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Govett, G.J.S. and Nichol, Ian, *Lithogeochemistry in mineral exploration; in Geophysics and Geochemistry in the Search of Metallic Ores; Peter J. Hood, editor; Geological Survey of Canada, Economic Geology Report 31, p. 339-362, 1979.*

Abstract

Lithogeochemistry, as used in this presentation, is defined as the determination of the chemical composition of bedrock material with the objective of detecting distribution patterns of elements that are spatially related to mineralization.

Mineralogical alteration zones in host rocks around mineral deposits have long been recognized and used as indicators of ore. Such alteration zones are the visible manifestations of physical and chemical changes in the host rocks resulting from either primary reactions associated with ore formation or subsequent secondary reactions between the ore and the host rocks. Chemical alteration halos may be more intense, and therefore detectable, over greater distances than mineralogical halos, since the lattice substitution of elements may be detected chemically without having any mineralogical representation. The scale and intensity of changes in the chemistry of the host rock is a function of the genesis of the ore, the chemistry of the host rock, and the nature of the secondary processes. Appreciation of these factors is fundamental to the successful application of lithogeochemistry to mineral exploration.

Lithogeochemistry has application at three levels of exploration: identification of geochemical provinces, favourable ore horizons, plutons or volcanic horizons on a regional reconnaissance scale; recognition of local halos related to individual deposits on a local reconnaissance or follow-up scale; and wall-rock anomalies related to particular ore-shoots on a mine scale.

Lithogeochemistry has been applied on a regional scale to the identification of mineralized areas in granitic and gneissic terrane (Sn, W, Mo, Cu, and U); in areas of basic intrusions (Ni, Cr, and Pt) and basic volcanic rocks (Cu); and in areas of sedimentary rocks (Cu, Pb-Zn, and Au-U). In other cases favourable geological environments have been recognized on the basis of some diagnostic geochemical parameter of lithological units spatially, and probably genetically, associated with mineralization. For example, productive greenstone belts can be distinguished from nonproductive greenstone belts, and cycles of volcanism containing significant massive sulphide deposits can be distinguished from equivalent nonproductive cycles on the basis of enhanced background contents of certain elements; areas of black shale horizons enriched in chalcophile elements may be readily identified, and these horizons may be spatially associated with more favourable horizons – such as quartzite and limestone – for the emplacement of mineralization.

On a more local scale, geochemical dispersion halos of both major and minor elements have been shown to be associated with porphyry copper deposits. Similarly, depletion of Na and Ca, and enhancement of Fe, Mg, and K – together with characteristic distribution patterns of a wide range of trace elements – appear to be a general local-scale feature associated with volcanogenic massive sulphide deposits. Wall-rock dispersion halos have proved useful in detailed exploration, although their nature is very much dependent on local geological conditions.

Various techniques have been employed to detect bedrock anomalies related to mineralization; these include whole rock analysis, measurement of water-soluble elements (especially halogens), and analysis of mineral separates. In some cases multivariate statistical techniques have been used to identify otherwise unrecognized, subtle features of the data or as a means of enhancing very weak anomalies.

The results cited are examples where lithogeochemistry has been or could have been used successfully for the location of particular types of mineralization. They are also indications of the diversified role lithogeochemistry could have in mineral exploration.

Exploration requirements in the future will demand techniques to find mineral deposits in situations where current methods have failed. In particular, presently available routine geochemical methods are unsuitable, or have limited application, for the location of deeply-buried or blind deposits – these are the types of deposits that probably will become common targets for mineral exploration as the more easily detected near-surface targets are exhausted. The subtle lithogeochemical anomalies and element zoning found in the cap-rocks of some types of blind deposits offer scope for their detection, and may also be useful in drill-hole control.

The application of lithogeochemistry is largely a function of the availability of adequate samples either from suitable bedrock exposure or drill core; obviously, it must have limited potential in areas of deep weathering and areas of extensive overburden or soil cover. However, within these constraints, recent developments offer convincing evidence of the potential power of lithogeochemistry as an exploration method.

Résumé

Dans ce rapport, on définit la lithogéochimie comme la détermination de la composition chimique de la roche en place; par cette méthode, on peut déceler le mode de distribution des éléments dans l'espace, dans la mesure où la distribution est liée à la minéralisation.

On a reconnu il y a longtemps l'existence de zones d'altération minéralogique dans les roches favorables qui renferment les gîtes minéraux; on les utilise comme "indicateurs" du minerai. Ces zones d'altération sont les manifestations visibles des modifications physiques et chimiques que subissent les roches favorables par suite des réactions secondaires ultérieures qui ont eu lieu entre le minerai et les roches favorables. Les auréoles d'altération chimique sont parfois plus intenses, par conséquent plus facilement décelables, et cela, sur de plus grandes distances que les auréoles minéralogiques, puisque toute substitution d'éléments apparaît à l'analyse chimique, sans qu'il soit nécessaire d'effectuer des observations minéralogiques. L'étendue et l'intensité des variations de la composition chimique de la roche favorable dépendent du mode de genèse du minerai, de la chimie de la roche favorable et de la nature des processus secondaires. Il est essentiel d'évaluer chacun de ces facteurs, pour pouvoir appliquer avec succès la lithogéochimie à la recherche minière.

