occurred because of varying depths of recent ?alluvium which was essentially barren of trace metals. When the alluvium depth exceeded 15 inches values were unusually low and deeper samples were collected. Lead anomalies were found and new orebodies were discovered in the northern prospecting area. This work was used as a test case for geochemical prospecting in Australia and Debnam appeared well satisfied with his results.

Near Cloncurry, Ivanac and Branagan (1960) investigated an area with copper, lead and zinc mineralisation. Soils were collected at 18-inch depth and assayed for these metals and cobalt. High values were found adjacent to three out of four prospects. The authors concluded (page 34) –

> "geochemical prospecting was useful because of its speed and accuracy ... (and) ... it pinpointed areas worthy of detailed examination and proved useful in the selection of drilling sites. ... Geochemical anomalies are a guide to favourable zones but may not indicate the presence of ore."

The Cloncurry area was also the site for the first combined soil-geobotany-biogeochemistry survey in Australia (Nicolls et al. 1965). The Dugald River lode is mainly zinc with some lead and minor silver. Copper mineralisation is known in the area. The biogeochemistry/geobotany of the area are discussed later in the report (Section 6.3). Soil investigations were carried out at the Dugald River and at the Little Eva prospect (copper) and descriptions of the soils and their pHs are given in the paper. The results are not easily reduced to tabular form and the reader is referred to the paper for details. Minus 80-mesh soil from the surface 4 to 6 inches was assayed. Lead threshold values at Dugald River were found to be about 25 ppm with anomalies extending up to over 1,600 ppm. For zinc the threshold was about 50 ppm and maxima of over 1% were recorded. Zinc and lead showed approximately the same sized anomalies. For copper the threshold value was about 30 ppm and maxima of over 1,600 ppm were obtained, however, the anomalies are small in area and are displaced laterally away from the lode. At the Little Eva prospect total and cold extractable copper (cx Cu) were measured. Maximum values exceeded 1,000 ppm total copper and 100 ppm cx Cu. Anomalies were found to be 500 to 1,000 feet wide with several localised maxima. Nicolls et al. favour reconnaissance stream sediment prospecting with judicious use of biogeochemistry/geobotany on interfluve areas or on level sites. By sampling the areas least affected by streams, Nicolls et al. believe that biogeochemical/geobotany complements the more simple stream sediment survey.

Crohn (1970) reports that work has been carried out in the Ayr area (see also the paper by Marshall, 1967), but no details of this work are given. Further work is in progress at Mount Isa.

New South Wales/Australian Capital Territory. Only one relevant major report has been discovered which discusses the geochemistry of the base metals in NSW and the ACT. Oldershaw (1965) investigated the geology and geochemistry of an area near Captains Flat, NSW. He reports on geochemical surveys over gossans and on the results of other geochemical surveys. The initial surveys sampled soil, bedrock, and gossans at intervals of 50 ft along traverses 200 feet apart. Sites of anomalous values were drilled and found to be associated with narrow lodes of chalcopyrite, sphalerite and galena. Later reconnaissance surveys sampled soil, water, salt concentrations and gossans. The samples were assayed for copper and zinc. One hundred and ten anomalous values were reported of which ninety-three were associated with the Copper Creek Shale (of high background) and only four were large enough to warrant further investigation. The area has a highland temperate climate with an annual rainfall of 23 inches. Main streams are perennial. Oldershaw believes high soil values are due to one of two causes:

a. fragments of metal-rich rock adjacent to ore; and
b. copper or zinc trapped on clay.

Water from the area was tested for copper, zinc, sulphate and pH, and encrustations were tested for copper and zinc. Soil samples were taken, using a post hole digger, from the B horizon of residual soils. The local A horizon is a leached grey silt and is underlain by a layer rich in stones. Below the stones the B horizon has been enriched with metals and clays. Local background was found to be low; copper had a mode of 10 ppm and 94% of the soil samples contained less than 40 ppm copper; zinc had a mode of 20 ppm and 90% of the soil samples contained less than 40 ppm zinc. Threshold values for both elements were taken as 100 ppm. It was possible to show that many of the higher zinc values were related to a high background in the Keatings Shale member. Some segregation of high values on the basis of host rock was attempted.

Anomalous areas varied in size. Maximum zinc values up to 5,000 ppm and copper values of 300 to 400 ppm were reported. Drilling showed modest values of lead and zinc.

The mineralisation of this part of the Captain's Flat area occurs as masses of sulphides up to 40-ft thick and several hundred feet long within the Keating Shale member of the Kohinoor Volcanics. In addition, there are mineralised shear zones within the volcanics. Small masses of sulphides, up to several feet thick, occur in the Copper Creek Shale and the Bullongong Shale members of the Foxlow beds. There are localised areas of disseminated sulphides in the Copper Creek and Bullongong Shales. Many showings are capped by gossans which appear to be leached at the surface. Typical gossan values are 400 to 800 ppm copper and 200 to 400 ppm zinc. Lead assays over gossans rarely exceeded 200 ppm.

Donovan (1969) reported that at Cobar surface soils gave no indications of mineralisation. Geochemical anomalies were obtained by drilling to 30 feet with auger drills and sampling either buried residual soil or weathered bedrock. Details of his procedures are not available.

Tasmania. No reports devoted to geochemical prospecting for copper, lead and/or zinc have been received. Hughes (1957) is considered in Section 4.3 under papers on nickel.

Western Australia. Three papers deal with soil and rock geochemical prospecting; these are written by Soufoulis, Williams and Rowston (1968, pub. 1969), Soufoulis and Williams (1969, pub. 1970) and Williams (1969, pub. 1970).

Soufoulis et al. (1968) investigated an area on the northern shores of Lake Yindarlgooda, Bubong, WA. Gossans had previously been recognised within a mixture of igneous rocks (acid to basic), chert, conglomerate, graphite shale, dolomite and jaspilites. All igneous rocks have been metamorphosed at the greenschist facies level. Isoclinal folds trend north-south. Local rock alteration has been caused by faulting. Gossans vary from a few inches to over 20 feet wide in lenses from a few feet to over 1,000 feet long. Samples were taken from the lake floor on two grids, over areas where EM anomalies had been found. Gossans were sampled at 100 to 200-ft intervals along their lengths. Lake floor samples were collected at 25 foot intervals along irregularly disposed lines; superficial material was removed and the samples were collected from the weathered suboutcrop at 3 to 12 inches. The fine fraction was assayed. Simplified results were obtained as follows:

	Gossans, Values in ppm			% Anomalous Results
	Mean	Range	Threshold	
Cu	153	15-400	270	12.4
Co	15	5- 60	30	11.5
Ni	68	20-280	140	6.2
Zn	152	5-850	300	10.6
Pb	62	20-400	130	8.0
Ag	1.4	nd- 6	3	8.0

	Lake Floor, Values in ppm					% Anomalous Results
	Grid 1		Grid 5		Overall	
	Mean	Range	Mean	Range	Threshold	
Cu	68	5-550	177	0-1100	310	5.8
Co	18	0-100	58	0-1060	100	5.9
Ni	34	0-180	81	0- 780	130	7.6
Zn	117	5-800	291	0-2400	100	4.0
Pb	46	0-250	59	0- 200	110	4.3
Ag	0.77	0- 4	0.46	0- 3	2	4.3

Grid 1 proved to have few anomalous values. Grid 5 contained one major anomaly, of irregular shape, but with maximum dimensions exceeding 400 by 350 ft. These anomalies, not drilled at the time of writing the report, were attributed to:

a. leakage anomalies from underlying sulphides (similar to gossans but in the lake);

b. the presence of near-surface, high-background conductive rocks, such as graphitic shale;

c. secondary zones of concentration ('collection phenomena') related to the weathering of adjacent gossanous/mineralised materials.

Soufoulis and Williams (1969) repeated this type of exercise at Twin Peaks in the Yalgoo Goldfield. Archaean acid to intermediate volcanic rocks (now greenschist facies) have been intruded by dolerite and ultramafic dykes (now also, greenschist facies assemblages). There are also intrusions of granite (in tension fractures or in openings caused by sinistral drag folding). The granite is believed to have caused remobilisation of copper originally dispersed within the volcanics, particularly within the pyroclastics. Most significant mineralisation is localised at granite-pyroclastic contacts. The area has low relief (150 - 300 ft maximum). The soils are considered to be residual with little horizon development, no more than 2 feet deep. They are hard but porous when dry and friable when damp. The pH varies between 6.0 and 8.2 with a pH of 3.9 being recorded in a zone of oxidising sulphide. The rainfall is 5 to 10 inches per annum and the area is covered with low scrub.

An orientation traverse crossed the strike of the rocks near the shaft of the old Twin Peaks mine. Samples were taken at 50-ft intervals from the 'B' horizon and from in the regolith. Assays were carried out on the minus 200 fraction. Anomalous values of 350 ppm copper, 15 ppm lead, an estimated 80 ppm for zinc and 250 ppm nickel were defined. No anomalous cobalt values were recorded.

In the main survey samples were chosen at 50-ft intervals on lines 200 ft apart with a few interpolated 100-ft traverse lines. Samples were assayed for copper. If copper was high they were also assayed for zinc. Five populations were found. 'Threshold' was fixed at 675 ppm cppper (6.2% of all samples exceed this level) with an 'interest' zone of 300 to 675 ppm copper (25% of all samples); 2.9% of the samples exceeded 1,000 ppm copper. Three anomalies were recommended for testing by drilling.

Williams (1969) also investigated an area north of Northampton, WA. Five traverses were made and two grid areas examined in detail. The area is in a region of low rainfall, 5 to 10 inches per annum; it is covered with scrub. Soil pH varies from 5 to 7.7 except at the Nooka Mine where the pH is 4. The soil is a red podsol on the slopes and a gleyed podsol in the valleys. Underlying rocks are high-grade metasediments and metaigneous rocks. These have been intruded and migmatised by granite. After being folded the rocks have been intruded by dolerite dykes. Sampling was carried out at 50 by 200 ft intervals in the Nooka Mine area at 18-inch depth or immediately above bedrock, where soil cover was thin. The minus 200 fraction was assayed. Similar procedures were adopted at the Martins Spring Mine area.

A number of extended traverses were also made with samples being collected at approximately 2000-ft intervals. The following summary table is presented:

	Nooka, Chiverton		Martins Spring	
	ppm	% of Results	ppm	% of Results
Cu	0-130	84.2	0-110	91.7
	140-270	8.8	120-160	4.9
	280-590	5.7	170-250	2.1
	> 600	1.3	250-990	1.0
			1000	0.3
Pb	0-170	70.8	0-110	89.7
	180-390	14.3	120-330	6.0
	400-980	8.8	340-840	2.4
	>1000	6.1	>840	1.9
Zn	0-170	71.6	0-170	94.5
	180-440	20.1	180-270	3.9
	450-710	3.7	280-450	1.4
	> 720	4.6	>450	0.2

The results suggested that there is a subsurface zone of mineralisation at Nooka, with additional surface effects caused by a dyke. A mineralised zone connecting two shafts was inferred at Martins Spring and unusually high values were reported on one of the extended traverse lines. Further work was recommended in two of the three areas.

South Australia. The first published geochemical work in South Australia was that of Sokolov in Mining Review 88 (1948). This paper carried an appendix on sampling by Hargreaves (1948). Sokolov's more detailed study and conclusions were published in 1951.

The Moonta-Wallaroo area is flat to gently undulating with no outcrop and no significant drainage pattern. The mantle contains two superimposed soil profiles separated from one another by a flat, thick, layer of calcrete. The mean rainfall for the area is 15 inches. The maximum penetration of the rainfall has been estimated to be 2.4 to 4 feet, and groundwater is 20 to 100 ft below the present surface. The basement consists of Proterozoic sediments and volcanics, intruded and metamorphosed by acid and basic rocks. Copper occurs as chalcopyrite in a variety of associations, and is found in lode deposits.

Assay of the surface soil showed some copper, of uncertain source, to be bound with organic matter. There was no evidence of enrichment at lower levels in the soil and values of copper were generally very low, below 1 ppm, except near mineralisation. Sokolov expressed his results as 'high', 'low', 'medium' and 'absent'. 'High' indicated in excess of 1 ppm copper; 'medium' - fractions of 1 ppm; and 'absent' - less than 0.005 ppm copper.

The topsoil varies in depth from 0 to 12 inches, rarely to 30 inches, and is clay loam to loam. It is limey and contains a small amount of free salt (NaCl). Most roots stop in this horizon. Underlying the topsoil is a layer of calcrete, up to 10 ft thick, which grades into limey clay at depth. Below the calcrete are red brown clays (3 - 18 ft thick, variable) with minor kaolinite and with very small concretions of manganese dioxide. Below this again, at depths commonly between 6 and 20 ft from the surface lies bedrock. The top soil is considered by Sokolov to be a modified terra rossa type. Surface soils were essentially barren of copper. The calcrete also gave low values, but higher values were obtained from the red clay horizon. Problems of the origin of the calcrete remain. If it is derived largely from the bedrock there ought to be some mineralisation effects within it; if it is the product of leaching of calcareous materials now eroded, geochemical anomalies related to mineralisation are not to be expected.

This paper, though pessimistic about geochemical exploration in the area, except for the possible use of the red clay horizon, is of interest as Sokolov tried to establish the forms of copper in the soils and rocks. Copper is present in, or as:

a. organic compounds (surface soils);

b. as 'free' copper, water soluble. This is associated with mines and dumps;

c. exchangeable copper, available by cation exchange in neutral conditions. This is very rare at Moonta;

d. copper in crystal structures. This is surmised and is expected to be rare in the area;

e. unweathered copper minerals, both primary and secondary, and not present in any of the soil horizons;

f. adsorbed copper, extractable with mineral acids. Most of the copper in the red clay is of this form.

Assaying of the red clay horizon allowed the identification of a number of anomalous zones. Examination of these zones led to the discovery of several, non-economic, mineralised veins.

Most soil geochemistry in South Australia has been carried out on the Sellick's Hill area of the southern Mt Lofty ranges, and in the Flinders Ranges.

Johnson (1962, pub. 1964) wrote the first of a series of papers about the Sellick's Hill area. During an orientation programme he showed that vanadium, copper, zinc, nickel and cobalt concentrations all increased with decreasing grain size, chromium increased with increasing grain size. Lead and silver and, to a limited extent, copper and zinc, are localised in anomalously high quantities near the base of the Wangkonda formation in a zone 20-ft thick but extending laterally for 4 miles. Johnson sampled various sections across the base of the Cambrian rocks of the area. The basal rock is a coarse arkose which passes upwards into siltstones and shales with dolomites. This is the Wangkonda formation. It is succeeded by the Sellick's Hill and Fork Tree limestones, and, finally, in the Cambrian, by the carbonaceous and phosphatic Heatherdale Shales.

The copper, lead and zinc contents of these rocks were shown to be quite variable with a maximum lead value, in the arkose south-west of the oldest Sellick's Hill road, of 5,000 ppm. Normal values are low with typical ranges of 10 to 30 ppm copper, 5 to 100 ppm lead, and 15 to 200 ppm zinc. Only lead was deemed to be anomalous. The higher values of zinc and lead were not always entirely sympathetic but the cause was not determined. Nickel values were consistently below 50 ppm.

Verhofstad (1963, pub. 1965) continued the investigation with detailed mapping. He found no indications of a major orebody.

Wright (1967, pub. 1969) amended the stratigraphic sequence, the lower part of the Wangkonda formation becoming the Mt Terrible formation. This report discussed, for the most part, the stream sediment geochemistry of the area, though additional rock and soil sampling was carried out. Rocks were assayed at 5-ft intervals over the highest values reported by Johnson. Both soils and underlying rocks contain similar amounts of lead, however zinc is markedly leached from the soils. Five samples of soil/bedrock were taken at each point in an orientation soil survey, *viz:*

0- 1 inch
1-12 inch
below 12 inches
calcrete
bedrock

In most cases, metal values in the soil reflected those in the bedrock. The best values appeared to be present in the 1 to 12-inch sample. Only the minus 80-mesh fraction was assayed. The calcrete and the bedrock each contained similar amounts of lead.

Typical values are as follows:

Sample No.		Cu ppm	Pb ppm	Zn ppm
2/14	0- 1 inch	15	30	50
	1-12 inches	15	30	45
	Calcrete	<5	95	10
	Bedrock	<5	95	15
2/17	0- 1 inch	15	70	50
	1-12 inches	15	75	50
	Calcrete	<5	95	12
	Bedrock	<5	105	10

Values obtained from the soil survey were as follows:

	Pb ppm	Zn ppm	Cu ppm	Co ppm	Ni ppm
Background	20-30	25-35	10-15	10-20	15-25
Threshold	50-60	60-70	-	-	-
Anomalous	>60	>70	-	-	-

In a final report Wright (1968, pub. 1970) gave the results of additional soil sampling. Extended soil surveying was related to a new prospect, the Fork Tree prospect. Further work was recommended.

Also in the Mt Lofty Ranges, Mirams (1962, pub. 1964) used soil geochemistry to show that an aeromagnetic anomaly at Dawesley was probably related to copper mineralisation. Noakes (1962) used rock (and stream sediment) sampling to study part of the eastern Mt Lofty Ranges. Twelve hundred composite rock samples were assayed spectrographically for eight elements. The results showed that there was a marked association of copper, lead and zinc with the sedimentary facies. Superimposed on this pattern are regional variations in trace element content which Noakes believed indicated a primary sedimentary control.

In the Flinders Ranges most of the geochemical work has been carried out on, and in the vicinity of, diapirs. This work is continuing. Diapirs investigated, or partly investigated, include those of Lyndhurst, Mount Coffin, Burr, Boolooroo and Blinman. In addition work has been carried out at

Yudnamutana. The Mount Coffin, Burr and Boolooroo diapirs (Serle-Angepina area) were first prospected by Fairburn (1967a, pub. 1969) using stream sediment geochemistry. This was followed by soil survey work.

In this first paper Fairburn described the rock sequence. The diapirs occupy anticlinal or domal structures. The Umberatana and Wilpena Groups (Proterozoic) of the Adelaide System are relatively undisturbed and lie on the flanks of the diapirs. Basal Adelaidean beds,the Callana Beds, are restricted to the diapirs and are composed of brecciated dolomites, siltstones, sandstones and quartzites — in a dolomitic matrix. Plugs of microdiorite are recorded at Boolooroo. Within the brecciated material lie blocks of foundered younger material, notably shales of the Tindelpina Shale member. Burra Group rocks (dolomites and siliceous rocks) are poorly exposed but occur at the margins of the diapirs. The upper groups present are also sediments. The Umberatana Group has glacigene beds at its upper and lower limits. Mineralisation consists of epigenetic vein copper lodes, with areas of disseminated copper minerals. This first paper described reconnaissance soil traverses over the Burr and Mount Coffin diapirs. Samples were taken at 100-ft intervals, and at 3 to 6-inch depths, on two lines at the Burr diapir and one at Mount Coffin. The minus 80-mesh fraction was assayed and variations in copper content were found with peaks up to 730 ppm copper against a background of 20 to 40 ppm. Most of the higher values were represented by single samples.

In a second paper, Fairburn (1967b, pub. 1969) described more detailed geochemical work. Samples were taken over the Burr and Mount Coffin diapirs mainly, with but little work at Boolooroo. Samples were taken at 100-ft intervals on twenty-seven traverse lines 800-ft apart and copper and zinc were determined on the minus 80-mesh fraction. The report notes a slight analytical bias in favour of the nearest 10 ppm, when results were supposed to be recorded to the nearest 5 ppm. The distribution curve for copper proved to be highly skewed and the use of cumulative frequency probability paper showed that at least two populations were present. The distribution of zinc was essentially symmetrical and no sign of two populations was apparent. The upper limits of background were calculated for copper as 50 ppm as opposed to a mode of 30 ppm. The upper limit of background for zinc was established as 65 ppm zinc (with a mode value of 40 ppm). High values of copper were related to two anomalous zones. In one of these zones outcrop assayed 1.1% copper. No zinc anomalies were recorded.

Fairburn (1968, pub. 1970) turned his attention to the Nichol's Nob area at the western margin of the Burr diapir. The general rock types are those indicated in Fairburn (1967a); however, there are prominent black shale outcrops belonging, possibly, to the Tindelpina Shale, within the diapir, as well as similar outcrops outside the diapir. Within the diapir the shales once carried sulphides and malachite was visible on some exposed surfaces. Outside the diapir these shales appear to be unmineralised. Copper mineralisation is also present within the diapir, in dolomitic siltstones (Bighole Mine), and, possibly, in buried dolomites. (Above these residual soils contained high copper values - up to 290 ppm). Most ore has been taken from a ferruginous quartz lode (Nichol's Nob Mine). A copper anomaly in this area was shown by a stream sediment survey. It was explored by taking soil samples at 100 by 800-ft intervals. The minus 80-mesh fraction was assayed for copper, and, in some cases, for zinc and lead. No anomalies were found for the latter elements. The distribution of copper was again highly skewed and two populations were demonstrated. The upper limit of copper background was taken as 40 ppm; the mode was 20 ppm; and the mean was 23.5 ppm. Mean values for lead and zinc were 14.1 and 39 ppm, respectively. Further work was recommended.

At Lyndhurst, Martin (1967, pub. 1969) assayed both stream sediments and soils. The stream sediment investigations are discussed elsewhere (Section 5). The climate is arid with approximately 6 inches of rain per annum. The relief is 400 to 500 ft with concave to planar hills slopes. The rocks are similar to those of the Mount Coffin and Burr diapirs. Siliceous and dolomitic beds of the Burra Group are overlain, unconformably, by glacigene sediments of the Yudnamutana Sub-Group. These are succeeded by the dominantly argillaceous Umberatana Group and the lower Wilpena Group. One phase of the diapirism predates the Yudnamutana sediments, a second phase postdates them. The diapir contains shale, quartzite, and dolomitic breccias. Copper is the main mineralisation (as malachite and cuprite) occurring over a wide area as veins cutting a variety of rocks. Lead-zinc mineralisation also occurs in two places. Soil samples were collected in a number of traverse lines. All plus 60-mesh fractions were crushed to minus 80 mesh and assayed (by atomic absorption spectroscopy) for copper, lead, zinc, cobalt and nickel. Martin discussed the results of sieving in a series of histograms, noting that dry sieving was inefficient, because of particle aggregation. The histograms show the proportions of the various elements plotted against fraction size. Metal distributions in the histograms were bimodal. Coarse material (rock fragments not yet broken down) and very fine material (clay) both gave high values. Values were at a minimum in the fine sand (-120 +200 mesh) fraction. In mineralised areas these proved to be a characteristic bimodal distribution as described above; in non-mineralised areas the metals are concentrated in the clays and exhibit a unimodal distribution. Some variation was present in the soil profile with generally higher proportions of each metal near the base. Despite the variation of metal content with size fraction, Martin preferred to use the minus 60-mesh fraction because of simple sample preparation and the fairly even distribution of metals in the dry sieved finer fractions. Extraction was carried out using hot perchloric acid, hence, values reported represent total metal contents present. The values of zinc vary from less than 100 to greater than 2,000 ppm; of copper from 10 to 1,000 ppm, of nickel from 10 to 160 ppm and of lead from 10 to 1,500 ppm. No mean or threshold values were given. Martin's conclusion was that, at Lyndhurst, dispersion is mainly mechanical, modified somewhat by chemical processes. The chief erosional mechanism is believed to be sheet flooding with the light clay surface material being subjected to the greater movement and disintegration. Further recommendations were made which included tests on cold extractable copper. Figure 6 is taken from Marin's paper and it summarises his data graphically.

Fairburn (1968, pub. 1970) has conducted a preliminary geochemical survey at Yudnamutana in the Flinders Ranges. The oldest rocks in this area are the Wooltana Volcanics. These are overlain by the Paralana Quartzite and this is itself overlain by the Wywyana Formation. The latter contains actinolite marble with magnetite-rich zones, bands of hornfels, quartz veins and quartz fissure lodes. Mineralisation is copper, of ?epigenetic origin, in faults, stockworks, shear zones and veins. Soil sampling has revealed, in addition, anomalous copper-rich zones within the Wywyana Formation and at its basal contact. Minor copper soil anomalies also occur over apparently barren quartz veins. Soils were collected at 100-ft intervals on lines 400-ft apart in an area 1 mile by 1,400 ft wide. The minus 80-mesh fraction was assayed for copper, lead, zinc and vanadium. Samples were taken from a "few inches" depth. The mode of the copper was 50 ppm and the upper limit of background 85 ppm. There was a positive skew in distribution with maxima exceeding 1,000 ppm. There were no really anomalous values for zinc and lead. Mean and "threshold" values for these elements were calculated as 15.1 and 24.5 ppm for lead, and

32 and 48 ppm for zinc.

One other major paper, that of Whitten (1967, pub. 1969) on the soils of the Clare area, has been discussed previously (Section 4.1.2). One paper about nickel (Waine, 1967) is discussed in Section 4.3.

Papua and New Guinea. Little material has been obtained on prospecting in Papua and New Guinea. Yates and de Ferranti (1967) have carried out extensive work near Port Moresby (Kemp Welch area). The first worker in the area was Mather (1964) who carried out orientation work on gossans, rocks and stream sediments. Yates and de Ferranti add further data on stream sediments, rocks and gossans, and they include an important section on the trace element content of magnetites. The mineralisation of the area is copper, which occurs in lutites of the Port Moresby beds, commonly close to a contact with gabbro (the Sadowa gabbro). Trace element studies of igneous and sedimentary rock samples showed no unusual values.

4.3 Prospecting for Nickel

Comparatively few papers have been written specifically about prospecting for nickel under any climatic conditions; however, there are two factors, which are well known, which can be used for prospecting purposes. One factors is the property of ultrabasic rocks to be rich in nickel. As pointed out in Section 2.1.2 the abundance of nickel in these rocks is about 2,000 ppm. Most nickel deposits are associated with olivine-rich ultrabasic rocks (dunites, peridotites and serpentinised derivatives), with the prime exception of the Sudbury, Canada area where the rock is an (olivine) norite. The first aim of much primary nickel prospecting has been to locate ultrabasic rocks.

As far as the literature is concerned there is little additional information which assists in the diagnosis of:

a. whether an ultrabasic rock is potentially nickel-bearing; or
b. where the nickel deposits lie in a nickeliferous ultrabasic rock.

One paper, Polferov and Sustova (1966), discusses, in general terms, the nickeliferous potential of ultrabasic rocks. Other papers discuss segregation processes of nickel-bearing magmas (eg. Wager and Mitchell, 1948; Emlie and Moore, 1961), but do not specifically refer to techniques for prospecting for the nickel-rich component.

The other well-established factor in nickel-prospecting is the concentration of nickel in laterites. A number of papers, particularly Zeissink (1969, 1971), Hotz (1964), Heidenreich and Reynolds (1959), Bonifas (1959) and Santos-Yungo et al. (1961) have indicated that the general level of nickel in nickeliferous laterites is between 0.1 and 2% at the surface. It is evident that in the tropical conditions of formation of these laterites, nickel tends to be concentrated at or near the surface; compare the concentration with values of 0.1 to 0.2% nickel in unweathered ultrabasic rocks.

These two factors have facilitated geochemical prospecting for nickel. Chip sampling of rocks has been carried out to indicate ultrabasic rocks or nickeliferous laterites. Further exploration has tended to involve detailed geophysics and soil geochemistry over the ultrabasic rocks. (Much of this work is not published, but remains in restricted company files.) Since magmatic nickel is commonly found with the cumulate minerals, costeaning at regular intervals across the basal portions of ultrabasic intrustions/?extrusions is common practice.

Nickel can be concentrated in soils. Mitchell (1945) reports soil values reaching 500 ppm over basic rocks which have a mean value of 160 to 200 ppm nickel. Leaching of nickel can occur over any rock; as an example, figures of 200 to 600 ppm are not uncommon in soils directly over ultrabasic rocks in Western Australia (unpublished Amdel reports). Turekian and Carr (1960) write that nickel is normally easily removed from surface environments - a statement which appears to need some qualification as far as arid and tropical weathering conditions are concerned.

One of the more unusual methods of prospecting for nickel has been used in Egypt where Nassin (1949) discovered nickeliferous copper ores by assaying prehistoric slags.

Papers of interest which are available and deal with prospecting for nickel include the following.

Fawley (1957) found 0.2 to 0.3% nickel in serpentine in Tanganyika, together with magnetite float assaying 2 to 16.4% nickel. Soil samples over the same material assayed between 900 and 3,400 ppm.

Miller (1957) in a PhD thesis (unpublished) devoted to prospecting methods for nickel, has summarised previous prospecting literature. In particular, he quotes Sergeev (1941) Malyuga (1944), Golobov (1952) from the USSR, Leutwein and Pfeiffer (1955) from Germany, Warren and Delavault (1954) from Canada and Harbaugh (1950) from the USA. Burrell and Wright (1945) have found 1,300 ppm nickel over serpentinite in New Caledonia, and Miller himself has found 6,000 ppm metal in soil over a nickel deposit in Oregon. In his thesis Miller describes a number of selected areas in terms of rocks, soils and plant assays. A summary of his soil data is presented in Table 13. The areas studied contain serpentine-laterite, silica carbonate and ultrabasic nickel deposits. Miller found that geochemical prospecting was most successful in locating serpentine-laterite deposits, since, by the very nature of the deposit, nickel is concentrated in the soils. Soil samples were used:

a. to outline general areas of interest, and
b. in areas of shallow weathering with limited surface leaching (in deeply weathered/leached area Miller prefers biogeochemical prospecting.)

No significant element ratios were discovered in the soils. Copper may be used to prospect for nickel in areas of sulphide mineralisation but not elsewhere.

Heidenreich and Reynolds (1959) examined various laterite and weathered serpentinite metal-bearing deposits in Puerto Rico. Though they were not specifically prospecting soils or surface rocks (but drilling) they present assay figures which include surface or near surface samples. Surface values for nickel range from 0.05 to 0.75% with most values lying between 0.2 and 0.4%. The profiles down the hole show that the nickel is more concentrated at depth; however, it is clear from the surface values that there has been some enrichment in the area and that further prospecting, in the form of drilling and assay of core, is needed.

Bonifas (1959) studied the lateritic alteration with depth of a profile through dunite at Conakry, Guinea. Surface concentration of 800 ppm nickel (0 - 1 metre) shows enrichment up to 0.4 - 0.5% over 40 m depth, compared to a figure of 700 ppm in the fresh dunite. This is an interesting paper from the point of view of the chemical changes involved during the transformation of dunite to laterite.

In Jamaica, Hill (1961) found 0.15 to 0.4% nickel over serpentinite whereas non-serpentine rocks had a background mode of 300 ppm nickel in lateritic soils. In the absence of outcrops a suitable cut-off point useful in separating mineralised serpentinites from other rocks was shown to be 1600 ppm. The mean value for soils over serpentinite is 1316 ppm (232 samples) and is 270 ppm over other rocks (277 samples). Nickel was later shown to be present in both magnetite and silicates.

Sinclair (1967) in the Cave Valley area found 380 ppm nickel over bauxite (over limestone) and less than 10 ppm in non-lateritic soils over 'volcano-clastic' rocks.

A similar pattern of behaviour was shown in Nonoc, Philippines by Santos-Yunigo and Esguerra (1961). Weathered serpentinite contains 0.75 to 2.5% nickel. Laterite and lateritic soils contain 500 to 1000 ppm nickel at the surface.

Polferov (1961) used primary and secondary haloes to detect patterns of nickel mineralisation adjacent to copper-nickel sulphide ores.

Worthington (1964) prospected an area in the south-eastern United States in a humid (40-50 inches of rain) temperature climate. Thick red soil is present as well as podsols and laterite. Certain laterites and 'lateritic soils' average 1% nickel in samples collected by auger to 20 ft. Parent rock averages 0.2%. In at least three cases the soil has been enriched three to four times compared with the parent rock.

In California, Hotz (1964) examined nickeliferous laterites. The overlying 17 feet of laterite and soil ranges from 1.4 to 2.2% nickel over a rock containing 0.3 to 0.4% nickel. Some leaching of the previously enriched nickel was noted in the top foot.

Similar properties are shown by Lewis of the US Geological Survey in an area near Bahia, Brazil (1966).

Kilpatrick (1964) examined nickel, cobalt and chromium in tropical soils in Guyana, using minus 80-mesh material from 2-ft depth. As is now well-established, nickel follows suboutcropping serpentinite and ranges from 300 to more than 2,000 ppm nickel over and adjacent to serpentine. The relatively low values were shown to be a feature, not of weathering, but of the narrowness of the serpentinite which occurs as dykes in amphibolite.

Other papers of interest include Dowsett and Reid (1967) who, having assayed 39,000 soil samples, found no mineralisation; however, the survey delineated the basal zone of a thick basic intrusive (cumulate zone). The highest values in soils were related to nickel in silicate minerals with sulphides almost absent.

Gregory and Tooms (1969) used nickel in soils as a means of identifying kimberlites.

In a different area of study Chamberlain (1968) advocated identification of potentially nickeliferous ultrabasic rocks by a study of:

a. sulphide content (which must be high overall), and

b. a nickel:copper ratio greater than unity.

Follow-up prospecting is apparently by more conventional means.

Townend and Turner (1968) have surveyed the geochemistry of nickel and its distribution in rocks and weathered products in some detail. This paper is notable for its bibliography of 477 references.

Information on Australia and Australasia is sparse. In a paper on general concentrations in soils, and different types of soils, Wells (1960) gives values of nickel over different types of igneous rocks from New Caledonia, the Solomon Islands and New Zealand and discusses the influence of organic matter on the values obtained.

The CSIRO publications considered earlier in the general soil geochemistry of copper, lead and zinc also have figures for nickel (see Tables 8 & 9). These figures are for nickel in 'agricultural' soils unrelated to mineralisation. Tiller (1959) shows that in Tasmania there is little difference in concentration down the profile in soils formed over dolerite. Giles (1960, 1965), Blackburn and Giles (1963) and McKenzie (1958) show that values of nickel in miscellaneous podsols, terra rossa, brown earths, rendzina and groundwater rendzina soils are very low, commonly below 10 ppm. Near the volcanoes of the south-east of South Australia below aeolian deposits, nickel is present in buried residual soils at concentrations of 100 to 400 ppm (over olivine basalts and tuffs) (Tiller, 1957).

Ridley (1969) has investigated the distribution of copper, nickel, cobalt, chromium and manganese over serpentinite and other rocks at Pine Mt, Queensland. He used metal values to define five different unmapped rock types. No nickel mineralisation was found.

Papers giving laterite assays have been written by Townend and Schultz (1966) and Turner (1968) - the samples having been collected from the Giles Complex, South Australia. Zeissink has written two papers (1969, 1971) concerning the Greenvale and Rockhampton lateritic deposits in Queensland. Both Townend and Schultz (1966) and Turner (1968) sampled down the profile. These authors showed that a relatively large proportion of nickel in laterites is incorporated (by a little-understood mechanism) into/onto manganese oxide/hydroxide nodules.

Warne (1967, pub. 1969) investigated nickel in surface soil and trenched chip samples over weathered jaspilised rock containing chrysoprase at Kenmore Park, South Australia. Rock cuttings assayed from 0.06 to 0.42% nickel with the chrysoprase assaying between 0.19 and 1.50% nickel. Soil geochemistry showed background values of less than 100 ppm nickel and anomalous values were as high as 1,700 ppm in places. The area is of interest as no ultrabasic rocks or their derivatives are known in the area. The zone of interest is in siliceous-laterite material which overlies calc-silicate marble, amphibolite, a felsic granulite and quartzite. Float of massive magnetite has been found. No source for the nickel is suggested.

Zeissink (1969) found that the bulk of the nickel is concentrated in the lattice of goethite. The surface of the Greenvale laterite (0 - 5 ft) assayed 2.27% NiO (1.78% Ni). Fresh serpentinite at 60 ft assayed 0.42% NiO. At Rockhampton (Zeissink, 1971) the surface concentration of nickel (2530 ppm) is near background for fresh serpentinite (mean 2640 ppm). There is a zone of major nickel enrichment (to 2.1%) at 55 to 60 feet below the main zone of iron enrichment. Fresh rock occurs at 90 feet.

Hughes (1957) has described a nickeliferous serpentinite at Beaconsfield, Tasmania. Samples from trenches varied between 0.07 and 6.7% nickel averaging approximately 0.5%. Laterite nearby is also known to be nickeliferous.

4.4 Float and Colluvium

Two papers have been found in which loose weathered material was used in prospecting.

Lotspeich (1956, pub. 1960) conducted an interesting experiment on the metal-rich Phosphoria beds of western USA. Two locations were selected; one in a semi-arid region where soils are primitive and saturated with calcium. Lotspeich analysed the shallow colluvium (ie. detrital material) in the semi-arid and more humid site, both overlying similar Phosphoria beds. In the semi-arid area there is twice as much copper and nickel as at the humid area. Most interesting are the zinc results: 75 ppm in the humid area and 500 to 600 ppm at the semi-arid site. Lotspeich believes that the zinc enrichment is related to plant activity. Such an enrichment only occurs when element concentrations exceed certain 'threshold' values: 250 ppm Cu, 150 ppm Ni and 3,500 ppm Zn.

Erickson et al. (1966) analysed iron-stained, discoloured and altered pebbles and cobbles found in major drainages. These are derived from fracture fillings and anomalous metal values probably represent primary dispersion haloes. Stream sediment samples (145) gave very 'flat' distributions for all metals whereas the float samples contain a wide range of values, especially for lead and zinc. The former, for example, ranges from less than 10 ppm to greater than 1%

in float, but only from 10 to 50 ppm in stream sediments. Both this study and that of Lotspeich were carried out in carbonate terrains where the interpretation of stream sediment data is likely to be difficult.

5. STREAM SEDIMENT GEOCHEMISTRY

5.1 General

In stream sediment prospecting methods,actively moving gravel and sand is collected from stream beds and assayed. The stream water and sediment are in contact with each other and presumably reach equilibrium under specific conditions of Eh, pH, etc. so that the chemistry of the water is reflected, in a complex way, in that of the sediment. In turn the water's composition is derived from that of weathering rock in contact with stream or ground water. Hence the chemistry of the water is related to that of all material in weathered rock and soil in the drainage basin above any sampled site.

If an element moves in the aqueous phase and in sediment in equilibrium with the water, for a sufficient distance then only one sample would need to be taken, at the lowest point of each drainage basin. However, other factors (discussed below) make it necessary to sample more frequently than this: the principle remains, that a sediment sample represents the integral of all the rocks weathered above it in the drainage basin.

The population of assay data that we receive is derived from the ore by geomorphic processes and by laboratory extraction processes. Tracing back the anomalous reading to the ore is more difficult than in, say, soil geochemistry, in which the anomalous metal ions are residual.

If this tracing back is to be successful then it is essential that some knowledge of the length of dispersion be obtained and this, in turn, requires knowledge of the mode of dispersion.

Purely mechanical dispersion reduces stream sediment collection to a sampling problem, discussed by Brown (1970). He shows that error can be reduced significantly by multiple sampling at each site, assuming that grains of one mineral are randomly distributed in the sediment. However this will rarely be the case because of 'placering effects' by which ore grains are concentrated in certain parts of the stream sediment because they have a relatively high weight. The length of the dispersion train is controlled by this difficult sampling problem, since if a barren part of an otherwise ore-rich sediment is collected, it will be assumed that dispersion from an upstream orebody will have ceased (values below threshold) at that site. Further increments of ore values downstream that could be thought to be due to another occurrence of ore, may simply be due to sampling a rich-part of sediment at the site. There seems to be a case here for consistent sampling, particularly with respect to depth and position in the stream or for multiple samples or for bulking and homogenising of several samples from one site.

Chemical dispersion tends to be free of these problems, since the ore-metal - usually in the form of absorbed ions - is dispersed throughout all sediment in contact with stream water.

If dispersion is chemical, movement of metals occurs mainly in water, whereas during mechanical dispersion, movement of metals relies solely on physical displacement of the sediment. The length of chemical dispersion trains is dependent on environmental and chemical factors of which the most important is pH. If the pH is unusually low, many metals remain in the aqueous phase and would pass out of the survey area in this form and no stream sediment anomaly could be measured. Only when ions are bonded in the sediments are they intersected on their journey to the sea by the stream sediment sampler.

Factors which affect both mechanical and chemical dispersion are those of dilution and the size of the ore deposit being weathered. The anomalous ion (or grain) population, the size of which depends on the second of these factors, is diluted by barren sediment from upstream sources, tributaries and banks of the sampled stream. If a source of anomaly exists near a tributary only 500 feet, say, from the much larger main stream, then a dispersion train of only 500 feet might well be recorded, since the anomalous ions from the tributary, on entering the main stream, will be 'swamped' by a great volume of barren sediment. This leads to an important conclusion: that increases in concentrations in streams are important in direct proportion to the size of the stream in which they occur. A corollary is that large streams normally give reliable readings of the regional background values.

Many of these factors are intuitively recognised and allowed for by geochemists, but attempts have been made to measure some of them. Horsnail et al. (1969), Horsnail and Elliot (1970), Webb et al. (1968) and Canney (1966) consider the effect of precipitated manganese oxide/hydroxide on removal of copper and other elements from the stream water. The effects of this factor and other chemical factors (such as local geology) can be allowed for by using the major element concentrations to adjust background values for minor elements, as suggested by Rose and Suhr (1970).

Four papers deal with several elements relevant to this study, but only their abstracts are available. The papers are: Murata (1952), Albul and Petersel (1961), Bohmer and Mechaceck (1965) and Sahinen et al. (1965). All claim to have delineated anomalous areas.

5.2 Nickel

Only a limited amount of work has been done on the use of nickel in stream sediment geochemistry. Both Boyle et al. (1966) and Williams (1966) have worked in cool, wet areas: New Brunswick and New Zealand, respectively. Boyle et al. found a background of approximately 45 ppm, using emission spectrography techniques on minus 80-mesh material. No analytical method is quoted by Williams and she obtained background values of only 10 ppm approximately. Even though the maximum value obtained by Boyle et al. was 300 ppm, they write that no nickel anomalies are associated with the sulphide mineralisation in New Brunswick. Williams obtained a maximum value of 40 ppm nickel.

Martin's (1967) results from Lyndhurst, South Australia (Figure 7) show that nickel is strongly concentrated with clay material in the minus 2-micron fraction; however, since this fraction represents only a small weight percentage of the sediments, most nickel occurs in minus 14 plus 60-mesh material.

Some relevant data is summarised in Table 14.

5.3 Copper

A considerable amount of work has been done on copper in stream sediment and the method has met with success as a prospecting tool in many kinds of environments. Table 15 summarises some of the information in important papers.

In regions of tropical weathering where neutral or acid conditions are likely to prevail, most total copper occurs in the fine size fractions as the following tabulation shows (data from Africa):

Hawkes & Webb (1962)		Webb (1956)		Webb (1956)		Size Fraction
(a)	(b)	(a)	(b)	(a)	(b)	Mesh
80	180	30	100	-	-	- 20 + 35
40	160	30	150	-	-	- 35 + 80
40	210	30	210	50	750	- 80 +135
80	250	40	260	-	-	-135 +200
110	360	90	500	100	750	-200

(a) Background.
(b) Anomalous.

Webb et al. (1959) give background values of 40 ppm Cu and quote values of

250 to 750 ppm in anomalous river sediments. In Ecuador, Kroon and de Grys (1970) measured a background of 50 ppm and threshold of 100 ppm after extraction with hot nitric acid (this is assumed to give values close to 'total' concentration). Tan and Yu (1970) used minus 80-mesh material in Taiwan and found backgrounds of 43 and 5 ppm for total and cold extractable copper, respectively.

In the tabulation on page 77, the anomalous and background values tend to increase similarly so that contrasts are independent of the size fraction selected. This suggests that in acid or neutral environments the copper is in the same form even where values of 500 ppm occur; since highest values are in the minus 200-mesh fraction it seems probable that copper is associated with clays or some form of bonding not related to its original form in the ore.

Cold extractable copper in acid or neutral conditions has a similar pattern:

Hawkes & Webb (1962)		Webb (1956)		Webb (1956)		Size Fraction
(a)	(b)	(a)	(b)	(a)	(b)	mesh
8	80	0.2	5	-	-	- 20 + 35
2	35	0.4	9	-	-	- 35 + 80
3	70	0.4	16	4	120	- 80 +135
12	110	0.6	30	-	-	-135 +200
22	170	2.5	55	20	145	-200

(a) Background.
(b) Anomalous.

Webb et al. (1959) found a background of cold extractable copper of 3 ppm, compared with 100 ppm in anomalous streams (size fraction unspecified). As might be expected the increase in concentrations in fine fractions is more marked than for total copper, and there is a marked difference between total and cold extractable values in the coarse fractions. Most notable, however, is the contrast between background and anomaly in cold extractable values, which is commonly greater than 10, whereas for the 'total' values a contrast of 3 to 7 was recorded.

In summary, both total and cold extractable copper are associated principally with the fine size fractions of the sediment but contrast is approximately constant in different size fractions. Greater contrast occurs with cold extractable determinations.

With respect to acid, alkaline environments, much work has been done by the South Australian Department of Mines, particularly in connection with diapiric structures in the Flinders Ranges.

Binks (1968) and Martin (1967) are particularly valuable papers: results of 'total' copper determinations are given below:

Size Fraction	Binks (1968)		Martin (1967)*		Size Fraction
mesh	Background	Anomalous	Background	Anomalous	mesh
- 9 + 16	13	21	55	750	- 8 +14
- 16 + 32	9	21	50	330	-14 +32
- 32 + 60	8	22	55	430	-32 +60
- 60 +115	8	19	45	150	-60 +80
-115 +250	9	15	45	60	-80
-250	13	11			

* Values estimated from diagrams (see Figure 7).

Clearly a most significant difference exists between the two sets of results, which presumably reflects differences in climate, nature of orebodies and possibly the type of country rock.

Binks asserts that alkaline conditions occur in the Adelaide Hills which have a temperate - Mediterranean climate, 20 to 30 inches of rain per annum. Carbonate (calcrete) is found at shallow depths in the soils, and is almost certainly present in the flatter parts of stream courses.

It seems certain that similar or more alkaline conditions occur at the even more arid Lyndhurst locality from which Martin's samples were collected. However, there are similarities between the data; in contrast to arid environments, the background values are independent of the size fraction, and the anomalous concentrations are greatest in the coarsest sizes. This latter fact implies that weathering is predominantly mechanical in semi-arid to arid, alkaline regions. Contrast between background and anomaly is greatest in the coarse fractions. In the minus 80-mesh fraction commonly used in stream sediment surveys, the 'anomalous' values fall to background levels.

Binks (1968) also analysed his samples by cold extraction techniques. Background values were the same as those for total copper (8 - 12 ppm) and the anomalous values were only 9 to 13 ppm. Consequently, the anomalous copper is 'fixed' (not cold-extractable) and probably represents mechanically-moved, primary minerals. Background copper, on the other hand, seems to be at least partly cold-extractable.

Govett and Hale (1967) working in the Philippines, found that the environment is alkaline (pH 7.8 - 8.0) and cold extractable background copper concentration is 7 ppm (threshold 11 ppm) compared with a 'total' copper background of 55 ppm (threshold 85 ppm).

Other values for copper in stream sediments are given in Table 15. Govett's (1960) determinations indicate that the organic components of a stream sediment can be instrumental in fixing copper in the sediments. This is clearly important, since differences between 3 ppm and 10 ppm could be mistaken as indicating an anomaly. Govett recommends cold extractable copper assays on organic-free stream sediments.

Dispersion train lengths may depend, as do absolute values, on the size fraction selected, the method of analysis and the size of the anomaly. Coope and Webb (1963) report that, in the Philippines anomalies of both total and cold extractable copper in minus 80-mesh fractions extend from 1,000 feet to more than 1 mile whereas Kroon and and de Grys (1970) in similar terrain and with total extraction from the minus 80-mesh fraction, report that anomalies of the same size are detectable for 15 km and then become indistinguishable from background levels.

Binks (1968) reports that an orientation survey in the Blinman area showed that sporadic high values for copper occurred in thecoarsest fraction of stream sediments, but, otherwise the size fraction affected the values only slightly. Contrasts of the order of two to four times the background were obtained, ('total' methods of extraction were used). In the actual survey itself only very weak anomalies are associated with known mineralisation and dispersion trains of less than ¼ mile are typical. The highest value from the Blinman Mine is 90 ppm Cu, but in other parts of the area values of approximately 300 and 200 ppm Cu, occur, not associated with any but trivial copper prospects. The immobility of copper is demonstrated quite clearly by this data; the 200 and 300 ppm values may result from sampling of cupriferous sediments, undiluted by 'immobile' material. An unnoted source of contamination may also be present. In this area there are both carbonate rocks and also calcrete. Both of these if present in stream sediments, may be instrumental in fixing the copper.

In New Guinea Dow et al. (1968) found in the south Sepik area, that sulphide mineralisation contributes up to 1,000 ppm copper to the stream sediment. Background values are only 40 ppm.

Yates and de Ferranti (1969) report on stream sediment prospecting in the Port Moresby/Kemp Welch area of Papua. Both total and cold extractable determinations were carried out on minus 80-mesh material. For the latter a low threshold value of 5 ppm was obtained and the authors doubt the usefulness of cold extraction methods in the Papua area. The total copper has a mean of 85 ppm and threshold of 180 ppm. Two new anomalous areas were detected, as well as several minor high values, probably not related to ore. The authors experimented with the analysis of magnetite taken from the stream sediments. The magnetite concentrates copper but has too variable a distribution to be useful.

Hosking et al. (1964), in Cornwall, found cold extractable : total copper ratios of nearly unity in some places. These sites suggest the presence of ore when both types of copper are present in anomalous quantities.

Coope and Webb (1963) have related the pH of stream sediments to the cold extractable copper : total copper ratio in an area where extreme leaching is evident (Cebu, Philippines).

Their results may be summarised thus:

pH of Water	cx Cu : total Cu, %		No. of Observations
	Range	Mean	
3.5 - 5.0	1.5 - 6.4	2.7	22
5.0 - 6.0	2.4 - 16.2	8.8	9
7.0 - 8.5	5.2 - 29.0	12.0	43

Clearly in acid environments proportionately more copper is dissolved from the stream sediment. High cx Cu : total Cu ratios will occur in alkaline conditions. This conclusion is borne out by the data quoted earlier in this section (Pages 77 & 78) and indicates that, in studying cold extractable copper in stream sediments, care must be taken that pH is relatively constant in different parts of the drainage system.

Webb et al. (1968) have indicated the variations in stream sediment chemistry with the different Basement lithologies of Zambia. Their paper is not directly related to prospecting problems.

5.4 Zinc

Zinc is reputed to be one of the most useful metals in stream sediment geochemistry, since dispersion trains can be very long indeed. However, such generalisations must be viewed sceptically and, in fact, the data collected here do not confirm this reputation (Table 16).

Use of the fine size fractions has been widespread, but Binks (1968) has suggested that the zinc content of different size fractions is the same in the Mt Lofty Ranges of South Australia. The most significant result obtained, however, is that 'total' analyses give far better contrasts than cold extractable techniques. In the minus 60 plus 115-mesh fraction, the cold extractable background and anomalous values are 8.3 and 12 ppm, respectively, whereas total values are 13 and 78 ppm. The discrepancies in absolute levels indicate that much zinc is tightly bounded in the stream sediments, possibly as detrital ore grains. Cold extractable zinc represents only 20% of the zinc in the anomalous samples.

Martin's (1967) experiments on stream sediment from Lyndhurst, South Australia, show further aspects of zinc's behaviour in arid conditions (Figure 7). In two samples, seived into five fractions, from minus 8 plus 14-mesh to minus 80 mesh, maximum zinc values occurred in the minus 14 plus 32-mesh fractions; However, two samples seived down to 2 microns showed maximum values in the minus 2-micron fractions. This apparently anomalous result depends on values from only two sediments; furthermore, if the weight percentage of minus 2-micron material is considered, then it can be concluded that only a very small fraction of the total zinc is associated with the minus 2-micron material. Most zinc is associated with the minus 8 plus 60-mesh material which makes up the bulk of the sample.

Muller and Donovan (1970) carried out a reconnaissance survey for willemite deposits near Beltana, South Australia. They found that coarse fractions defined areas of interest better, since aeolian dilution of fines occurred. In the richer samples willemite was distinguished from zinc-bearing limestone microscopically.

Part of the coarser, dry sieved, material may represent clots of clay. Some proportion of the higher values in the coarser fraction may be due to this feature.

Most of the other papers dealing with zinc in stream sediments are case histories from relatively wet areas; perhaps the most outstanding feature of these is the high contrasts obtained between background and maximum value (Table 16). Where the lengths of dispersion trains are either quoted or can be estimated from maps, they do not exceed 3 km and are sometimes much less than this. Yates and de Ferranti working in Papua, note that zinc has longer dispersion trains than copper, down to a threshold of 120 ppm.

Binks (1968) noted in the Blinman area, that zinc has only limited mobility so that a sampling density of 25 samples per square mile was probably insufficient. Orientation surveys suggested that where anomalies did occur contrasts would be of the order of two to four times the background, but in the main survey only two high values were obtained in an otherwise very 'flat' distribution. These two values are probably due to contamination from old settlements. Pavlides and Canney (1964) found an even flatter distribution, all values but one falling in the range 50 to 110 ppm zinc. They analysed samples collected in two consecutive summers from the same sites. Zinc values were in close agreement from year to year, in contrast to most other elements sought. As might be expected Hosking et al. (1964) found few zinc anomalies in south-west England. Most base-metal bearing lodes contain only minor amounts of sphalerite and the anomalies are probably related to contamination from tailings dumps containing this mineral. The authors assert that in sediments containing background quantities of zinc, most of this element is held in biotite; they do not indicate whether this zinc is leached out in the hot nitric acid digestion they used.

Williams (1966) in New Zealand, and Boyle et al. (1964) in eastern Canada, analysed both stream sediments and waters for zinc. Williams used the hydrogeochemical method as a preliminary survey, followed-up by stream sediment methods. Only one hydrogeochemical zinc anomaly was detected in the sediments, whereas Boyle et al. report that zinc in the sediments and heavy metals (mainly zinc) in the water are positively correlated. Where waters are acid, however, zinc will stay in solution, and only in this circumstance should there be a lack of correlation. Williams attributes this absence of correlation to "the disturbing effect of excessive vegetation". Presumably, this is a reference to the fact that zinc is absorbed and held by plants; however, zinc will return to the aqueous phase via leaf-fall and leaching from the resulting humus.

Kroon and de Grys (1970) carried out a large-scale survey in Ecuador, and despite the wide variety of environments involved, found several anomalous zones. At San Fernando, for example, a dispersion train of values of 250 to 600 ppm zinc could be followed for 6 km and as the anomaly was approached, the pH of the water decreased from 7 to 4. Anomalies recognisable in both total and cold extractable determinations suggest that dispersion is mainly by solution. In the Bulman area, Northern Territory (Cole et al. 1968) dispersion is mainly mechanical, the length of the dispersion train being related to the extent and grade of ore. One of the most reliable indicators of anomalous zones was the Zn/Pb ratio, which increases towards ore-bearing sites.

5.5 Lead in Stream Sediments

Lead is not a very mobile element and consequently is not entirely satisfactory in stream sediment surveys, the principle of which, is that each sample integrates a large area of the region being surveyed. Lead is readily precipitated from solutions and although high contrasts can be obtained, dispersion trains are limited in extent (Table 17).

Wright (1967), working in semi-arid conditions of Sellick's Hill, South Australia, found that the size fraction selected for assay had little effect on the anomalies obtained. The values of lead concentration in the coarsest fraction were only slightly higher than those in other fractions. He used the minus 80-mesh fraction in the main survey.

Antropova (1969) also concluded that lead concentration is independent of size fraction. In fractions from less than 0.002 mm to greater than 2 mm, the minimum lead value occurred in the 0.05 to 0.075-mm (300 - 200 mesh) fraction and the maximum in the 0.18 to 0.25 mm (85 to 60 mesh) fraction, but the range of values is only 0.015 to 0.04%.

With respect to the method of extraction employed, almost all workers have used 'hot acid' or 'total' methods. De Grys (1961) used hot nitric acid and methods range from this to bisulphate fusion (Nicholls et al. 1966) and emission spectrography (Solovov and Kunin, 1961).

Antropova (1969) has carried out a detailed study of the form of lead in stream sediments in Estonia. In quartzitic sands most lead occurs in the 'ferruginised quartz' fraction, but organic, hydrogoethite and magnetic fractions each contain relatively high concentrations of lead.

The following tabulation summarises Antropova's data on two contrasting sediments:

	Sample 20842-1			Sample 20842-2		
	(a)	(b)	(c)	(a)	(b)	(c)
organic	60.5	1.0	0.605	4.6	0.6	0.028
hydrogoethite	9.5	1.0	0.095	3.05	0.8	0.024
magnetic	1.0	1.0	0.010	1.0	1.0	0.010
quartz, calcite, albite	28.5	0.02	0.006	6.5	0.001	0.00006
ferruginised quartz	0.5	0.1	0.0005	84.06	0.1	0.084
whole sample	100.0	0.8	0.72	99.21	0.15	0.146

(a) % fraction in sample.
(b) % lead in fraction.
(c) % lead as whole sample.

The different lead contents are related to the differing composition of the samples, especially with respect to their content of organic matter. Antropova discovered that lead associated with organic material occurs as fulvate or humate complexes and that found in the hydrogoethite is mainly adsorbed lead.

Hot acid (especially oxidising nitric or perchloric acids) would dissolve both kinds of lead.

In arid, warm regions, background values of lead in stream sediments are varied; Cole et al. (1968) quote measurements of 70 ppm as background in the Bulman area, Northern Territory. In western Queensland, however, Nicholls et al. (1966) obtained a background of only 5 ppm and other workers in South Australia have obtained intermediate values: 17 ppm (Binks, 1968); 40 ppm (Wright, 1967); and 20 to 30 ppm (Martin, 1967). It is probable that, as indicated in the paper, Cole and co-workers did not sample the full length of the dispersion train.

Twenty-five ppm lead seems to be a typical background level in wetter areas (Boyle et al., 1966, Canada; Kroon and de Grys, 1970, Ecuador; de Grys, 1961, Chile).

Dispersion trains are invariably short and various authors (Table 17) quote ¼ mile to 4 km as measured distances from anomaly to the site where values fall below threshold level.

6. BIOGEOCHEMICAL PROSPECTING

6.1 General

Plants respond to the chemistry of soil (including soil water) either in their morphology or distribution or in their chemistry. By sampling and assaying plant material data pertinent to the chemistry of the soil can be obtained.

The prospecting technique whereby the areal distribution of plants is studied is generally referred to as geobotanical prospecting; when the plant material is assayed, the term biogeochemistry is preferred. The former method relies on the ability of plants either to tolerate abnormally high concentrations of metal in soil or not to grow where such concentrations exist. Some plants show characteristic forms and leaf-colours when the soil is enriched in a particular metal.

Both biogeochemistry and geobotany are more indirect than soil geochemistry since they rely on the addition assumption that plants will reflect the soil chemistry. Apart from rare instances where indicator plants occur, most attention has been applied to biogeochemistry. Geobotany has proved useful mainly when species such as *polycarpaea* sp. occur — these plants being known to thrive in copper-enriched soils. Cannon (1960) and Douglas (1968) are useful reviews of geobotany.

The procedure commonly used in sampling during a biogeochemical survey depends mainly on collection of material from the same organ from the same species, Warren et al. (1955). Where possible plants of the same age only are sampled. Commonly several plants around one sampling site are sampled and the leaves, say, are bulked to form one sample for analysis. As will be noted below, various workers use leaves, one-year old twigs, etc.

An important field aspect in biogeochemistry is that of contamination. There are two ways in which contamination can occur; one is by spattering of soil during heavy rain — this is particularly important when low-growing plants are sampled, the other major contaminant is wind-blown material, especially from dumps, smelters, etc. In order to suppress these effects, washing of the sampled organ has been attempted. A dilute solution of hydrochloric acid or dilute detergent seems to be most satisfying. Certainly metal values are so low that extreme caution is required in handling the material.

Briefly, the advantages of biogeochemical methods are:

1. several plants provide a better sample than a few grains of soil;
2. sampling is rapid and easy;
3. plant roots sample the lower parts of the soil profile.

The principle disadvantage is that there are many factors which influence the metal content of plants and many of these are not fully understood. Soil geochemistry also has some unknown variables which must be added to those of the biogeochemical method. One of these factors, which illustrates the complexities of the interaction between plant and soil, is the so-called "Goldschmidt effect" by which the plant extracts a metal from the soil and subsequently returns the metal to the upper layers of the soil by leaf-fall.

The most important step in the transport of metal from orebody to laboratory is its uptake by the plant, from the soil. This step is accomplished by four different processes: ion accumulation, ionic exchange, chemical combination and diffusion. The first of these is an active process which uses the plant's energy to accumulate relatively high element concentrations in growing cells, especially in young roots. Since the process requires energy from the plant its rate depends on the rates of photosynthesis and transpiration. Ionic exchange is a physical process occurring independently of the plant's metabolism.

Hydrogen ions on the root are exchanged for cations in soil fluid or absorbed on soil particles. Other processes are thought to be less important than these two.

It must be recognised that, when assaying plant material, the prospector is measuring the efficiency of factors affecting the uptake of metals, as well as the broad chemistry of the soil itself.

As mentioned above different workers sample different parts of the plant. If the element sought is a nutrient it is logical to assume that the element travels to the young parts of the plant. Many ore metals, however, are not nutrients and their concentration in the plant is less easy to understand theoretically. It seems likely (Carlisle and Cleeveland, 1958) that, in trees the organs, in decreasing metal concentrations, are: leaves, twigs, cones, wood, roots, bark; and for smaller plants: leaves, roots and stems.

Some empirical studies have been performed on the seasonal variation of metals in plants. Small, flowering plants have highest concentrations at the time of flowering, since this is the period when new growth is most abundant and leaves are fully developed. Trees tend to show maximum values in the autumn (Robinson et al. 1942; Carlisle and Cleeveland, 1958).

A further factor is the response of the plant itself to metals in the soil. Whereas some plants may absorb only a limited amount of a metal, even from anomalous soil, another species may tolerate such high concentrations. Even so, a tolerant species may not absorb metal in proportion to its content in the soil. In carrying out biogeochemical surveys, it is important to establish, by pilot studies, that the concentration of metal in soil is reflected by that in the plant, whatever the level of concentration in the soil and in each soil type in the area. Then, providing healthy, apparently normal plants of the same species are sampled, interpretable results should be obtained.

Two final points may be mentioned briefly: analytical methods and interpretation of assay results. Analyses are usually performed on ashed plant material. Considerable care is needed so that all samples receive exactly the same ashing treatment, otherwise some spurious results may occur. Generally, some extremely sensitive assay method is required since concentration levels are generally low.

Recognition of anomalies is carried out as in other geochemical surveys. In biogeochemical methods one often has high contrast ratios so that anomalous areas are distinct from usually very low background levels.

Shacklette (1967) has suggested that mosses may indicate exceptionally high values of copper, vanadium, silver and lead in the rocks on which they grow.

General references on biogeochemical and geobotanical methods are: Warren et al. (1965) - on sampling methods; Marmo (1956; Canney (undated); Cannon (1960); Rommel et al. (1968); Cole (1970); and Carlisle and Cleveland (1958); other references will be mentioned in the following sections.

6.2 Nickel

Marmo (1953) has reported on early work he carried out in Finland. At Nokia leaves of *Vaccinium vitis idaea* were assayed and high nickel values occur over ground showing magnetic anomalies. The background level appears to be less than 20 ppm, whereas the highest contours shown on Marmo's map are 30 ppm (nickel in ash).

Warren and Delavault (1954) examined three tree species over both mineralised and unmineralised ground with the results tabulated below:

	Mountain Hemlock		Mountain Fir		Western Red Cedar	
	(a)	(b)	(a)	(b)	(a)	(b)
1st year stems	360	-	870	-	-	-
2nd year stems	320	10-30	1230	50	-	-
3rd year stems	240		1260	-	590	-
4th & 5th year	250	-	1000	-	250	-
Mixed needles	400	-	1200	-	-	-
Older stems	-	-	-	-	140	-
Leaves	-	-	-	-	840	50

(a) Mineralised.
(b) Unmineralised.

The values are averages and represent ppm nickel in ash. Samples were also collected over a lead/zinc orebody in order to investigate nickel's pathfinding potential:

	Engelmann Spruce		Mountain Balsam		Western Red Cedar	
	(a)	(b)	(a)	(b)	(a)	(b)
2 year needles	185	30	145	50	-	-
Green twigs and leaves	-	-	-	-	195	50

(a) Mineralised.
(b) Unmineralised.

Note: Data in ppm nickel in ash.

Clearly, although nickel is not a major constituent of the ore, it does behave as a pathfinder. Warren and Delavault assert that this is due to the element's low background value. Deciduous trees also showed anomalies but the general level of the nickel content is lower.

A considerable amount of work has been performed in New Zealand by Timperley, Brooks and Peterson in three papers (1970a, 1970b, 1971).

In the work reported in the 1970 paper, four tree species were sampled for their leaves and assayed for nickel. Samples of nearby soil were also collected. All species show high positive correlations between nickel in leaves and soil. Threshold values are 100 to 200 ppm nickel in ash (varying with species).

Timperley et al. (1970b) report on work on the same tree species in the same area of New Zealand. A regression equation relating nickel in plant/nickel in soil (called "relative accumulation") to several independent variables, was calculated. Despite considerable 'management' of the new data only 34% of the variance of the dependent variable was accounted for by the significant variables; nickel abundance in the plant and attitude of sampling point. The authors then attempt to 'explain' the significance of this regression equation.

Finally, (Timperley et al. 1971) the same data is considered further: a graph relating relative accumulation to the concentration of the metal in the soil showing a hyperbolic form indicates that the element is essential to the plant's metabolism; straight-line graphs indicate that the element is non-essential. Also, using logarithmic data, a correlation coefficient near minus 1 indicates that the element is essential to the plant. The authors assert that, if an element is essential, it cannot be used in prospecting unless the soil values are greater than that value where the linear part of the graph begins. Another measure of essentiality is the ratio of coefficients of variation of the element in plants and in soil. The nickel values obtained from the leaves are as follows:

Species	No. of Analyses	Mean Ni ppm in Ash
Nothofagus fusca	49	163
N. menziesii	48	193
Quintinia acutifolia	93	92
Wimmannia racemsa	103	126

Most experience of biogeochemical prospecting for nickel has been obtained by Malyuga and his co-workers in the USSR. This work is reviewed in Malyuga

(1964). At the Taiketkenskii nickel deposit many grasses and herbs show enhanced values over the orebody:

		Ni, ppm	Cu, ppm
Feather grass	- unmineralised	6	9
	mineralised	21	20
Desert oats	- unmineralised	20	16
	mineralised	90	10
Pasqueflower	- unmineralised	-	-
	mineralised	250-370*	80-130

* Endemic forms.

However, simultaneous sampling of plants and soil shows that far greater contrasts are obtained from soils. From study in the Taiketkenskii and Chugaevskii nickel deposits, Malyuga concludes that soil geochemistry is more effective than plants (1964, p 91). Aleskovskii (1959) found that birch leaves concentrate most nickel in the conditions of the Kola Peninsula. The nickel content is related to that of the 'matrix rock' and hence is useful in prospecting.

Harbaugh (1950) studied the concentration of nickel in the ash of *Quercus marilandica* twigs from an area in the Tri-State lead/zinc region. Samples collected over anomalous regions and those over barren regions both show values within the range 37 to 45 ppm.

Miller wrote a PhD thesis (Miller, 1957) on biogeochemical prospecting at eight nickel deposits in the USA. At only one of these (the only nickeliferous laterite deposit) were biogeochemical anomalies recognised, in twigs of various pine and spruce species. Anomalous values are 30 to 40 ppm nickel in dry plant compared with background values of 5 to 15 ppm. At the remaining seven areas no anomalies were recognised and concentrations exceeding 10 ppm are rare.

Hornbrook (1970) has reported work in the Cobalt area of Ontario; there birch spurs and aspen twigs define anomalous areas with respect to their silver, cobalt and nickel contents.

Little biogeochemistry seems to have been done in Japan, but Yamagata et al. (1960) obtained valuable results from *Cletha barbinervis*, the leaves of which contained sufficient nickel to define anomalous areas. Other plants analysed showed many flat distributions of nickel in leaves.

6.3 Copper

Deficiencies of copper in plants has long been recognised in Australia (Riceman, 1950) and one might therefore expect copper-rich areas to be distinctive. Sommer (1945) and Repp (1963) have considered the effect of copper in soil on the growth of plants.

Nicholls et al. (1966) carried out extensive biogeochemical studies in the area of the Dugald River lode. Because tree species are absent from the lode area itself their attention was directed to herbs and grasses. The dominant grass species, *Triodia pungens*, gave the following results (ppm in ash-leaves): copper 47 ppm, zinc 178 ppm and lead less than 10 ppm. Over the lode higher values for zinc only, were measured. In general, flowers and leaves of grasses are richer in copper than are the stems, and species confined to the lode area show much higher copper values than *Triodia pungens* of the background vegetation. It is possible that plants in the lode assemblage are more deeply rooted than *Triodia pungens* and therefore draw on high copper values at depth. In some areas copper is so high that species such as *Triodia pungens* and *Tephrosia sp. nov.* give way to *Polycarpaea glabra* and *Eriachne mucronata.* The latter two species, tolerate high copper values in soil (1% measured) but do not absorb the metal themselves. The plants are indicators rather than accumulators and appear to be most useful in geobotanical prospecting rather than biogeochemistry. Nicholls et al. emphasise that only small variations in soil chemistry have strong effects in controlling the vegetation pattern.

A similar survey has been carried out by personnel from Imperial College, London, in the Bulman-Waimuna Springs area, Northern Territory (Cole et al. 1968). The mineralisation is of the lead/zinc type and few plants contain high copper values. Exceptional are the stems of *Polycarpaea spp.* the well-known copper indicator, which contain 600 ppm copper.

Blissett (1968) has reported a copper accumulator plant observed in South Australia; this is *Millotia myosotidifolia*, the ash of which contains up to 4% copper.

Tooms and Jay (1964), examined the distribution of copper in twigs and leaves of several tree species over orebodies in Northern Rhodesia. The average values for all species are (copper, ppm in ash-leaves):

600 feet upslope,	505 ppm
200 feet upslope,	625 ppm
over ore,	910 ppm

200 feet downslope,	655 ppm
600 feet downslope,	850 ppm
800 - 1400 feet downslope,	580 ppm

The copper in twigs is highly erratic in distribution. Tooms and Jay were particularly interested in the effect of leaf-fall on A horizon anomalies (the Goldschmidt effect) and present the following data from Minbula in Northern Rhodesia:

	No Trees	Sparsely Wooded	Wooded
$\frac{\text{Cu in A}_2\text{ horizon}}{\text{Cu in C horizon}}$	0.06	0.25	0.45

Finally, the authors emphasis the need to study the vegetation densities in different areas so that care will be taken in examining the significance of geochemical anomalies.

Millman (1957) has carried out some fairly systematic studies on biogeochemical prospecting in Cornwall, England. In both birch and oak trees, copper is concentrated preferentially in the leaves. Despite this the author presents background values in twigs, which for copper are less than 1 to 6 ppm in oven-dried material from several tree species. The highest anomaly value recorded is 12 ppm copper from an oak tree. It is notable that the twigs have copper concentrations of less than 1 to 6 ppm, whereas the underlying soil has a value of 20 to 100 ppm copper.

Marmo's early work in Finland (1953) showed broad anomalies in the ashed leaves, generally corresponding in position to magnetic anomalies. Small amounts of chalcopyrite in granitic rocks are reflected in the copper content of leaves of *Ledum palustre.*

In the Tri-State district, Harbaugh (1950) sampled an oak species, *Quercus marilandica*, utilising young twigs. Not surprising, in an area of predominantly lead-zinc mineralisation, the copper distribution is 'flat' with values of 210 to 220 ppm copper in ash. The San Manuel copper deposit was the site of the work reported in Warren et al. (1951). Samples of various organs of California poppy, Palo Verde, Scrub Oak, Sagnaro and Ocotillo and Creosote bush were assayed. Generally, unusually high concentrations were obtained, up to 1100 ppm copper in ash of stems and leaves of Scrub Oak. Contrasts between mineralisad ground and barren ground is of the order of 1 to 7. The authors attempted to classify the plants collected from this arid region into three categories:

1. those basically similar (and behaving similarly biogeochemically) to more humid region plants;
2. the Paloverde, a leafless bush, the branches of which behave as would be expected; and
3. the cacti.

The latter absorb as much copper (and zinc) as more ordinary plants. Too few samples of cacti were collected for a more precise appraisal of their prospecting value, to be made.

Hornbrook et al. (1970) worked on a copper-molybdenum stock in western Canada. They found that copper in twigs gives excellent results and accurately reflected the copper content of the B horizon of the soil. The authors consider the significance of careful plotting of the results and of judicious choice of sampling sites - the latter with respect not only to the trees, but also to the condition of the soil. The copper anomaly defined a rim of altered mineralisation around a stock,but not the disseminated chalcopyrite within the igneous body itself.

Warren and Howatson (1947), apart from reviewing much early geobotanical and biogeochemical work, assayed parts of several plant species from five areas. Where satisfactory samples could be collected (Britannia and Texada Island) large contrasts between material collected from barren and mineralised ground were obtained. Other experiments suggested that most copper occurs in leaves and cones of these trees.

Warren and Delavault (1949) present the continuation of this work in British Columbia. From the Britannia area an average value of copper in dried leaves from the mine area is 186 ppm, compared with a background average of 34 ppm.

Timperley et al. (1970b)(New Zealand) were particularly concerned with correlating copper in plants (leaves and twigs of several species) with total copper in the soil. Significantly high correlations were obtained for the *Nothofagus* species and *Quercus acutifolia* only.

The authors conclude that *Nothofagus fusca* and *N. menziesii* give best results if leaf ash is analysed. A later paper, Timperley et al. (1971), has been mentioned with reference to nickel. Relative accumulation of copper was regressed against seven significant variables (although the regression 'accounted for' less than 35% of the variance of this dependent variable) of which the most important are concentrations of chromium, nickel and copper in vegetation. The explanations forwarded to interpret these variables are hardly convincing and for one variable, the authors (having written that seven variables contributed significantly to the variance) state that it makes a 'negligible' contribution to the regression.

Finally, Timperley et al. (1970b) claim that copper is an essential element in the tree species studied and that, no matter how cupriferous the soil is, the tree will absorb only its required amount and no more. Consequently these tree species may not be expected to be useful in biogeochemical prospecting.

Malyuga (1964) describes biogeochemical prospecting work carried out at Tuvinskii. Most time was spent on soil sampling, but an anomalous vegetation population characterised by abundant *Alyssum biovulatum* and members of the pink family was noted. These plants have ash only slightly enriched in copper (compared with background values) and clearly 'tolerate' copper rather than accumulate it. Unfortunately, the data on the commoner plants is not associated with any background values so that comparisons of biogeochemical significance cannot be made. Other Soviet papers which claim to have obtained successful results with copper are: Paskotin (1963), who recommends the use of spruce needles and birch leaves in the Middle Urals; Lynbofeev et al. (1962), in the Caucasus; anomalies 50 to 100 times background were measured in beeches and firs. Talipov (1964) suggested that leaves and stems of herbaceous plants should be sampled in an area in Uzbekistan.

The studies of Nicholls et al. (1966), Cole et al. (1968), Chafee and Hessin (1970), El Shazly et al. (1970), Missaghi (1968) and Lovering et al. (1950), all indicate that prospecting for copper (and, in some cases, for lead and zinc) is practicable and useful in arid areas. Some emphasis has been placed on the sampling of trees: acacias (El Shazly, 1970), and aspen (Missaghi, 1968). Desert plants are often morphologically different from plants growing in wetter areas and the work on creosote, paloverde, etc. is of a preliminary nature as little is known concerning the best organs to sample and the optimum time of the year.

Lovering et al. (1950) is one of the few papers which suggests that biogeochemistry is not useful in arid areas. The paper by Warren et al. (1951), described above, tends to question this result. Since both groups of authors analysed plants from the San Manuel deposit, the discrepancy in their conclusions is most disturbing and suggests that a more detailed study of seasonal soil, analytical and other factors, is required. It may be that desert plants are more susceptible (in their copper content) to sudden flooding rains or to the soil pH or humus content.

6.4 Zinc and Lead

These elements are considered together following the greater part of the literature; however, from a botanical viewpoint, lead and zinc differ considerably. Lead is well-known to be toxic to most plants and tends to be precipitated in roots (Hammett, 1928) rather than to reach the actively growing parts of the plants. Zinc, on the other hand, is commonly relatively enriched in leaves, twigs, etc. Zinc is also essential to most plants whereas this has not been shown for lead (but see Hawkes & Webb, 1962; p 295).

Nicolas and Brooks (1969) have performed a detailed study of biogeochemical prospecting in the Te Aroha area of New Zealand. For the bush *Schefleva digitata*, for example, a significant positive correlation between zinc in soil and zinc in the leaves was obtained. However, although a straight line can be fitted to the data, the plotted points have a wide scatter. No significant correlation occurs for lead. Both zinc and lead showed two populations (anomalous and background) with threshold values of 540 ppm zinc and 250 ppm lead in the ash.

Work on wood and leaves of *Beilschmiedia tawa* showed that where the soil is highly enriched in lead and zinc, low concentrations of these elements occur in the wood. Nicolas and Brooks postulate that in the sulphide-rich environment over the lode, lead (zinc, to a lesser extent) would be precipitated, and hence rendered unavailable to the plants. The author's "critical analysis of the statistical data" (page 64) is an excellent summary of the dangers of misinterpreting statistical phraseology such as 'highly significant' in a natural system.

Later work in New Zealand is reported by Timperley, Brooks and Peterson (1960a, 1970b, 1971). In the earliest paper, the four tree species *Nothofagus fusca*, *N. menziesii*, *Quintinia acutifolia* and *Weinmannia racemosa* showed no correlation between the zinc content of the leaves and that of the soil. No relationship was found between the pH of the soil and the zinc uptake by the trees. The paper published by these authors (1971) on essential and non-essential elements has been described in the section on nickel's biochemistry; zinc is an essential element and hence care is required in interpreting biogeochemical results for this element.

In western Canada Warren and Howatson (1947) measured very high zinc values in various organs of tree species:

		Zinc in Ash, ppm	
		Anomalous Area	Background Area
Pinus contorta,	cones	19,780	6,750
	bark	2,780	1,960
Populus trichocarpa,	leaves	7,760	-
	wood	-	370
Salix sp.	bark	490	40
Larix occidentalis,	leaves	2,540	2,390
Populus tremuloides,	leaves	4,000	1,640
Larix occidentalis,	bark	2,690	1,130
Sheperdia canadensis,	leaves	1,090	740

All organs show some enhancement near zinc mineralisation, although contrasts between background and anomaly are not very high. In the copper-rich areas examined by Warren and Howatson, similar high zinc values were obtained, but anomalies were not recorded. As other authors note, the Cu : Zn ratio can be more important than absolute values since it is less variable at background levels and generally sensitive to small changes in the metal content of soil.