La lithogéochimie s'applique à trois niveaux d'exploration: l'identification des provinces géochimiques, des horizons minéralisés favorables, des plutons ou des horizons volcaniques, à une échelle de reconnaissance régionale; l'identification des auréoles locales liées à des gîtes particuliers, à l'échelle de la reconnaissance locale ou des travaux d'exploration détaillée; et l'étude des anomalies qui caractérisent la roche encaissante et sont liées à l'existence de colonnes minéralisées, cela à l'échelle de l'exploitation minière.

On a appliqué, à l'échelle régionale, la lithogéochimie à l'identification de zones minéralisées dans des terrains granitiques et gneissiques (Sn, W, Mo, Cu et U); dans des zones d'intrusions basiques (Ni, Cr et Pt) et de roches volcaniques basiques (Cu); et enfin dans des zones de roches sédimentaires (Cu, Pb-Zn, et Au-U). Dans d'autres cas, on a identifié des milieux géologiques favorables, en fonction de certains paramètres géochimiques diagnostiques caractérisant des unités lithologiques spatialement et sans doute génétiquement associées à une minéralisation. Par exemple, on peut distinguer les zones de roches vertes productives des zones équivalentes non productives, et distinguer les cycles volcaniques pendant lesquels se sont constitués d'importants gîtes sulfureux massifs, des cycles équivalents non productifs, après accentuation des valeurs de fond de certains éléments; on peut facilement reconnaître les secteurs à horizons d'argile litée noire enrichis en éléments chalcophiles, lesquels peuvent être spatialement associés à des horizons plus favorables – tels que quartzites et calcaires – pour la mise en place de minéralisations.

A une échelle plus locale, les auréoles de dispersion géochimique des éléments importants et secondaires sont parfois, comme on l'a démontré, associées à des gîtes porphyriques de cuivre. De même, l'appauvrissement en Na et Ca, et l'enrichissement en Fe, Mg et K – en même temps que le mode de distribution typique d'une vaste gamme d'éléments-traces – semblent constituer un caractère local dû à la présence de gîtes sulfureux massifs, de types volcanogénique. Les auréoles de dispersion dans la roche encaissante se sont avérées utiles pour l'exploration détaillée, bien que leur nature dépende beaucoup plus des conditions géologiques locales.

On a employé diverses techniques pour déceler les anomalies que présente la roche en place du point de vue de la minéralisation; parmi ces techniques, citons l'analyse de la roche entière, la mesure des éléments solubles dans l'eau (en particulier les halogènes), et l'analyse des diverses fractions minérales. Dans certains cas, on a employé des méthodes utilisant plusieurs variables statistiques, pour mettre en relief des résultats moins évidents, jusque là ignorés, ou bien des anomalies très faibles.

Les résultats cités représentent des cas où la lithogéochimie a ou aurait pu donner des résultats satisfaisants pour localiser certains types de minéralisation. Ils indiquent aussi le rôle multiple que pourrait jouer la lithogéochimie dans l'exploration minière.

A l'avenir, il sera nécessaire d'employer de nouvelles techniques d'exploration là où les méthodes habituellement ont échoué. En particulier, les méthodes géochimiques couramment employées actuellement sont inadéquates, ou n'ont que des applications restreintes, pour la localisation des gîtes profondément enfouis ou tout simplement dissimulés – c'est-à-dire les sortes de gîtes qui probablement constitueront les principaux objectifs d'exploration, à mesure que s'épuiseront les minéralisations proches de la surface, plus facilement détectables. Les anomalies lithogéochimiques de faible intensité, et la zonalité des éléments qui caractérisent le chapeau (cap-rock) de certains types de gîtes dissimulés favorisent la détection de ces gîtes, et peuvent sans doute permettre un meilleur choix de l'emplacement des trous de forage.

L'usage de la lithogéochimie dépend largement de la mesure dans laquelle on peut obtenir des échantillons adéquats, provenant soit d'affleurements favorables de la roche en place, soit de carottes de forage; il est évident que la lithogéochimie offre moins de possibilités, dans les zones d'altération profondes, et celles cachées par de vastes terrains de couverture ou une importante couverture de sol. Cependant, malgré ces limitations, les développements récents démontrent de façon convaincante le potentiel de la lithogéochimie en tant que méthode d'exploration.

INTRODUCTION

Litho geochemistry, or rock geochemistry, as used in this paper, is defined as the study of the chemical composition of bedrock with particular reference to the search for ore deposits. Geochemical patterns in bedrock that can be related to mineralization are referred to as primary patterns or primary dispersion, irrespective of whether the reactions causing the element distribution patterns are syngenetic or epigenetic (James, 1967).

Mineralogical alteration zones in host rocks around mineral deposits have long been recognized and used as indicators of ore. Such alteration zones are the visible manifestations of physical and chemical changes in rocks associated with mineralization. Chemical alteration halos may be more extensive and therefore detectable over greater distances than mineralogical halos, since lattice substitution of elements may occur without any mineralogical change. Recognition of this possibility and the need to develop techniques capable of detecting deeply buried and blind deposits and to improve exploration capabilities have led to the recent widespread interest in litho geochemistry.