Hornbrook (1969) has reported on pilot studies of bark, twigs, needles and current growth of trees over a lead deposit on Cape Breton Island.

Over the San Manuel copper deposit consistently high Cu : Zn ratios are obtained, an effect which may be related indirectly to the more arid regions near this porphyry copper mine.

Warren et al. (1961) report, for example, that California Poppy *(Eschscholtzia mexicana)* leaves and stems have a Cu : Zn ratio of 0.48 over the suboutcrop of ore, but a ratio of only 0.08 away from known mineralisation. Absolute zinc values are 66 and 153 ppm, respectively. As New Zealand examples (see above) have indicated, over copper prospects the uptake of zinc is inhibited in some way and enhanced values of the Cu : Zn ratio are obtained. Other species sampled by Warren et al. showed a similar pattern of behaviour, although in a less marked fashion.

The distribution of lead and zinc in plants may be expected to be of importance in the other well-known ores of the USA: the Tri-State lead and zinc deposits. Harbaugh (1950) analysed twigs of *Quercus marilandica* and found in samples near to known orebodies, an average zinc value of 1100 ppm in ash (56 samples), away from ore a mean of 850 ppm zinc (101 samples) was recorded. Lead shows no variation with respect to ore, and concentrations of 300 to 350 ppm were recorded.

Harbaugh also analysed leaves and twigs of 24 tree species for zinc. Although the average zinc concentration is 28% greater for leaves and 25% greater for twigs in samples from mineralised areas, the trees differed considerably. Not all species, nor the same organ consistently gave contrasts. As an example *Rhus capallina* leaves contain 600 ppm zinc over both mineralised and barren areas, whereas twigs over mineralised ground contain 600 ppm and those over barren ground have 800 ppm. (These figures are all means of three values.) Exactly similar conclusions can be arrived at from Harbaugh's data on grasses and herbaceous plants. Although there is a relationship between mineralisation and zinc in the ash, not all the species show contrasts.

When values of zinc and lead are mapped only a poor correlation between high values in *Quercus marilandica* and mineralised zones is shown. In particular, the lead distribution is irregular and the metal appears to have little value in this type of prospecting in the Tri-State area.

Marmo (1953) found that zinc in plants (in this case *Vaccinium vitis idaea*) bore only moderate correlation to areas showing magnetic anomalies. He introduced the useful concept of considering the direction of groundwater flow. This can be most important, especially when trees are sampled.

Workers in Canada and the USA, referred to above, analysed leaves and twigs and found them to be similar in their response to metalliferous soils and in their absolute contents of trace metals. Millman (1957), however, has found considerable differences:

		ppm in Dried Sample	
		Zn	Pb
Birch:	leaves - 3 samples	520	5.9
	twigs - 3 samples	290	16
	soil	<300	20
Oak:	leaves - 3 samples	130	3
	twigs - 3 samples	44	9.3
	soil	<300	10

Zinc is preferentially concentrated in leaves, lead in twigs. Whereas Millman (south-west England) quotes background levels (1 - 10 ppm for lead, less than 100 ppm for zinc), values from anomalous areas are not quoted. He does imply, however, that unremarkable anomaly contrasts were obtained. Birch trees have the highest concentrations of zinc and lead. These rather negative results are probably due to the low grade (with respect to lead and zinc) of the Cornwall deposits. Millman had previously worked on the Nigerian lead-zinc belt (Webb and Millman, 1951) when much greater contrasts were obtained.

In Nigeria, the savannah trees sampled yielded backgrounds of 1 ppm lead in twigs and 1 to 2.5 ppm in leaves and contrasts, particularly for lead, reach values of 30 or even 100. Dispersion lengths of 200 feet were inferred. Less satisfactory zinc results were obtained, possibly because of the poor sensitivity of spectrographic analysis to zinc. Occasionally the authors resorted to mixed-species traverses; this procedure involves some risks but Webb and Millman have collected some data suggesting that individual species have comparable lead and zinc contents.

Webb and Millman suggest that no 'external' factors, eg. general geology, topography, season, etc. affect the prospecting results. Their main conclusion (that lead is a satisfactory index element) is based on a comparison with zinc measured spectrographically. Colourimetric zinc analyses probably render this conclusion invalid.

Robinson et al. (1947) tested the biogeochemical prospecting value of zinc by analysing plants growing on slime ponds which contain 12.5% zinc. In such ponds only plants tolerating high zinc can survive and one can measure whether such plants, as well as tolerating zinc, also accumulate this element. Presumably any maximum zinc value in the plant represents the limit of the plant's accumulating capacity rather than a measure of zinc in the soil. The highest concentration measured was 4,900 ppm (in dry plant) zinc in horsetail *(Esquisetum sp.)*. Away from zinc-rich areas this plant contains 50 to 110 ppm zinc. Unfortunately, the slime ponds are not entirely typical of soil over mineralised areas, since they have low hydrogen ion contents and pH in the range 7.9 to 8.1. It is even more surprising that at such a pH 4,900 ppm zinc is available to plants; it must be borne in mind that this (superficially high) figure represents only 4% of the concentration of zinc in the slime ponds.

Most of the work in England and the USA has not compared the usefulness of lead and zinc prospecting in vegetation with soil sampling methods. Keith (1969) found that, although anomalies in soil were also recorded in leaves and twigs of trees, the A and C soil horizons provide more reliable figures.

Only in less-covered areas was biogeochemical sampling more useful than soil sampling.

Keith's data is summarised below:

		Lead		Zinc	
		Mineralised	Non-mineralised	Mineralised	Non-mineralised
Elm:	stems	78	102	1240	604
	leaves	26	29	266	138
Maple:	stems	135	119	490	555
	leaves	62	44	370	347
Oak:	stems	99	150	614	440
	leaves	57	61	554	356
Soil horizon:	A	124	18	1007	58
	B	67	13	144	8
	C	117	13	1019	49

Note:
1. Soil values in ppm in dried soil.
2. Plant values in ppm in ash.
3. The values are means of 152 to 368 samples.

It can be seen that both lead and zinc are preferentially concentrated in stems rather than leaves and that anomalies between background and mineralised areas are, in many cases, insignificant.

Nesvetaylova (1961) is a review paper concerned principally with geobotanical methods and relating to much early work on 'indicator' species. Stanikov et al. (1964) succeeded in delineating several orebodies using biogeochemical methods in the USSR. In one area Alder leaves gave values of 0.06 to 0.02% zinc and 0.02% lead in the ash - clearly defining anomalies. No background values are given, however. A fault, associated with polymetallic mineralisation was discovered by values of 0.03 to 0.3% lead and 0.01 to 0.1% zinc in *Saxifraga, Centaurea* and *Carnpanula.*

Malyuga et al. (1959) considered the correlation between geological maps and vegetation maps of areas and found that some vegetation associations are restricted to certain rock types. In the field they noted various morphological changes in plants, particularly the large-pod poppy *(Papaven macrostomum B. et H.).* This flower develops large black spots on petals - referred to as modified form in the following tabulation:

	Ash Content, %		
	Cu	Zn	Pb
Normal poppy, from ore zone	0.016	0.006	0.003
Modified poppy, from ore zone	0.012	0.031	0.015
Normal poppy, from Cu-orebody	0.294	0.003	0.004

Malyuga (1964) mentions lead and zinc biogeochemical prospecting in only one area, that of the Varaz polymetallic deposit in Georgia. One figure shows anomalies in lead content over a vein, but the plant used is not specified (either cherry, laurel or rhododendron). The contrast is about 4 for lead in leaves and less than 1.5 for lead in roots.

Vakhromeer (1962) has shown that zinc is preferentially concentrated in pine needles; however, no information is available to indicate what other organs or plants were analysed.

Biogeochemical studies on lead and zinc in Australia are those of Nicholls et al. (1965) and Cole et al. (1968).

As explained in the section on copper, in the Dugald River lode area (Nicholls et al. 1965) the absence of background vegetation renders comparison between 'anomalous' and background areas impossible. The main background species, *Triodia pungens* contains 178 ppm zinc and less than 10 ppm lead in the ash; where it grows near the lode the plant can assimilate large amounts of zinc. The local indicator species all accumulate zinc, especially in the flowers. None of the indicator species accumulates much lead even when growing over lead-rich soils. Only when the lead content in the soil exceeds 1,000 ppm do *Tephrosia sp. nor* and *Eriachne micronata* disappear; otherwise they can tolerate this lead, presumably by excluding it in some way. Some evidence obtained from dead *Triodia pungens* suggests that this species does not grow on the lode because it has no excluding mechanism.

In the Bulman area (Cole et al. 1965) the seasonal variations in metal uptake were examined. *Gomphrena canesceus* accumulates up to 1% zinc in its leaves and even higher values occur at the end of the dry season. There is evidence that zinc is moved to the flowers from April to August. With regard to lead, relatively low values occur in the plants in August. *Polycarpaea synandra var. gracilis* accumulates lead when growing on very lead-rich soils and consequently tolerates this lead in its tissue (rather than excludes the lead). High lead concentrations in April may indicate greater lead availability after the wet season; an effect probably combined with translocation within the plant.

In summary; the beginning of the dry season is the best time to sample for lead and the end is the most suitable time for zinc.

Many of these papers on lead and zinc point to problems of inadequate contrasts, especially for zinc. It appears that this metal is entirely different from lead, copper and nickel in that relatively large quantities are required by most plants.

7. HYDROGEOCHEMICAL PROSPECTING

7.1 General

This technique has been of some use in the more humid areas of the world. The principle is that oxidising sulphide orebodies give rise to anomalous concentrations of appropriate trace elements in waters. These concentrations should show a dispersion pattern, similar to that in stream sediments, related to the position of the original ore. The problems involved include the sampling of uncontaminated specimens and their subsequent assay. The concentrations in water are at least as subject to climatic variation as concentrations in sediments and contamination is possibly even more likely. A prime prerequisite is an oxidising orebody which is releasing cations to ground waters.

A general discussion of the technique is offered by Saukov (1956). General assay values of the elements in water are given by Livingstone (1963). In fresh waters copper values range from 0 (<0.05) to 600 ppb (mean estimated 10 ppb); nickel is reported as from 0 to 300 ppb (mean 5 ppb), however, zinc values near 1 ppm have been reported in natural waters as far apart as the USA and Nigeria with most values between 10 and 100 ppb.

Lead is the least soluble in water but has been reported as having values between 0.03 and 115 ppb in lakes in Maine, USA (Kleinkopf, 1955, 1960 - quoted by Livingstone). Most common values for lead are between 2 and 5 ppb. No mean values are reported for ground waters by White et al. (1963), but values for copper and zinc vary from not detectable (<10 ppb) for both elements to maximum values of 360 ppb for zinc in ?unmineralised ground waters associated with shale in Kentucky, and 120 ppb in ?unmineralised ground waters associated with shale in New Carolina. In mineralised areas White et al. report values of 0 to 0.6 ppm for nickel (?copper mineralisation), 1 to 852 ppm for zinc and 2 to 148 ppm for copper in waters associated with ores.

7.2 Discussion of Main Papers

Among the authors that have discussed water sampling De Geoffroy et al. (1967) found that assay of spring water for zinc was a suitable exploration technique for buried lead-zinc ores in south-west Wisconsin. This is a fairly comprehensive paper and includes discussion of the bonding of cations to the soil, the pH and total salt content of the waters and adds the measurement of zinc and iron. Relatively advanced statistical analysis was used in the data treatment with the construction of trend surfaces and trend surface residuals.

Other papers which have used water assays in the USA include those of Kennedy (1956), Kleinkopf (1960) and Van Price and Ragland (19). Kleinkopf evaporated waters to dryness and spectrographed the residues. Van Price and Ragland used atomic absorption on the waters. In both papers the writers found the method worthwhile. Kennedy's main contribution is his discussion of potential and actual contamination.

Water sampling is used extensively by the Geological Survey of Canada, who use it as one technique together with stream sediment and soil sampling. Representative papers are those of Boyle et al. (1955, 1958, 1966). The first paper discusses an area underlain by permafrost (Yukon) and finds that zinc is a useful sulphide indicator element in the summer wet season. The second paper discusses a more humid temperate area (Nova Scotia) and the behaviour of zinc, copper and lead. Three anomalous zones were delineated in the waters. The authors suggest that better results might more possibly have been obtained with stream sediments. Boyle et al. (1966) give figures of less than 1 ppb lead, 1 to 350 ppb copper, and 2 ppb to 330 ppm zinc in drill-hole waters which intersected sulphide ore. Background values were: lead, not detectable; copper ≤5 ppb; and zinc 1 ppb.

Most papers from the USSR have dealt not only with water analyses, but also with the modes of migration of cations through the waters. Bughelskii (1951) gave figures for copper, lead and zinc as follows:

	Pb, ppm	Zn, ppm	Cu, ppm
Background	nd	0.04-0.1	trace-0.06
Aureoles	0.01-0.02	0.04-0.15	0.03-0.1
Orebodies	0.01-1.5	0.1 -1.0	0.1 -0.2

These are the ranges of figures found for five orebodies in semi-arid areas of Kazakhstan. One locality only gave lead - 1.5 ppm, the highest of any of the other localities was 0.12 ppm. The high value was found in water circulating through oxidised lead ores.

Belyakova (1958) discussed a different area in Kazakhstan and noted that lead, zinc and copper have only background values even at the deposit. Nickel is present locally in the district but not in the waters of the deposit.

In Transbaikalia, a region with seasonal rainfall, Polikarpochkin et al. (1960), found that waters were best tested after rain when springs are flowing. The zinc content of bicarbonate-sulphate-rich waters was 14 to 60 ppb. Polikarpochkin et al. used total base metals as indicators of mineralisation. Dispersion traces were found 1.5 km away from the nearest known mineralisation. Concentrations fluctuated with the volume of the water flowing.

Udodov and Pasilov (1961) give average contents in water as: copper - 0.0103 ppm; zinc - 0.0130 ppm; nickel - 0.0021 ppm and lead - 0.0015 ppm. Waters from mineralised zones reached up to an order of magnitude higher than this. The pH varied from 5.8 to 7.2. Belyakova (1961) asserts that copper is mobile up to pH 7, lead to pH 7.2 and zinc to pH 7.5. This is not borne out in the author's experience. If the figures of Belyakova are correct, it may mean that the base metals have been travelling in colloidal form.

Williams (1967) and Williams and Wood (1967) used water assays in conjunction with soils and stream sediments in the Longwood Range, Southland, New Zealand and in Western Otago, New Zealand. Copper values in waters at Longwood ranged from 4 to 15 ppb (background), to 30 to 108 ppb (anomalous). In western Otago stream water contained from zero (not detectable) copper to 12.3 ppm copper immediately below the lode.

In Africa investigations have been carried out by Webb and Millman (1950) and by Atkinson (1951). Webb and Millman assayed for total heavy metals and expressed the results as ppm zinc equivalent. Values obtained were 0.05 ppm upstream from a lode to 0.5 ppm immediately downstream from the lode (Nigeria). A different area showed a rise from 0.06 ppm heavy metals to 0.6 ppm downstream for the lode.

Atkinson worked in Angola and found very variable concentrations of the total heavy metals in streams. In the dry season concentrations were low but stable. In early rains they become high and very variable; later in the wet season they fell irregularly to very low but stable values.

No papers on prospecting using water assays have been discovered for Australia or Papua/New Guinea, though it is known that such work has been attempted, with little success, in New Guinea and also in Tasmania.

8. INDICATOR ELEMENTS

8.1 General

In geochemical prospecting for copper, nickel, lead and zinc it is possible to use other, related elements, as pathfinders or indicators. This is especially useful when copper, nickel, etc. have unusual distributions or high background values. Anomalies in the indicator element are then much greater than in the relevant element. Boyle (1969) presents a general and wide-ranging discussion.

Indicators discussed below are $SO_4^=$, mercury, cobalt and chromium, arsenic, selenium, molybdenum and zinc.

8.2 Sulphate

During the weathering of sulphide ore deposits (including pyrite) oxidation to sulphate ions occurs, consequently groundwaters, and hence river water, are enriched in this component. Sulphate tends to remain in solution in water in contact with the atmosphere unless it precipitates with lead or calcium (in such circumstances anomalies could be recognised in the stream sediments). In order to provide a control on the sulphate variation, the $SO_4^=:Cl^-$ ratio may give anomaly patterns more stable than those of sulphate alone.

8.3 Mercury

This element is thought to be associated with many sulphide ore deposits, although in very low concentrations. As analytical techniques of improved sensitivity have become available, so interest in mercury has quickened. Normally a limit of detection of 1 to 10 ppb is required if large haloes are to be detected, since, due to the high vapour pressure of mercury the haloes can be very large indeed. One of the most significant advantages of mercury's mobility is that deeply buried orebodies may be detected at the surface.

Fursov (1958) is a classic early paper; later work is typified by Friedrich and Hawkes (1966) and Erickson et al. (1966). Warren et al. (1966) analysed vegetable matter for mercury and found somewhat inconclusive results. It appears that biogeochemical methods will only be of use where soil concentrations of mercury are very low. Ozerova (1971) presents an up-to-date review of primary haloes of mercury.

8.4 Cobalt and Chromium

Both of these elements have affinities with nickel and are associated with it in orebodies. Occasionally cobalt and, more important, the Co : Ni ratio has been used in geochemical prospecting. Malyuga (1964) presents several examples. On the whole nickel behaves at least as well as cobalt and the latter's use is limited. Chromium is commonly concentrated in nickeliferous laterite profiles (Zeissink, 1971) and it may be particularly useful in mature, deeply-weathered laterites.

8.5 Arsenic

This metal is well-known as a pathfinder for gold deposits (Mazzuchelli and James, 1966). Presant and Tupper (1966) have shown that extremely high contrasts occur when arsenic over sulphide orebodies is compared with that in barren areas. Some analyses of soils from their paper are shown in the following tabulation:

	Mean As, ppm	
	Normal Bedrock	Over Sulphide Deposits
No. of analyses	13	7
A_0 horizon	2	530
A_2 horizon	5	620
B_1 horizon	22	927
B_2 horizon	14	1101
C horizon	11	1270

Presant and Tupper (1966) recommend sampling of the B or C horizons. Mitcham (1952) has worked on the Coeur d'Alene district and found that arsenopyrite is an indicator mineral, forming envelopes around the ore shoots.

8.6 Selenium

This rare element may be found as a component of sulphide ores. Usually its concentration varies widely up to 1%, depending on the particular mineral. Sulphides of nickel and copper are richer in selenium than those of zinc. In the highly oxidising conditions associated with the weathering of sulphide deposits, selenium is readily transported as $SeO_4^=$ and $HSeO_3^-$, (Sindeeva, 1964 and Coleman and Delavaux, 1957). The Eh must be greater than plus 0.5 to plus 0.1, depending on pH.

Most prospecting for selenium (as a pathfinder) has been through the use of *Astragalus pattersoni* which requires relatively large amounts of selenium in order to survive, (eg. Cannon, 1960).

Goleva and Lushuikov (1967) discuss the mode of transport of selenium in groundwaters emanating from ore deposits. Most selenium is sexivalent and forms haloes around oxidising chalcopyrite-pyrite deposits, with maximum concentrations of 300 μg per litre (0.3 ppm).

8.7 Molybdenum

Molybdenum occurs in porphyry copper ores, sometimes as a trace element, sometimes in economic proportions. Since it can form anionic complexes, such as the molybdate ion, in some circumstances it is more mobile than copper. Warren and Delavault (1958) suggest molybdenum's use in biogeochemical prospecting and also point out that it sometimes forms a halo around porphyry copper, which effectively widens the zone of interest.

Huff and Marranzino (1961) found molybdenum in mesquite useful in tracking a buried porphyry copper deposit at Puma, Arizona. Hansuld (1966) suggests the use of molybdenum in soils to 'home in' on the target areas of porphyry coppers where copper anomalies have been recorded in stream sediments.

8.8 Zinc

Zinc has some use as an indicator in geochemical prospecting, since, particularly in sulphate-rich waters, it is more soluble than lead and copper and hence forms wider secondary dispersion haloes. This can have disadvantages, since all the zinc may pass out of the survey area in river waters rather than become detectable in stream sediments. The details of zinc's behaviour are discussed elsewhere in this report. It is noteworthy that few stream sediment or hydrogeochemical surveys are carried out without the use of zinc analyses.

9. FUTURE TRENDS IN PROSPECTING

Current activity in new prospecting methods is devoted to remote sensing. This may be chemical in its approach or devoted to recognition of anomalous or unusual physical features by infrared, side-looking aerial radar or other physical methods (Canney, 1969). Porphyry copper deposits have been sought, and located by photographing anomalous colours in arid red soils in Arizona (Reeves, 1969), but in general these methods are not specific for any element.

The chemical remote sensing techniques have been largely developed by Barringer (1969). Mercury in the atmosphere has been used to detect hydrothermal alteration zones and orebodies. Sulphur dioxide in the atmosphere can possibly be related to oxidising sulphide deposits and iodine is of possible prospecting use. Kremar (1968) has applied geothermal methods for detecting heat from oxidising sulphide deposits. These methods to date have not proved very reliable and much further research is needed before they become adequate exploration tools.

Weiss (1967) has worked on the detection of aerosol particles of high metal content as direct indicators of ore.

None of these methods are likely to be specific for prospecting for the elements under consideration in this report. If workable they will apply more to the conditions of mineralisation or to a sulphide deposit of any sort, than be restrictive to one or two elements.

10. DISCUSSION

10.1 General

The survey of the literature has shown the incompleteness of our understanding of geochemistry applied to prospecting. It is clear that in the majority of cases only the geochemical successes have been published and that many failures have been ignored. Of the papers published many discuss the results in terms of anomalous areas found, (usually in relation to known orebodies) but few papers discuss, or have any interpretation of the behaviour of the elements. It is all too clear that Hawkes and Webb (1962), admirable though this book is, has been used indiscriminately and the instructions prescribed in it have been carried out without sufficient thought. From the Australian point of view, this is regrettable since most of the papers to which Hawkes and Webb refer concern humid climates (both tropical and temperate). With the exception of a few papers about the south-western United States, there is scarcely any reference to arid regions in the book. Hawkes and Webb are the perpetrators of the almost universal use of the minus 80-mesh fraction. This fraction is certainly useful from analytical purposes in that no further preparation is required, however it is not necessarily the best fraction to use, particularly in arid areas such as South Australia. Martin (1967) pointed to some of the differences between size fractions, and the authors have found from their personal experience that in many areas coarser fractions give more meaningful results. Hawkes and Webb also advocate the comparison of cold extractable heavy metals to total heavy metals. Their hypothesis is that the cold extractable metal values are derived from oxidising sulphide material, carried in solution, and precipitated loosely on the surface of clays or sesquioxides. Total values of metals are considered to represent broken down rock and indicate the traces of metals concealed in the structure of silicates or various oxide minerals. The only published paper which discusses this topic in Australia is that of Binks (1968), where, in the Adelaide Hills, he shows that there is no point in analysing for cold extractable material and the total heavy metals (copper in this case) gives better ratios of anomaly to background. This again has been borne out in the experience of the authors of this report. The cause of the lack of definition in cold extractable metal is possibly that during the long dry periods to which most of continental Australia is subjected, an irreversible change takes place and the metal, which was loosely adsorbed on the surface of the clays, etc. is "fixed" within the framework of the supporting minerals, and not available to cold extraction techniques. It is worthy of note that Govett and Hale (1960) in the Phillipines, Yates and de Ferranti (1967) in New Guinea, found that cold extractable techniques were of little use, and this in a climate considered by Hawkes and Webb to be ideal for such methods.

In part, therefore, a plea for adequate orientation, where this is possible, is made so that when geochemical work is carried out, the optimum methods, size fractions, depths (or profiles), elements for assay, and sample intervals may be used. This is necessary for interpretation of the results. In too many cases geochemical data are expressed as a series of numbers (in ppm), some conventional statistics may be applied, some anomalies located and the results assessed simply on whether the anomalies, if any, yield ore. This is too glib. The interpretation should cover an understanding of the geochemistry such that if no anomalies are found an assessment may be made of whether this means that there are no orebodies in the area, or whether surface chemical processes such as intensive leaching, with or without silicification, have conspired to give a geochemical pattern which is little related to conditions at a depth of a few feet. The orientation survey should determine whether geochemical prospecting is a suitable tool for locating ore.

One problem in Australia is that many of the present surfaces are believed to relate to the late Tertiary, a time when the climate was more humid. Most surface or near-surface sulphide oxidation is believed to have taken place during the development of the Tertiary landscape and little oxidation of sulphides is believed to be taking place at the present day in the arid regions. Consequently, there is now little release of trace elements to the drainage systems from this type of source. In certain areas values must be further depressed by the addition of barren windblown material. For example, it is a common occurrence for dust from the Lake Torren's area to be blown onto the Flinders Ranges in the area between Wilpena Pound and Parachilna. A considerable increment of dust must have been added to soils and sediments here.

It is generally considered that, in the arid regions, the main erosive forces are mechanical. The wind and the abrasive power of sand in dust storms are quoted. There is so little rain that chemical weathering has been accepted as minimal. It is clear, however, that much of the topography has been highly influenced by water. The periodic torrential downpours are sufficient to move mechanically vast quantities of material loosened and/or oxidised during the previous dry period. The part played in weathering by dew, even in these regions, has probably been underestimated, for example, the 'onion' weathering of granites and dolerites is essentially a hydration process.

With these preliminary remarks in mind, some consideration should now be given to the methods of geochemical prospecting. These are:

a. Rock geochemistry
b. Soil geochemistry
c. Stream sediment geochemistry
d. Hydrochemical geochemistry
e. Biogeochemical geochemistry and geobotany
f. Use of indicator elements in any of the above techniques

10.2 Rock Geochemistry

The literature has offered little advice on the problems of rock geochemistry. In a few papers discussion of primary dispersion in rocks is included (eg. Lovering et al. 1948; Morris and Lovering, 1952; Cooper and Huff, 1951). Many papers dealing with exploration for nickel show that ultrabasic rocks, believed to be host rocks for nickel, can often be located by rock chip sampling (eg. Polferov and Suslova, 1966; Hotz, 1964; Turekian and Carr, 1960). This applies not only to ultrabasic rocks but also to prospecting of laterites for nickel. Laterite may be considered to be part of an unusual soil profile, but commonly it is sufficiently coherent to be included among the rocks. Papers which have used assays of laterite for nickel include: Miller (1957), Fawley (1957), Heidenreich and Reynolds (1959), Hill (1961) and Zeissink (1969, 1971). Rock sampling at depth below overburden has been advocated and used by Van Tassell (1969) and Donovan (1970) and is known to be used elsewhere.

Problems involved with rock sampling are:

a. the inherent variation of composition within the rock itself;

b. the influence of climatic features which have possibly leached or transformed surface or near-surface rock; and

c. the frequency of sampling.

The problem of inherent variation of composition may be resolved statistically. Tests of this variation by the analysis of several samples from the one area may be made. These tests must take into account the variations in, and absolute values of, grain size within the rock.

The influence of climate may be more difficult to determine or interpret. In much of Australia, rock trace element values are low because of leaching and/or silicification, although values may yet be higher than the values in the sediment adjacent and it may be beneficial to sample rock in some areas instead of the soils or drainage sediments.

Rocks outcrop irregularly, and not on a standard-sized or shaped grid. Sample distribution is therefore likely to be erratic. Providing enough samples are available from a reasonably small area, judicious use of statistical techniques can be used on the raw data and give indications, at least, of any trends which are present.

Another problem in rock geochemistry in Australia is that of distinguishing laterite, gossans, ironstone and weathered rocks. It is the authors' opinion that any "ironstones" found in the course of mapping or surveying should be assayed.

Of the four elements under discussion lead is the least mobile and may be concentrated in laterites. Nickel is more mobile and though it tends to be concentrated in laterites may have its maximum values below the surface (Zeissink, 1971). Copper and zinc are normally mobile though, again, there is some concentration of these elements in ironstones. During the leaching of rock (with non-production of ironstone) copper, nickel and zinc are fugitive, but little has been written to indicate whether lead remains in the leached rock or goes into the soil above it. It is agreed that little lead is transported in solution.

10.3 Soil Geochemistry

Soil sampling is one of the two most favoured techniques in geochemical surveying; where it is now commonly used in follow-up work (after a reconnaissance stream sediments survey) in areas with a well-developed drainage pattern or as a primary reconnaissance tool in generally flat areas with few drainage channels.

Problems to be resolved before adequate use in a particular area are:

i. the nature of the soil (residual or transported);
ii. optimum depths or position in the profile;
iii. optimum grain sizes;
iv. elements to be sought;
v. distribution of elements within the soil.

The first problem is difficult to determine in the field but may be resolved by study of aerial photographs. The position is complicated by the lack of stratification in many desert soils and their contamination (dilution) by wind-blown material.

The optimum depth for sampling is a function of the soil chemistry. It is this which has provoked the discussion between Boyle and Dass (1967) on the one hand and Roy and Paul (1967) on the other. Boyle and Dass prefer to use the A horizon; Sinha and Roy the B horizon. Meanwhile in the Rum Jungle area of the Northern Territory Semple (1968) finds that the C horizon gives the best results. There is little doubt that in any given area this problem should be resolved by orientation investigations.

In general, rain leaches soils through which it passes. The leached ions pass down until they are either precipitated as oxides/hydroxides, trapped by evaporation or flow away in groundwater. Hawkes and Webb (1962, p 98) give a qualitative diagram showing the effect of rainfall on the position of hard pan horizons or zones with accumulation of calcium salts. In general in areas of relatively high rainfall, the soil profile is deeper. On page 111 they give a diagram from Jenny (1941) showing more quantitatively the relationship between depth of lime accumulation and rainfall. The latter diagram is effectively a straight line graph with a positive slope. In arid zones carbonate/lime accumulates at about 10 inches depth for 15 inches of rain or less. This layer is believed (Twidale, 1968) to be forming in Australia at the present time. Laterite represents a former hard pan zone now fossil and laterite is not believed to be forming today over much of Australia. Both of these zones (of lime accumulation and laterite) collect or have collected most of the mobile cations. The hard pan horizon which is composed to a large extent of iron oxides/hydroxides with clay is responsible for a similar precipitation of cation in the podsol soils of Australia. It appears possible that analysis of either of these two horizons may give an indication of trace elements in the rocks below, provided the cover is residual.

There has been much debate about the wisdom of assaying calcrete (on the grounds that both it and material above it may have little relationship to the rock below), but its use is advocated by Sokolov (1949) and assays of either calcrete or the calcite-cemented fraction of alluvium or soil has been used, with effect, by Malyuga and Makarova (1956), Erickson and Marranzino (1960), Huff and Marranzino (1961) and Huff (1970). All were working in arid regions. Huff, Marranzino and Erickson were investigating the dispersion of copper above or away from concealed (but known) porphyry copper deposits.

There are also problems of consistent sampling of soil horizons, if the sampling is left to technical assistants. This problem is discussed by Warren et al. (1966), specifically in Canada, but applicable elsewhere. Many anomalies can be related to sampling at constant depths but not constant parts of profiles. This is of less importance where the soils are little stratified, but is applicable where there is a choice of sampling calcrete, hard pan or laterite or loose soil above or below.

Drilling through alluvium or other transported material to residual soil may prove to be an acceptable exploration technique. Examination of the various Bureau of Mineral Resources records which deal with exploration in the Rum Jungle area has indicated that in this area it is advantageous to drill through to the C horizon, a depth variously given as 5 to 30 feet.

10.4 Stream and Drainage Sediment Geochemistry

This technique is universally accepted as the leading reconnaissance tool for geochemical prospecting. It also appears to be one of the most abused. The underlying principle is that at any given site in a drainage system the sediment represents an integration (a mixture) of sediment and fugitive (mobile) elements derived from all upstream parts of the drainage system. This is reflected in the trace element values. In particular, comparison of trace element values obtained at one site with values obtained at the next site upstream allows the interpreter to deduce whether there has been any significant influx of the trace elements sought between the two samples. Comparison of values from one drainage system to the next reveals whether there are significant regional changes or allows comparison of values in sediments derived from different rock types. As in all interpretations, a prime aim is to establish the 'natural' geochemical patterns of an area and then to determine discrepancies (anomalies) in the pattern which are caused by mineralisation. As always an understanding of the geology and of chemical behaviour of the elements sought is necessary in this interpretation.

Most of the papers collected have reported the use of minus 80-mesh sampling (in many cases using the non-existant 80-mesh BSS sieve!). Many have tried various partial extraction techniques as well as total extraction methods. There have been varying and irregular sample densities, and sampling has been at irregular intervals along streams.

Low density sampling (1 to 4 samples per square mile) has been used in the UK by Horsnail, Nichol, Tooms and others (1956, etc.) from the Imperial College, London. This low density sampling is rarely successful in locating specific orebodies but is adequate for regional reconnaissance, to assess the general levels of trace elements in a given area and to assist (possibly) in mapping (Garrett and Nichol, 1967; Reedman and Gould, 1970).

It appears from the literature that too little regard has been paid to the type of orebody sought in a given area, and the contribution such an orebody makes or has made to the local drainage, the state of dispersion profiles away from the ore, the manner of dispersions, the optimum sample interval and the optimum size fraction.

Relatively little emphasis has been placed on how the cations get into the streams and even less on the manner of migration and removal of ions from stream waters and sediments. Many of the papers and books which do discuss these are theoretical, (for example Garrels and Christ, 1965) and only a few attempt to relate the theoretical behaviour to practical problems (eg. Hansuld, 1966). Baas Becking et al. (1960) provided some excellent measurements of natural aqueous environments. When these observations and the more theoretical works of Sato (1960a, 1960b), Anderson (1955) and Garrels and Christ (1965) are taken into account field geologists and geochemists should be able to make pH and Eh assessments in the field and at least arrive at some qualitative assessment of the likely chemical behaviour in any given environment. Earlier sections of this report have discussed this more specifically for each element.

The problems of having non-anomalous sediments co-existing with mineralised outcrops in stream banks has been pointed out by Brown (1970). His technical note attempts to deal mathematically with the increments, in terms of parts per million, expected in a drainage sample below mineralised outcrops. This treatment is not comprehensive but illustrates the variables which need to be considered in such an exercise. His argument is such that one is surprised to find stream sediment anomalies at all.

From his discussion it is clear that both the sample interval used, and the sample fraction assayed should be related to the expected size of the target as well as to the manner of transport and precipitation of the various ions. The relationships between these are not simple, and where possible should be determined as closely as possible by measurement in the vicinity of a known orebody.

Dilution of increments of anomalous sediments is always an important factor in the conduct of stream sediment surveys. Transport may have been effected in solution or on clay, etc., or have been by mechanical movement of primary minerals, or as secondary minerals. Whatever the method of transport, "concentrated" material from a lode is distributed over a wide area and hence diluted. Anomalies, away from headwaters which contain much primary material, are apt to have a low contrast with background. It may be better therefore to try to accent the contrast by using one or more concentrating techniques. One technique is to use the placering effect of streams in the search for heavy minerals. This placer effect, involving the collection of heavy minerals in areas of quiet water, can disturb surveys when samples are taken at fixed intervals without thought, but by deliberate use of this effect streams may be sampled, more irregularly yet more meaningfully.

If unoxidised sulphides are present (Hawkes, 1953) lead, zinc and copper sulphides will be found this way. The useful collection of heavy minerals for the indirect tracking of an element has been shown by Yates and de Ferranti (1967). They assayed for copper in panned concentrates of magnetite and related high values to mineralisation.

Similarly, spurious anomalies can be generated in streams where there are either local deposits of calcrete/travertine or the creek flows over carbonate rocks which are either exposed or contribute to the sediment. This normally has the effect of shortening dispersion trains of mobile base metals and must surely be one of the factors whereby Binks (1968) and others of the South Australian Department of Mines, working on diapirs, found dispersion trains of copper to be so short and why so few anomalous values were detected. Once the copper has been precipitated on carbonate it may be either lost to the sediment or travel mechanically. In regions of periodic downpour, this is likely to result in a low anomaly.

It may be that in areas of largely non-calcareous rocks, deposits of calcrete/travertine in stream courses may be specifically sampled to determine whether they have collected the mobile base metals. This is known to the authors to have been noted in Queensland and to have been used in Western Australia.

In regions of dominant carbonate rocks it is therefore likely to be necessary to shorten sampling intervals in order to get meaningful results.

On the whole, however, satisfactory results have been obtained on stream sediment surveys for copper and zinc. Limited success has been obtained from lead and little has been written about nickel in drainage sediments.

One possibility not normally used in drainage prospecting, is the use of laterite or, iron-enriched material or iron-stained float. This technique has been found to be feasible in Nevada by Erickson et al. (1966) in an area which is semi-arid to arid. In this area fine-grained material shows no recognisable anomalous values, having apparently been too thoroughly diluted. The ore metals sought, zinc and lead, are most concentrated in coarse float of gossan and of silicified carbonate rock. The major problems of this survey appear to be two-fold:

1. the problem of adequate sampling to get a representative proportion;
2. difficulties in Australia of discriminating laterite or other ironstones from gossan.

Erickson et al. made sampling deliberately selective by choosing iron-enriched boulders. It is probable that following assay of a mixture of laterites with gossan that elemental patterns would emerge to separate the two.

10.5 Hydrogeochemistry

The papers which deal with hydrogeochemistry indicate that this technique, perhaps above all other techniques is subject to variation between samples and to contamination of samples. The technique is probably only feasible in regions with a moderately constant/regular supply of water. As such it has been extensively used in Canada, the USSR and various parts of the tropics. One main problem is the variation not only of the flow but of concentrations of cations within the waters. Polikarpochkin et al. (1960) in the USSR and Atkinson (1957) in Angola found very marked variations of concentration with the season. Warren et al. (1966) point to the severe problems in sampling water, including the possible disruptive effects of suspended sediments or of colloids in the water. There are variations in both Eh and pH over the year (commonly depending on the relationships of wet and dry 'seasons'). Although Warren et al. do not quote it, there are also problems of adsorption from the waters on to walls of containing vessesl, changes of Eh and pH on prolonged standing in sample containers, and the solution of material from the walls of containing vessels. As the normal concentrations are of the order of few parts per billion (10^{-7}%), even small changes in the samples can have very marked effects on the assays.

In South Australia it is apparent that water sampling can only be carried out in the wet season, if any, or by putting bores into groundwater, although bore waters are particularly subject to contamination from drills, well casings, and bailers.

Cu and Zn are the only two of the four elements which are commonly found in natural waters to any large extent; many bore fittings are made of brass and anomalous readings are known from this cause.

Another problem in Australia may be that of access which can be difficult following rain.

Overseas, Huff and Marranzino (1961) have noted that copper can move substantially in groundwater in arid lands but in general this technique is not recommended.

10.6 Biogeochemistry/Geobotany

Two separate influences are involved when considering the biogeochemical behaviour of the four elements. These are the fact that copper and zinc are necessary trace elements for plant growth (whereas lead and nickel are probably not), and the fact that all the elements can be toxic to plants if large quantities, varying with the plant, are ingested.

It is clear that there are strong convictions about the worth of botanical/biogeochemical prospecting. Cannon (1960) in the USA and Nesvetaylova (1961) in the USSR have praised the merits of geobotany. Nicholls et al. (1965) and Cole et al. (1968) have found geobotanical variations and associations in Australia. The investigations detailed in the two latter papers covered copper, lead and zinc, and distinctive botanical lode assemblages were found at both the Dugald River of Queensland and the Waimina Springs-Bulman area of the Northern Territory. It appears that in any given area it is pertinent to consider the possibilities of geobotanical associations even though many variations of association may be caused more by groundwater or other geomorphic factors than by mineralisation.