The improved understanding of ore genesis during the last decade is also a significant factor in the increased interest in litho geochemical techniques. The general features of porphyry ore deposits have been characterized in terms of pre-ore host rock, igneous host rocks, the orebody, hypogene alteration, mineralization and occurrence of sulphides (Lowell and Guilbert, 1970). Whereas a considerable degree of similarity exists among the deposits, aspects in the detailed geological history of a particular deposit (e.g., nature of fluids, degree of fracturing and postmineralization history) might be expected to give rise to significant differences between geochemical responses and mineralization. Understanding of the genesis of volcanic-sedimentary massive sulphide deposits has also vastly improved over the past decade; they are generally regarded as having originated from metal-bearing fumarolic exhalations on the sea floor that were coeval with the associated volcanic or sedimentary activity (Sangster, 1972). Notwithstanding a common genesis, detailed variations in the character of the host rock, tectonic, and postmineralization history of different deposits could be expected to result in variations between the geochemical responses in the wall rock and mineralization.

The chemical composition of a sample of rock reflects the entire geological history of the rock. For example, the composition of a sample of a particular granite may reflect the composition of the primary magma (possibly modified by assimilation of country rock), metasomatic and postmagmatic processes, metamorphism, and, in the case of surface samples, the effects of weathering. The extent to which the effect of a mineralizing event is recognizable in the composition of the host rock depends upon the actual processes that affected the rock. It is thus of critical importance in the evaluation of any litho geochemical data to consider the nature and effects of all processes that may have affected the sample.

In view of the importance of geological environment on the nature of geochemical dispersion associated with mineralization the main body of this review is divided into two parts: (1) geochemical response in intrusive rocks; and (2) geochemical response in extrusive and sedimentary rocks. Within each geological group, geochemical response is considered in terms of exploration scale:

Regional – large-scale, geochemical responses that are capable of discriminating between productive and barren terrain.

Local and Mine Scale – geochemical responses around individual deposits that can be detected up to 1 to 2 km from a deposit, and the geochemical responses that are limited to the immediate wall rock of a deposit.

This classification is necessarily somewhat arbitrary, and there is some overlap between the two scales of investigation.

The objective of the paper is to present a state-of-the-art review of litho geochemistry; the source of much of the data, therefore, is published papers, augmented by our personal experiences. The works that we cite were carried out in many different ways – in terms of sampling, analysis, data presentation – and, indeed, with many different objectives. Our lack of first-hand knowledge of many of the areas makes comparisons and evaluation difficult; to minimize some of the problems and to achieve more meaningful comparisons, some of the data have been replotted from the published work and, in so doing, we trust that neither the character of the original data nor the intent of the authors have not been misrepresented.

A number of investigations have been concerned with the distribution of stable isotopes (sulphur, oxygen, hydrogen, and lead) associated with various types of deposits and mineral provinces. The results of these investigations are not considered here, although stable isotope studies may provide a better understanding of the genesis of mineral deposits – information that would be useful in selecting areas for exploration. In a limited number of cases, isotope zoning around mining districts has been noted.

Litho geochemistry has received considerable attention within the Soviet Union. Although reports indicate notable success and some innovative approaches, the work, in general, is difficult to evaluate and discussion is limited to a consideration of some of the principles of the Soviet work.

The technical viability of litho geochemistry in mineral exploration is dependent on the existence of some geochemical signature in the rocks associated with mineralization – which normally requires a genetic relationship between the geochemical patterns and the ore-forming processes. A major factor affecting the applicability of litho geochemistry in exploration is the extent to which features are of general occurrence. The economic viability is related to the cost effectiveness of the procedure in relation to other techniques, and is dependent on the nature of the appropriate sampling, analytical and interpretational procedures.

GEOCHEMICAL RESPONSE TO MINERAL DEPOSITS IN INTRUSIVE ROCKS

Regional Scale

Prior to the present upsurge of interest in litho geochemistry, geologists and geochemists have sought criteria to discriminate between productive and barren intrusions on a regional scale. Tin seems to be the only element that generally – but not universally – shows enrichment in intrusions associated with tin mineralization in many parts of the world. Quartz-cassiterite-bearing granite bodies have Sn variations in the range 20-30 ppm, compared to 3-5 ppm in barren intrusions (Barsukov, 1967). Granite associated with tin deposits in Transbaikaliya (U.S.S.R.) has 16-32 ppm Sn, compared to barren granite that has less than 5 ppm Sn (Ivanova, 1963).

Tin-bearing granite of northeast Queensland has been shown to have significantly higher Sn contents than nonstanniferous granite (Sheraton and Black, 1973). A granite with a high proportion of samples with Sn contents above background values appears a criterion of potential tin

mineralization. The variation in tin content of granite with mineralization is ascribed to a primary uneven distribution of tin in the crust or mantle that was the magma source. Although the areal extent of the granite bodies is not given the Sn content of individual intrusions was characterized on the basis of an average of some 25 samples per intrusive but ranging from 6 to 73 samples for individual bodies. None of the mineralized granite is uniformly high in tin and the characteristic feature is a very variable tin content amongst samples necessitating that sampling must be reasonably extensive if the tin-bearing potential is to be realistically assessed. On the basis of a wider study of granitoids from the Tasman geosyncline in Eastern Australia, granitic rocks associated with cassiterite mineralization have a higher mean Sn content (26 ppm) relative to similar but barren granitoids (3.4 ppm) (Hesp and Rigby, 1975). The samples were collected from outcrops some distance from locations where cassiterite mineralization was observed to avoid the effect of the latter on Sn values. However, the extent to which the higher Sn values are characteristic of the mineralized granite as a whole is not known as the sampling was biased to some extent towards areas of Sn mineralization rather than being representative of the granitoid rocks as a whole (Hesp and Rigby, 1975). Although there are some exceptions to the generalization, particularly in the low range of Sn concentration, all the granitoid samples that have more than