Similar arguments apply to biogeochemical prospecting. It appears that it is a potentially useful technique particularly in areas of relatively shallow transported soils overlying residual soils or rock, where the latter are no more than 30 ft in depth. Even in these situations deep auger drillings for soil or rock may prove to be a better sampling technique.

The success of the biogeochemical technique lies in finding appropriate plants, with suitable root depths, high tolerances to the metals sought, and of sufficient density over the search area that an adequate sample interval can be maintained. The most useful trees and shrubs in Australia are likely to be the eucalypts or the acacias. The latter have been used with some success in Egypt (El Shazly et al. 1970). A point in favour of a biogeochemical technique is that plants tend to 'integrate' values by collecting their cations from a considerable volume of soil. On the other hand it has been reported in conversation that material of the same type and age collected at various parts round the circumference of a shrub may have a variation of concentration of up to 100%. Warren et al. (1965, 1966, 1967) have discussed admirably many of the problems of collection and of choice of shrub. In the 1965 paper they noted that material of the same age from top and bottom branches of the same tree may contain variable concentrations of trace elements. In the 1966 and 1967 papers they illustrate some of the changes of copper concentration in pine tree stems over the year. Variations of up to 400% are apparently not uncommon.

It seems clear that before biogeochemical surveys are carried out plants must be found which collect the elements sought. In the Australian arid areas these remain largely unknown. In addition, an experimental survey is needed which will determine the optimum part of the plant for analysis.

Other factors which need consideration both at the commencement of a survey and during the interpretation of data obtained are the possibilities of contamination. Thus Marmo (1956) gives a table showing variations between values reported for washed and unwashed leaves. Warren et al (1965) argue convincingly, that assays of plant material should be standardised and expressed as ppm of the ash content.

Despite these sampling problems the most important feature which has not been fully investigated is the behaviour of the various trace elements in the plants, and the relationship which plant values show in relation to subsoil or rock values. Timperley et al. (1970) discuss the role of essential (copper and zinc) and non-essential trace elements in plants. It has been noted in Sections 6.2 and 6.3 that they claim that as copper is an essential trace element a tree (as studied) will absorb only its required amount and no more. Plots of relative accumulation (amount in plant (leaf-ash) divided by amount in soil) plotted against amount in the soil of essential trace elements are hyperbolic (negative) for essential elements on an arithmetic scale; and are linear with a negative slope on a log-log scale. By contrast plots of relative accumulation against soil content for non-essential trace elements are alleged to be a straight line. This argument is only in the hypothesis stage and may yet be challenged. Meanwhile Timperley et al. conclude that non-essential trace elements may be the most useful in biogeochemical prospecting.

On the other hand it is clear that certain plants are accumulators of copper (Blisset, 1966; Cole et al. 1968; Warren et al. 1951, etc.) and that zinc is accumulated by some tree species (Warren and Howatson, 1947; Harbaugh, 1950, etc.)

There is clearly much work to be carried out before biogeochemical prospecting as a whole becomes a viable tool, able to be used with confidence. From the literature it appears that it ought to be possible to use biogeochemical prospecting for copper, zinc and nickel. Work has been published on lead in plants (for prospecting purposes) and the information obtained to date tends to show that lead in plants is not suitable for prospecting purposes.

10.7 Indicator Elements

Some use has been made of indicator elements, but this is obviously a matter which depends on the area under examination and suitable indicator elements/ions must be found by experiment.

The element most recommended in the literature is zinc. This element is more mobile in supergene environments than copper, nickel or lead, and may be expected to be detected further from the source than the other elements. The element is not expected either to be specific for the elements under discussion, but is a general indicator for sulphide deposits, or to lead directly to the sulphide deposits, but merely to indicate areas of interest. Most hydromorphic surveys have used zinc as the main element of interest.

The other elements/ions discussed in Section 8 all have their uses. In Australia sulphate prospecting is less feasible than in more humid areas because of the relatively high concentration of sulphate in the soils. It is possible, however, that it could be of use on slopes or when testing salt seeps. Selenium and arsenic are both common associates of sulphides in general. These elements, together with tellurium are associated with both gold and sulphide mineralisation in Western Australia. Chromium is of extensive use in locating ultrabasic rocks, for it collects in residual soils, and the effective position of the ultrabasic rock may be outlined by high chromium contents. This feature is applicable in both humid and arid climates and is a feature of the relative stability of chromite. No general rules can be applied for cobalt though it is a common associate of (copper-) nickel mineralisation. Hansuld (1967) has argued convincingly that, when prospecting for porphyry copper mineralisation, copper can be used to delineate the area of interest (because of its moderate dispersion) while molybdenum can be used to locate the area of mineralisation. This hypothesis has been tested in one area in Australia and appears to be of some value.

The indicator element of most current interest is mercury. Much enthusiasm has been raised by this element, but many people have affirmed in conversation that they have found it of little use. Discussion of the true worth of the mercury prospecting technique needs a more adequate basis of fact on which to work. Until relatively recently assay methods for mercury were unreliable with considerable interference from other elements, and with considerable possibilities of contamination. Until more data can be collected on the mercury content of ores and on the mercury content of soils, and soil air above the ores no definite conclusions can be made. It is suggested that a systematic survey of South Australian deposits be made for the specific purpose of clarifying this problem.

11. CONCLUSIONS

11.1 General

1. In no circumstances are water surveys recommended.
2. Wherever possible orientation surveys should be carried out.
3. Biogeochemical surveys show such variability of analysis that values obtained should be treated as effectively semiquantitative. Once an area of interest is located, auger drilling or some other more positive method of approach is recommended in locating a target.
4. When carrying out stream sediment surveys more consideration than has been shown in the past should be given to the choice of size fractions and sample intervals.
5. As an alternative to conventional stream sediment surveys, sampling of iron-stained or iron-enriched float (or laterite) may lead more directly

to mineralisation.

6. There is no positive evidence that the cold extractable heavy metal survey techniques work in arid regions.

7. Despite differences in leaching properties all four elements tend to collect on/with iron and manganese oxides/hydroxides. In any geochemical survey iron-enriched material should be tested for its trace element content.

11.2 Copper

1. Copper is relatively easily oxidised from its primary occurrence in sulphide ores. It is capable of migrating in acid solutions, and after precipitation or adsorption it travels mechanically. It is an essential constituent of plants and is ubiquitous, at detectable levels, in plant ash.

2. Copper tends to be leached from the surface of residual soils but may be collected in a hard pan or calcareous 'B' horizon, or in calcrete. Soil geochemistry with samples collected from the appropriate part of the profile, is a suitable method of prospecting for copper.

3. Copper may be found in coarse or in very fine fractions in stream sediments. In the coarse fractions (+60 mesh) it is likely to be a component of partly broken down rock, in the fine fractions most of the copper is secondary and is a product of either precipitation or adsorption onto (secondary) minerals. Copper in solution is readily trapped by carbonates. Hence in any stream sediment survey prior consideration must be given to the optimum size fraction and to the optimum sample interval.

4. Indicator elements may be useful in the search for copper deposits. In particular molybdenum may be expected to be present in residual soils near the focus of porphyry copper mineralisation. Zinc and mercury are possible alternative indicator elements. However, zinc is so mobile that it tends to be dispersed too widely in arid conditions, so that no anomaly is detectable. The case for mercury as an indicator of copper is not proven.

5. It appears to be possible to use either or both geobotany and biogeochemistry in the search for copper deposits. All plants contain copper and

several are known which are accumulator plants. In any given biogeochemical survey thorough orientation work must be carried out.

6. There appears to be no great value to be obtained using cold extractable methods for determining copper.

7. The possibilities of either using calcrete (massive or in stream courses) or the calcite of calcite-cemented alluvium in the search for copper should not be ignored. Care is needed to obtain consistent samples.

8. The possibilities of using heavy minerals (eg. iron oxides) in placer deposits in creeks should be considered. In areas of generally low values, assay of these minerals may produce sharper contrasts.

9. Copper may be collected on iron/manganese oxides/hydroxides and in laterites.

11.3 Zinc

1. The behaviour of the zinc in the supergene environment is very similar to that of copper except that it is more mobile. Zinc is more readily leached from rock and less easily precipitated.

2. Dispersion trains of zinc tend to show a wide low level distribution. Stream sediment surveys are therefore appropriate, subject to the correct choice of size fraction and sample interval. Zinc is also precipitated readily onto carbonate. This fact may be used to advantage or else taken into account when interpreting results.

3. Zinc is so mobile in soils that soil surveys using zinc are less effective for this element than others. If soil surveys are to be carried out samples need to be collected in hard pan or carbonate layers. Zinc soil anomalies are commonly offset, by the drainage, from the mineralisation to which they are related.

4. Zinc may be collected in iron/manganese oxides/hydroxides. All iron-rich outcrops should be sampled. However, because of the mobility of zinc, iron enriched outcrops, *per se*, are not likely to lead directly to zinc mineralisation.

5. Biogeochemistry is a possible tool in the search for zinc deposits. However, because zinc is an essential element at trace to minor levels

in plants, care should be taken in interpreting assay values obtained.

6. Mercury appears to be a possible indicator element for low temperature, hydrothermal, lead-zinc deposits. Mercury is sold as a by-product of Rosebery ore (Argall, 1971) and as a by-product of lead-zinc deposits elsewhere in the world.

7. There appears to be no value in using cold extractable zinc survey methods in arid regions.

8. As for copper, the possibilities of using heavy minerals in placer-type deposits should be considered. However, zinc is more likely than copper to be leached from iron oxides, etc.

11.4 Lead

1. Lead is less easily oxidised from its ores than other metals under discussion. This is not because galena is less reactive but because a lump of ore is quickly coated with either cerussite or anglesite. Both of these are almost insoluble and impede further reaction. Lead does not travel in solution to any large extent, but does travel mechanically.

2. Lead is less susceptible to leaching than either copper or zinc. This makes it a suitable element to be sought in residual soil surveys. Because of its relative lack of mobility there is little tendency to concentrate in certain parts of the profile.

3. Lead is present with iron and manganese oxides, possibly because of its lack of mobility rather than an inherent concentration effect. Values recorded tend to be rather erratic; however, all ironstone/laterite outcrops should be sampled for lead.

4. Lead is not a particularly suitable element for stream sediment surveys. Reconnaissance is better with zinc or copper and lead used in follow-up work on soils. Because of its lack of mobility, little lead gets into streams. When in streams lead minerals tend to travel mechanically. the three main lead minerals galena, cerussite and anglesite all have good/excellent cleavage and grains are quickly broken down. Consequently lead in streams tends to be found as a low wide, very low-level anomaly. Lead in the coarse fractions can be used to locate a source.

5. Lead is a suitable element for consideration using heavy minerals from 'placer' deposits in streams. This may be a suitable technique for

enhancing the contrast in stream sediment surveys.

6. Zinc and mercury are potentially useful indicators of lead mineralisation. If any showing is present a test survey of the values of these elements can be made.

7. There appears to be no merit in using hydrogeochemistry or cold extractable methods in the search for lead.

8. The usefulness of biogeochemistry in the search for lead is of questionable value. However, because of lead's highly toxic nature to many plants there are likely to be variations in ecological patterns in the vicinity of lead deposits.

11.5 Nickel

1. Though nickel can be leached from its ores it is not one of the most mobile elements. It is capable of migrating in acid solutions, of travelling mechanically after precipitation or adsorption. It is also capable of being absorbed into plants.

2. A first approach to the search for nickel is the search for ultrabasic rocks. Because nickel can be leached at the surface, where there is no outcrop high chromium values are considered to be a good indicator of the presence of ultrabasic rocks.

3. Nickel is commonly leached from the upper parts of residual soils, but it is collected by hard pan or calcareous layers in the lower parts of the profile. Sampling for nickel in well stratified soils in arid/semi-arid regions should be restricted to the 'B' or even 'C' horizons.

4. Though nickel may show a relative displacement in the profile compared with iron, it tends to remain concentrated in laterite, and ironstone soil profiles. All outcrops of this material should be sampled and assayed for nickel. If nickel is present in concentrations greater than 1,000 ppm at the surface, trial drill holes should be made to test whether there has been any concentration at depth.

5. Most nickel in stream sediments is related to outcropping ultrabasic or basic rocks. Relatively unaltered rock may be found in the coarser fractions. These may show reasonable nickel values. Secondary nickel is concentrated in the finer fractions.

6. No direct way is known for prospecting for nickel. The current technique appears to be to find a magnesium-rich ultrabasic/basic rock, preferably with high sulphur values, and then to drill the rock systematically paying particular attention to any basal contact zone.

7. Apart from chromium, copper, selenium, sulphur and arsenic have all been used as indicators of nickel mineralisation. Whether these are suitable needs to be determined by trial and error in any given area. Primary nickel deposits are believed to be emplaced at high temperatures, therefore, it is not likely that mercury will be a suitable indicator element.

8. Biogeochemical and geobotanical prospecting have been used with success in some areas, and so these techniques should be considered as possible tools.

12. BIBLIOGRAPHY

ABABI, V. and DONOS, M. (1963). Geochemical distribution of Mn, Zn, Cu, Co and Mo in some chermozyems of South Dobrogea. Acad. Rep. Populare Romine, Filiala Iasi, Studii Cercetarii Stiint., Chim. 14 (2), 191-201.

ABDULLAEV, Z.B. et al. (1967). The geochemistry of nickel and cobalt in ultrabasic rocks of the ophiolite formation of the Lesser Caucasus (Azerbaidzhan). Geokhimiya (4), 425-32 (Russ).

AGNEW, A.G. (1955). Application of geology to the discovery of lead-zinc ore in the Wisconsin-Illinois-Iowa District. Min. Eng. 7. 781-799.

AKRIGHT, R.L. (1969). Exploration Geochemistry. Min. Eng. 21 (2), 75-76.

ALBUL, S.P. and PETERSEL, L.Kh. (1961). Geochemical studies of river-bed deposits of drainage systems in districts of polymetallic ore manifestations in the Estonian SSR. Tr. Vses. Nauchn.-Issled. Inst. Metodiki i Tekhn. Razvedki (3), 304-316.

ALBUL, S.P. et al. (1961). Hydrochemical prospecting of ore deposits in the basin of the Budyemkan River (E. Transbaikal). Tr. Vses. Nauchn.-Issled. Inst. Metodiki i Tekhn. Razvedki (3), 295-303.

ALESKOVSKII, V.B. et al. (1959). Applications of the biogeochemical method to prospecting for nickel on the Kola Peninsula. Geokhimiya (3), 266-271 (Russ).

ALEVA, G.J.J. (1960). Geochemical and geophysical exploration of the Nigadoo base metal deposit. N.B. Canada. Geol. en Mijn. 39, 492-499.

ALIEVA, M.M. et al. (1964). Content and conversion of copper and zinc in irrigated soils in the Fergana Valley of the Uzbek SSR. Tr. Nauchn.-Issled. Inst. Pochvoved. Gos. Kom. po Khlopkovodstrvu. Sredu. Azii pri Gosplane SSSR (4), 108-112.

ALMOND, H. and MORRIS, H.T. (1951). Geochemical techniques as applied to recent investigations in the Tintic District, Utah. Econ. Geol. 46, 608-625.

AMMON-CHOKROUM, M. (1969). Contribution a l'etude de la distribution du nickel dans les ferrallites de Nouvelle Caledonie. C.R. Acad. Sci. Paris ser. D 268, 1563-1566.

ANDERSON, C.A. (1955). Oxidation of copper sulphides and secondary sulphide enrichment. Econ. Geol. 50th Anniversary Volume 324-340.

ANDERSON, D.H. and HAWKES, H.E. (1958). Relative mobility of the common elements in weathering of some schist to granite areas. Geochim. et Cosmochim. Acta 14, 204-210.

ANDREWS-JONES, D.A. (1968). The application of geochemical techniques to mineral exploration. Colorado School of Mines, Mineral Industries Bull. 11 (6), 31 pp.

ANNAMALAI, A. (1969). Geochemical study on part of the Mantan Grid, Rum Jungle area, NT. BMR Records 1969/18.

ANTROPOVA, L.V. (1968). Forms of occurrence of lead in dispersion trains (Estonia). Int. Geol. Review 11, 24-30.

ARCHER, A.R. (1967). Geochemical prospecting in the Ketca River District. Western Miner 40 (4), 29-37.

ARINUSHKINA, E.V. and LEVIN, F.I. (1961). Contents of V, Cu, Mn, Co and Ni in soils of the Agrobiological Experimental Station of Moscow State University. Poryshenie Plodorodiya Pochv. Nechernozemnoi Polosy No.1, 69-79.

ARKHANGEL'SKY, A.D. and SOLOVIEV, N.V. (1938). Experimental investigations of the mechanism of accumulation of copper in sedimentary rocks. Bull. Acad. Sci. USSR Ser. Geol. (2), 279-294.

ATKINSON, D.J. (1957). Heavy metal (Cu) concentration in streams in North Angola. Econ. Geol 52, 652-667.

AUBAGUE, M. et al. (1964). Sur les anomalies de fiute en prospection geochimique strategique. Un exempler pris dans la bordure sedimentuire du Vivarais. Bull. Soc. fr. Mineral Paris 38 (1), 20-27.

AUSTIN, C.F. and NACKOWSKI, M.P. (1958). Geochemical exploration at Darwin Mines, California (abs). Bull. Geol. Soc. Amer. 69, 1531.

BAAS BECKING, L.G.M. et al. (1960). Limits of the natural environment in terms of pH and oxidation-reduction potentials. Jour. Geol. 68, 243.

BABAEV, F.M. (1969). Biogeochemical surveys in the Katsdag deposit of the Belokansk area. Uch. Zap. Azerb. Gos. Univ., Ser. Geol.-Geogr. Nauk. 5, 107-108 (Russ).

BALDOCK, J.W. (1969). Geochemical dispersion of copper and other elements at the Bukusu carbonatite complex, Uganda. Trans. Inst. Min. Metall. (Lond.) 78, B12-28.

BARAGAR, W.R.A. and ANNELLS, R.N. (1969). Geochemistry of Coppermine River basalts. Can. Dep. Energy, Mines Resour., Geol. Surv. Can., Pap. No.69-44, 43 pp (Eng).

BARR, D.A. and HAWKES, H.E. (1963). Seasonal variations in copper content of stream sediments in British Columbia. Trans. AIME 226, 342-346.

BARRINGER, A.R. (1969). Remote sensing techniques for mineral discovery. 9th Commonwealth Mining and Metallurgical Congress.

BARRINGER, A.R. (1970). Optical detection of geochemical anomalies in the atmosphere. 3rd Inst. Geochem. Expl. Symposium, Toronto (Abs).

BARSUKOV, V.L. and VOLOSOV, A.G. (1967). Geochemical method of mineralisation prognosis into depth and of blind orebody detection on sulfide-cassiterite deposits. Geokhimiya 11, 1370-1380 (Russ).

BASITOVA, S.M. et al. (1964). Biogeochemical research in Northern Tadzhikistan. Izv. Akad. Nauk Tadzh. SSR Otd. Fiz.-Tekhn. i Khim. Nauk (1), 30-40.

BATESON, J.H. (1969). Geochemical investigation of the Eagle Mountain area. Red., Geol. Surv. Brit. Guiana 6, III-1 - III-8 (Eng).

BAYROCK, L.A. and PAWLUK, S. (1967). Trace elements in tills of Alberta. Canadian Jour. Earth Sci. 4, 597-607.

BEAR, F.E. (Ed.) (1955). Chemistry of the Soil. Reinhold, New York, 373 pp.

BEAUMONT, C. (1956). Prospections Geochimique pour plomb et zinc sur des mineralisations d'impregnations (abs). Int. Geol. Congr. Rept 20th Sess.

BEERS, A.H., NACKOWSKI, M.P. and PARRY, W.J. (1970). Trace element study of the Oquirrh Mts, Utah. 3rd Internal Geochem. Expl. Symp. Toronto.

BEEVERS, J.R. (1966). Kalgoorlie Geochemical Project Report. BMR Records 1966/130.

BELYAKOVA, E.E. (1961). Hydrochemical method of prospecting for ore deposits in arid regions. Materialy Vses Nauchn-Issled Geol Inst. 46, 47-82.

BELYAKOVA, E.E. and KRONIDOVA, T.F. (1968). Study of the metal content of natural waters. Geol. Metallogeniya Uspensk. Tekton. Zony (Tsent. Kaz.) 4, 94-111 (Russ).

BELYAKOVA, Ye, Ye. (1958). Migration of elements in underground and surface waters of the Upper Kairakty District, Central Kazakhstan. Geochemistry 176-188.

BELYAKOVA, Ye, Ye. (1961). Some laws governing the migration of copper, lead and zinc in water and their significance in prospecting. Sovetskaya Geologiya No.1, 98-108.

BERGEY, W.R. (1966). Geochemical prospecting for copper in Puerto Rico. In "Caribbean Geol. Conf. 3rd Kingston, Jamaica 1962". Trans. Jamaica Geol. Surv. Pub. 95, 113-119.

BINKS, P.J. (1968). Comparison of total and partial extraction techniques on drainage sediments in the Adelaide Hills. SADM Quart. Geol. Notes No.27.

BINKS, P.J. (1968). Geochemical survey of the Blinman Dome Diapir. SADM Mining Review No.128, 86-90.

BIRRELL, K.S. and WRIGHT, A.C.S. (1945). A serpentinous soil in New Caledonia. N.Z. Jour. Sci. and Tech. 27A, 72-76.

BLACK, C.D. and BAILEY, B.V. (1968). Investigation of the Barbecue copper prospect. Jamaica Geol. Survey Econ. Geol. Report 2 (Pub. 103), 11 pp.

BLACKBURN, G. and GILES, J.B. (1963). Trace element concentrations in certain soils of the lower south east of South Australia. CSIRO Div. of Soils, Adelaide, Divisional Report 2/63, 10 pp.

BLANCHOT, A. and CLERGUE, I. (1956). Utilisation des methodes de prospection geochimique en A.D.F. (French West Africa). Rev. l'Industrie Minerale. Cong. Centinaire No. Special 1 R 37, 310-314 (French).

BLISSETT, A.H. (1966). Copper tolerant plants from the Ukaparinga copper mine, Williamstown, SA. SADM Quart. Geol. Notes No.18, 1-3.

BLOOM, H. (1966). Geochemical Exploration in 1965. Min. Engr 18 (2), 75-78.

BLOOM, H. (1966). Geochemical Exploration as applied to copper-molybdenum deposits. In " Geology of the Porphyry Copper Deposits of Western North America." Ed. Titley and Hicks, Univ. of Arizona Press.

BLOOM, H. et al. (1956). Geochemical Reconnaissance in Eastern Canada (abs). Int. Geol. Congr. Rept 20th Sess.

BLOOMFIELD, K. et al. (1970), Geochemical exploration of carbonatite complexes: Eastern Uganda. 3rd Int. Geochem. Exp. Symp. Toronto.

BLOSS, F.D. (1956). Water analyses as an aid to geochemical prospecting for zinc in east Tennessee. Tennessee Acad. Sci. Jour. 31, 306-312.

BOHMER, M., and MECHACEK, E. (1965, pub. 1967). Metallometric survey of the drainage of neovolcanics of the Kemnica Mts. Geochem in Czech Trans 1st Conf. Geochem Ostrava, Sept 20-24 (Eng).

BOHMER, M. and MECHACECK, E. (1966). Some results of geochemical drainage survey in neovolcania of Kremnicke Hory Mtns. Geol. Sbor. Ceskosl. 17 (1), 7-16.

BOLVIKEN, B. (1967). Recent geochemical prospecting in Norway. "Kvalheim volume" 225-254.

BONDARENKO, G.P. (1968). An experimental study of the solubility of galena in the presence of fulvic acid. Geochem. Int. 525-531.

BONIFAS, M. (1959). Geochemical study of lateritic alteration. Mem. Serv. Carte Geol. Alsace Lorraine 17, 1-159.

BORUCKI, J. and RATSIMBAZAFY, C. (1969). Geochemical mapping of the Horombe Plateau (southern Madagascar). Quart. Colo. Sch. Mines 64 (1), 75-87 (Eng).

BOSE, S.K. (1964). Recent advances in geochemical prospecting in India for metalliferous ores. Indian Mineralogy 18, 1.

BOURY, M. (1938). Le plomb dans le milieu marin. Rev. trav. Office sci. et techn. peches maritimes 11, 157.

BOWEN, H.J.M. (1966). Trace elements in biochemistry. Academic Press, London and New York.

BOYLE, R.W. (1966). Geochemical prospecting research in 1966, Cobalt area, Ontario. Geol. Survey, Canada. Paper 66-46, 15 pp.

BOYLE, R.W. (1967). Geochemical prospecting in retrospect and prospect. Canadian Inst. Min. Bull. 657, 44-49.

BOYLE, R.W. (1968). The source of metals and gangue elements in epigenetic deposits. Mineralium Deposita 3, 174-177.

BOYLE, R.W. (1969). Elemental associations in mineral deposits and indicator elements of interest in geochemical prospecting. Can., Dep. Energy, Mines Resour., Geol. Surv. Can., Pap. No.68-58, 45 pp (Eng).

BOYLE, R.W. and CRAGG, C.B. (1957). Soil analysis as a method of geochemical prospecting in Keno Hill-Galena Hill area, Yukon Territory. Geol. Survey Canada Bull. 39, 27 pp.

BOYLE, R.W. and DASS, A.S. (1967). Geochemical prospecting - use of the A horizon in soil surveys. Econ. Geol. 62 (2), 274-6 (Eng).

BOYLE, R.W. and GARRETT, R.G. (1970). Geochemical prospecting - A review of its status and future. Earth Science Reviews 6, 51-75.

BOYLE, R.W. et al. (1955). Geochemical investigation of the heavy metal content of stream and spring waters in the Keno Hill-Galena Hill area, Yukon Territory. Geol. Survey Canada Bull. 32, 34 pp.

BOYLE, R.W. et al. (1958). Heavy metal (Zn, Cu, Pb) content of water and sediment in the streams, rivers and lakes of south-western Nova Scotia. Geol. Survey Canada Paper 58-1.

BOYLE, R.W. et al. (1966). Geochemistry of Pb (sic), Zn, Cu, As, Sb, Mo, Sn, W, Ag, Ni, Co, Cr, Ba and Mn in the waters and stream sediments of the Bathurst-Jacquet River District, New Brunswick. Can. Dept Mines Techn. Serv., Geol. Surv. Can. Paper 65-42; 50 pp.

BOYLE, R.W. et al. (1968). Minor and trace element distribution in the heavy minerals of the rivers and streams of the Bathurst-Jacquet River Districts, New Brunswick. Geol. Survey Canada Paper 67-45.

BOYLE, R.W. et al. (1969). Geochemical prospecting methods for native silver deposits in the Cobalt area of Ontario in 1966. Can., Dep. Energy, Mines Resour., Geol. Surv. Can., Pap. 67-35, 91 pp (Eng).

BOZHKO, M.G. (1964). Certain geochemical characteristics of the forest-steppe landscapes in the Cu district of the S. Urals. Int. Geol. Rev. 6, 238-253.

BRADBURY, J.C. (1955). Geochemical prospecting in the zinc-lead district of north-western Illinois. State of Illinois Geol. Survey, Rept of Investigation 179, 11 pp.

BRADSHAW, P.M.D. and STOYEL, A.J. (1968). Exploration for blind orebodies in south-west England by the use of geochemistry and fluid inclusions. Trans. Inst. Min. metall. 77, 144-152.

BRAZ da SILVA, A. (1969). Geochemical prospecting for lead and zinc in Malhada D'Arcia, Pernambuco, Brazil. Mineracao, Met. 49 (292), 139-144 (Port).

BRODERICK, T.M. (1929). Zoning in Michigan copper deposits and its significance. Econ. Geol. 24, 149-162, 311-326.

BRODSKII, A.A. (1962). Fundamentals of the hydrogeochemical method of prospecting for ore deposits. Tr. Vses. Nauchn-Issled Inst. Gidrogeol i Inzh Geol. No.20, 99-110 (Russ).

BROOKS, R.R. (1968). Plants as a guide to mineralisation. Austral. Jour. Sci. 31 (4), 137-140.

BROTZEN, O. and OBIAL, R. (1964). Geochemical prospecting applied in the Philippines. Philippines Geol. 17, 26-40.

BROTZEN, O. et al. (1967). Development, Status and possibilities of geochemical prospecting in Fennoscandia. "Kvalheim Volume" 99-112.

BROWN, B.W. (1964). A statistical case study in geochemical prospecting for copper. Econ. Geol. 59, 492-500.

BROWN, B.W. (1970). Error in lead anomalous stream sediments. Econ. Geol. 65, 514-515.

BROWN, J.S. and MEYER, P.A. jnr. (1956). Geochemical prospecting as applied by the St Josephs Lead Co. (abs). Int. Geol. Congr. Rept 20th Sess, p 359.

BRUNDIN, N.H. (1969). Experiences in geochemical and heavy mineral prospecting. Quart. Colo. Sch. Mines 64 (1), 89-94.

BUGEL'SKII, Yu, Yu. (1965). Formation of the chemical composition of natural waters in serpentinite massifs. Kora Vyvetrivaniya, Akad. Nauk SSSR Inst. Geol. Rudn. Mestrozhd., Petrogr., Mineralog. i Geokhim. 9, 37-41.

BUGEL'SKII, Yu, Yu. (1965). Chemical composition of pore solutions in weathering products of ultrabasic rocks. Kora Vyvetrivaniya, Akad. Nauk. SSSR, Inst. Geol. Rudn. Mestorozhd., Petrogr., Mineralog. i Geokhim. 9, 42-7 (Russ).

BUGHELSKII, Y.Y. (1960). Some characteristics of zinc, lead and copper migration in ground waters in complex ore deposits of Central Kazakhstan. Geochemistry 1957, No.1, 102.

BUSH, J.B. et al. (1960). The chief Oxide-Burgin area discoveries, East Tintic District, Utah; a case history. Pt II, Bear Creek Mining Co. studies and exploration. Econ. Geol. 55, 1507-1540.

BUTLER, J.R. (1953). The geochemistry and mineralogy of rock weathering (1) The Lizard area, Cornwall. Geochim et Cosmochim Acta 4, 157-178.

BYERS, A.R. (1956). Geochemical investigations in the Flin-Flon area. Can. Min. Jour. 77, 83-86, 101.

BYERS, A.R. (1956). Geochemical prospecting in the Flin Flon-Amisk Lake base metal area, northern Saskatchewan (abs). Int. Geol. Congr. Rept 20th Sess, p 359.

CACHAU-HERREILLAT, F. (1969). Geochemical prospecting for lead-zinc stratiform deposits: nonlinear correlations between the content of soils and rocks in lead and zinc and their use in separating stratiform and hydrothermal deposits. Quart. Colo. Sch. Mines 64, (1), 95-110.

CAMERON, E.M. (Ed) (1967). Geochemical prospecting. Geol. Surv. of Canada Paper 66-54, 282 pp.

CAMERON, R.E. (1966). Properties of desert soils. NASA Accession No.N66-36474, Rept No.NASA-CR-77938, 164-86.

CANNEY, F.C. (1963). Soil sampling experiments in the Mission Mine area, Pima County, Arizona (abs). AIMM Petrol. Eng. Dallas, Texas, February.

CANNEY, F.C. (1965). Geochemical prospecting investigations in the copper belt of Vermont. US Geol. Survey Bull. B-1198, 28 pp.

CANNEY, F.C. (1966). Hydrous manganese-iron oxide scavenging: its effect on stream sediment surveys (abs). Canadian Geol. Survey Paper 66-54.

CANNEY, F.C. (1969-70). Remote detection of geochemical soil anomalies. Source unknown.

CANNEY, F.C. and WING, L.A. (1966). Cobalt: useful but neglected in geochemical prospecting. Econ. Geol. 61 (1), 198-203.

CANNON, H.L. (1955). Geochemical relations of zinc-bearing peat to the Lockport Dolomite, Orleans Country, New York. US Geol. Survey Bull. 1000-D, 119-185.

CANNON, H.L. (1960). Botanical prospecting for ore deposits. Science 132, Nr. 3427.

CANNON, H.L. et al. (1968). Metal absortion by Esquisetum (horsetail). US Geol. Survey Bull. 1278-A, A1-A21.

CARLISLE, D. and CLEVELAND, G.B. (1958). Plants as a guide to mineralisation. California, Div. of Mines, Special Report 50, San Francisco, 31 pp.

CARPENTER, R.H. and HALE, R.C. (1967). Nickeliferous soils and stream sediments associated with peridotites near Democrat, North Carolina. Southeast Geol. 8 (1), 9-18.

CARROLL, D. (1958). Rainwater as a chemical agent of geologic processes - A review. US Geol. Survey, Water Supply Paper 1535-G, 18 pp.

CARTER, E.K. (1959). Kohinoor copper deposit, Cloncurry mineral field, Queensland. BMR Record 1959/155.

CARTER, G.S. and KING, A.J. (1959). Geochemical and geophysical investigations at Mpanda, Tanganyika. Rec. Geol. Surv. Tanganyika 9, 40-46.

CHAFEE, M.A. and HESSIN, T.D. (1970). An evaluation of some geochemical sampling in the search for concealed 'porphyry' copper-molybdenum deposits on pediments in Southern Arizona, USA. 3rd Int. Geochem. Expl. Symp., Tornonto.

CHAKRABARTI, A.K. (1969). Geochemical exploration of the ore-bearing horizons at Zawar mines, India, and its possible bearing on metallogenesis. Quart. Colo. Sch. Mines 64 (1), 111-138.

CHAMBERLAIN, J.A. (1968). Some geochemical factors in nickel exploration. Canadian Mining Journal, 61, 54-57.

CHAN, S.S.M. (1969). Guides for exploration from geochemical investigation of ore veins at the Galena Mine deposits, Shoshone County, Idaho. Quart. Colo. Sch. Mines 64 (1), 139-168.

CHAPMAN, R.M. (1958). Geochemical exploration in the Kantishna Area, Alaska (abs). Geol. Soc. of America, Bull. 69, (2),

CHAPMAN, R.M. and SHACKLETTE, H.T. (1960). Geochemical exploration in Alaska. US Geol. Survey Prof. Paper 400B, B104-107.

CHERNYAEV, A.M. et al. (1968). Comparative evaluation of hydrogeochemical conditions of prospecting for sulfide deposits in arid regions of the Urals, areas east of Urals, and northern Kazakhstan. Gidrogeol. Sb 5, 17-86 (Russ).

CHISHOLM, E.O. (1950). A simple chemical method of tracing mineralisation through light non-residual overburden. Trans. Canadian Inst. Min. Metall. 53, 44-48.

CHISHOLM, E.P. (1957). Geophysical exploration of a lead-zinc deposit in Yukon Territory. 6th Commonwealth Mining and Metallurgy Congress, 269-277.

CHOWDBURY, M.K.R. et al. (1956). Geochemical prospecting in the Singhbin copper belt, Bihar, India (abs). Int. Geol. Congr. Rept 20th Sess, p 360.

CHOWDBURY, M.K.R. and BOSE, B.B. (1970). Role of 'humus matter' in the formation of geochemical anomalies. 3rd Int. Geochem. Expl. Symp., Toronto.

CLARK, O.M. Jnr (1953). Geochemical prospecting for copper at Ray, Arizona. Econ. Geol. 48, 39-45.

CLARKE, O.M. (1957). Geochemical prospecting for copper at Ray, Arizona. Geochimica et Cosmochimica Acta 12, 39.

CLARKE, O.M. (1970). Geochemical prospecting in laterite soils of Alabama. 3rd Int. Geochem. Expl. Symp., Toronto.

CLEAVES, E.T. et al. (1970). Geochemical balance of a small watershed and its geomorphic implications. Bull. Geol. Soc. Amer. 81, 3015.

CLEWS, D.R. (1968). Geochemistry, present and future. Can. Min. Jour. 89 (4), 110-113.

COALDRAKE, J.E. (1951). Ecology of part of the Ninety-mile Plain, South Australia. CSIRO Bulletin 266, Melbourne.

COLE, M. (1970). The importance of environment in biogeographical, geobotanical and biogeochemical investigations. 3rd Int. Geochem. Expl. Symp., Toronto.

COLE, M.M. et al. (1968). Geobotany, Biogeochemistry and Geochemistry in mineral exploration in the Bulman-Waimuna Springs area, Northern Territory, Australia. Trans. Inst. Min. Metall. 77, B81-104.

COLEMAN, R.G. and DELAVAUX, M. (1957). Occurrence of selenium in sulphides from some sedimentary rocks of the Western United States. Econ. Geol. 52, 499-527.

COLLENETTE, P. and BRYANT, R.N. (1968). Geochemical prospecting in the Buri area, West Sarawak. Bull. geol. Surv. Borneo, Reg. Malaysia J, Kuching, 74-79.

CONNOR, J.J. and MIESCH, A.T. (1964). Analysis of geochemical prospecting data from the Rocky Range, Beaver County, Utah. US Geol. Survey, Prof. Paper 475-D, 136.

COOPE, J.A. and WEBB, J.S. (1964). Copper in stream sediments near disseminated copper mineralisation, Cebu, Philippine Republic. Trans. Inst. Min. Metall. (London) 12, 397-406.

COOPER, J.R. and HUFF, L.C. (1951). Geological investigations and geochemical prospecting experiment at Johnson, Arizona. Econ. Geol. 46, 731-756.

COOPER, R.A. et al. (1965). A geochemical reconnaissance survey of part of the Labuk Valley, Sabah, Malaysia, Borneo region. Geol. Surv. Ann. Rept 1964, 176-185.

CORBETT, D.W.P. (1960). Geochemical prospecting in the Katherine-Darwin region, NT. BMR Record 1960/72.

CORNWALL, F.W.D. (1969). Discovery and exploration of the Fitula copper district, Nchanga area, Zambia. Ninth Comm. Min. Metall. Congress, Min. and Pet. Geol. Sec. Paper 21, 26 pp.

CROCKER, R.L. (1946). Post Miocene climatic and geologic history and significance in relation to the genesis of major soil types of South Australia. C of Aust. CSIRO Full 1946, 193.

CROHN, P.W. et al. (1959). The geology of the Tennant Creek gold and copper field. BMR Record 1959/49.

CROHN, P.W. et al. (1967). The Woodcutters L5 prospect, Rum Jungle area, NT. BMR Record 1967/154.

CRONAN, D.S. (1969). Average abundance of manganese, iron, nickel, cobalt, copper, lead, molybdenum, vanadium, chromium, titanium and phosphorus. Geochim. Cosmochim. Acta 33 (12), 1562-5 (Eng).

DAS SARMA, B. and CHOWDHURY, A.N. (1966). Experimental study on the formation of geochemical anomaly. Indian Miner. 20 (1), 26-31.

DAVLETGALIEVA, K.M. and DIVEEV, I.G. (1969). Hydrogeochemical prospecting indexes of Mugodzhar and little Kara-Tau minerals. Tr. Inst. Gidrogeol. Gidrofiz., Akad. Nauk Kaz. SSR 3, 86-100 (Russ).

DEBNAM, A.H. (1954). Geochemical prospecting at Mt Isa, Queensland. Bull. Inst. Min. Metall. No.568 (6), 269-283.

DEBNAM, A.H. (1955). Biogeochemical prospecting investigations in the Northern Territory, 1954. BMR Record 1955/43.

DEBNAM, A.H. (1956). Report on overseas trip January - April 1956. BMR Record 1956/156.