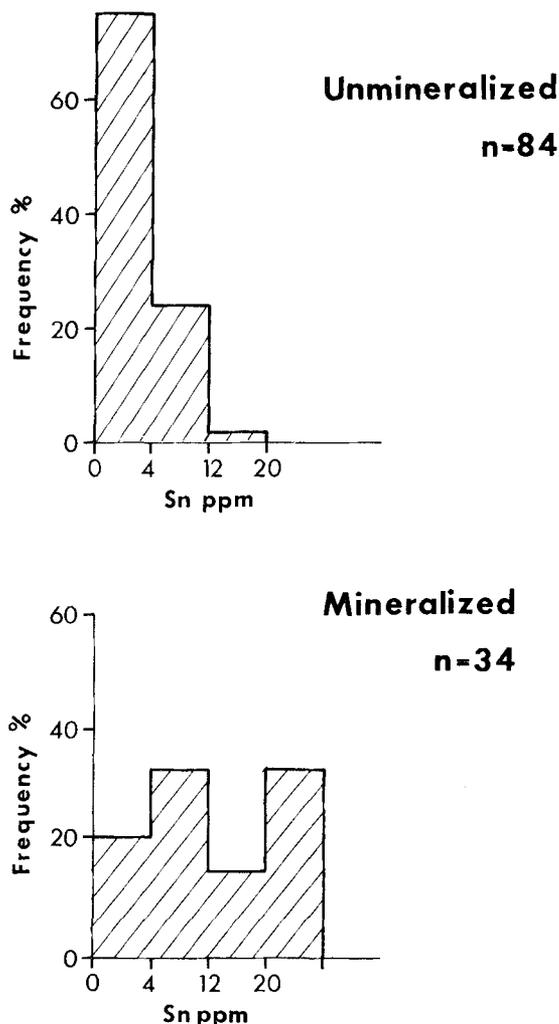


Figure 15.1. Frequency distribution of Sn in mineralized and barren granitic intrusions, Tasman Geosyncline, Eastern Australia (data from Hesp and Rigby, 1975).

Table 15.1
Variations in composition of mineralized and unmineralized intrusives – Allen et al., 1976

		Mineralized	Unmineralized
K ₂ O	\bar{x}	2.31	1.47
	σ	0.80	1.12
	R	1.12 - 2.77	0.28 - 5.36
Cu	\bar{x}	1450	57
	σ	1785	73
	R	17 - 7400	0 - 350
CaO	\bar{x}	3.58	4.85
	σ	1.17	1.80
	R	2.0 - 3.62	0.50 - 9.28
Na ₂ O	\bar{x}	2.27	3.67
	σ	1.40	1.82
	R	0.50 - 4.52	0.22 - 6.48
MnO	\bar{x}	0.12	0.18
	σ	0.04	0.09
	R	0.07 - 0.21	0.06 - 0.42
Zn	\bar{x}	36	92
	σ	14	67
	R	17 - 70	30 - 270
n		20	27

20 ppm have associated tin mineralization (Fig. 15.1); this finding is consistent with most of the work carried out in the U.S.S.R.

Many workers have observed that, aside from tin, there is no noticeable correlation between the abundance of elements in granitic rocks and the presence or absence of mineralization; the lack of correlation is documented for lead and zinc (Tauson, 1967), and for lead, zinc, molybdenum, and tungsten (Barsukov, 1967). In the investigation of mineralized granitic rocks of northeast Queensland referred to earlier, no relation between the lead, zinc, and copper contents of the granite and lead/zinc and copper mineralization was noted, (Sheraton and Black, 1973). This feature was ascribed to the mineralization resulting from processes unrelated to the differentiation of the intrusive.

On the other hand, in situations where there has been hydrothermal alteration, significant differences in mean element content have been observed between mineralized and barren intrusions. For example, the intrusion that hosts the Coed-y-Brenin copper porphyry-type deposit in North Wales (U.K.) is enriched in K₂O, Cu, and Mo, and is depleted in MnO, Na₂O, CaO, and Zn relative to similar but barren intrusions in the same region on the basis of a comparison of mean element content (Allen et al., 1976). With the exception of Cu and Zn, the differences in mean content are slight, and there is considerable overlap in the ranges of the mineralized and unmineralized populations (see Table 15.1). The authors drew attention to the fact that the distribution of the data within the data sets is not normal and thus the statistical data should be treated with caution. The enhancement and depletion effects are interpreted as a reflection of the effects of mineralization and associated hydrothermal alteration. The K₂O, Na₂O, and CaO variations are associated with phyllic alteration, whereas the Zn depletion possibly reflects Zn migration to the pyrite and propylitic zone.

In certain cases, the form of the frequency distribution of an element in a region or a particular rock unit is more diagnostic of mineralization than the mean value of the element (Beus, 1969; Bolotnikov and Kravchenko, 1970;

Tauson and Kozlov, 1973). The form of frequency distributions for W has been shown to differ between barren and mineralized acidic plutons in the Yukon and Northwest Territories in Canada (Garrett, 1971). The distribution of W in barren plutons (Fig. 15.2) is only slightly skewed, whereas the distribution in mineralized plutons has a more marked positive skew; this is interpreted as reflecting the occurrence of a tungsten mineralizing event due to magmatic processes superimposed upon the primary tungsten distribution. Plutons that are host to porphyry-type disseminated tungsten mineralization, and therefore presumably were closely allied to primary magmatic processes, are more clearly distinguishable from barren plutons than those associated with more local skarn-type mineralization. Garrett concluded that an "average" size pluton could be geochemically characterized by collecting duplicate samples from 15 samples sites in an unzoned pluton.

Attempts have also been made to use variations in element content of a particular mineral phase in a rock to discriminate between barren and productive plutons. Most of the work has been done on biotite (although trace element distribution in feldspar and magnetite have also been investigated). The rationale behind the investigations is the fact that the structure of biotite can readily accommodate minor elements in different states within the lattice and that biotite in productive stocks might contain characteristic minor element contents as a result of hydrothermal alteration associated with the mineralization. Some early work on the distribution of Cu and Zn in biotite from acidic intrusions in the Basin and Range Province of the U.S.A. (an area of major base and precious metal production) by Parry and Nackowski (1963) showed an apparent relation between the contents of Cu and Zn in biotite and the presence of base metal mineralization within a particular stock. The high copper values in biotite from the Basin and Range intrusions were ascribed to the deposition of sulphides in biotite by hydrothermal solutions. Subsequent investigations on biotite from the Basin and Range Province, however, have indicated that there is no clear relation between minor element contents of biotite in intrusions hosting porphyry copper deposits and unmineralized stocks (Jacobs and Parry, 1976); this is attributed to the existence of three genetic types of biotite (magmatic, replacement, and hydrothermal), the composition of which reflects the physical and chemical conditions of crystallization and the postmagmatic history of a stock. Systematic variations in biotite composition of the three types of biotite may be characteristic of individual porphyry copper deposits and thus may serve to distinguish intrusions genetically related to porphyry copper deposits from barren intrusions.

The halogen distributions in biotite within individual plutons of the Basin and Range area are distinctive, but there is no systematic distinction between barren and mineralized intrusions (Parry, 1972; Parry and Jacobs, 1975). The mean Cl content of biotite from intrusions in western North America and the Caribbean was shown to be similar in barren and mineralized plutons, and there is a greater range of values in the former than in the latter (Fig. 15.3) (Kesler et al., 1975a). Similarly neither water-soluble nor total Cl and F content in whole rock is consistently different in barren and mineralized intrusions (Kesler et al., 1973, 1975b). The lack of a clear relation between halogen content and mineralization is attributed to the halogen content of the biotites also being related to magmatic processes.

Some differences have been noted in major and trace element contents in feldspar, biotite, and muscovite from five granite bodies associated with tin, copper, zinc, and lead mineralization in Devon and Cornwall (southwest England) compared to nonmineralized granite elsewhere in England and Scotland (Bradshaw, 1967). An average of eleven samples per

stock was used to characterize specific stocks. In the case of biotite, higher mean Rb and Sn contents and lower Sr contents are characteristic of mineralized granite relative to barren granite. In feldspars, mean contents of Rb, Zn, and, to a lesser extent, K, Mn, Pb and Sn are higher and Ca and Sr are lower in mineralized than in nonmineralized stocks. The mean contents of Pb and Zn in feldspar from the granite show a clear distinction in Zn content between barren and mineralized intrusions (Fig. 15.4). The mineralized and barren intrusions, however, are not strictly comparable, since the mineralized intrusions are more highly fractionated than the barren intrusions; only the Weardale granite (identified on Fig. 15.4) is petrochemically similar to the mineralized granite – but has an even lower Zn content than other barren granite. The study was based on relatively few samples (a total of 55 samples from the five mineralized granite bodies