DEBNAM, A.H. (1956). Geochemical prospecting for lead at Namoona, NT (abs). Int. Geol. Congr. Rept 20th Sess., p 36.

DE GEOFFROY, J. (1969). Geochemical prospecting by spring sampling in the southwest Wisconsin zinc-mining area. Wis., Geol. Natur. Hist. Surv., Inform. Circ. 10, 28 pp.

DE GEOFFROY, J. et al. (1967). Geochemical coverage by spring sampling method in the southwest Wisconsin zinc area. Econ. Geol. 62 (5), 679-97.

DE GEOFFROY, J. and WIGNALL, T.K. (1970). Application of statistical decision techniques to the selection of prospecting area and drilling targets in regional exploration. Canadian Inst. Min. Metall. Bull. 73, 196-202.

DE GRYS, A. (1961). Copper, lead and zinc in rivers draining Chilean Andes. Econ. Geol. 56, 1456-64.

DE GRYS, A. (1964). Copper distribution patterns in soils and drainage in central Chile. Econ. Geol. 59, 636-46.

DERPGOLITS, V.F. (1962). Geochemistry of sub-surface (mine) waters and atmospheric precipitations in the Enisei Region of the Arctic. Dokl. Nauk. SSSR 147, 469-470.

DE WEISSE, G. (1967). Sur la presence de nickel dans un gisement de bauxite pres de Megare. Mineralium Deposita 2, 349-56.

DIJKSTRA, S. and BOT, A.C.W.C. (1968). Geochemical investigation in an area with low anomaly contrast in S. Limburg (Netherlands). Geol. Mjnbonw 47 (6), 401-468.

DOBRITSKAYA, Yu.I. et al. (1963). The content of zinc, copper, cobalt and molybdenum in some soils of the European part of the USSR. Mikroelementy v. Selisk. Khoz. i Med., Ukr. Nauchn.-Issled. Inst. Fiziol. Rast. Akad. Nauk. Ukr. SSR, Materialy 4-go Vses. Soveshch., Kiev 1962 391-7.

DODSON, R.G. and SHATWELL, D.O. (1965). Geochemical and radiometric survey, Rum Jungle, NT, 1964. BMR Record 1965/254.

DOLUKHANOVA, N.I. (1957). The application of hydrochemical surveys to copper and molybdenum deposits in the Armenian SSR. Akad. Nauk Armyanskoy SSR (Yerevan), 90 pp (Russ); (Partial English translation in Int. Geol. Rev., 2, 20-42, 1960).

DONOVAN, P.R. (1969). Geochemical prospecting at Cobar, NSW. Lecture to ANZAAS section C, Adelaide (unpublished).

DONOVAN, P.R. and JAMES, C.H. (1967). Geochemical dispersion in glacial overburden over the Tynagh (Northgate) base metal deposit, west-central Eire. Can., Dep. Energy, Mines Resour., Geol. Surv. Can., Pap. No. 66-54, 89-110.

DORFMAN, M.D. (1958). Geochemical characteristics of weathering processes in nepheline syenites of Khibina Tundra. Geochemistry 537.

DOUGLAS, J.S. (1968). Geobotany: a valuable aid in prospecting and mining. Mining Mag. 118 (2), 93-95.

DOW, D.B. and DEKKEN, F.G. (1964). The geology of the Bismark Mountain, New Guinea. Aust. Bur. Miner. Resour., Geol. Geophys. Rep. 76, 1-45.

DOWSETT, J.S. and REID, N.T. (1967). An exploration programme for nickel and copper in the differentiated intrusives of E. Griqualand and Pondoland. Trans. Geol. Soc. S. Af. 70, 67-79.

DREIMANIS, A. (1958). Tracing ore boulders as a prospecting method in Canada. Trans. Canadian Inst. Min. Metall. 61, 49-56.

DREIMANIS, A. (1960). Geochemical prospecting for Cu, Pb and Zn in glaciated areas, eastern Canada. Int. Geol. Congr. Rept 21st Sess, Pt II, 7-19.

DREWES, H. (1967). A geochemical anomaly of base metals and silver in the southern Santa Rita Mountains, Santa Cruz County, Arizona. US Geol. Survey Prof. Paper 575-D, 176-182.

DREWES, H. (1970). Structural control of geochemical anomalies in the Greaterville mining district, SE of Tucson, Arizona. US Geol. Survey Bull. 1312-A.

DURUM, W.H. and HAFFTY, J. (1963). Implications of the minor element content of some major streams of the world. Geochim. et Cosmochim. Acta. 27, 1-11.

DUTT, G.N. (1960). Geochemical prospecting for nickel ores at Kwatha and Nampesha-Humine area. Manipur State. Indian Minerals 14, 246-58.

DZHURKO, M.S. (1960). Content of certain trace elements in soils of the Kostroma Region. Sb. Nauchn.-Issled. Rabot Kostromsk. Sel'skokhoz. Inst. "Karaveavo" Kostroma, 115-119.

EAKINS, P.R. (1956). Geochemical prospecting for porphyry copper deposits in southern Peru (abs). Int. Geol. Congr. Rept 20th Sess.

EAKINS, G.R. (1968). A geochemical investigation of the Wood River-Tikchik Lakes Area, SW Alaska. Alaska, State Rep. Natur. Resourc. Div. Mines. Miner. Geochem. Rep. No.17, 1-31.

EDEL'SHTEIN, I.I. (1960). Geochemistry of nickel. Geokhimiya 601-9.

EDEL'SHTEIN, I.I. (1965). Oxide type of supergene nickel mineralisation. Akad. Nauk Doklady NS 165 (2), 918-920.

ELGABALY, M.M. (1950). Mechanism of Zn fixation by colloidal clays and related minerals. Soil Sci. 69, 167-173.

ELINSON, M.M. et al. (1970). Gas haloes around copper molybdenum orebodies. Ocherki Geokhim. Rtuti Molibdena Sery Gidroterm. Protserse 217-36 (Russ).

ELISEEV, E.N. (1961). The geochemistry of nickel. Trudy Lab. Geol. Dokembriya, Akad. Nauk SSSR 297-325.

ELLIS, A.J. et al. (1967). Application of solution experiments in geochemical prospecting. Trans. Inst. Min. Metall. (London) 76, B25-39.

ELLIS, M.W. and McGREGOR, J.A. (1967). The Kalengwa copper deposit in northwestern Zambia. Econ. Geol. 62, 781-797.

EL SHAZLY, E.M. et al. (1970). The use of acacia trees in biogeochemical prospecting. 3rd Int. Geochem. Expl. Symp., Toronto.

EMSLIE, R.F. and MOORE, J.M. (1961). Geological studies of the area between Lynn Lake and Fraser Lake. Granville Lake Mining Division, Manitoba. Dept. Mines and Nat. Resources Pub. 59-4.

ENGEL, A.E.J. and ENGEL, C.G. (1956). Distribution of copper, lead and zinc in hydrothermal dolomites associated with sulfide ore in the Leadville limestone (abs). Bull. Geol. Soc. Amer. 67, 1692.

ENGEL, E.A.J. et al. (1956). Variations in the Isotopic Composition of oxygen in the Leadville limestone (Mississippian) of Colorado as a guide to the location and origin of its mineral deposits. Int. Geol. Congr. Rept 20th Sess, Pt 3, 3.

ERICKSON, R.L. (1969). US geological survey programme in geochemical exploration research. Quart. Colo. Sch. Mines 64 (1), 237-244.

ERICKSON, R.L. and MARRANZINO, A.P. (1960). Geochemical prospecting for copper in the Rocky Range, Beaver County, Utah. Geol. Surv. Research 1960. US Geol. Survey Prof. Paper 400-B, 98-101.

ERICKSON, R.L. et al. (1966). Geochemical reconnaissance in the Pequoy Mountains and Wood Hills, Elko County, Nevada. US Geol. Survey Bull. 1198-E.

ERIKSON, J.E. (1953-8). Geochemical Prospecting Abstracts July 52 - December 54. US Geol. Survey Bull. 999-1002.

ERMENGEN, S.V. (1957). Geochemical prospecting in Chibougamau. Canadian Mining Journal 78 (4), 99-104.

ERNST, Th. and HORMANN, H. (1936). Nachr. Ges. Wiss. Gottingen, math-phys. Kl. Fachgr. iv, No.16 (quoted in Goldschmidt, 1954).

FAIRBURN, W.A. (1966). The Serle-Angepena Area. First Geochemical Report. SADM Mining Review, No.126, 33-47.

FAIRBURN, W.A. (1967). Geochemical and geological investigation of the Serle-Angepena Area, Mt Coffin diapir. SADM Mining Review No.127, 47-60.

FAIRBURN, W.A. (1968). A preliminary geochemical survey in the Yudnamutana area. SADM Mining Review No.128, 54-63.

FAIRBURN, W.A. (1968). Geochemical investigation ot the Burr Diapir-Nichols Nob anomaly. SADM Mining Review No.128, 104-113.

FINNELL, T.L. et al. (1963). Geology, ore deposits and exploratory drilling in the Deer Flat area, San Juan County, Utah. US Geol. Survey Bull. 1132.

FISHER, N.H. (1970). Recent research in geochemical prospecting in Australia. BMR Record 1970/14.

FISHER, R.B. and DRESSEL, W.M. (1959). The Nicaro (Cuba) ores. US Dept. Int. Bur. Mines Rept of Invest. 5496.

FLEISCHER, M. (Ed.) (1963). Data of geochemistry. US Geol. Survey Prof. Paper 440.

FORTESCUE, J.A.C. (1967). Research programme for examination of scope of geobotanical and biogeochemical prospecting in Canada. Geol. Survey Canada Paper 66-61, 32-35.

FORTESCUE, J.A.C. (1967). The role of geochemistry in exploration architecture. Canadian Min. Metall. Bull. Jour. 50-53.

FORTESCUE, J.A.C. (1968). A small-scale stream-sediment geochemical survey in the Moose River area. In "A preliminary study of the Moose River belt, northern Ontario". Geol. Survey Canada Paper 67-38, 45-48.

FORTESCUE, J.A.C. and HUGHES, O.L. (1965). Copper, zinc, nickel and lead in lower till material collected near a massive sulphide orebody in the clay belt of northern Ontario. Geol. Surv. Canada Paper 65-2, 23-27.

FREDRIKSSON, K. and LINDGREN, I. (1967). Anomalous copper content in glacial drift and plants in a copper-mineralised area of the Caledonides (Sweden). "Kvalheim Volume" 193-202.

FRIEDRICH, G.A. and HAWKES, H.E. (1966). Mercury as an ore guide in the Pachucha Real del Monte District, Hidalgo, Mexico. Econ. Geol. 61, 744-753.

FRIEV, T.A. (1960). Zinc content of soils in the Chuya Valley. Byul. Kirgizsk. Nauch.-Issled. Inst. Zemledeliya 5, 67-71.

FULTON, R.B. (1950). Prospecting for zinc using semiquantitative analyses of soils. Econ. Geol. 45, 654-670.

FULTON, R.B. et al. (1958). Frequency distribution of zinc-lead-copper values in soils of eastern United States. Int. Geol. Congr. Rept 20th Sess., 81-97.

FURSOV, U.Z. (1958). Haloes of dispersed mercury as prospecting guide at the Achisai lead-zinc deposits. Geochemistry 1, 338-344.

GAEV, A.Ya. (1969). Geochemical barriers. Sb. Nauch. Tr., Perm. Politekh. Inst. No.48, 165-71 (Russ).

GAINUDINOVA, F.Kh. and KRUGLOVA, E.K. (1962). Copper and its forms in the irrigated soils of the Fergana Valley. Uzbeksk. Khim. Zh. 6, 23-7.

GARDNER, W.R. and BROOKS, R.H. (1957). A descriptive theory of leaching. Soil Sci. 83, 295-304.

GARLICK, W.G. (1954). Reflection on prospecting and ore genesis in northern Rhodesia. Trans. Inst. Min. Metall. 63, 9-20.

GARRELS, R.M. (1944). Solubility of metal sulphides in dilute vein-forming solutions. Econ. Geol. 39, 472-483.

GARRELS, R.M. (1954). Mineral species and functions of pH and oxidation-reduction potentials, with special reference to the zone of oxidation and secondary enrichment of sulphide ore deposits. Geochim. et Cosmochim. Acta 5, 153-168.

GARRELS, R.M. and CHRIST, C.L. (1965). Solutions, minerals and equilibria. Harper and Row, New York, 450 pp.

GARRETT, R.G. (1970). The dispersion of copper and zinc in glacial overburden at the Louvem deposit, Val d'Or, Quebec. 3rd Int. Geochem. Expl. Symp., Toronto.

GARRETT, R.G. and NICHOL, I. (1969). Factor analysis as an aid in the interpretation of regional stream sediment data. Quart. Colorado Sch. Mines 64 (1), 245-264.

GAVRILIN, R.D. et al. (1967). Behaviour of lead and zinc in the hydrothermal alteration of intrusive rocks. Geochem. Int. 4 (4), 790-799.

GERMANOV, A.I. (1956). On the possible hydrogeochemical cause of the development of leached horizons. Geochemistry No.7.

GERMANOV, A.I. and PANTELEYEV, V.M. (1968). Behaviour of organic matter in groundwater during infiltrational epigenesis. Int. Geol. Review 10 (7), 826.

GERMANOV, A.I. et al. (1970). Geochemistry of supergene migration of copper in the Dzhezkazgan ore field. Geokhimiya 3, 358-63 (Russ).

GHOSH, A.K. (1968). Quantitative analysis of polymetallic orebody zoning at Rangpo, Sikkim. Econ. Geol. 63, 682-687.

GILBERT, R.E. (1951). Geochemical prospecting in the Park City district. Min. Congr. Jour. 37 (9), 58-61.

GILES, J.B. (1960). Trace element profiles of some ground water rendzina and terra rossa soils from County Grey, SE, South Australia. CSIRO Soils Division, Adelaide, Divisional Report 9160.

GILES, J.B. (1968). Total concentrations of Co (sic), Cu, Fe, Mn, Mo, Ni, V, Zn and Zr in surface soil samples from 78 sites in SE South Australia and Western Victoria. CSIRO Division of Soils, Adelaide, Technical Memorandum 27/1968.

GINZBURG, I.I. and KORIN, I.Z. (1951). Problems of mining geology in the exploration of nickel deposits connected with the weathering crust. Gorngi Zhur. 125 (5), 7-10.

GLAZOVSKAYA, M.A. (1964). Biological cycle of elements in various landscape zones of the Urals. Fiz., Khim. Biol. i Mineralog. Pochr. SSSR. Akad Nauk. SSSR Dokl. k VIII-mu (Vos'monun) Mezhdunar, Kongr. Pochvovedov, Bucharest 148-157.

GLEESON, C.F. (1966). The distribution and behaviour of metals in stream sediments and waters of the Keno Hill area, Yukon. Canada Geol. Survey Paper 66-54.

GLINSKI, J. (1967). Effects of some soil-forming factors on the content and distribution of trace elements in soil profiles. I. Dependence of copper and manganese contents on local relief. Ann. Univ. Mariae Curie-Sklodowska, Sec. E 22, 21-35 (Pol).

GLOVER, R.E. (1964). Dispersion of dissolved or suspended materials in flowing streams. US Geol. Survey Prof. Paper 433-B, 32 pp.

GOLDSCHMIDT, V.M. (1954). Geochemistry (Ed. A. Muir). Clarendon Press, London, 730 pp.

GOLEVA, G.A. (1964). Formation of hydrous dispersion halo over blind copper pyrite deposits in the southern Urals. Tr. Vses Nauchn.-Issled. Inst. Gidrogeol i Inzh Geol 9, 21-39; (Russ).

GOLEVA, G.A. and LUSHNIKOV, V.V. (1967). Occurrence of selenium in the ground waters of ore deposits and in some types of mineral waters. Geochem. Int. 4, 378-385.

GOLEVA, G.A. and VOROB'YEVA, I.N. (1967). The migration of germanium in the ground waters of ore deposits. Geochem. Int. 4, 809-817.

GOLEVA, G.A. et al. (1968). Occurrence and migration forms of copper in groundwaters. Geochem. Int. 5, 496.

GOLEVA, G.A. et al. (1970). Distribution and migration of lead in ground waters. Geochem. Int. 7, 256-268.

GOLEVA, R.V. (1963). Prospecting for lead/zinc deposits in sedimentary rocks of the Northern Ossetia (Northern Caucasus). Geol. Rudn. Mestorozhd 5 (6), 87-92 (Russ).

GOLOBOV, A.D. (1952). A nickel enriched biogeochemical province in the southern Urals. Byull. Moskov. Obshchestva Ispytatel Prirody, Otdel. Biol. 57 (3), 3-4 (Russ).

GOLUBEV, V.S. (1968). Diffusional theory of formation of secondary dispersion haloes in ore deposits. Int. Geol. Review 10, 1103-1107.

GONCALVES, G.N.D. et al. (1968). Prospecting for occurrence of copper in Fazenda Matinos, Bahia, Brazil. Mineracao, Met. 48 (286), 159-62 (Port).

GOTT, G.B. and ZABLOCKI, C.J. (1968). Geochemical and geophysical anomalies in the western part of the Sheep Creek range, Lander County, Nevada. US Geol. Survey Circular 595, 17 pp.

GOVETT, G.J.S. (1960). Geochemical prospecting for copper in Northern Rhodesia. Int. Geol. Congr. Rept 21st Sess. 44-56.

GOVETT, G.J.S. and BROWN, W.W. (1968). Geochemical prospecting. Philippines Bureau of Mines R I, 66.

GOVETT, G.J.S. and HALE, W.E. (1967). Geochemical orientation and exploration near a disseminated copper deposit, Luzon, Philippines. Trans. Inst. Min. Metall. 76, B190-B201.

GOVETT, G.J.S. et al. (1967). Geochemical prospecting by determination of cold-extractable copper in stream silt and soil. Philipp. Geologist 21 (1), 41-60.

GREEN, J. (1959). Geochemical table of the elements for 1959. Bull. Geol. Soc. Amer. 70, 1127-1184.

GRIFFITTS, W.R. and ALMINAS, H.V. (1968). Geochemical evidence for possible concealed mineral deposits near the Monticello Box, Northern Sierra Cuchillo, Socorro County, New Mexico. US Geol. Survey Circular 600, 13 pp.

GRIFFITTS, W.R. and NAKAGAWA, H.M. (1960). Variations in base-metal contents of monzonitic intrusives. US Geol. Survey Prof. Paper 400B, B93-B95.

GRIGORYAN, L.A. et al. (1968). Topographic-geochemical mapping during geochemical prospecting from secondary dispersion haloes. Izv. Akad. Nauk Arm. SSR, Nauki Zemle 21 (5), 66-79 (Russ).

GRIMME, H. (1967). Fractional extraction of soil copper. Z. Pflanzenernaehr. Dueng. Bodenk. 116 (3), 207-22.

GRIP, E. (1953). Tracing of glacial boulders as an aid to ore prospecting in Sweden. Econ. Geol. 48, 715-725.

GREGORY, P. and TOOMS, J.S. (1969). Geochemical prospecting for kimberlites. Quart. Colorado Sch. Mines 64, 265-305.

GUCKER, F.T. and GARRELS, R.M. (1949). Activity coefficients and dissociation of lead chlorite in aqueous solutions. Chem. Rev. 44, 117-134.

HABASHI, F. (1966). The mechanism of oxidation of sulphide ores in nature. Econ. Geol. 61, 587-591.

HALDON, A.D. (1965). Geochemical prospecting at McArthur River, NT. BMR Record 1965/158.

HAMMETT, F.S. (1928). Studies in the biology of Metals. I The localisation of lead by growing roots. Protoplasma 4, 183-186.

HANSULD, J.A. (1966). Eh and pH in geochemical exploration. Can. Mining and Metall. Bull. 647, 77-84.

HARBAUGH, J.W. (1950). Biogeochemical investigations in the Tri-State district. Econ. Geol. 45, 548.

HARBAUGH, J.W. (1953). Geochemical prospecting abstracts through June 1952. US Geol. Survey Bull. 1000-A, 1-50.

HARDING, R.R. (1965). Geochemical investigation of aeromagnetic ridge, Tennant Creek. BMR Record 1965/27.

HARDING, R.R. and DUNNETT, D. (1965). Geochemical sampling of the Golden Mile and Jubilee area, Tennant Creek, NT. BRM Record 1965/143.

HARGREAVES, A.J. (1948). Geochemical sampling at Wallaroo-Moonta. SADM Mining Review 88, 64-71.

HAWKES, H.E. (1948). Annotated bibliography of papers on geochemical prospecting for ores. US Geol. Survey Circular 28.

HAWKES, H.E. (1949). Geochemical prospecting for ores; a progress report. Econ. Geol. 44, 706.

HAWKES, H.E. (1950). Geochemical prospecting for ores. Trask P.D. (ed). In "Applied Sedimentation." Wiley, New York.

HAWKES, H.E. (1957). Principles of geochemical prospecting. US Geol. Survey Bull. 1000-F, D225-355.

HAWKES, H.E. (1958). Geochemical prospecting in the Nyeba lead-zinc district, Nigeria. US Geol. Survey Bull. 999-1002, 51.

HAWKES, H.E. (1970). Recent articles on geochemical prospecting 1965-1969. 3rd Int. Geochem. Expl. Symp., Toronto.

HAWKES, H.E. and BLOOM, H. (1956). Heavy metals in stream sediments used as exploration guides. Mining Eng. 8, 1121-1127.

HAWKES, H.E. and LAKIN, H.W. (1949). Vestigial zinc in surface residuum associated with primary zinc ore in east Tennessee. Econ. Geol. 44, 286-295.

HAWKES, H.E. and SALMON, M.L. (1960). Trace elements in organic soil as a guide to copper ore. Int. Geol. Congr. Rept 21st Sess. 38-43.

HAWKES, H.E. and WEBB, J.S. (1962). Geochemistry in mineral exploration. Harper and Row, New York; 415 pp.

HAWKES, H.E. et al. (1957). Stream sediment analysis discovers two mineral deposits. Sixth Commonwealth Mining Metallurgy Congr. 259-268.

HAYASHI, H. (1961). Geochemical cycles of nickel and cobalt. Nagoya Kogyo Gijutsu Shikensho Hokoku 10, 837-48 (Jap).

HEIDENREICH, W.L. and REYNOLDS, B.M. (1959). Nickel-cobalt-iron bearing deposits in Puerto Rico. US Dept Int. Bur. Mines Report Invest.5532.

HIEMSTRA, S.A. (1969). The geochemistry of the uraniferous conglomerate of the Dominion Reefs Mine, Klerksdorp area. Trans. Geol. Soc. S. Afr. (Pub. in Trans. Proc. Geol. Soc. 71, 67-100. (Eng).

HEM, J.D. (1950). Geochemistry of ground water. Econ. Geol. 45, 72.

HENKENS, Ch.H. (1962). Vertical migration of copper in soils. Landbollusk Tijdschr. 74 16-23 (Dutch).

HERMAN, L.D. (1958). Geochemical zonations in the Blyava deposit on the western slope of the Southern Urals. Geochemistry 430.

HERREID, G. (1968). Geological and geochemical investigations south of Farewell, Alaska. Alask. Div. Mines Miner. Geol. Rept No.26, 1-23.

HERREID, G. (1968). Geology and geochemistry of the Sinak area, Seward Peninsula, Alaska. Alaska Div. Mines Miner. Geol. Rept No.29, 1-13.

HEVESY, G. et al. (1931). Lead content of rocks. Nature 128, 1038.

HILL, V.G. (1961). Geochemical prospecting for nickel in the Blue Mountain Area, Jamaica, West Indies. Econ. Geol. 56, 1025-32.

HOLMAN, R.H.C. (1956). Dispersion of copper in the drainage system. Part I of Geochemical prospecting studies in the Kilembe area, Uganda. Imp. Coll. Sci. Technol. Geochem. Prosp. Research Centre, Tech. Comm. No.9, 136 pp.

HOLMAN, R.H.C. (1963). Copper in bedrock. Canada Dept Mines, Tech. Surv. Geol. Surv. Can. Geol. Surv. Maps 50-1963-56.

HOLMES, R.S. (1943). Copper and zinc contents of certain United States' soils. Soil Sci. 56, 359.

HORN, M.K. and ADAMS, J.A.S. (1966). Computer-derived geochemical balances plus element abundances. Geochim et Cosmochim Acta 30, 279-298.

HORNBROOK, E.H.W. (1967). Biogeochemical prospecting research. Geol. Survey Canada Paper 67-68, Part A, 61.

HORNBROOK, E.H.W. (1967). Biogeochemical prospecting methods. Geol. Survey Canada Paper 67-1, Part B, 22.

HORNBROOK, E.H.W. (1969). Pilot project at the Silvermin lead deposit, Cape Breton Island, Nova Scotia. Geol. Survey Canada Paper 67-23, 65-94.

HORNBROOK, E.H.W. (1970). Biochemical investigations in the Perch Lake area, Chalk River, Ontario. Geol. Survey Canada Paper 70-43.

HORNBROOK, E.H.W. (1970). Effectiveness of geochemical and biogeochemical exploration methods in the Cobalt area, Ontario. 3rd Int. Geochem. Expl. Symp., Toronto.

HORNBROOK, E.H.W. et al. (1970). Biogeochemical prospecting for copper in west-central British Columbia. Geol. Surv. Canada Paper 69-49; 39 pp.

HORNE, R.G. (1968). Geochemical orientation survey, Wau, New Guinea. BMR Records 1968/133.

HORSNAIL, R.F. and ELLIOTT, I.L. (1970). Some environmental influences on the secondary dispersion of molybdenum and copper in western Canada. 3rd Int. Geochem. Expl. Conf., Toronto.

HORSNAIL, R.F. et al. (1969). Influence of variations in secondary environment on the metal content of drainage sediments. Quart. Colorado Sch. Mines 64, 307.

HOSKING, K.F.G. (1959). Applied geochemistry: Studies in Cornwall. Trans. Roy. Soc. Cornwall 19, 52-83.

HOSKING, K.F.G. and OBIAL, R. (1966). A preliminary study of the distribution of certain metals of economic interest in the sediments and waters of the Carrick Roads (W. Cornwall) and of its "feeder" rivers. Camborne Sch. of Mines Mag. 66, 17-37.

HOSKING, K.F.G. et al. (1964). The distribution of tin, copper, zinc, beryllium and phosphorus in the stream sediments of the Land's End Peninsula, Cornwall. Camborne Sch. of Mines Mag. 64, 15-32.

HOTZ, P.E. (1964). Nickeliferous laterites in southwestern Oregon and northwestern California. Econ. Geo. 59, 355-396.

HUFF, L.C. (1952). Abnormal copper, lead and zinc content of soil near metalliferous veins. Econ. Geol. 47, 517-542.

HUFF, L.C. (1955). Preliminary geochemical studies in the Capitol Reef area Wayne County, Utah. US Geol. Survey Bull. 1015-H, 247-256.

HUFF, L.C. (1955). A Paleozoic geochemical anomaly near Jerome, Arizona. US Geol. Survey Bull. 1000-C, 105-118.

HUFF, L.C. (1956). Comparison of soil analysis with other prospecting methods at a small, high-grade copper lode (abs). Int. Geol. Congr. Rept 20th Sess, 364.

HUFF, L.C. (1963). Comparison of prospecting methods at the Malachite mine Jefferson County, Colorada. US Geol. Survey Bull. 1089-C, 161-179.

HUFF, L.C. (1970). A geochemical study of alluvium covered copper deposits in Pima County, Arizona. US Geol. Survey Bull. 1312-C, 31 pp.

HUFF, L.C. (1970). A comparison of alluvial exploration techniques for copper deposits. 3rd Int. Geochem. Expl. Symp., Toronto.

HUFF, L.C. and MARRANZINO, A.P. (1961). Geochemical prospecting for copper deposits hidden beneath alluvium in the Pima District, Arizona. US Geol. Survey Research 308-310.

HUGHES, T.D. (1957). Nickel near Beaconsfield (Tas). Tas. Dept Mines Tech. Rept 1, 19-22.

HULSBOS, W.C. and BOUMANS, J.H. (1960). Leaching of saline soils in Iraq. Neth. J. Agric. Sci. 8, 1-10.

HYRARINEN, L. (1967). Geochemical prospecting for lead ores at Korsnas (Finland). "Kvalheim Volume" 171-180.

IVANAC, J.F. and BRANAGAN, D.F. (1960). A case history of geochemistry and prospecting in north-west Queensland. Proc. Aust. Inst. Min. Metall. 195, 25-35.

IVANAC, J.F. and LANGRON, W. (1968). Discovery of silver-lead-zinc mineralisation at Woodcutters. Australian Mining 60, 62-69.

IVANAC, J.F. and MARSHALL, N.J. (1965). Geochemical sampling Michelago area, NSW. BMR Records 1965/204.

IVANOV, L.B. et al. (1966). Endogenic dispersion haloes in the Batystan orefields. Izv. Akad. Nauk Kaz SSSR Ser. Geol. 23, 70-74.

JENNE, E.A. (1968). Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water. In "Trace inorganics in water." Am. Chem. Symposium, Washington, DC. Am. Chem. Soc. (Adv. Chemistry Ser. 73) 337-387.

JENNY, H. (1941). Factors of soil formation. McGraw Hill, New York.

JEROME, S.E. (1963). Some features pertinent in exploration of porphyry copper deposits. Western Miner and Oil Review Feb. 28-37.

JESSUP, R.W. (1960). The lateritic soils of the south-eastern portion of the Australian arid zone. Jour. of Soil Sci. 11, 106-113.

JOHNSON, D.H. et al. (1970). Geochemical investigations of base metal occurrences in western Liberia. 3rd Int. Geochem. Expl. Symp., Toronto.

JOHNSON, J.E. (1964). Geochemical lead anomaly, Sellick Hill, SA. SADM Mining Review 116 (for 1962), 23-27.

JONASSON, I.R. (1970). Mercury in the natural environment. Geol. Survey Canada Pap. 70-57, 39 pp.

KALMET, R. (1964). Trace elements for the fields of Estonia. Zemledelie 9, 72-5.

KAPRANOV, S.D. (1969). Interpretation of the results of hydrogeochemical exploration surveys. Izv. Vyssh. Uchev. Zaved., Geol. Razved. 12 (4), 82-7 (Russ).

KARAMATA, S. (1969). Geochemical prospecting of ore deposits in Yugoslavia. History and some examples. Berg. Huettenmaenn. Monatsh. 114 (12) 453-9 (Ger).

KASHIRTSEVA, M.F. (1959). Experimental data on sorption of copper by various minerals and organic sorbing agents. Sovetskaya Geologiya No.5, 131-141 (Int. Geol. Review 1959, 52-59; Eng).

KEITH, J.R. (1969). Relationships of lead and zinc contents of trees and soils, Upper Mississippi Valley District. Am. Inst. Min. Engrs 244, 353-6.

KELLY, W.C. et al. (1958). Progress in studies on leached outcrops. Bull. Geol. Soc. Amer. 69.

KENNEDY, V.C. (1952). Geochemical studies in the Coeur d'Alene mining district, Idaho. US Geol. Survey Circular 168.

KENNEDY, V.C. (1956). Geochemical studies in the southwestern Wisconsin zinc-lead area. US Geol. Survey Bull. 1000-E, 187-223.

KETNER, K.B. et al. (1968). Geochemical anomalies in the Swales Mountain area, Elko County, Nevada. US Geol. Survey Circular 588, 13 pp.

KHOLNOV, G.V. (1958). Geological foundations for prospecting of sulphide copper-nickel deposits based on their genesis. Sbornik Tekh. Inform. Prockt. i Nauch.-Issled. Inst. Gipronikel (4-5), 23-31.

KILPATRICK, B.E. (1969). Nickel, chromium and cobalt in tropical soils over serpentinites, NW District, Guyana. Quart. Colorado Sch. Mines 64, 323-332.

KIRKPATRICK, I.M. (1965). A geological and geochemical survey of the western Tambani area, Blantyre district. Malawi Geol. Surv. Rec. 6 (1963), 80-99.

KLEIBER, J. (1964). The use of geochemical prospecting in the search for nickel on the east coast of Madagascar. Compt. Rend. Semaine Geol. Comite Natl. Malgache Geol. 136-140.

KLEINKOPF, M.D. (1960). Spectrographic determination of trace elements in lake waters of northern Maine. Bull. Geol. Soc. Amer. 71, 1231-1242.

KOCHENOV, A.V. and KRESHTAPOVA, V.N. (1967). Rare and dispersed elements in the peats of the northern part of the Russian platform. Geochemistry Int. 4.

KOEHLER, G.F., HOSTETLER, P.B. and HOLLAND, H.D. (1954). Geochemical prospecting at Cobalt, Ontario. Econ. Geol. 49, 378-388.

KONONOVA, R.S. (1942). Efficiency of hydrochemical and metallometric methods of prospecting. Int. Geol. Review 5, 192-196.

KOTEL'NIKOV, V.V. et al. (1965). Use of radiometric methods in prospecting for deposits of non-ferrous metals. Metod. Ukazaniya po Primeneniyu Radiometr. Metodov pri Poiskakh i Razvedke Rud Neradioaktivn. Elementov, Gos Geol. Kom. SSSR 2.

KOVALEV, V.F. (1965). Hydrochemical exploration indexes and water dispersion haloes of copper in area of the Makansk deposit in the southern Urals. Tr. Inst. Geol. Akad Nauk SSSR Ural'sk Filial 76, 277-283 (Russ).

KOVALEV, V.F. et al. (1968). Experimental use of hydrogeochemical methods for seeking minerals on the eastern and western limbs of the Turgai syncline. Gidrogeol. Sb. 5, 3-16 (Russ).

KOVDA, V.A. et al. (1968). Geochemical differentiation of products of weathering and soil formation on the Russian Great Plain. Trans., Int. Congr. Soil Sci., 9th 4, 293-301 (Eng). (Edited by Holmes, J.W., Amer. Elsevier Publ. Co., Inc., New York).

KRAINOV, S.R. (1962). Geochemical topographic factors in geochemical prospecting for lead in the Northern Armenian ore zone. Tr. Vses Nauchn-Issled. Inst. Gidrogeol. i Inzh Geol. 20, 111-120.

KRAMAR, B. (1968). Application of geothermal method for geological prospecting. Freiburg Forschungsh C. 238, 45-53 (Ger).

KRAMER, J.R. (1968). Mineral-water equilibria in silicate weathering. Int. Geol. Congr. Rept 23rd Sess 6, 149-160.

KRASOVSKII, V.F. and LUKASHEV, K.I. (1968). Mineralogical and geochemical criteria of searches for deeply buried copper-nickel sulfide ores in the Belorussian crystalline massif. Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk 5, 87-94 (Russ).

KRAUSKOPF, K.B. (1956). Factors controlling in concentrations of thirteen rare metals in sea-water. Geochim. et cosmochim. Acta 9, 1-32B.

KRAUSKOPF, K.B. (1967). Introduction to geochemistry. McGraw-Hill Inc., New York, 721 pp.

KRAYNOV, S.R. et al. (1966). Distribution and the mode of migration of trace elements Zn, Cu, Hg, Li, Rb, Cs, As and Ge. Geochem. Int. 3, 108-123.

KRITSUK, I.N. (1962). Dispersion haloes of lead and zinc over one polymetallic deposit in Eastern Transbaikal. Zap. leningr. Gorn Inst. 43, 112-21, (Russ).

KROON, T.P. and DE GRYS, A. (1970). A geochemical drainage survey in Central Ecuador. Econ. Geol. 65, 557-563.

KVALHEIM, A. (Ed.) (1967). Geochemical prospecting in Fennoscandia. "Kvalheim Volume". Interscience Publishers, New York, 350 pp.

KVYATKOVSKI, F.M. and KRITSUK, I.N. (1963). Quantitative interpretation of secondary dispersion haloes of lead. Zap. leningr. Gorn Inst. 45 (2), 3-9 (Russ).

LAKIN, H.W. and TRITES, A.R. Jnr. (1956). The behaviour of selenium in the zone of oxidation. Int. Geol. Congr. Rept 20th Sess. 1.

LAKIN, H.W. et al. (1963). Variation in minor-element content of desert varnish. US Geol. Survey Prof. Paper 475-B, 28-29.

LAPP, M.A. and SUDOV, B.A. (1963). Prospecting for deep seated orebodies and deposits by using broad dispersion haloes. Sovetskaya Geol. 6 (10), 113-119 (Russ).

LEDUC, C. and BOUCETTA, M. (1970). A study of the distribution and localisation of lead and zinc in the weathered mantle of the Granite de Fougeres, N.W. Brittany. 3rd Int. Geochem. Expl. Symp., Toronto.

LE RICHE, H.H. and WEIR, A.H. (1963). A method of studying trace elements in soil fractions. Jour. Soil Sci. 14, 225.

LE ROUX, N.W. (1966). Geochemical investigations in the Kalgoorlie and Norseman areas, Western Australia. BMR Rrecord 1966/96.

LE ROUX, N.W. (1966). Geochemical investigations in the Kalgoorlie area, Western Australia - progress report. BMR Record 1966/97.

LEUTWEIN, F. and PFEIFFER, L. (1954). The possible usefulness of geochemical prospecting methods for hydrous nickel silicate ores. Geologie 3, 950-1008 (Eng).

LEWIS, R.W. (1966). A geochemical investigation of the Caraiba deposit, Bahia, Brazil. US Geol. Survey Prof. Paper 550-C, 190-196.

LISITSYNA, N.A. (1968). Geochemistry of the weathering profile developed on basic rocks. Geokhim. Osad. Porod Rud. Mater. Vses. Litol. Konf., 7th, 5-47 (Russ).

LISTOVA, L.P. (1966). Experimental data on the solubility of lead sulphide under oxidising conditions. Geochem. Int. 3, 25-33.

LITTLE, H.W. and SMITH, A.Y. (1968). Techniques currently used in prospecting in Canada. Nucl. Tech. Miner Resour. Proc. Symp., 131-145.

LOTSPEICH, F.B. (1956). Movement of metallic elements in shallow colluvium. Int. Geol. Congr. Rept 20th Sess. 1, 125-142.

LOUNAMAA, J. (1967). Trace elements in trees and shrubs growing on different rocks in Finland. "Kvalheim Volume", 287-320.

LOUP, A. and WOODTLI, R. (1965). Two examples of geochemical prospecting in Valais, France. Bull. Soc. Vandoise Sci. Nat. 69 (318), 111-116 (French).

LOVERING, T.S. (1952). Mobility of heavy metals in ground water. Part I of Supergene and hydrothermal dispersion of heavy metals in wall rocks near ore bodies, Tintic district, Utah. Econ. Geol. 47, 685-698.

LOVERING, T.S. (1959). Significance of accumulator plants in rock weathering. Bull. Geol. Soc. Amer. 70, 781-800.

LOVERING, T.S. et al. (1948). Heavy metals in altered rock over blind ore bodies, East Tintic district, Utah. Econ. Geol. 43, 384-399.

LOVERING, T.S. et al. (1950). Dispersion of copper from the San Manuel copper deposit, Pinal County, Arizona. Econ. Geol. 45, 493-514.

LOVERING, T.S. et al. (1970). Cu in biotite from igneous rocks in southern Arizona as an ore indicator. US Geol. Survey Prof. Paper 700-B, 1-8.

LUNDEGARDH, P.H. (1949). The geochemistry of chromium, cobalt, nickel, and zinc. Sveriges Geol. Undersokn., Ser. C., Avhandl. och Uppsat., No.513; Arsbok 43 (11), 56 pp (Eng).

LYUBOFEEV, V.N. et al. (1962). A biogeochemical method. Tr. po Geol. i polezn. Iskopaemym Ser. Kavkaza, 281-7 (Russ).