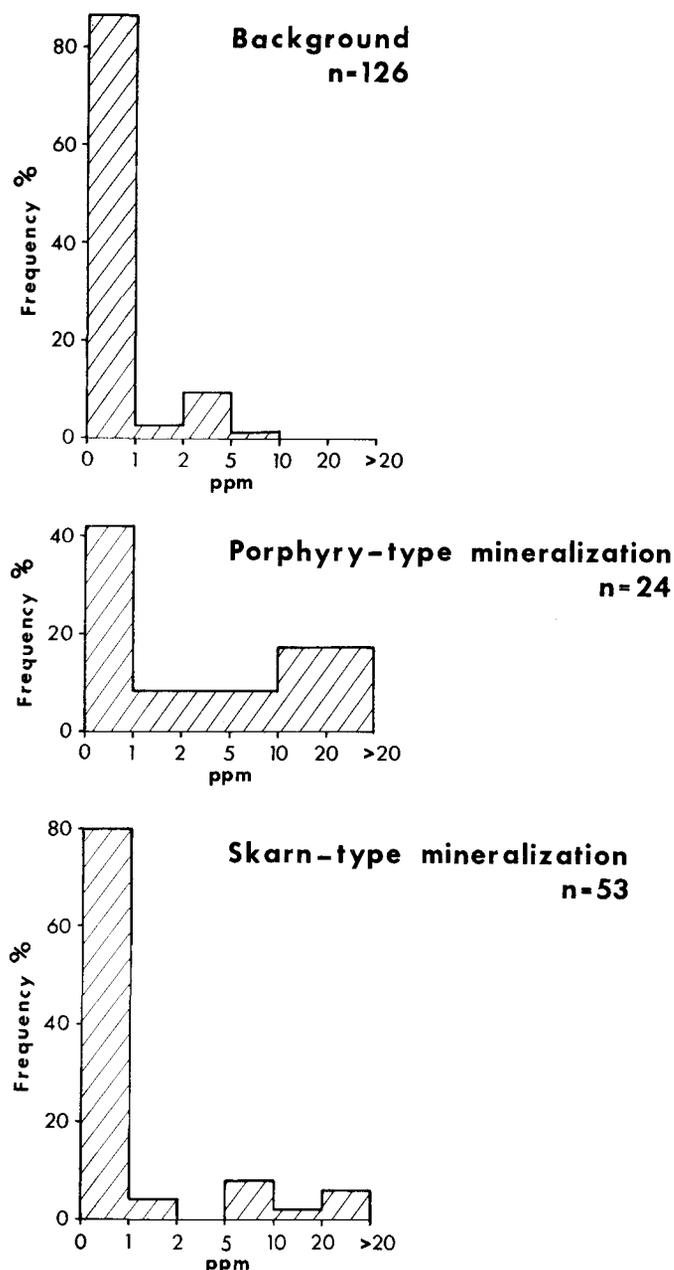


Figure 15.2. Frequency distribution of W in mineralized and barren granitic intrusions, Northern Canadian Cordillera (data from Garrett, 1971).

and a total of 94 from the eight barren granite bodies); although there are clear differences in the mean element contents, there is also considerable overlap between the two groups of granite in terms of element content of individual samples. The differences in mean contents of the ore metals Sn, Pb and Zn between mineralized and unmineralized stocks are attributed to effects of mineralization whereas variations in the mean contents of K, Rb, Sr and Ca are related to varying degrees of fractionation of the granite.

A rather different approach, based on determining the metal content of sulphide minerals, has been adopted to discriminate significantly mineralized from unmineralized ultramafic bodies of the Canadian Shield (Cameron et al., 1971). A total of 1079 samples from 61 locations were investigated and each location classified according to importance of mineralization: an ORE group contains ore grade deposits with more than 5000 tons nickel-copper, a MINORE group contains deposits of ore grade with less than 5000 tons nickel-copper, and a BARREN group contains only minor amounts of sulphide. The samples collected varied according to restraints on sampling imposed by sample availability but attention was focused on obtaining a suite of samples as representative as possible of the individual areas. A sulphide-selective digestion was used to determine the Cu, Ni, and Co contents present in sulphide minerals, based on the assumption that for an ultramafic magma to give rise to significant copper-nickel mineralization, the magma must be enriched in sulphur to such an extent that the solubility products of the metal sulphides will be exceeded, causing metal sulphides to separate. The content of sulphur or metals held as sulphides should be indicative of this condition and hence of possible mineralization. The frequency distributions of sulphide-held Cu, Co, and Ni, and of total sulphur, are all

positively skewed; the results are summarized in Table 15.2. Ore-bearing localities (ORE group) are enriched in sulphide-held Ni and Cu (and, to a lesser extent, Co) and total S relative to mineralized localities (MINORE group) and to barren localities (BARREN group). The MINORE and BARREN localities are only distinguishable from one another on the basis of higher sulphide-held Ni content of the MINORE group.

The importance of recognizing the mineralogical site of trace elements has been demonstrated by variations in the mineralogical form of uranium in granite bodies in the U.K. (Simpson et al., 1977); delayed neutron analysis and Lexan plastic fission track studies were carried out to determine the content and form of the uranium. The geometric mean of U content of the Caledonian granite is 3.9 ppm U (118 samples, range 0.5-15.2 ppm), compared to Hercynian granite of southwest England that has a geometric mean of 10.8 ppm U (66 samples, range 3.2-35.5 ppm). The difference between the two granite suites is significant at the 99 per cent confidence level (based on the two-tailed Kolmogorov-Smirnov test). In the Caledonian granite, U occurs in postmagmatic secondary minerals, such as hematite and chlorite, in alteration zones associated with major faults. In southwest England, uranium occurs as mainly primary accessory minerals such as zircon, apatite, and sphene in vein-type deposits closely associated with the granite. It was concluded that the U vein-type mineralization of the Hercynian granite is comagmatic with the uranium-enriched granite and is not attributable to later kaolinization or weathering. Analyses of granite can serve to identify primary uranium provinces with associated vein-type mineralization. In the Caledonides, where uranium is principally associated with later faults and molasse facies sediments, granite sampling can help to identify the enrichment processes and thus aid in the definition of economic targets.

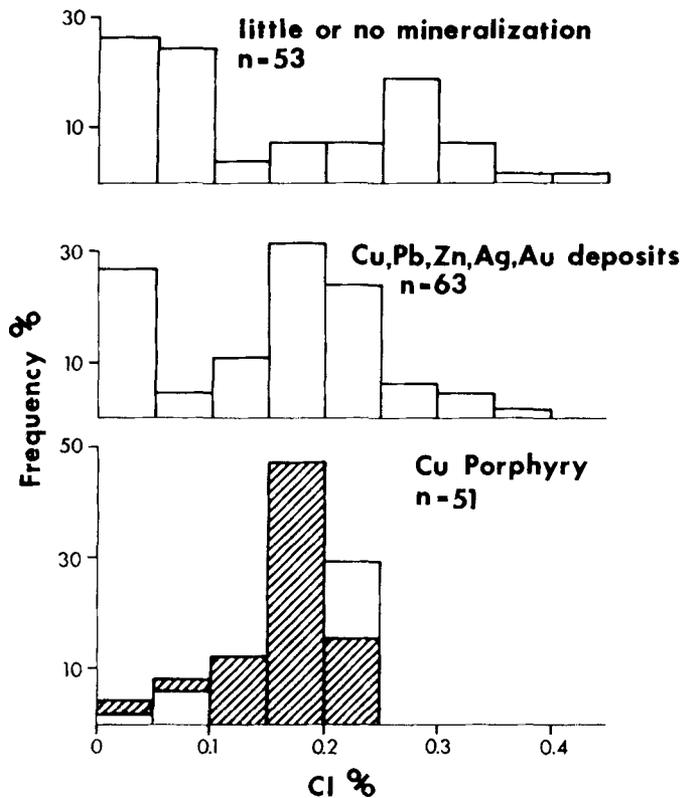


Figure 15.3. Frequency distribution of Cl in biotite from mineralized and barren granitic intrusions, Basin and Range Structural Province, U.S.A. (redrawn from Parry and Jacobs, 1975).

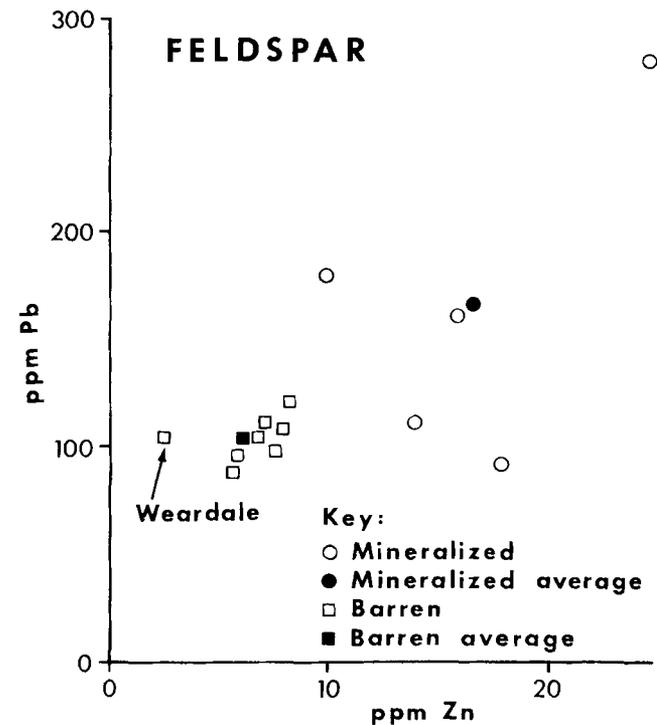


Figure 15.4. Mean contents of Pb and Zn in biotite from mineralized granitic intrusions of southwest England and barren granitic intrusions from northern England and Scotland (data from Bradshaw, 1967).

Table 15.2
Geometric mean content of sulphur and sulphide-held Cu, Ni, and Co in ore-bearing mineralized, and barren ultramafic intrusions in the Canadian Shield
(from Cameron et al., 1971)

	Number of bodies	Number of Samples	Cu, ppm	Ni, ppm	Co, ppm	S, %
ORE groups: (deposits with >5000 tons Ni-Cu)	16	372	67.8	715	57.4	0.166
MINORE group: (deposits with <5000 tons Ni-Cu)	5	91	6.8	560	25.2	0.036
BARREN group:	40	616	6.9	354	31.3	0.031
All deposits:	61	1079	15.2	469	37.9	0.056

Local and Mine Scale

There have been a variety of investigations of geochemical patterns associated with specific mineral deposits within, or closely associated with, intrusive rocks. Porphyry-type ore deposits constitute an important ore type where in the exploration stage it is frequently of significance to distinguish areas of mineralization within intrusions (Lowell and Guilbert, 1970). An evaluation of the nature of geochemical dispersion associated with porphyry copper deposits as a whole is difficult due to variations in sampling procedures and in the elements that have been analyzed by various workers. In view of the importance of porphyry copper deposits as sources of Cu and Mo, it is somewhat surprising that relatively few litho geochemical studies have been reported. Available data for the distribution of major and trace elements in rocks around copper porphyry deposits are given in Table 15.3. Perhaps the most comprehensive investigations are those carried out on the Highland Valley deposits of British Columbia (Brabec and White, 1971; Olade and Fletcher, 1975, 1976a, 1976b; and Olade, 1977). A total of 1860 samples were used in the study, comprising 1800 from the mineralized areas and 60 from background areas of the Guichon Creek. Surface outcrop samples consisted of 4 kg composites of several fist-sized chip samples and drill core samples comprising composites of 5 cm lengths of drill core taken over 3 m. Analysis was carried out for 30 elements or forms of elements (e.g., total and water extractable Cl). In the Highland Valley, geochemical dispersion in proximity to porphyry copper deposits is related to primary lithology, hydrothermal alteration, and mineralization (Fig. 15.5) Olade and Fletcher (1976a). Anomalous halos of Cu, S, and B variously extend beyond the alteration zones and thus constitute larger exploration targets than the visible alteration halo (Table 15.4), (Fig. 15.5). Rb, Sr, and Ba distributions are closely related to alteration and thus provide useful guides of porphyry zoning. Element ratios were found to be more consistent indicators of mineralization than single element patterns, which show erratic trends due to mineralogical variations.