McKENZIE, R.M. (1956). Trace element distribution in some South Australian red brown earths. CSIRO Division of Soils, Adelaide, Divisional Report 9/56.

McKENZIE, R.M. (1957). The distribution of trace elements in some Australian red-brown earths. Aust. J. agric. Res. 8, 246-252.

McKENZIE, R.M. (1958). The trace element status of some South Australian terra rossa and rendzina soils. CSIRO Division of Soils, Adelaide, Divisional Report 12/57.

McKENZIE, R.M. (1966a). Copper, zinc and molybdenum analyses in some Victorian soils. CSIRO Division of Soils, Adelaide, Technical Memorandum 7a/66.

McKENZIE, R.M. (1966b). The relation of laboratory analyses for copper, zinc and molybdenum in some Victorian soils to the results of field trials. Aust. J. Exp. Agr. and Animal Husb. 6, 170.

McMILLAN, N.J. and DEBNAM, A.H. (1961). Geochemical prospecting for copper in the Tennant Creek gold-field, NT. BMR Record 1961/101.

McPhar Geophysics Ltd (1956). The problem of variation in geochemical soil sample field tests. Int. Geol. Congr. Rept 20th Sess. 1, 339.

MAGAK'YAN, I.G. (1961). Ore deposits, Terevan. Int. Geol. Review 10, 72-170.

MAIOROV, N.F. (1966). Selection of moraine fractions for analyses in lithiochemical survey involved in search for copper nickel sulphide ores. Zap. Leningrad. Gorn. Inst. 51, 62-65.

MAKEEV, O.V. and SENICHKINA, M.G. (1963). Dynamics of the content of available forms of trace elements in soils in the Buryat Autonomous SSR. Mikroelementy v Sel'sk.-Khoz. i. Med. Sb. SSR 458-60.

MAKSIMOVIC, Z. et al. (1966). Geochemical prospecting for copper in the region Cavka Mountain-Teslic-Zavidovici, Bosnia. Geol. Glas. (Sarajevo) 11, 417-32 (Serb).

MAKUNINA, A.A. et al. (1962). Secondary dispersion haloes in the southern Ural copper-cobalt deposit. Vopr. Georgr. Nauchn. Sb. Mosk. Filiala. Geogr. Obshchestva SSSR 59, 53-87.

MAKUNINA, A.A. (1962). A topographical-geochemical survey in copper-pyrite deposit of the southern Urals. Vopr. Geogr. Nauchn. Sb. Mosk. Filiala Geogr. Obshchestva SSSR 59, 132-44.

MAKUNINA, A.A. (1962). Certain results of landscape geochemical investigations in the vicinity of a chalcopyritic ore deposit in the southern Urals. Int. Geol. Review 6, 379-386.

MALLORY, E.C. Jnr. (1968). Spectrochemical analysis of stream waters in geochemical prospecting north-central Colorado. In "Geological Survey Research" US Geol. Survey Prof. Paper 600-B, B115-B116.

MALYUGA, D.P. (1944). On the problem of cobalt, nickel and copper content of soil. Doklady Akad. Nauk USSR 43.

MALYUGA, D.P. (1946). Geochemistry of disseminated nickel and cobalt in the biosphere. Trudy Biogeokhim. Lab., Akad. Nauk SSSR 8, 75-141.

MALYUGA, D.P. and AYVAZYAN, A.D. Biogeochemical investigations in the Rudnyy Altay.

MALYUGA, D.P. (1947). Chemical composition of soils and plants as indicators in prospecting for metals. Izvest. Akad. Nauk SSSR, Ser. Geograf. i Geofiz. 11, 135-8.

MALYUGA, D.P. (1954). Experimental application of the biogeochemical method of search for ore locations in South Ural. Akad. Nauk SSSR Biogeokhim. Lab., Trudy 10, 28-59.

MALYUGA, D.P. (1958). An experiment in biogeochemical prospecting for molybdenum in Armenia. Geochemistry 314-337.

MALYUGA, D.P. et al. (1950). Biogeochemical investigations at Kadzharan, Armenian SSR. Geochemistry 519-528.

MALYUGA, D.P. and MAKAROVA, A.I. (1956). An experiment in biogeochemical prospecting for ore deposits in Tuva. Geochemistry No.1.

MARKWARD, E.L. (1961). Geochemical prospecting abstracts January 1955 - June 1957. US Geol. Survey Bull. 1098-B.

MARMO, V. (1953). Biogeochemical investigations in Finland. Econ. Geol. 48, 211-224.

MARMO, V. (1956). On biochemical prospecting of ores. Int. Geol. Congr. Rept 20th Sess.

MARSHALL, N.J. (1967). Regional geochemical survey Ayr 1:250,000 sheet, Queensland. BMR Records 1967/129.

MARTIN, J.E. (1967). The distribution of metals in soils and stream sediments near Lyndhurst. SADM Mining Review No.126, 86-96.

MASHEV, N.P. (1965). Trace zinc in the soils of Bulgaria. Pol'nohospodarstvo 11, 136-40.

MATHER, A.L. (1964). Regional geochemical sampling methods. BMR Record 1964/57.

MATHER, A.L. (1964). Geochemical orientation survey, Astrolabe, Papua, 1964. BMR Records 1964/100.

MATHER, A.L. (1965). Regional chemical sampling methods used by the Bureau of Mineral Resources. BMR Record 1965/72.

MATHERON, G. (1956). Prospection geochimique du gisement d'Ain-Barbar (Algerie) (abs). Int. Geol. Congr. Rept 20th Sess.

MELCHER, G.C. (1956). Geochemical prospecting in the Rio Ribeira de Iguape district, Brazil (abs). Int. Geol. Congr. Rept 20th Sess.

MELENT'YEV, B.N. et al. (1965). Investigation of the solubility of sphalerite in aqueous solutions of different acidity. Doklady Akad. Nauk SSSR 161, No.3.

MENZEL, R.G. and JACKSON, M.L. (1950). Sorption of copper from acid systems by kaolinite and montmorillonite. Trans. Int. Congr. Soil Sci. Amsterdam 1.

MIESCH, A.T. and CONNOR, J.J. (1964). Investigation of sampling-error effects in geochemical prospecting. US Geol. Survey Prof. Paper 475-D, D84-D88.

MILLAR, C.E. et al. (1958). Fundamentals of soil science. J. Wiley and Sons Inc., New York.

MILLER, C.P. (1957). Geochemical and biogeochemical prospecting for nickel. Unpublished PhD thesis, Stanford University, 166 pp.

MILLER, C.P. (1961). Plant and soil prospecting for nickel. Trans. Am. Inst. Min. Metal. Eng. 220, 255-260.

MILLMAN, A.P. (1957). Biogeochemical investigations in areas of copper-tin mineralisation in southwest England. Geochim. et Cosmochim. Acta 12, 85-93.

MIRAMS, R.C. (1962). Investigation of Dawesley aeromagnetic anomaly. SADM Mining Review 116, 10-13 (pub. 1964).

MIRANDA, F.E. and GARCIA, M.V. (1968). Geological-geochemical investigation of the zinc-lead-copper prospect in Palanas, Kawit, Ayala District, Zamboanga City. Philipp. Geol. (Manila) 22 (3), 133-47.

MISSAGHI, F. (1968). Geochemical anomalies in the Philmont Range region, New Mexico. N. Mex., Bur. Mines Miner. Resour., Circ. 92, 1-12.

MISSAGHI, F. (1968). Geochemical and biogeochemical studies in the Eagle Nest Quadrangle, New Mexico. New Mexico Bur. Mines Miner. Resour. Circ. 94, 1-24.

MITCHAM, T.W. (1952). Indicator minerals, Coeur d'Alene silver belt. Econ. Geol. 47, 414-450.

MITCHELL, R.L. (1964). Trace elements in soils. In "Chemistry of the Soil" Bear, F.E. ACS Monograph No.160.

MOELLER, T. (1952). Inorganic chemistry. John Wiley and Sons Inc. New York, London; 966 pp.

MORRIS, H.T. and LOVERING, T.S. (1952). Supergene and hydrothermal dispersion of heavy metals in wall rocks near orebodies, Tintic District, Utah. Econ. Geol. 47, 685-716.

MUELLER-KAHLE, E. (1966). Geochemical prospecting in Province Mendoza, Argentina. Z. Erzbergbau Metallhuettenw. 9, 330-9 (Ger).

MULCAHY, M.J. (1960). Laterites and lateritic soils in south-western Australia. Jour. of Soil Sci. 11, 206-225.

MULLER, D.W. and DONOVAN, P.R. (1970). Stream sediment reconnaissance for zinc silicate (willemite) in the Flinders Ranges, S. Australia. 3rd Int. Geochem. Expl. Symp., Toronto.

MUNG K'O-K'O. (1970). Quantitative interpretation of secondary dispersion haloes of a complex ore deposit (abs). Mat. Metody Geol. 7, 72-82 (Russ).

MURATA, A. (1952). Chemical prospecting in the northeastern district of Mt Zao, Miyagi Prefecture, Japan. Tohaku Univ. Research Inst. Min. Dress. and Met. Bull. 8, 73-76.

NAUMOV, V.N. et al. (1969). Behaviour of copper, bismuth, silver, lead and zinc in the oxidation of copper-bismuth deposits of Eastern Karamazar. Geochem. Int. 6, 1049-1054.

NEELKANTAN, V. and MEHTA, B.V. (1962). Distribution of copper in typical soil profiles of Gujarat. Indian J. Agr. Sci. 32, 39-46.

NESVETAYLOVA, N.G. (1955). Geobotanical method of prospecting for copper and polymetallic ores. Razvedka i Okhrana Nedr., 4, 17-20 (Russ).

NEWBERG, D.W. (1967). Geochemical implications of chrysocolla-bearing alluvial gravels. Econ. Geol. 62, 932-56.

New Jersey Zinc Co. Staff Of. (1956). a. Frequency distribution of zinc, copper, lead values in soil; b. Metal content of mine waters (abs). Int. Geol. Congr. Rept 20th Sess.

NICHOL, I. et al. (1966). Studies in regional geochemistry. Trans. Inst. Min. Metall. 75, B106-107.

NICHOL, I. et al. (1966). Regional geochemical reconnaissance in Sierra Leone. Trans. Inst. Min. Metall. 75, B147-161.

NICHOL, I. et al. (1970). Regional geochemical reconnaissance of the Derbyshire area. Rept Inst. Geol. Sci. No.70/2; 37 pp.

NICHOL, I. et al. (1970). Regional geochemical reconnaissance in the Denbighshire area. Rept Inst. Geol. Sci. No.70/8, 40.

NICHOLLS, O.W. et al. (1966). Geobotany and geochemistry in mineral exploration in the Dugald River area, Cloncurry District, Australia. Trans. Aust. Inst. Min. Metall. 75, 695-799.

NICOLAI, J. (1956). Les recherches geochimiques au Niari (Afrique Equatoriale Francaise) realisees par le bureau minier. de la France d'outremer (abs). Int. Geol. Congr. Rept 20th Sess.

NICOLAS, D.J. and BROOKS, R.R. ((1969). Biogeochemical prospecting for zinc and lead in the Te Aroha region of New Zealand. Proc. Aust. Inst. Min. Metall. No.231, 59-66.

NIGRINI, A. (1970). Investigations into the transport and deposition of copper, lead and zinc in the surficial environment. 3rd Int. Geochem. Expl. Symp., Toronto.

NOAKES, L.C. (1962). Liaison symposium on regional geochemistry in the British Commonwealth, 1962, by Commonwealth Geological Surveys. Brit. Comm. Geol. Liaison Office, Lond; 82 pp.

NOCKOLDS, S.R. and MITCHELL, R.L. (1948). The geochemistry of some Caledonian plutonic rocks; a study of the relationship between the major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edin. 61 (iii), 533.

NODDACK, I. and NODDACK, W. (1939). Arkiv. Zool. 32A, No.1, Act 4. (Quoted in Goldschmidt, 1954).

NOVIKOV, Yu.A. et al. (1969). Evaluation of native copper ore shows by geochemical surface sampling. Geokhimiya 1, 96-103 (Russ).

OBIAL, R.C. (1970). Cluster analysis as an aid in the interpretation of multi-element geochemical data. Trans. Inst. Min. Metall. (London) 79, B175-180.

OERTAL, A.C. and GILES, J.B. (1964). A study of some Brigalow soils based on trace-element profiles. Australian J. Soil. Res. 2, 162-172.

OJA, R.V. (1967). Geochemical investigations of the Thunder Bay silver area. Can., Dep. Energy, Mines Resour., Geol. Surv. Can., Pap. No.66-54, 211-21.

OLDERSHAW, W. (1964). Report on the 1961-2 geological and geochemical survey of the Captain's Flat area, NSW. BMR Record 1964/99.

ONG, H.L. and SWANSON, V.E. (1966). Adsorption of copper by peat, lignite and bituminous coal. Econ. Geol. 61, 1214-1231.

OZEROVA, N.A. (1959). On the use of primary dispersion haloes of quicksilver in search for lead-zinc deposits. Geokhimiya 638-645 (Russ).

PADGET, P., EK, J. and ERIKSSON, L. (1969). Vargistrask, a case-history in ore prospecting. Geoexploration 7, 163-175.

PATTERSON, E.M. (1952). A petrochemical study of the Tertiary Lavas of north-east Ireland. Geochim. et Cosmochim. Acta 2, 291.

PAULI, F.W. (1966). Some recent developments in biogeochemical research. Bull. Serv. Carte Geol. Alsace-Lorraine 19, 221-240 (Eng).

PAVLIDES, L. and CANNEY, F.C. (1964). Geological and geochemical reconnaissance, southern part of Smyrna Hills, Quadrangle, Aroostook County, Maine. US Geol. Survey Prof. Paper 475-D, D96-99.

PECK, A.J. (1967). Mass transport in porous rocks. Mineralium Deposita 2, 243-7.

PHILLIPS, W.S. (1963). Depth of roots in soil. Ecology 44, 424.

PICOTTI, M. and BALDASSI, G. (1942). Mikrochemie ver. Microchim. Acta 30, 77. (Quoted in Goldschmidt, 1954).

POLFEROV, D.V. (1962). Geochemical prospecting for copper and nickel sulfide ores. Byul. Nauchn.-Tekhn. Inform. Min. Geol. i Okhrany Nedr SSSR 1, 26-30 (Eng).

POLIKARPOCHKIN, V.V. et al. (1958). Geochemical prospecting for polymetallic ore deposits in the eastern Transbaikal by means of the muds and waters of the drainage system (translation from Russian). Int. Geol. Review 2, 237-253 (Eng).

POLIKARPOCHKIN, V.V. et al. (1965). Dispersion haloes in plants in areas in eastern Transbaikal ore deposits. Vopr. Geokhim. Izverzhennykh Gorn. Porod i Rudn. Mestorozhd. Vost. Sibiri. Akad Nauk SSSR, Sibirsk Otd. Inst. Geokhim. 242-270 (Russ).

POSKOTIN, D.L. (1961). Geochemical prospecting of non-ferrous metal deposits in large-scale charting in the Pyshna ore district in the middle Urals. Tr. Sverdlovsk. Gorn. Inst. 38, 94-105.

POSKOTIN, D.L. (1963). Use of metallometric and biogeochemical methods in prospecting for copper-pyrite deposits in the middle Urals. Tr. Sverdl. Gorn. Inst. 42, 81-94.

POSKOTIN, D.L. (1964). Geochemical prospecting for non-ferrous metals by using secondary haloes. Isv. Vysshikh. Uchebn. Zavedenii, Geol. i Razvedka 7, 67-73.

PRESANT, E.W. (1966). A trace element study of podsol soils, Bathurst district, New Brunswick. Geol. Survey Canada Paper 66-54, 222.

PROTOPOPOV, V.N. (1967). Lead, copper and zinc in the waters of one of the regions of the Enisei Ridge. Sb. Aspir. Rab., Kazan. Gos. Univ., Khim., Geol. 175-9 (Russ).

RACE, W.H. (1962). Preliminary geochemical investigation, Tracy and Endicott Arm area. Alaska Dept. Nat Resources Div. Mines Minerals Rept 68-74.

RAKHIMOV, Sh.Kh. (1966). Primary dispersion haloes in the Kurusai-I-lead-zinc deposits. Izv. Vysshikh. Uchebn. Zavedenii, Geol. i Razvedka 9, 70-76 (Russ).

RANDHAWA, N.S. and KANWAR, J.S. (1964). Zinc, copper and cobalt status of Punjab soils. Soil Sci. 98, 403-7.

RANKAMA, K.K. (1947). Some recent trends in prospecting: chemical, biochemical and geobotanical methods. Mining and Metallurgy 28, 282-284.

RANKAMA, K.K. and SAHAMA, Th.G. (1950). Geochemistry. Univ. Chicago Press (Chicago and London).

REEDMAN, A.J. and GOULD, D. (1970). Low sample density stream sediment surveys in geochemical prospecting: an example from northwest Uganda. Trans. I.M.M. London 74 (4), B246-248.

REICHE, P. (1950). A survey of weathering processes and products. Univ. New Mexico Pub. in Geol. No.3, 95 pp.

REPP, G. (1963). The copper resistance of the protoplasm of higher plants on soils containing copper. Protoplasma 57, 643-659.

RICEMAN, D.S. (1950). Copper, zinc, manganese and molybdenum deficiencies in Australia. Proc. Soil Sci. Soc. of Florida X, 203-217.

RICHARDSON, P.W. and HAWKES, H.E. (1958). Adsorption of copper on quartz. Geochim. et Cosmochim. Acta 15, 6-9.

RIDDELL, J.E. (1954). Geochemical soil and water surveys in Lemieux township, Gaspe, North County. P.R. No.302, Quebec Dept of Mines.

RIDDELL, J.E. (1967). Geochemical dispersion patterns in soils at Mount Pleasant Mines, Charlotte County, New Brunswick. Geol. Survey Canada Paper 66-54, 233-248.

RILEY, G.A. (1937/38). J. Marine Research 1, 60. (Quoted in Goldschmidt, 1954).

RILEY, J.P. and SKIRROW, G. (Eds) (1965). Chemical Oceanography. Volume 1. Academic Press Inc. New York.

ROBERTSON, F. (1956). Geochemical prospecting by soil analyses in Montana. Montana Bur. Mines and Geol. Bull. 7, 1-78.

ROBINSON, W.O. et al. (1947). The zinc content of plants of the Friedensville zinc slime ponds in relation to biogeochemical prospecting. Econ. Geol. 42, 572-582.

ROMMEL, M.A. et al. (1968). Application of biogeochemistry to mineral prospecting. NASA Spec. Publ. SP-5056, 134 pp (Eng).

ROSE, A.W. (1965). Geology and mineral deposits of the Rainy Creek area, Mt Hayes Quadrangle, Alaska. Alaska Div. of Mines Minerals Geochem. Rept 14, 1-46.

ROSE, A.W. and SUHR, N.H. (1970). Major element content as a means of allowing for background variation in geochemical exploration. 3rd Int. Geochem. Expl. Symp., Toronto.

ROSLYAKOV, N.A. (1965). Distribution and form of occurrence of copper, lead and zinc in dispersion haloes of the sulphide deposits in Western Altai. Geol. i Geokhim. Rudn. Mestorozhd. Sibiri, Akad. Nauk SSSR Sibirsk, Otd. 165-186 (Russ).

ROSZYK, E. (1968). Vanadium, chromium,manganese, cobalt, nickel and copper contents in some Lower Silesian soils developed from silty loams and silt formations. I. Total content of the micro-elements. Rocz. Glebozn. 19, 224-47 (Pol).

ROY, S.S. and PAUL, D.K. (1967). Geochemical prospecting - use of A horizon in soil surveys. Econ. Geol. 62, 1102-3 (Eng).

ROZHKOVA, D.A. (1965). Hydrochemical prospecting for buried ore deposits in the Belokan ore field. Tr. Kankaz In. Miner. Nogo Sur'ya 6, 111-114.

RUCHKIN, G.V. and SERGEYEVA, N.Ye. (1967). Primary aureole parameters and hypogene mineral zoning of the Yaman Kasa chalcopyrite deposit (southern Urals). Doklady Akad. Nauk SSSR 178, 191-194.

RUDAKOVA, E.V. and SHIRYAEVA, I. (1963). Zinc content in soils of the Ukraine. Mikroelementy v. Sel'sk.-Khoz. i Med. Sb. 407-11.

RUDOLFS, W. and HELBRONNER, A. (1922). Oxidation of zinc sulfide by microorganisms. Soil Sci. 14, 459-464.

RUSSKII, V.I. and ZHURAVLEVA, N.A. (1969). Migration of elements in a weathering crust developed on ultrabasic rocks in the southern part of the Kola massif, northern Urals. Geol. Polez. Iskop. Urala 1969, No.1, 153-4 (Russ).

RUXTON, B.P. (1963). Some aspects of detailed geochemical testing of Rum Jungle, NT, Australia. Proc. Seminar on Geochem. prospecting methods and techniques, Bangkok, Min. Res. Dev. Ser. 21, 104-111.

SAHAMA, T.G. (1945). Spurenelemente der Gesteine im sudlichen Finnisch-Lappland. Bull. Comm. geol. Finl. 135. (Quoted in Rankama and Sahama, 1950).

SAHINEN, U.M. et al. (1965). Geochemical reconnaissance stream sediment sampling in Flathead and Lincoln Counties. Mont. Bur. Mines. Geol. Bull. 48, 1-16.

SAINSBURY, C.L. et al. (1970). Geology, mineral deposits, geochemical and radiometric anomalies, Serpentine Hot Springs area, Seward Peninsula, Alaska. US Geol. Survey Bull. 1312-H.

SALMI, M. (1967). Peat in prospecting: applications in Finland. "Kvalheim Volume" 113-126.

SANDELL, E.B. and GOLDICH, S.S. (1943). The rarer metallic constituents of some American igneous rocks. J. Geol. 51, Part I 99; Part II 167.

SANTOS-YNIGO, L. and ESGUERRA, F.B. (1961). Geology and geochemistry of the nickeliferous laterites of Nonoc and adjacent islands, Surigao Province, Philippines. Philippines, Dept. Agr. Nat. Resources, Bur. Mines, Spec. Projects Ser., Publ. 18, 1-90 (Eng).

SATO, M. (1960). Oxidation of sulphide ore bodies II, Oxidation mechanisms of sulphide minerals at 25°C. Econ. Geol. 55, 928-961.

SATO, M. (1960). Oxidation of sulphide ore bodies I, Geochemical environments in Terms of Eh and pH. Econ. Geol. 55, 1202-1231.

SAUKOV, A.A. (1956). Hydorgeochemical method for mineral deposit prospecting (abs). Int. Geol. Congr. Rept 20th Sess.

SAUKOV, A.A. (1960). Migration of chemical elements as a theoretical basis of geochemical search methods. Int. Geol. Congr. Rept 21st Sess. Pt 2, 14-26.

SAUKOV, A.A. (1963). Geochemical methods of prospecting for useful mineral deposits (ed. Valyashko). Moscow State University Print (English translation).

SCHWARTZ, G.M. (1949). Oxidation and enrichment in the San Manuel copper deposit, Arizona. Econ. Geol. 44, 253-277.

SCOTT, B.P. and BYERS, A.R. (1965). Trace copper and zinc in the Coronation Mine overburden. Can. Min. Metall. Bull. 58 (637), 534-7.

SELEGEAN, E. and BARNEA, M. (1964). Diffusion of Pb and Zn in the air around non-ferrous metal foundries. Igiena (Bucharest) 13 (2), 137-44.

SEMPLE, D.G. (1967). Geochemical and radiometric investigation, Gould area, NT. BMR Records 1967/41.

SEMPLE, D.G. (1967). Geochemical and radiometric investigations, Prospects L1, L2, L3 and L6, northern part of Woodcutters area, Rum Jungle east, NT, 1966. BMR Records 1967/42.

SEMPLE, D.G. (1968). Geochemical and radiometric investigations, Acacia area, NT. BMR Records 1968/8.

SEN, N. et al. (1959). Trace elements in minerals from rocks of the S. Californian batholith. Geochim. et Cosmochim. Acta 16, 58-78.

SERGEEV, E.A. (1941). Geochemical prospecting for ore deposits. In Sokolov, V.P. "Selected Russian papers on geochemical prospecting for ores". US Geol. Survey (1950), 15-87.

SERYKH. V.I. (1964). Geochemistry of nickel in granitic rocks. Geokhimiya 9, 898-907 (Russ).

SHACKLETTE, H.T. (1960). Soil and plant sampling at the Mahoney Creek lead-zinc deposit, Revillagigedo Island, SE Alaska. In Geol. Survey Research 1960. US Geol. Survey Prof. Paper 400-B, 102-104.

SHACKLETTE, H.T. (1967). Copper mosses as indicators of metal concentrations. US Geol. Survey Bull. No.1198-G, 18 pp.

SHANNON, S.S. (1970). Evaluation of copper molybdenum geochemical anomalies at the Cuno prospect, Boise County, Idaho. 3rd Int. Geochem. Symp., Toronto (Abstract only).

SHARP, W.N. and GUALTIERI, J.L. (1968). Lead, copper, molybdenum and zinc geochemical anomalies south of the Summitville district, Rio Grande County, Colorado. US Geol. Survey Circ. No.557, 7 pp.

SHATWELL, D.O. (1966). Geochemical and radiometric investigations, Rum Jungle East area, 1964. BMR Records 1966/34.

SHAW, D.M. (1954). Geochemistry of pelitic rocks. Part III. Major elements and general geochemistry. Bull. Geol. Soc. Amer. 67, 919-934.

SHCHERBINA, V.V. (1962). On compounds in which elements are transported in geochemical processes. Geochemistry 1069-1076.

SHEPARD, W.A. (1966). Geochemical studies in E. Tintic District, Utah. Min. Eng. 18, 68-72.

SHIRINYAN, K.G. (1961). Significance of depth assimilation for prospecting ore bearing zones buried under lava. Dokl. Akad. Nauk. USSR 33, 61-66, (Russ).

SHORT, N.M. (1958). Element variations during weathering of four residual soils. Bull. Geol. Soc. Amer. 69.

SHTEINBERG, D.S. and MALAKHOV, I.A. (1963). Distribution of nickel in ultramafic rocks of the Urals. Geokhimiya 11, 982-95 (Russ).

SINCLAIR, I.G.L. (1967). Distribution of nickel in the soils of the Cave Valley area. J. Geol. Soc. Jamaica 9, 11-16 (Eng).

SINCLAIR, I.G.L. (1967). Geochemical stream sediment survey of the Yallahs Valley. Jamaica Geol. Survey Econ. Geol. Rept 1, (Pub. 100), 4 pp.

SINDEEVA, N.D. (1964). Mineralogy and types of deposits of selenium and tellurium. Interscience Publishers, New York, London and Sydney, 363 pp.

SINIAKOVA, S.I. (1945). On the distribution of lead in soils. Dokl. Akad. Nauk USSR 48, 648-650 (Russ).

SMIRNOV, V.I. (1967). Primary aureole parameters and hypogene mineral zoning of the Yaman Kasa Chalcopyrite Deposits (Southern Urals).

SMITH, K.H. (1966). Some field methods used in prospecting for nickel. BMR Records 1966/215.

SMITH, W.H. (1968). Geochemical investigation of a portion of the Forty-mile district, east central Alaska. Alask, State, Dep. Natur. Resour., Div. Mines Miner., Geochem. Rep. 16, 1-17 (Eng).

SOFOULIS, J. and WILLIAMS, X.K. (1969). The geology and geochemistry of a cupriferous area at Twin Peaks, Yalgoo Goldfield, W. Australia. Annual Report, Dept of Mines, WA 71-76.

SOFOULIS, J. et al. (1968). Investigation of Ministerial Reserve 4538H, Yindarlgooda, Bulong District, WA. Annual Report, Dept of Mines, WA 82-86.

SOKOLOFF, V.P. (1949). Geochemical reconnaissance in the Wallaroo Mining District. SADM Mining Review 88, 32-64.

SOKOLOFF, V.P. (1950). Sampling and testing of soil and rock for copper, lead and zinc in geochemical reconnaissance. Mines Mag. 40 (11), 15-22.

SOKOLOFF, V.P. (1951). Geochemical exploration for copper in the Wallaroo mining district, South Australia. Geochim. et Cosmochim. Acta 1, 284-298.

SOKOLOFF, V.P. and HAWKES, H.E. (1950). Selected Russian papers on geochemical prospecting for ores. Translations into English. US Geol. Survey.

SOLOVOV, A.P. and KUNIN, N.Ya. (1961). Metallometric surveying in mountainous areas based on alluvial deposits. Int. Geol. Review 3, 998-1010.

SOMMER, A.L. (1945). Copper and plant growth. Soil Sci. 60, 71-79.

SPRIGG, R. (1953). Report No.36/99 SADM 215/53 (unpublished).

STARIKOV, V.S. et al. (1964). Biogeochemical prospecting and the results of its use in Gornaya Osetiya (Russ). Geokhimiya No.10, 1070-1072.

STEWART, A.L. et al. (1967). Prospecting for minerals. Kenya, Colony Protectorate, Min. Commer. Ind., Geol. Surv. Kenya, Bull. 5, 1-58 (Eng).

STRACZEK, J.A. et al. (1956). Geochemical prospecting in the Khob-Dariba copper area. Alwar district, Rajasthan, India (abs). Int. Geol. Congr. Rept 20th Sess.

SUSPITSIN, N.V. (1965). Deposits of nickel silicate ores in the Char belt. Izv. Akad. Nauk Kaz. SSR, Ser. Geol. 22 (4), 23-34 (Russ).

SVEDAS, A. (1961). Copper in Lithuanian soil. Lietvos TSR Aukstuju ju Mokylu Mokslo Darbai, Biologija 1, 85-97.

SVERDRUP, H.A. et al. (1942). The oceans, their physics, chemistry and general biology. New York.

SVESHNIKOV, G.B. (1960). Electrochemical solution of sulfide ores and its role in the formation of heavy-metal dispersion halos. Mezhdunarod. Geol. Kongress, 21 (Dvadtsat Pervaya) Sessiya, Doklady Sovet. Geologov 2, 71-7 (Russ).

SVESHNIKOV, G.B. and DOBYCHIN, S.L. (1956). Electrochemical solution of sulphides and dispersion aureoles of heavy metals. Geochemistry 413-419 (Eng).

SVESHNIKOV, G.B. et al. (1960). Role of electrochemical dissolution of sulphides in the formation of nickel matter dispersion haloes. Uch. Zap. Leningr. Gos. Univ. (286) Ser. Fiz. i Geol. Nauk (12) 142-148.

SWAINE, D.J. and MITCHELL, R.L. (1960). Trace element distribution in soil profiles. J. Soil Sci. 11, 347-368.

Symposium on Geochemical Prospecting. Two volumes (1956). 20th Int. Geol. Congr. Mexico, 725 pp (published 1960).

SZUCS, L. and ELEK, E. (1962). Trace-element contents of Hungarian chernozem soils. Agrokem. Talajtan 11, 311-22.

TALIPOV, R.M. (1964). Concentration of nonferrous metals in soils and plants of the Sany-Checku and Uch-Kulach deposits (Uzbekistan). Geokhimiya 457-467 (Russ).

TAN, L.P. (1966). Stream sediment prospecting for the copper deposits in the Southern Appalachians. Proc. Geol. Soc. China 10, 115-24 (Pub. 1967) (Eng).

TAN, L.P. (1968). Geochemical study of soil and gossan and their significance in Cu exploration in the S. Appalachians. Sci. Rep. Nat. Taiwan Univ., 1st Ser. Acta Geol. Taiwan 12, 21-33.

TAN, L.P. and YU, F.S. (1968). Heavy-mineral reconnaissance for gold and copper deposits of the Chinkuashih area, Taiwan. Sci.Rep. Nat. Taiwan Univ., First Ser. Acta Geol. Taiwan No.12, 41-57 (Eng).

TAN, L.P. and YU, F.S. (1970). Geochemical exploration of the Chimei copper deposit, Taiwan. Proc. Geol. Soc. China, 13, 90-107.

THOMSON, B.P. (1965). Weathering and related nickel mineralisation, Mt Davis area. SADM Quart. Geol. Notes 16, 6.

THORNE, D.W. et al. (1942). Zinc relationships of some Utah soils. Soil Science 53, 463-468.

THURLOW, E.E. (1965). Geochemical prospecting applied to geologic reconnaissance. Trans. A.I.M.E. 229, 225-229.

TILLER, K.G. (1957). The geochemistry of basaltic tuff and basalt and associated soils in the Mt Burr area of SE South Australia. CSIRO Division of Soils, Divisional Report 3/57.

TILLER, K.G. (1959). Distribution of some trace elements in soils developed on dolerite in Tasmania. CSIRO Division of Soils, Adelaide, Divisional Report 6/58.

TIMPERLEY, M.H. et al. (1970a). The significance of essential and non-essential trace elements in plants in relation to biogeochemical prospecting. J. Appl. Ecol. 7, 429-439.

TIMPERLEY, M.H. et al. (1970b). Prospecting for copper and nickel in New Zealand by statistical analysis of biogeochemical data. Econ. Geol. 65, 505-510.

TIMPERLEY, M.H. et al. (1971). The improved detection of geochemical soil anomalies by multiple regression analysis of biogeochemical data. Aust. Inst. Min. Metall. Conference 1971.

TOLSTOY, M.P. (1967). Azonal phenomena in hydrogeology, their place among zonal phenomena and significance for mineral prospecting. Dokl. Akad. Nauk. SSSR Earth Sci. Sec. 173, 52-54.

TOOMS, J.S. and JAY, J.R. (1964). The role of the biochemical cycle in the development of Cu/Co anomalies in the freely drained soils of the N. Rhodesian copperbelt. Econ. Geol. 59, 826-34.

TOOMS, J.S. and WEBB, J.S. (1961). Geochemical prospecting investigations in the Northern Rhodesian Copperbelt. Econ. Geol. 56, 815-846.

TOWNEND, R. and SCHULTZ P. (1965). An investigation of nickel-bearing ultrabasic rocks and their weathered derivatives using the electron probe microanalyser. Bull. Aust. Min. Dev. Labs 1, 1-9.

TOWNEND, R. and TURNER, A.R. (1968). Some aspects of the geology and geochemistry of nickel. In "Nickel, a Review". Amdel unpublished report.

TUCKER, B.M. (1956). Basaltic soils of the Lismore district, NSW. CSIRO Soil Pub. 7.

TUREKIAN, K.K. and CARR, M.H. (1960). The geochemistries of chromium, cobalt and nickel. Intern. Geol. Congr., Rept 21 Sess. Copenhagen 14-26 (Eng).

TUREKIAN, K.K. and SCOTT, M.R. (1967). Concentrations of Cu, Ag, Mo, Ni, Co and Mn in suspended materials in streams. Environmental Science and Technology 1 (11), 940-942.

TUREKIAN, K.K. and WEDEPOHL, K.H. (1961). Distribution of the elements in some major units of the earths' crust. Bull. Geol. Soc. Amer. 72, 175-192.

TURNER, A.R. (1968). The distribution and association of nickel in the lateritic ochres of the Giles complex, north-west South Australia. Bull. Aust. Min. Deve. Labs 5, 72-89.

TURTON, A.G. et al. (1961). Morphological, chemical, physical, clay mineralogy and minor element data on lateritic profiles from SW Australia. CSIRO Division of Soils, Adelaide, Divisional Report 8/61.

TURTON, A.G. et al. (1962). The chemistry and mineralogy of lateritic soil in the south west of South Australia. CSIRO Soil Pub. 20.

TWIDALE, C.R. (1968). Geomorphology. Nelson, 406 pp.

UDODOV, P.A. and PARILOV, Yn.S. (1961). Certain regularities of migration of metals in natural waters. Geochemistry 763-771.

UDODOV, P.A. et al. (1968). Development of a hydrochemical method in prospecting for ore deposits. Itogi Issled. Geol. Georgr. 50 Let. 1917-1967, 142-51 (Russ).

United Nations, E.C.A.F.E. (1963). Proceedings of the seminar on geochemical prospecting methods and techniques, held at Bangkok, 5-14 August; UN, New York.

USIK, L. (1968). Botanical investigations at 3 known mineral deposits. Geol. Surv. Canada Paper 68-71, 32 pp, pub. 1969.

USIK, L. (1969). Review of geochemical and geobotanical prospecting methods in peatland. Geol. Surv. Canada Paper 68-66, 43 p.

VAKHROMEEV, G.S. (1962). Biogeochemical exploration methods in a mass of ultrabasic alkaline rocks and carbonatites. Zap. Vost-Sibisk. Otd-Vses. Mineralog. Obshchestva Akad. Nauk SSSR 196-197.

VAN PRICE and RAGLAND, P.C. (1968). Ground water chemistry as a tool for geologic investigation in the southwestern Piedmont. Southeastern Geology _9_ (1), 21-38.

VAN TASSELL, R.E. (1969). Exploration by overburden drilling at Keno Hill Mines Ltd. Quart. Colorado Scho. Mines _64_ (1), 457.

VERHOFSTAD, J. (1963). Sellick's Hill lead anomaly area. SADM Mining Review _118_, 127-133.

VIEWING, K.A. (1968). Regional geochemistry and the Rhodesian basement complex. Symp. Rhodesian Basement Complex, Pap. Discuss., Geol. Soc. S. Africa, Rhodesian Br., 1st. 1967, 21-32, (Eng).

VINOGRADOV, A.P. (1959). The geochemistry of rare and dispersed chemical elements in soils. 2nd Ed. Consultants Bureau, New York, 209 pp.

VINOGRADOV, A.P. (1962). Average contents of chemical elements in the principal types of igneous rocks of the earth's crust. Geochemistry _7_, 641-664.

VOGT, T. and BRAADLIE, O. (1942). Geokjemisk og geobotansk malmeting IV. Plantevekst og jordbunn ved Rorosmalmene. Kgl. Norske Videnskab. Selskabs Forh. 15 No.7, 25.

VOSTROKNUTOV, G.A. (1968). Formation and geochemical characteristics of ores and halo waters of sulfide deposits of the urals. Gidrogeol. Sb. No.5, 87-102 (Russ).

WAGER, L.R. and MITCHELL, R.L. (1951). The distribution of trace elements during strong fractionation of basic magma - a further study of the Skaergaard instrusion, E. Greenland. Geochim et Cosmochim. Acta _1_, 129-208.

WALENCZAK, Z. (1955). Biogeochemical methods of determining the nickel content of Lower Selesian Serpentinites. Polska. Akad. Nauk Kom. Geol., Arch. Mineralog. 18, 302-317.

WALPOLE, B.P. (1964). Development of geochemistry, Bureau of Mineral Resources. BMR Records 1964/176.

WARK, W.J. (1955). Geochemical prospecting in lakes and rivers. Can. Min. Met. Bull. 48, 195-8.

WARNE, K.R. (1967). Kenmore Park nickel prospect, northwest province. SADM Mining Review No.127, 61-68.

WARREN, H.V. and DELAVAULT, R.E. (1949). Further studies in biogeochemistry. Bull. Geol. Soc. Amer. 60, 531-560.

WARREN, H.V. and DELAVAULT, R.E. (1954). Variations in the nickel content of some Canadian trees. Royal Soc. Canada Trans. 48, Sec.IV, 71-74.

WARREN, H.V. and DELAVAULT, R.E. (1956). Soils in geochemical prospecting. Mining Eng. 8, 992-996.

WARREN, H.V. and DELAVAULT, R.E. (1958). Pathfinding elements in geochemical prospecting. Int. Geol. Congr. Rept Sess. 20th, p 225.

WARREN, H.V. and DELAVAULT, R.E. (1960). Aqua regia extractable copper and zinc in plutonic rocks in relation to ore deposits. Trans. Inst. Min. Metall. 69, 495-504.

WARREN, H.V. and HOWATSON, C.H. (1947). Biogeochemical prospecting for copper and zinc. Bull. Geol. Soc. Amer. 58, 803-820.

WARREN, H.V. et al. (1951). Further biogeochemical data from the San Manuel copper deposit, Pinal County, Arizona. Bull. Geol. Soc. Amer. 62 (8), 919-929.

WARREN, H.V. et al. (1953). Sampling in biogeochemistry. Bull. Geol. Soc. Amer. 66, 229-238.

WARREN, H.V. et al. (1966). Some observations on the geochemistry of mercury as applied to prospecting. Econ. Geol. 61, 1010-1028.

WARREN, H.V. et al. (1967). Some problems in applied geochemistry. Geol. Surv. Can. Paper 66-54.

WARREN, H.V. et al. (1968). The arsenic content of Douglas Fir as a guide to some gold, silver and base metal deposits. Canadian Inst. Min. Bull. 675, 860-868.

WATSON, J.P. (1970). Contribution of termites to the development of a zinc anomaly in Kalahari sand. Trans. Inst. Min. Metall. 79, 53-59.

WATTENBERG, H. (1943). Z. anorg. Chem. 251, 71. (Reference from Goldschmidt, 1954).

WATTS, M. (1968). Prospecting copper mines river area, N.W. Territory. Can. Min. Jour. 89, 116-118.

WEBB, J.S. (1953). A review of American progress in geochemical prospecting and recommendations for future British work in this field. Trans. Inst. Min. Metall. (London) 62, 321-348.

WEBB, J.S. (1956). Observations on geochemical exploration in tropical terrains. Int. Geol. Congr. Rept 20th Sess. 380.

WEBB, J.S. et al. (1958). Geochemical drainage reconnaissance for copper in Northern Rhodesia. Trans. Inst. Min. Metall. (London) 68, 125-44.

WEBB, J.S. (1959). Notes on geochemical prospecting for lead-zinc deposits in the British Isles. Inst. Min. Metall (London) 419-436.

WEBB, J.S. and MILLMAN, A.P. (1950). Heavy metals in natural waters as a guide to ore. A preliminary investigation in W. Africa. Trans. Inst. Min. Metall. 59, 323-336.

WEBB, J.S. and MILLMAN, A.P. (1951). Heavy metals in vegetation as a guide to ore. Trans. Inst. Min. Metall. (London) 60, 473-504.

WEBB, J.S. et al. (1968). The broadening scope of regional geochemical reconnaissance. Int. Geol. Congr., Rep. Sess., 23rd, Sec. 6, 131-47.

WEDEPOHL, K.H. (1958). Investigations on the geochemical distribution of lead (abs). Bull. Geol. Soc. Amer. 69.

WEISS, O. (1967). Method of aerial prospecting which includes a step of analysing each sample for element content, number and size of particle. US Patent 3,309,518.

WELLS, J.D. et al. (1969). Geology and geochemistry of the Cortez gold deposit, Nevada. Econ. Geol. 64, 526.

WELLS, R.C. (1946). Analyses of petroleum-coke ashes. US Geol. Survey Bull. 950, 3.

WENNERVIRTA, H. (1968). Application of geochemical methods to regional prospecting in Finland. Bull. Comm. geol. Finl. 234, 91 pp (Eng).

WHITE, D.E. et al. (1963). Chemical composition of subsurface waters. US Geol. Survey Prof. Paper 440-F.

WHITE, M.L. (1957). The occurrence of zinc in soil. Econ. Geol. 52, 645-651.

WHITE, W.H. and ALLEN, T.M. (1954). Copper soil anomalies in the Boundary District of British Columbia. Mining Eng. 6, 49-52.

WHITTEN, G.F. (1967). Regional geochemical investigation on the Clare One-Mile-Sheet area. SADM Mining Review No.127, 34-46.

WILLIAMS, X.K. (1967). Geochemical prospecting for copper, nickel and zinc in the Longwood Range, Southland, N.Z. N.Z. Jl for Geol. and Geophys. 10 (3), 742-58.

WILLIAMS, X.K. (1967). Chemical variations in stream waters and sediments in the Moke Creek area, West Otago. N.Z. Jl. Geol. Geophys. 10 (3), 759-70.

WILLIAMS, X.K. (1969). Geochemical prospecting for copper, lead and zinc in the Northampton mineral field. Annual Report, W. Australian Dept of Mines, p 105.

WILLIAMS, X.K. and WOOD, B.L. (1967). Geochemical prospecting for copper, West Otago. N.Z. Jl. Geol. Geophys. 10 (3), 798-830.

WILSON, H.D.B. (1953). Geology and geochemistry of base metal deposits. Econ. Geol. 43, 370-407.

WIRAKUSUMAH, W. (1967). Geochemical and radiometric results from three areas, Woodcutters, Prospect, Rum Jungle East, NT. BMR Records 1967/5.

WONG, N.P.Y. (1966). Geology and copper mineralisation of the Bambangan Valley, Kinabalu, Sabah. Malaysia, Geol. Surv., Borneo Reg., Bull. 1966 (Pub. 1967) 8, 81-8 (Eng).

WORT, M. (1966). Geochemical drainage sampling. Personal communication.

WORTHINGTON, J.E. (1962). Geochemical prospecting for nickel in the Blue Mountain area, Jamaica, W.I. Econ. Geo. 57 (4), 637.

WORTHINGTON, J.E. (1964). An exploration program for nickel in the S.E. United States. Econ. Geol. 59, 97-109.

WRIGHT, R.G. (1966). Geological and geochemical report on the Sellick Hill Area. SADM Mining Review No.126, 21-32.

WRIGHT, R.G. (1968). Second geological and geochemical report on the Sellick Hill area. SADM Mining Review No.128, 119-126.

YAKHONTOVA, L.K. (1958). Experimental studies in oxidation of cobalt and nickel arsenides in solution containing oxygen and carbonic acid. Geochemistry 1, 95-108.

YAMAGATA, N. et al. (1960). Biogeochemical investigation in serpentine-chromite ore district. Geochim. et Cosmochim. Acta 18, 23-35.

YARDLEY, D.H. (1958). Significance of geochemical distribution trends in soil. Mining Eng. 10, 781-6; Trans. AIME 211, Tech. Publ. 4765-1.

YATES, K.R. and de FERRANTI, R.Z. (1967). Geology and mineral deposits Port Moresby/Kemp Welch area, Papua. BMR Report No.105 (PNG 1), 117 pp.

YOUSSEF, M.S. and EL-KAHWAGY, A.S. (1966). Geophysical and geochemical investigations at Umm Gheig area, Eastern Desert. United Arab Republic, Geol. Survey Paper 33, 11 pp.

YUSHKOV, Yu.N. (1968). Hydrogeochemical prospecting for hidden pyrite mineralisation according to supergene dispersion haloes in soils and loose deposits of the central Urals. Gidrogeol. Sb. No.5, 103-9 (Russ).

ZEISSINK, H.E. (1969). The mineralogy and geochemistry of a nickeliferous laterite profile (Greenvale, Queensland, Australia). Mineralium Deposita 4, 132-152.

ZEISSINK, H.E. (1971). Trace element behaviour in two nickeliferous laterite profiles. Chem. Geol. 7, 25-36.

ZENTAI, P. (1964). A new method of hydrochemical prospecting of ore deposits. Razvedka i Okhrana Nehr 30, 62.

ZIMMERMAN, D.O. (1964). Papers on geochemical prospecting programme at Mt Isa, 1963. BMR Records 1964/128.

ZIMMERMAN, D.O. and HOWARD, E.J. (1962). Interim report on regional geochemical drainage sampling in the Chillagoe-Herbert River gorge area, N. Queensland. BMR Record 1962/142.

ARGALL, G.O. (1971). Byproduct mercury recovery from zinc and copper concentrates. World Mining, January, 33-35.

TABLES 1 to 17

FIGURES 1 to 10

TABLE 1: BASE METAL CONTENT IN SOILS OF SOUTHWESTERN AUSTRALIA (TURTON ET AL. 1961)

Fraction		Profile Number																	
		8			6			7			5			2			9		
		Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm
		Profiles 8, 6 - Sandy Laterites; Profiles 7, 5, 2, 9 - Gravelly Laterites																	
A_1	F	0.5	5	<20	0.7	38	<20	3	9	<20	1	16	<20	3	35	<20	24	18	31
	G	2	26	<20	0.6	18	25	2	17	43	2	123	35	2	20	38	9	9	37
A_2	F	0.6	8	<20	0.5	5	<20	1	11	<20	0.6	10	<20	2	27	<20	54	13	20
	G	2	4	<20	0.8	51	30	2	25	65	0.7	35	31	3	43	30	10	18	53
	F	0.8	9	<20	1	7	56	0.8	4	<20	0.8	33	39	1	32	27	25	15	31
	G	5	10	30	2	18	<20	0.3	12	29	0.3	71	40	0.9	35	49	9	25	44
	F							0.7	8	<20	0.8	41	59	2	27	25	30	16	31
	G							0.3	17	36	0.4	43	41	0.1	94	<20	13	11	54
	F							1	6	23	0.7	32	58	0.6	125	39			
	G							0.4	13	53	0.3	42	35	0.5	28	44			
	F										0.7	7	38	3	25	47			
	G										0.5	42	<20	1	30	23			
	F										0.7	21	58	6	24	36			
	G										0.3	42	40	0.7	31	33			
	F													2	32	39			
	G													1	124	26			
	F													2	30	36			
	G													1	18	39			

Continued

TABLE 1: CONTINUED

Profoles 1, 10 - Truncated Laterites; Profiles 12, 11, 4, 3 - Sands, Loams and Sandy Loams

Fraction		Profile Number																	
		1			10			12			11			4			3		
		Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm	Cu ppm	Zn ppm	Pb ppm
A_1	F	17	38	140	18	11	21	11	22	78	16	24	22	19	27	22	49	13	25
	G	4	25	<20	18	18	100	14	32	35	11	12	58	26	18	29	26	24	35
A_2	F	11	40	140	21	15	30	5	21	110	12	20	<20	29	15	32	65	21	32
	G	2	30	<20	20	19	110	9	11	29	14	23	55	38	9	40	35	19	38
	F	70	280	88	69	21	67	10	14	180	13	81	22	80	16	30	120	29	32
	G	4	35	<20	48	22	130	14	9	66	18	22	72	72	6	40	49	28	43
	F	6	35	94	46	18	67	72	30	290	210	44	35	130	17	24	70	35	28
	G	19	26	33	51	46	130	28	22	64	77	44	45	75	21	25	33	28	35
	F	11	36	120	81	21	57	47	30	190	360	81	<20	120	15	34			
	G	15	90	27	55	9	83	17	18	55	120	95	<20	70	19	36			
	F	6	39	95	59	29	62							56	25	24			
	G	12	62	27	50	24	1000							40	30	46			
	F	8	38	54															
	G	15	62	34															
	F	6	35	30															
	G	2	37	40															

Note: F = less than 2 mm fraction; G = greater than 2 mm fraction (gravel).

TABLE 2: COPPER (IN PPM) IN SOIL PROFILES IN SOUTH-EAST SOUTH AUSTRALIA (GILES, 1960)

Depth inches												
	Rendzinas											
0 - 4	13	3.9	6.6	11	4.0	1.5	5	14	7	8.1	8.3	12
4 - 10	3.6	4.1	14	2.6	5.7	0.8	5.5	9.3	9	6.8	6	8
10 - 20	3.0	1.1	9	-	-	0.9	3	8.6	8	4.9	2.2	5.4
	Terra Rossas											
0 - 3-4	8.3	0.9	2	5.3	2.2	7.2	4.2	4.7	8.3			
3-4 - 10-12	3.6	1.1	1.9	2.5	1.7	6	3	3	2.6			
10-12 - 20	1.2	2.2	1.8	1.5	-	3	-	-	2.7			

TABLE 3: COPPER (IN PPM) IN SOILS FROM TODD RIVER, NT (McKENZIE, 1958)

Desert Loam Solonetz				Brown Soils			
13	14	24	25	6	7.1	4.6	3.6
25	30	39	28	2.2	8.5	6.2	4.4
22	33	34	32	8.5	9.5	5.3	4.3
19	27	32	36	10.5	9.0	6.0	4.6
17	22	36	46	9.5	7.7	5.5	4.2
150	22	-	42	8.9	7.2	4.6	5.2

* Values given down profile, with final value that of the bedrock.

TABLE 4: ZINC (IN PPM) IN SOILS NEAR ALICE SPRINGS, NT (McKENZIE, 1960)

Rodinga				Brown Soils				
1	2	3	4	1	2	3	4	
33	29	46	54	19	19	12	13	Surface
66	60	72	51	18	22	13	14	
64	58	56	60	24	18	15	13	
50	52	56	68	30	21	18	15	
46	65	-	73	34	21	18	13	
-	-	-	-	33	-	-	-	
-	-	-	-	30	-	-	-	
86	54	60	47	31	18	11	13	C Horizon

TABLE 5: ZINC (IN PPM) IN VARIOUS SOILS OVER DOLERITE IN TASMANIA (TILLER, 1959)

Krasnozem				Podsol						Brown Earth					
Zn	pH	Zn	pH	Zn	pH	Zn	pH	Zn	pH	Zn	pH	Zn	pH	Zn	pH
58	5.1	44	5.8	68	-	92	5.7	49	5.7	76	6.1	78	5.4	58	6.1
78	5.0	37	6.0	79	5.7	62	6.2	45	6.0	69	7.0	70	5.8	40	6.6
71	5.1	39	6.1	58	-	64	6.5	47	8.2	47	7.9	53	6.6	65	6.8
42	-	57	-	-	-	-	-	55	-	70	-	70	-	63	-
-	-	-	-	73	-	84	-	57	-	-	-	-	-	-	-

Note: Values shown from surface downwards. Last value is that of the dolerite.

TABLE 6: ZINC (IN PPM) IN RENDZINAS AND TERRA ROSSAS OF SOUTH AUSTRALIA (GILES, 1960)

Depth	Soil Number 1		2		3		4		5		6		7		8	
inches	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH
								Rendzinas								
0- 3	64	8.2	22	8.2	13	8.2	27	8.2	17	8.3	5	8.2	29	8.1	18	6.7
3- 7	27	8.5	21	8.3	21	8.1	28	8.5	14	8.5	4	8.2	16	8.2	21	7.2
11-20	19	8.7	10	8.9	21	8.6	-	-	8	9.1	6	8.3	15	-	25	7.7
								Terra Rossas								
0- 3	17	7.3	9	8.3	13	7.2	17	7.3	7	6.7	18	6.7	26	7.5	20	7.9
3-10	17	7.5	13	8.5	10	7.2	8	7.3	6	6.6	9	6.7	15	7.8	18	7.9
10-20	17	7.4	14	8.5	10	7.2	12	7.6	7	-	13	6.7	6	-	9	-

TABLE 7: ZINC IN RENDZINA AND TERRA ROSSA PROFILES IN SOUTH-EAST SOUTH AUSTRALIA (McKENZIE, 1958)

Profile Number 1	2	3	4	5	6	7	8	9	10
				Terra Rossas					
75	56	51	86	50	59	11	24	21	21
79	56	55	70	71	39	9	27	19	15
18	65	21	72	56	45	7	8	10	29
22	35	46	110	68	4	11	6	4	11
26	20	-	42	9	-	7	-	-	4
-	-	-	52	36	-	18	-	-	-
-	-	-	-	-	-	8	-	-	-
-	-	-	-	-	-	8	-	-	-
				Rendzinas					
27	49	42	67	37	18	24	70	23	
26	56	65	69	33	16	20	38	25	
8	13	58	13	37	13	5	6	42	
14	90	25	43	18	11	5	10	7	
-	-	-	-	15	13	6	-	11	
-	-	-	-	-	7	-	-	-	

Note: Values are given (as in Tables 3 and 5) from surface to base of the soil profile.

TABLE 8: NICKEL IN SOILS IN TASMANIA (TILLER, 1959)

	Krasnozam		Grey-Brown Podsol		Brown Earth		Black Earth	
	Ni*	pH	Ni*	pH	Ni*	pH	Ni*	pH
Surface:	140	5.8	14	-	54	6.1	72	6.5
	130	6.0	13	6.2	54	6.1	79	6.7
Down Profile:	120	6.1	27	6.1	96	7.0	100	7.2
	150	6.0	39	-	78	7.5	110	8.0
	140	6.1	39	6.4	65	7.9	120	9.2
	170	6.1	91	8.1	-	-	-	-
Dolerite:	110	-	79	-	69	-	140	-

* Results in ppm.

TABLE 9: NICKEL IN GROUNDWATER RENDZINAS AND TERRA ROSSAS OF SOUTH AUSTRALIA (GILES, 1960)

Depth	Soil Number																			
	1		2		3		4		5		6		7		8		9		10	
inches	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH	Ni	pH
	Groundwater Rendzinas																			
0- 3	2.8	8.2	2.6	8.2	2.5	8.2	1	8.2	12	7.7	5.0	8.1								
3- 9	2.5	8.5	4.3	8.3	6.0	8.1	1	8.2	16	8.0	4.7	8.4								
9-18	2.5	8.1	1	8.9	8.9	8.3	1	8.3	11	8.4	5.1	8.5								
	2.0	8.8	1	-	2.0	8.6			13	8.6	4.1	8.8								
					2.0	8.7			16	8.6										
	Terra Rossas																			
down	2.3	7.3	1	8.3	1	6.5	2.7	7.3	<1	6.7	35	6.7	4.7	7.5	29	7.9	20	8.1	2.9	6.7
profile	2.8	7.5	1	8.5	1	7.2	2.2	7.3	1	6.6	34	6.7	5.4	7.8	31	7.9	17	7.9	3.7	6.6
	5.8	7.4	1	8.5	1	7.2	2.0	7.6	1	-	37	6.7	<1	-	1	-	1	-	5.6	6.8
	1.0*	-	1.5	8.6	2	7.2	1.0	-			7.1	-							1.0	-
			<1	-	<1	-														

* The last value in each column refers to a sample collected from bedrock.

TABLE 10: ZINC IN SOILS AND ROCKS

Author(s)	Date	Material Analysed	Rock Types	Locality	No. of Samples	Depth inches	Back-ground ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Mesh Size
					Zinc in Soils								
Blackburn & Giles	1963	terra rossa	limestone	south-east S. Australia	9	0- 5	14	-	26	6.7-8.4	semi-arid	total	-
		rendzina	marl, tuff	- ditto -	4	0- 8	50*	-	110	7.0-8.1	-ditto-	total	-
		groundwater rendzina	marl	"	11	0- 8	27	-	45	6.6-8.8	"	total	-
		- ditto -	extrusives	"	11	0- 8	17	-	34	8.1-8.4	"	total	-
		groundwater podsol	sands	"	5	0- 5	5	-	9	5 -6	"	total	-
		meadow podsol	sands	"	2	0- 6	16	-	18	6.0	"	total	-
		krasnozem	basalt	"	2	0- 5	37	-	50	6 -6.5	"	total	-
Baldock	1969	terra rossa	acid basement, carbonate	Uganda	1255	-	100*	250*	400-500	-	warm,humid	$K_2S_2O_7$	-150
Bose	1964	soil	-	India	-	15-30cm	-	-	4000	-	semi-arid	-	-
Beers et al.	1970	soil	-	Utah	300	8-12	244	-	-	-	semi-arid	XRF	-
Cole et al.	1968	skeletal soils	limestone	Northern Territory	-	-	30*	50*	150*	-	warm, arid	-	-
Dreimains	1960	glacial till	-	E. Canada	40	-	<150	150-600	-	-	-	-	- 80
Ermengen	1957	till & soil	-	Quebec	4300	B and A_0 horizons	-	50*	400*	-	cool, wet	hot HNO_3	-
Giles	1968	solodic soils	-	S. Australia	38	0- 6	3*	-	11	5.8-8.6	warm, dry	total	-
		podsols	-	Victoria	16	0- 7	5- 10*	-	55	5.1-6.7	-	total	-
		clays	-	Victoria	17	0- 7	5- 10*	-	24	7.8-9.6	-	total	-
		black earths	-	Victoria	2	0- 7	36*	-	37	6.0-6.1	-	total	-
		terra rossa	-	Victoria	2	0- 6	16*	-	17	6.5-7.3	-	total	-
Hawkes	1958	laterite	schists	Nigeria	-	down profile ↓	81 155 150	-	-	-	tropical	hot HNO_3	-
Hawkes and Lakin	1949	clayey soil	limestone	Tennessee	36	0- 6ft	400	700*	1000	-	-	-	-

Continued

TABLE 10: CONTINUED

Author(s)	Date	Material Analysed	Rock Types	Locality	No. of Samples	Depth inches	Back-ground ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Mesh Size
					Zinc in Soils								
Huff	1952	soil	-	USA	-	-	80-500	-	5500	-	mostly semi-arid	$K_2S_2O_7$	- 2 mm
Keith	1969	Brunizem & podsol	sediments, limestone	Tri-State USA	458	A horizon	58	-	1007	-	-	total	-200
						B horizon	48	-	144	-	-	-	-
						C horizon	49	-	1019	-	-	-	-
Nicolas & Brooks	1969	Brown earths	-	New Zealand	-	B horizon	-	250	-	-	warm, humid	HF/HNO_3	-
Padget et al.	1969	soil	-	N. Sweden	1710	≥0.5 m	70	-	2200	-	cold, wet	-	-
Thorne et al.	1942	topsoil	-	Utah	72	-	181 6.0	-	-	7	warm, dry	total Cx	-
		upper sub-surface	-	Utah	-	-	101 3.5	-	-	7.3	warm, dry	total Cx	-
		lower sub-surface	-	Utah	-	-	87 4.0	-	-	7.4	warm, dry	total Cx	-
Webb	1959	soil	shale, limestone	England	-	18-24	80*	150-200*	600*	-	cool, humid	-	- 80
			mudstones, grits	S. Wales	-	12-18	50-60*	100*	350*	-	cool, humid	-	- 80
Williams	1969	podsol	granite	W. Australia	-	-	0-170	-	710	5 -8	hot, arid	-	-
Wright	1967	skeletal soils	limestone	Sellicks Hill	-	-	25- 35	60- 70	450*	-	Mediter-ranean	$HClO_4$	- 80
Fairburn	1967	soil	limestones	Mt Coffin, SA	1395	few inches	40	65	-	-	semi-arid	-	- 80
	1968	residual soil	marble & metamorphics	Yudnamutana	227	few inches	32	48	-	-	semi-arid	-	- 80
	1968	residual soil	diapiric rocks	Burr, SA	278	few inches	39	60	-	-	semi-arid	-	- 80
Semple	1967	residual soil	dolomites & sediments	Northern Territory	930	several feet	60	300	3200	-	semi-arid	-	- 80
	1968	residual soil	-ditto-	-ditto-	774	several feet.	60	200	1000	-	semi-arid	-	- 80

Continued

TABLE 10: CONTINUED

Author(s)	Date	Material Analysed	Rock Types	Locality	No. of Samples	Depth inches	Back-ground ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Mesh Size
Zinc in Rocks													
Almond & Morris	1969	altered acid volcanics	-	Utah	25	-	5*	10*	37*	-	-	Acetic acid leach	-
		- ditto -	-	Utah	25	-	5-10*	20*	20	-	-	H_2SO_4	-
		intrusive monzonite	-	Utah	24	-	<1	1*	2	-	-	acetic acid	-
		- ditto -	-	Utah	24	-	1-5*	20-40*	70	-	-	H_2SO_4	-
Baldock	1969	carbonatite	-	Uganda	6-12	-	5-20*	-	340	-	-	total	-
		syenite	-	Uganda	-	-	10-20*	-	200	-	-	total	-
		ultrabasic	-	Uganda	-	-	50*	-	200	-	-	total	-
		alk. igneous	-	Uganda	-	-	70*	-	175	-	-	total	-
Cooper & Huff	1951	limestone	copper-manto	Arizona	8	-	25*	-	290	-	-	aqua regia	-
		hornstone	- ditto -	Arizona	7	-	40*	-	110	-	-	aqua regia	-
Huff	1955	sandstone	-	Arizona	24	-	30*	-	160	-	-	dil. HNO_3	-
Morris & Lovering	1952	quartz monzanite	-	-	-	-	10	-	200	-	-	-	-
		limestone wall-rocks	-	-	-	-	20-30	-	300-400	-	-	$HF/HClO_4$	-
Warren & Delavault	1960	granodiorite	-	W. Canada	19	-	50*	-	136	-	-	hot aqua regia	-
		quartz diorite	-	W. Canada	2	-	42*	-	92	-	-	- ditto -	-
		granite	-	W. Canada	8	-	25*	-	96	-	-	"	-
Wright	1967	limestone	-	Sellicks Hill	-	-	20	-	1400	-	-	$HClO_4$	-
		siltstone	-	Sellicks Hill	-	-	70	-	350	-	-	-	-

* Estimated values.

TABLE 11: COPPER IN SOILS

Author(s) Date	Material Analysed	Rock Types	Locality	No. of Samples	Background ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Depth inches
Almond & Morris, 1951	Altered rock	latite	Utah	23	8-10	20*	32	-	hot, arid	hot H_2SO_4	-
Blackburn & Giles, 1963	terra rossa	limestone	south-east S.Australia	15	5	-	-	6.7-8.4	-	total	0- 5
	rendzina	marl	- ditto -	2	7.5	-	9.3	7.1-7.5	-	total	0- 8
		tuff	"	2	30	-	45	7 -8.1	-	total	0- 6
	groundwater rendzina	marl	"	18	8	-	17	7.6-8.8	-	-	0- 8
	groundwater podsol	sil sand	"	5	3.7	-	6.5	5 -6	-	-	0- 5
	podsol	sil sand	"	2	6	-	7.2	6.0	-	-	0- 6
	krasnozem	basalt	"	2	76	-	130	6.0-6.5	-	-	0- 5
Clarke, 1953	soil	-	Arizona	17	60-100*	-	-	-	desert	10% H_2SO_4	-
Cole et al, 1968	soil	-	Bulman, NT	-	50	200	800	4.6-5.4 5.8-7.0	-	-	-
			Waimin Springs	-	15	40	45	6.4-7.0	Savannah	-	-
Coope & Webb, 1963	soil	porphyry copper	Philippines	-	100	1000	10000	-	-	-	-
Cooper & Huff, 1951	CO_3 rocks, hornstones	carbonates nr acid stock	Arizona	-	10-15*	100	-	-	arid	HNO_3	-
De Grys, 1964	soils	chalcopyrite in batholith	Chile	-	95-130	-	>1000	-	desert	-	-
							> 500	-	mediterranean	-	-
Dreimanis, 1960	soil and till	various	E. Canada	49	<50	50-150*	>4000	-	cool,humid	-	-
				68	<75	75	500				
				99	<75	75	150				
				17	<75	150	400				
				11	<75	75	200				
Ermengen, 1957	soil and till	-	N. Quebec	4300	5-15*	50*	220*	-	cool,humid	hot HNO_3	-
					<100	200*	1000*				
Fairburn, 1967a	soil**	various sediments	Serle-Angepena	-	20-40	>100*	420	-	-	-	3- 6
					30	>100*	260				
1967	**	-	Mt Coffin, SA	-	29	50	1000	5 -7	mediterranean	-	-
1968a	**	-	Yudnamutana, SA	193	50*	85	>260	-	mediterranean	-	-
1968b	**	-	Burr, SA	795	23	40	>170	-	mediterranean	-	-
Govett, 1960	polydrained soil**	-	Rhodesia	175	120	230	-	4.7-6.0	sub-tropical	total	0- 3
				175	80	170	-	4.7-6.0	sub-tropical	total	18
				175	35	70	-	4.7-6.0	sub-tropical	Cx	0- 3

Continued

TABLE 11: CONTINUED

Author(s) Date	Material Analysed	Rock Types	Locality	No. of Samples	Background ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Depth inches
Govett, 1960	poorly drained soil**	-	Rhodesia	175	15	40	-	4.7-6.0	sub-tropical	Cx	18
	well drained soil**	-	Rhodesia	275	110	190	-	4.7-6.0	sub-tropical	total	0- 3
				275	80	150	-	4.7-6.0	sub-tropical	total	18
				275	20	50	-	4.7-6.0	sub-tropical	Cx	0- 3
	bank soil**	-	Rhodesia	275	4	15	-	4.7-6.0	sub-tropical	Cx	18
Govett & Hale, 1964	immature soils**	-	Philippines	-	0- 10	25- 100	-	-	-	Cx	0- 3
					25-100	300-1000	-	-	-	Lx	18
Hawkes & Salmon, 1960	peat***	-	New Brunswick	183	12	60	-	-	cool,humid	total $K_2S_2O_7$	0-12
Hornbrook, 1969	hill & swamp soil	-	British Columbia	96	30*	55*	1000	-	cool,humid	HCl	A horizon
				96	150*	375*	>1000	-	cool,humid	-	B horizon
Hosking, 1959	soil on granite	-	Cornwall	-	50*	200*	500-600*	-	temperate	-	-
Huff, 1950	residual soil	-	Colorado	9	32	-	-	-	-	-	-
	soil	andesite	Arizona	10	-	100*	720	-	semi-arid	-	-
		limestone	Arizona	10	-	200*	930	-	arid	-	-
		quartzite	Idaho	16	<200	400	3000	-	arid	-	-
		gneiss	Colorado	12	<100	300	5300	-	arid	-	-
		quartzite & schist	N.Carolina	9	<150	200	720	-	temperate-humid	-	-
Lovering et al. 1950	soil & alluvium**	-	Arizona	-	20	50-100	8000	-	warm, arid	HCl	-
Makunina, 1962	humus horizon	-	S. Urals	-	<5	-	<1%	-	cool	total	-
	illuvial horizon	-		16	≤100	-	1%	-	-	-	-
	clays	-		(5)	50-1000	-	-	-	-	-	-
	illuvial on clay	-		7	50-1000	-	-	-	-	-	-
Malyuga & Makarova, 1956	chemozem	-	Tuva	-	20- 240	-	1700	7 -8	semi-desert	total	-
Padget et al. 1969	soils, some glacial till	-	N. Sweden	1710	40	50	250	-	-	-	below B horizon
Semple, 1967	residual soil**	-	Rum Jungle	930	100	300	1400	-	hot, semi-arid	hot $HClO_4$	variable several ft
1968	residual soil**	-	Rum Jungle	774	40	150	320	-	- ditto -	ditto	-ditto -
Shatwell, 1966	residual soil**	-	Rum Jungle	-	30-40	150	600	-	"	"	"
Sofoulis et al. 1968	lake floor sediment**	-	W.Australia	-	0-200*	310	1100	6 -8.2	hot, arid	-	3-12

Continued

TABLE 11: CONTINUED

Author(s) Date	Material Analysed	Rock Types	Locality	No. of Samples	Background ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Depth inches
Sofoulis & Williams, 1969	soil***	-	W.Australia	-	<300	675	7750	-	-	-	-
Tan & Yu, 1970	**	-	Taiwan	-	50-150	200	4000	-	temperate	total	0.3 m
					4-15	20	-	-	hot, humid	Cx	0.5 m
											0.9 m
Tooms & Webb, 1961	laterite**	-	-	>3000	45*	75*	700*	-	-	total	12-18
					0-5	10	100	-	-	Cx	
	poorly drained soil**	-	-	>3000	100	-	4500	-	-	total	
					110	-	1200*	-	-	Cx	
Tooms & Webb, 1961	organic topsoil**	-	-	-	90	1150	3500	-	-	total	0- 2
					4	360	1200	-	-	Cx	0- 2
	clayey subsoil	-	-	-	80	800	2500	-	-	total	2- 6
					4	170	900	-	-	Cx	2- 6
Webb, 1956	laterite soils**	-	-	-	50	-	-	-	hot,monsoonal	total	-
	A_0**	-	-	-	4	-	-	-	-	Cx	-
					35	-	-	-	-	total	-
	A_1**	-	-	-	1.5	-	-	-	-	Cx	-
					45	-	-	-	-	total	-
	B**	-	-	-	50	-	-	-	-	total	-
	C**	-	-	-	60	-	-	-	-	total	-
Williams, 1966	soil	-	Southland New Zealand	-	20*	60*	160*	-	humid	-	-
			McConnochies Otago, NZ	-	<50*	100*	>300	-	temperate	-	-
			Ironstone Creek	-	<100	170	>400	-	temperate	-	-
Williams, 1969	-	-	W.Australia	-	0-130	280	>600	5 -7	hot, arid	-	-
					0-110	170	>1000	-	-	-	-

* Estimated values.

** Minus 80 mesh.

***Minus 200 mesh.

TABLE 12: LEAD IN SOIL

Author(s)	Date	Soil Type	Rocks	Mineralisation	Locality	No. of Samples	Depth inches	Background ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Mesh Size
Boyle & Cragg	1957	glacial till	metamorphics	Pb/Zn lodes	Alaska	-	-	30*	50*	18000	5.2-7.2	permafrost	cold HNO_3	all sizes
Cole et al.	1968	skeletal	CO_3 and chert	Pb/Zn	N.Territory	-	-	-	100*	6000	5.8-7.0	dry, hot	-	-
Fairburn	1968	-	volcanics & marbles	-	north-east S.Australia	227	few inches	15	25	32*	-	hot, semi-arid	-	-80
			siltstones dolomites	Cu Veins	Burr	278	-ditto-	14	25	50*	-	- ditto -	-	-80
Hawkes	1958	laterite	shale sandstone	fault zones	Nigeria	-	varied	64-210 (~50)	-	20000	-	wet, hot	hot HNO_3	-
Hosking	1959	-	slate	galena lode	Cornwall	-	base of B horizon	20	400*	>1000	-	mild,damp	-	-
Huff	1950	lithosols	dolomite	Pb/Zn Veins	Colorada	-	0-12	⩽50*	1000*	4400	-	-	total	-
Nicholas & Brooks	1969	-	andesite	Pb/Zn lode	New Zealand	-	B horizon	170	300*	>10000	4.0-5.5	warm,humid	HF/HNO_3	-40
Nicholls et al.	1966	skeletal	various	-	W.Queensland	-	-	25*	100*	⩾1600	5.7-6.4	hot, semi-arid	$KHSO_4$	-80
Padget et al.	1969	-	acid igneous	-	N. Sweden	1710	>0.5 m	30	-	250	-	-	-	-
Semple	1968	skeletal soil	siltstones dolomites	-	Rum Jungle	774	variable	25-40	120	1050	-	-	hot $HClO_4$	-80
Semple	1967	-ditto-	-ditto-	-	Rum Jungle	930	-	25	100	8400	-	-	- ditto -	-80
Shatwell	1966	"	"	-	Rum Jungle	-	variable	40-50	100	>2000	-	hot, semi-arid	"	-80
Webb	?	-	mudstones grits	-	S. Wales	-	12-18	50*	100*	360*	-	cool,humid	-	-80
Webb	?	peat	schist	-	Scotland	-	deep	50*	100*	1600*	acid	cool,humid	-	-80
Williams	1969	podsols	metamorphics	PbS Veins	W.Australia	-	⩾18	170*	-	>1000	5 -7.7	hot,acid	hot $HClO_4$	-85
Wright	1967	residual	-	Pb Veins	Sellicks Hill	-	1-12	20-30	50-60	350	-	warm, semi-arid	hot $HClO_4$	-80

* Estimated values.

TABLE 13: NICKEL IN SOILS

Author(s)	Date	Material Analysed	Rock Types	Locality	No. of Samples	Depth in.	Background ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Mesh Size
Baldock	1969	-	Various igneous rocks	Uganda	680	18	70*	100*	200*	-	warm, humid	$K_2S_2O_7$	-150
Blackburn & Giles	1963	terra rossa	-	south-east S.Australia	14	0-5	5*	-	-	6.7-8.4	warm, humid	total	-
		rendzina	-	-ditto-	4	0-8	65	-	-	7 -8	-ditto-	total	-
		groundwater rendzina	-	"	20	0-8	4	-	-	6.6-8.8	"	total	-
		groundwater podsol	-	"	5	0-5	<2	-	-	5 -6	"	total	-
		podsol	-	"	1	0-6	10	-	-	6	"	total	-
		krasnozem	-	"	2	0-5	90-400	-	-	6 -6.5	"	total	-
Giles	1968	Solodic and solonete soils	-	S.Australia & Victoria	28	0-8	<1- 2	-	-	5.8-8.6	temperate	total	-
		podsols	-	-ditto-	16	0-7	<2	-	-	5.1-6.7	semi-arid	total	-
		clays	-	"	17	0-6	4- 7	-	-	6.2-9.6	semi-arid	total	-
		black earths	-	"	2	0-7	6- 13	-	-	6.0-6.1	semi-arid	total	-
		terra rossas	-	"	2	0-6	14- 22	-	-	4.5-7.3	semi-arid	total	-
Miller	1957	soil	dolomite	NW USA	-	0-6	<8*	30*	500*	-	-	hot H_2SO_4	-2mm
						0-6	<16 (all values)	-	-	-	-	-ditto-	-2mm
		lateritic soils	ultrabasics	Oregon	-	0-6	1500*	2500*	>5000*	-	-	"	-2mm
		soils	ultrabasics	Montana	-	0-6	<8*	10*	100	-	-	"	-2mm
		soils	norik	Montana	4	0-6	60	-	-	-	-	"	-2mm
						0-6	50*	150*	1400	-	-	"	-2mm
					21	0-6	30*	120*	500	-	-	"	-2mm
					5	0-6	10-30*	-	140	-	-	"	-2mm
Semple	1968	skeletal soils	dolomites, sediments	N.Territory	774	**	30-50	100	240	-	hot,arid	hot,$HClO_4$	-80
	1967	skeletal soils	-ditto-	N.Territory	930	**	50	100	1700	-	hot,arid	hot $HClO_4$	-80
Warne	1967	immature soils	calcrete sands etc.	north S.Australia	275	3-6	⩽200*	>200*	>1000*	-	hot,arid	-	-80

* Estimated values.
** Variable - several feet.

TABLE 14: NICKEL IN STREAM SEDIMENTS

Author(s)	Date	Locality	Mesh Size	No. of Samples	Climate	Extraction	Background ppm	Threshold ppm	Maximum ppm
Boyle et al.	1966	N. Brunswick	- 80	3550	cool, humid	total	45	-	300
Williams	1966	New Zealand	-100	37	cool, humid	-	10*	16	36
Williams	1966	New Zealand	-100	30	cool, humid	-	10*	15*	40

* Estimated values.

TABLE 15: COPPER IN STREAM SEDIMENTS

Author(s)	Date	Locality	Mesh Size	No. of Samples	Back-ground ppm	Threshold ppm	Maximum ppm	pH	Climate	Extraction	Length of Dispersion	Other Information
Baldock	1969	Uganda	- 80	~30	50*	50-100*	>200	-	warm,humid	-	-	-
Binks	1968	Blinman	- 80	450	25	50	315	-	semi-arid	-	-	-
Boyle et al.	1966	N. Brunswick	- 80	3550	12	-	4000	-	cool,humid	-	-	-
Coope & Webb	1963	Philippines	- 80	>500	75-100	-	5000	-	tropical,wet	total	1000ft-1mile	-
		Philippines	- 80	>500	4- 20	-	1000	-	tropical,wet	Cx	- ditto -	-
De Grys	1964	Chile	- 80	-	30*	-	100-200	-	cool,humid	-	-	-
	1961	Chile	-200	several hundred	40	50- 60*	100*	-	cool,humid	HNO$_3$	-	-
Fairburn	1967	Serle-Angepena	- 80	>1000	20	30	160	-	hot,arid	HClO$_4$	-	-
Govett	1960	N. Rhodesia	- 80	37	35	-	50	-	warm	total	-	non-organic sand
				7	40	-	60	-	warm	total	-	non-organic clay
				24	45	-	60	-	warm	total	-	organic-rich
				37	3	-	7	-	warm	Cx	-	non-organic sand
				7	3	-	5	-	warm	Cx	-	non-organic clay
				24	10	-	21	-	warm	Cx	-	organic-rich
Govett & Hale	1967	Philippines	- 80	-	6.6	11	>350	7.8-8.0	warm,humid	Cx	-	-
					55	85	-	7.8-8.0	warm,humid	Lx	-	-
Kroon & De Grys	1970	Ecuador	- 80	-	50	100	4500	-	tropical	hot HNO$_3$	15 km	-
Nicholls et al.	1965	W. Queensland	- 80	-	<30*	30	>120*	-	semi-arid	K$_2$S$_2$O$_7$	-	-
Pavlides & Canney	1964	Maine	- 50	41	10*	15*	40	-	temperate,wet	total	-	Cx <1 ppm
Webb et al.	1959	N. Rhodesia	-	-	110-125	-	250-700	-	warm,humid	K$_2$S$_2$O$_7$	-	-
					20	-	100	-	warm,humid	Cx	-	barren rivers Cx = 3 ppm. total 40 ppm
Williams	1966	N. Zealand	-100	25	10*	15*	35*	-	cool,humid	-	-	-

* Estimated values.

TABLE 16: ZINC IN STREAM SEDIMENTS

Author(s)	Date	Locality	Mesh Sizes	No. of Samples	Climate	Extraction	Background ppm	Threshold ppm	Maximum ppm	Length of Dispersion
Baldock	1969	Uganda	- 80	-	-	-	≤50*	~100	>200	>1 mile
Binks	1968	Adelaide Hills	- 9 + 16	6-10	warm, semi-arid	total	19	-	62	-
			- 16 + 32				16	-	76	-
			- 32 + 60				16	-	80	-
			- 60 +115				13	-	78	-
			-115 +250				15	-	62	-
			-250				18	-	54	-
			- 9 + 16			6N HCl (Cx)	9	-	12	-
			- 16 + 32				10	-	12	-
			- 32 + 60				11	-	12	-
			- 60 +115				8	-	12	-
			-115 +250				7.5	-	8.8	-
			-250				9	-	7	-
	1968	Blinman	- 80	-	semi-arid, hot	-	30	45	290	-
Boyle et al.	1966	New Brunswick	- 80	3550	cool, humid	-	150	-	34000	-
Cole et al.	1968	N. Territory	-	-	hot, semi-arid	-	85	-	>680	≥½ mile
Hosking et al.	1964	Cornwall	- 80	-	cool, wet	hot HNO_3	40- 50*	-	>500	-
Kroon & De Grys	1970	Ecuador	- 80	-	temperate, humid	hot HNO_3	100	200	900*	3 km
Pavlides & Canney	1964	Maine	- 50	41	cool, wet	Cx	75-100*	-	175	-
Webb	1959	England	- 80	-	wet and cool	-	100*	250*	1200	-
Williams	1966	New Zealand	-100	-	cool, wet	-	<20*	20	40	≤¼ mile

* Estimated values.

TABLE 17: LEAD IN STREAM SEDIMENTS

Author(s)	Date	Locality	Mesh Sizes	No. of Samples	Climate	Extraction	Background ppm	Threshold ppm	Maximum ppm	Length of Dispersion
Boyle et al.	1966	N. Brunswick	- 80	3550	cool, humid	total	25	-	3300	-
Cole et al.	1968	Bulman, NT	-	-	hot, arid	-	70	-	785	2000-3000ft
De Grys	1961	Chile	-200	-	temperate, humid	hot HNO_3	25	50*	100*	-
Kroon & De Grys	1970	Ecuador	- 80	-	hot, humid	aqua regia	-	100*	540	2 km
Nicholls et al.	1966	W.Queensland	- 80	-	hot, arid	$K_2S_2O_7$	-	5	⩾20	½ mile
Solovov & Kunin	1961	W.Tien-Sham	0.25-0.5mm	>5000	cold, wet	total	-	200	300	1-4 km
Webb	1959	England	- 80	-	cool, humid	total	20*	50*	200*	1 mile
Wright	1967	Sellicks Hill	- 9 +16	-	Mediterranean, dry	$HClO_4$	75	~90*	-	¼ mile
			-16 +32	-		-	65	-	-	-
			-32 +60	-		-	60	-	-	-
			-60 +115	-		-	62	-	-	-
			-115+250	-		-	62	-	-	-
			-250	-		-	55	-	-	-
Binks	1968	Blinman	- 80	450	warm, semi-arid	-	17	30	40	⩽½ mile*

* Estimated values.

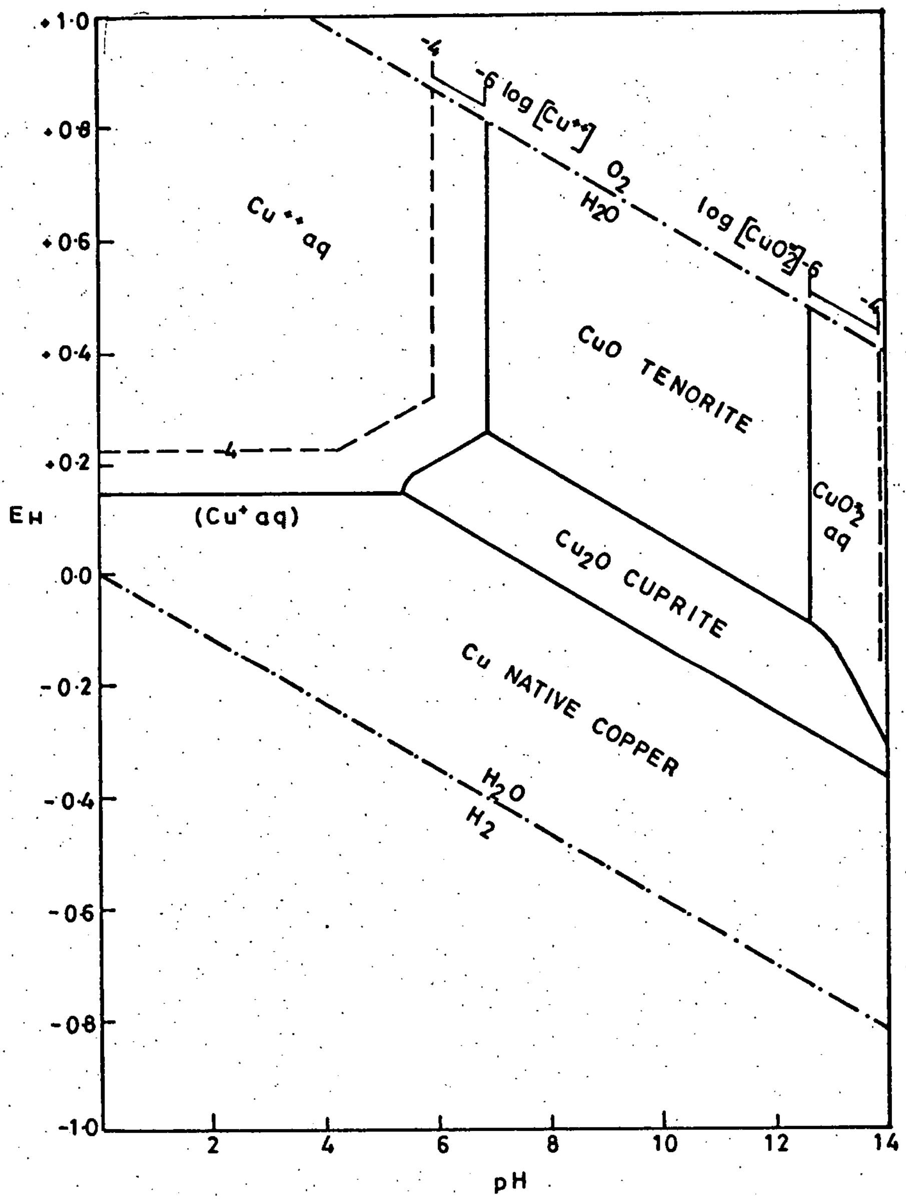


FIGURE 1: STABILITY RELATIONS AMONG COPPER COMPOUNDS IN SYSTEM Cu-H_2O-O_2 AT 25° C AND 1 ATMOSPHERE TOTAL PRESSURE. (Courtesy J. Anderson)

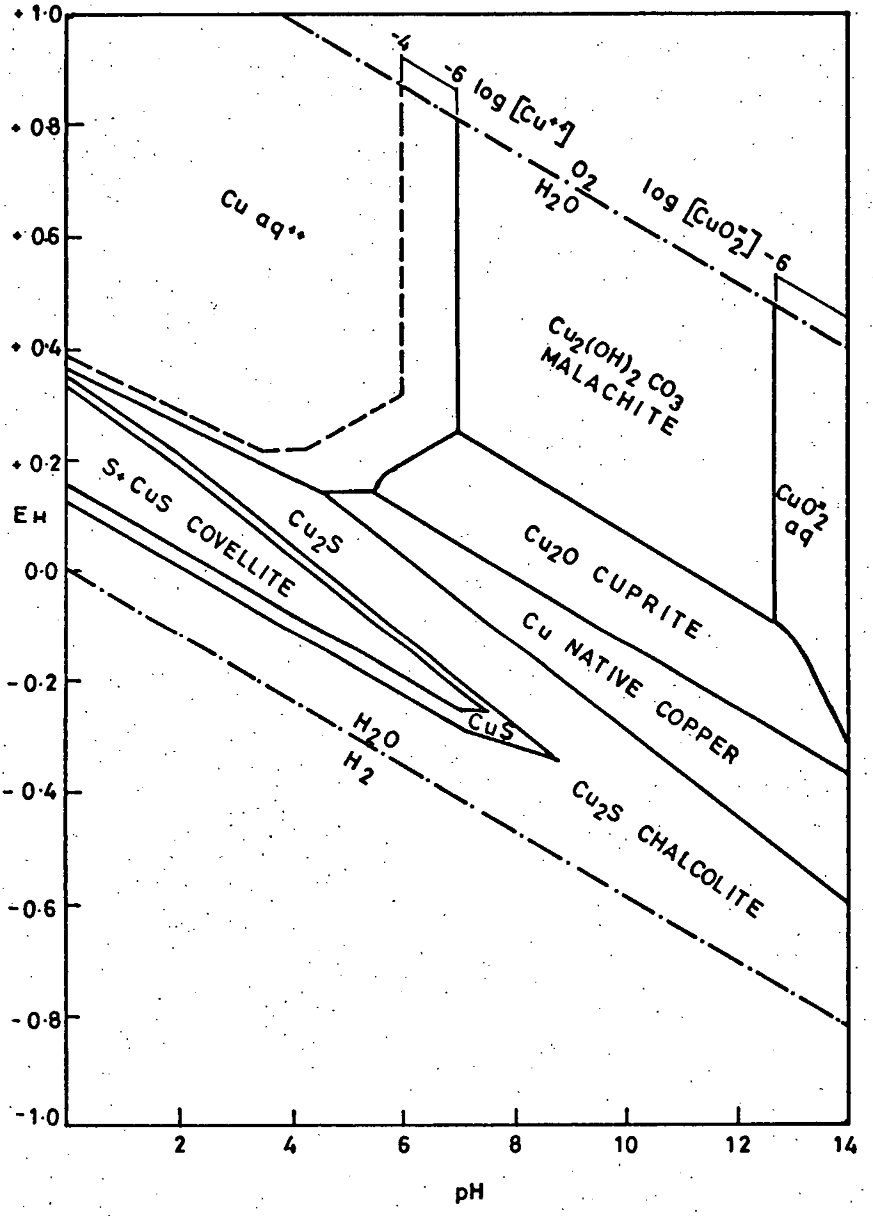


FIGURE 2: STABILITY RELATIONS AMONG SOME COPPER COMPOUNDS IN THE SYSTEM $Cu-H_2O-O_2-S-CO_2$ AT 25°C AND 1 ATMOSPHERE TOTAL PRESSURE. $P_{CO_2} = 10^{-3.5}$, TOTAL DISSOLVED SULPHUR SPECIES $= 10^{-1}$. (Courtesy J. Anderson)

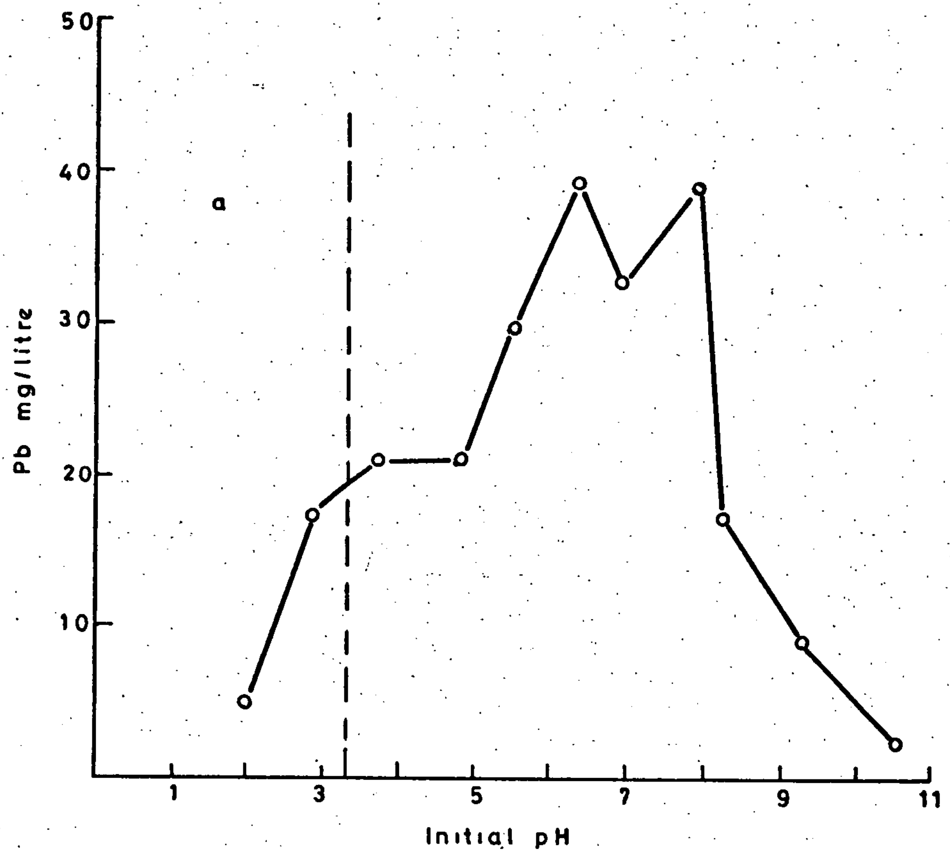


FIGURE 3: VARIATION IN THE CONCENTRATION OF LEAD DEPENDING ON THE INITIAL pH IN THE LIQUID PHASES OF EXPERIMENTS I-II
a = Region of high concentration of SO_4^{2-} ions

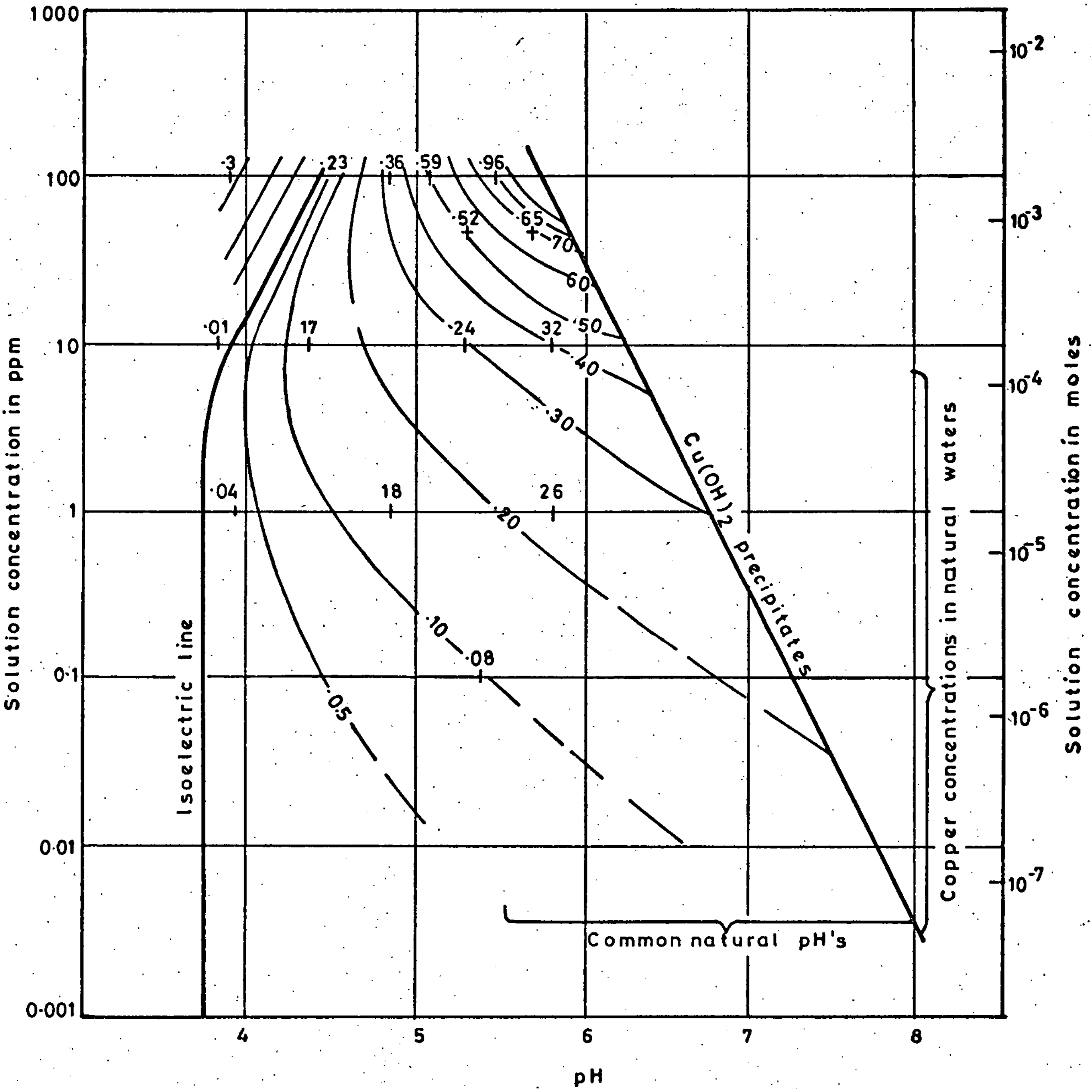


FIGURE 4: AMOUNT OF COPPER ADSORBED ON QUARTZ EXPRESSED IN µg OF COPPER PER g OF QUARTZ

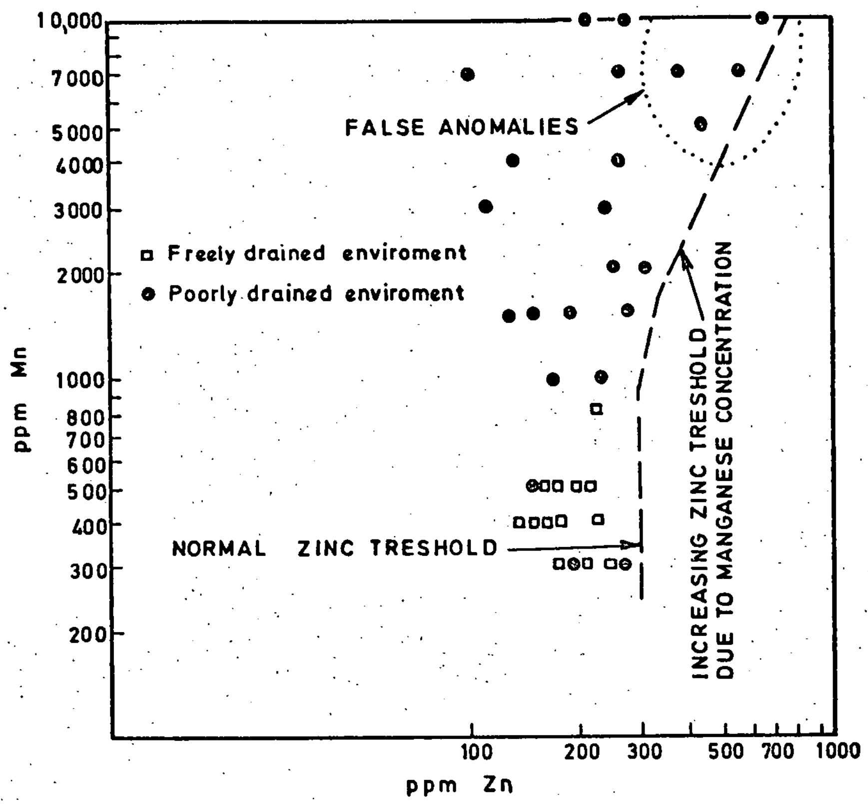
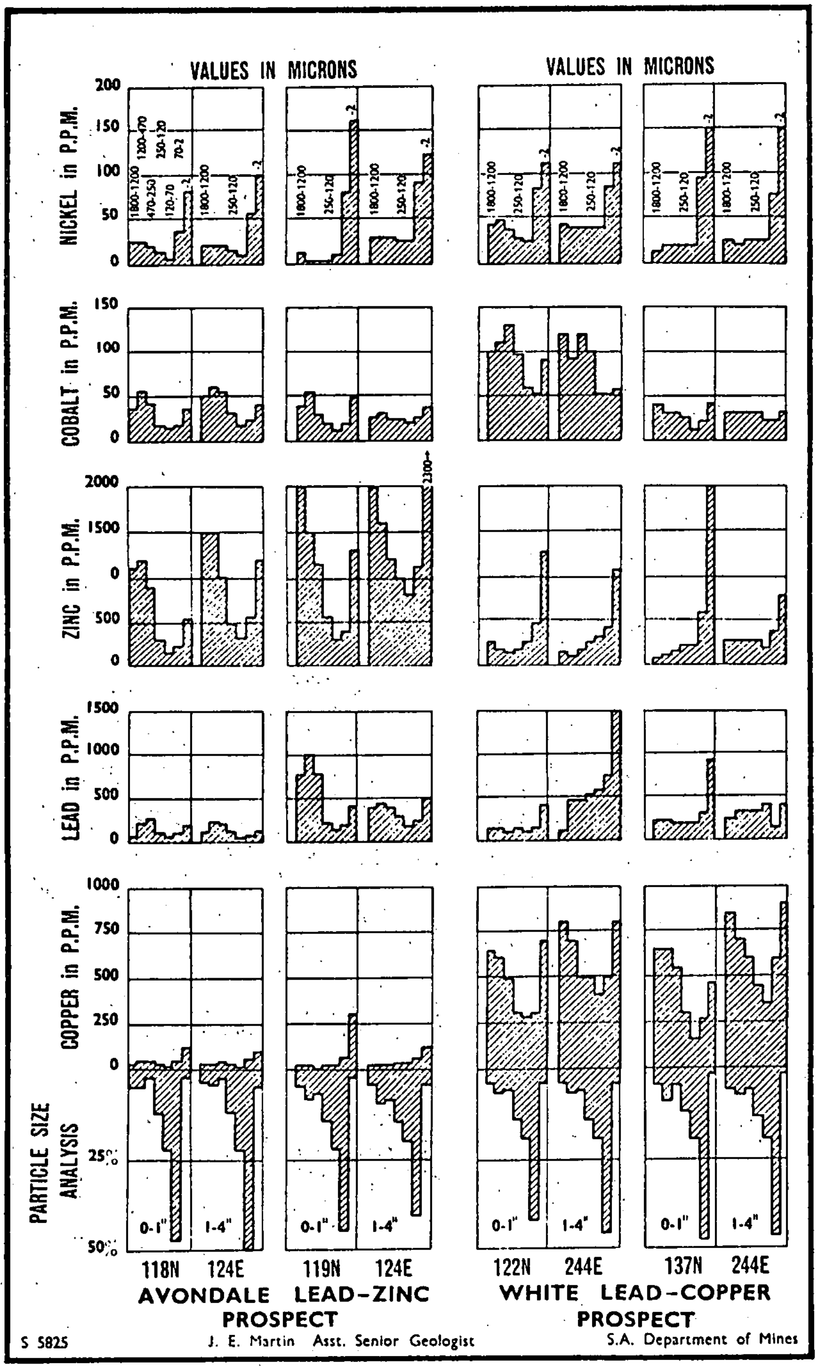


FIGURE 5: FALSE ZINC ANOMALIES IN DRAINAGE SEDIMENTS



S 5825 J. E. Martin Asst. Senior Geologist S.A. Department of Mines

FIG. 6—METAL CONTENT—WET SIEVED SOIL SAMPLES.
White Lead—copper prospect, and Avondale—lead-zinc prospect

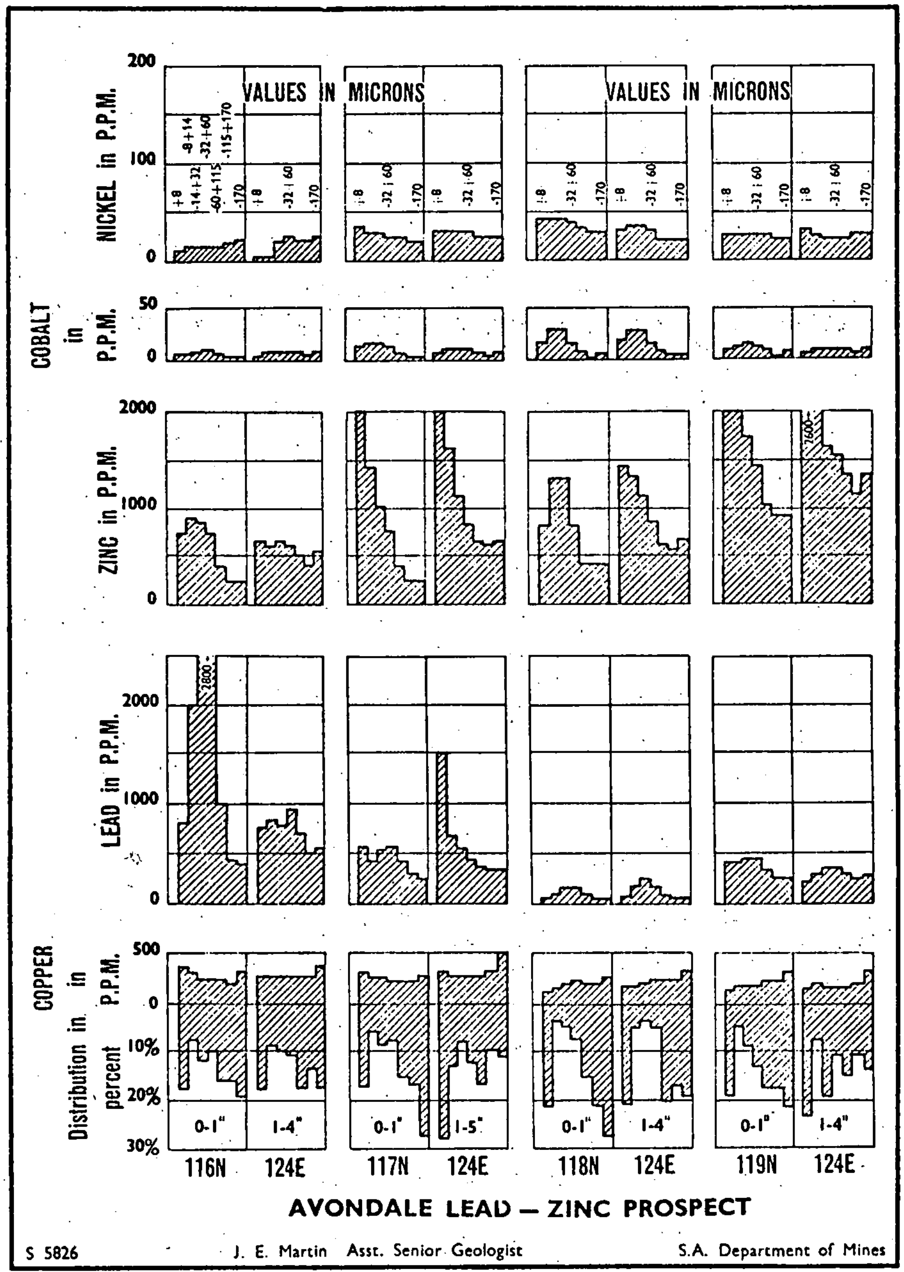


FIG.7 —METAL CONTENT—DRY SIEVED SOIL SAMPLES
Avondale lead-zinc prospect

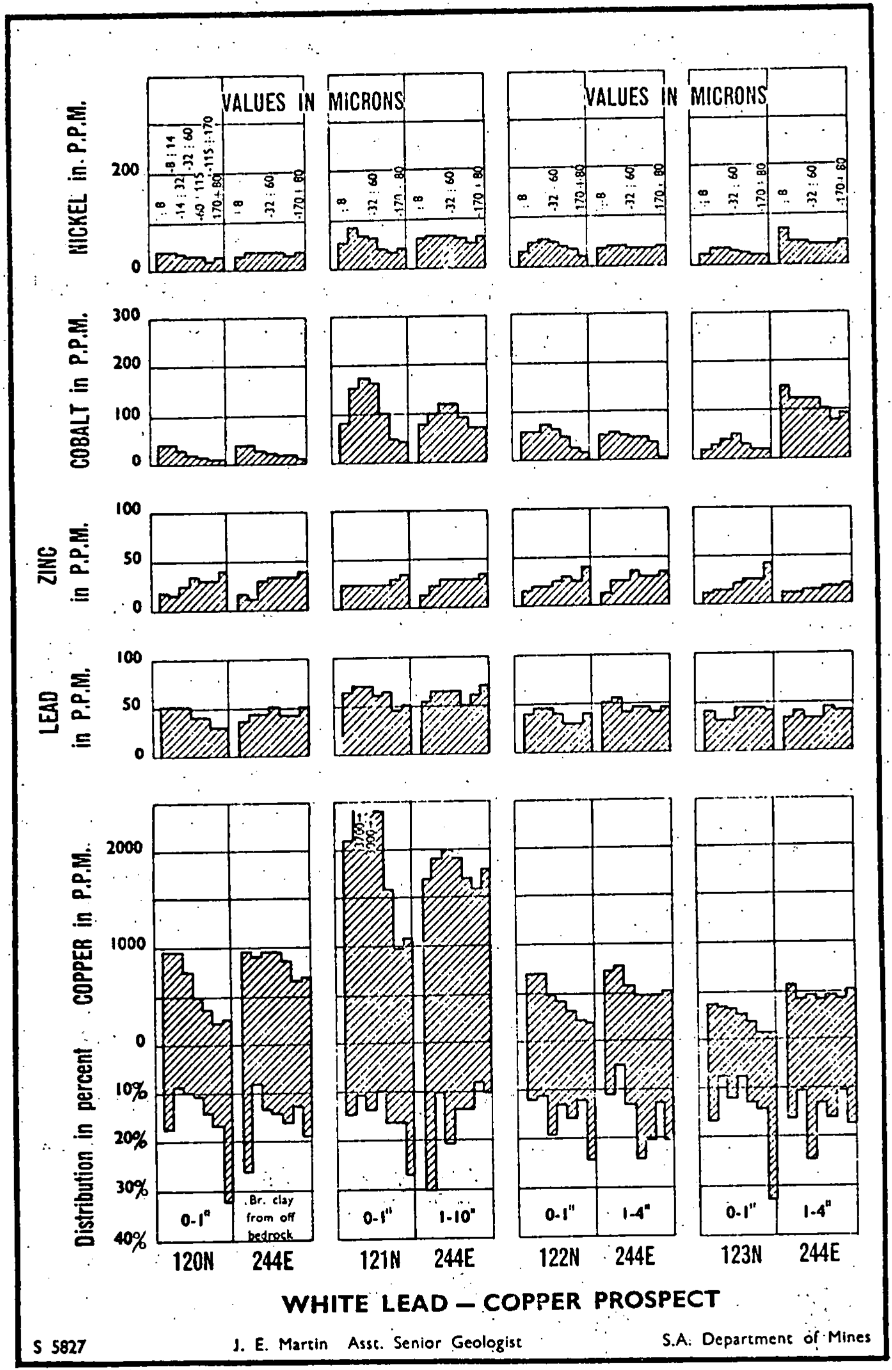


FIG. 8—METAL CONTENT—DRY SIEVED SOIL SAMPLES
White Lead—copper prospect

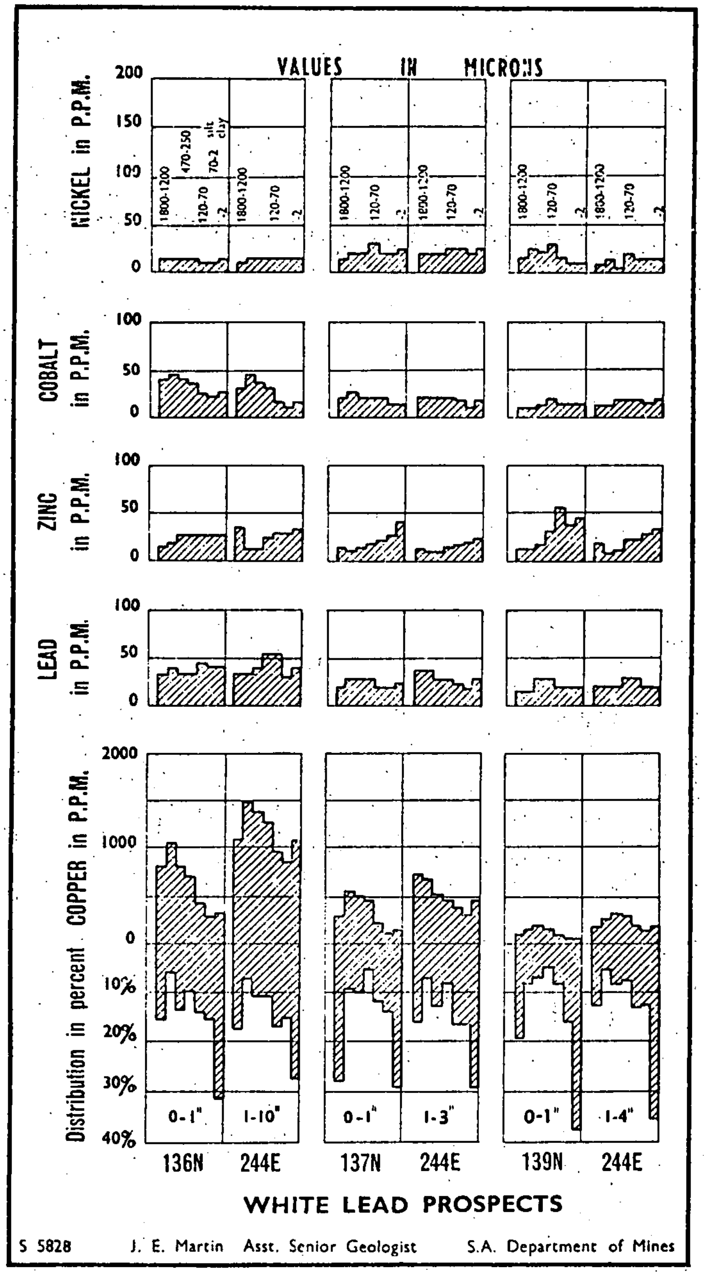


FIG. 9—METAL CONTENT—DRY SIEVED SOIL SAMPLES
White Lead—copper prospects inside diapir

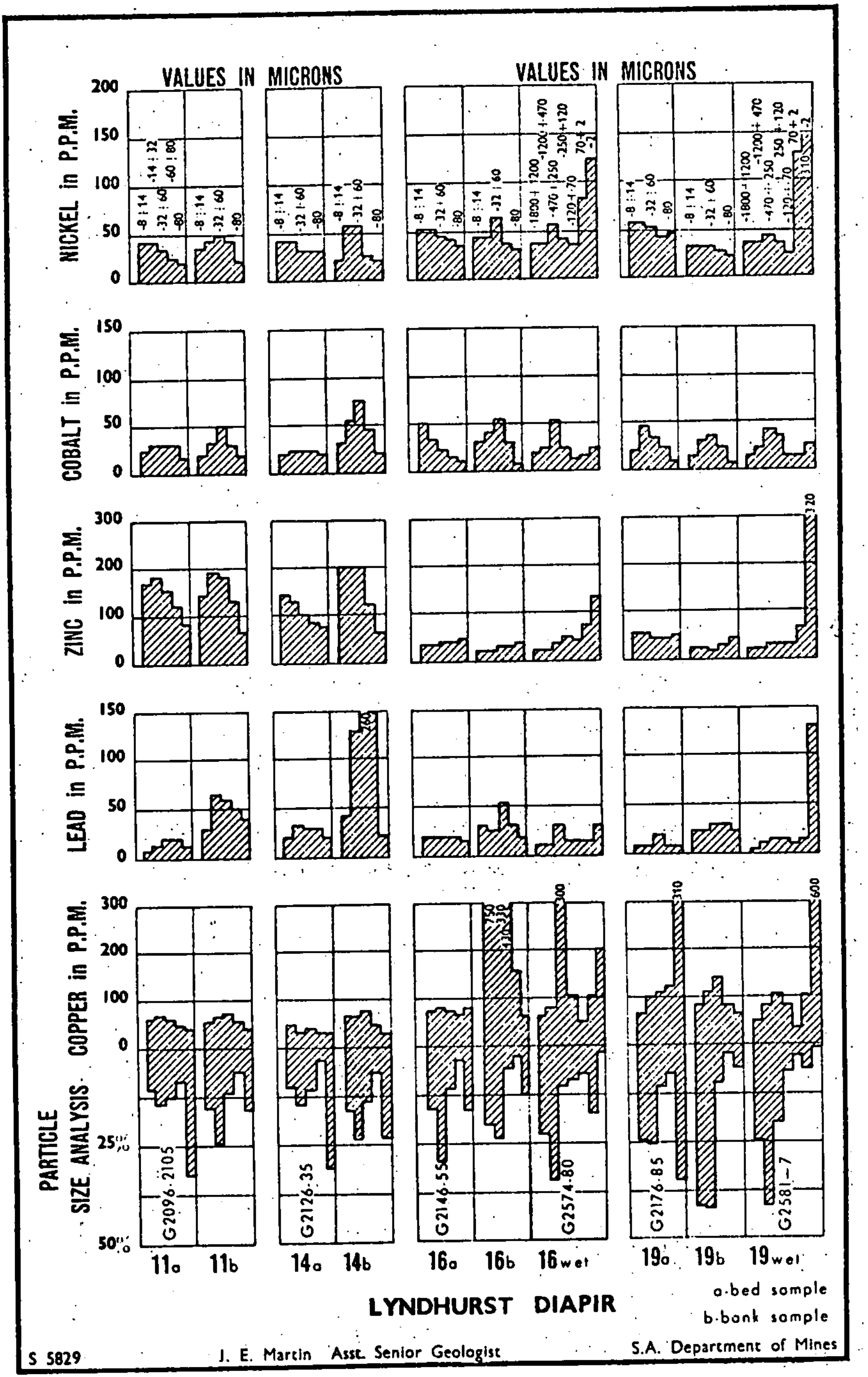


FIG. 10-PHYSICAL AND CHEMICAL ANALYSES OF TEN STREAM SEDIMENT SAMPLES LYNDHURST DIAPIR