In a preliminary investigation of geochemical dispersion associated with the Kalamazoo deposit (southwestern United States) whole rock samples of core and cuttings from 3 m intervals, spaced 15 m apart from two drill holes were analyzed for 60 elements (Chaffee, 1976). Trace element distributions, for the most part, are not related to lithology and are thus more significant in terms of mineral exploration than major element distributions. Increases in Cu, Co, B, S, or Se and decreases in Mn, Tl, Rb, and Zn occur with

proximity to mineralization within the alteration zone and may be useful in exploration for blind deposits.

The Copper Canyon porphyry copper deposit in Nevada occurs in fractured and altered sedimentary rocks associated with a granodiorite intrusion (Theodore and Nash, 1973). One kilogram composite rock chip samples from areas of 10 m² were collected over a 16 km² zone and analyzed for 20 elements. Highest copper concentrations occur over the nonproductive granodiorite rather than associated with the orebodies in the adjacent metasediments. The copper distribution within the sediment has also been affected by

premineralization structures and supergene enrichment. The abundance of metal dispersed through rocks at Copper Canyon rather than occurring as fracture fillings of coatings is a more specific indicator of ore deposits. The distribution of high salinity fluid inclusions outlines the orebodies in the metasedimentary rocks more precisely than the pyrite halo. The distribution of the high salinity fluids is considered to reflect the circulation limits of the fluids. These data draw attention to the limited effectiveness of exploration based solely on a consideration of geochemical data and the need for the additional consideration of the petrography of the fluids and alteration.

In the Copper Mountain area of British Columbia where porphyry-type mineralization in volcanic rocks surrounds the intrusive, patterns exist on various scales (Gunton and Nichol, 1975). An orientation survey was carried out to establish the nature of geochemical zoning associated with the deposits and identify appropriate geochemical exploration parameters. On the basis of these results 5 lb composite chip samples were collected as outcrop permitted from 500 foot grid cells and the samples were analyzed for 18 elements or forms of elements. High contents of Na, K, P, Rb, Sr, total Cu and sulphide-held copper are characteristic of the volcanics surrounding the stock relative to background areas thus providing a broader exploration target than the discrete deposits. In significantly mineralized areas surrounding the stock area the host rocks are characterized by 8-fold higher Cu and 1.5-fold higher Sr contents over three-fold more extensive areas than the economic mineralization. The volcanic host rocks associated with the individual Ingerbelle and Copper Mountain deposits are characterized by high soda and potash contents reflecting differences in the nature of metasomatic alteration associated with the two deposits. On the basis of these results it was concluded that in reconnaissance level exploration samples should be taken at a density of ten samples per square mile and in detailed level exploration at 80 samples per square mile with the samples being analyzed for P, Sr, Na, K, and Cu. During sampling attention should be given to recording dominant alteration types, degree of fracturing, and sulphide content.

In a study into the nature of primary dispersion associated with an early Precambrian porphyry-type molybdenum-copper mineralization in northwestern Ontario, fifty 500 g to 1 kg composite samples of rock chips were collected 5-15 m apart from the 5.7 km² area of the porphyritic granodiorite-quartz monzonite pluton (Wolfe, 1974). The samples were analyzed for Cu, Zn, Pb, Mn, and Mo. Strongly contrasting Cu and Mo dispersion within the stock partly

Table 15.3
Halos of selected elements around some copper porphyry and porphyry-type deposits

Deposit	Na	K	Ca	Mg	Fe	FeS	S	B	Cu	CuS	Zn	Mn	Mo	Hg	Au	Ag	Rb	Sr
Bethlehem JA ^(1,2,3,4)	-	+	-	-	-	+	+	+	+	+	-	-	+	+			+	-
Valley Copper ^(1,2,3,4)	-	+	-	-	-	+	+	-	+	+	m	-	+	0			+	-
Lornex ⁽²⁾	na	na	na	na	na	na	na	+	+	na	m	0	+	na			na	-
Highmount ⁽²⁾	na	na	na	na	na	na	na	+	+	na	+	-	+	na			na	-
Ingerbelle ⁽⁵⁾	+	+	0	0	0	0	na	na	+	+	na	0	na	na	na	na	+	+
Granisle ⁽⁶⁾	na	na	na	na	na	na	+	na	+	na	m	na	+	+	+	0	0	0
Bell Copper	na	na	na	na	na	na	+	na	+	na	m	na	+	+	+	0	0	0
Setting Net Lake ⁽⁷⁾	na	na	na	na	na	na	na	na	+	na	0	0	+	nd	na	nd	na	na
Kalamazoo ⁽⁸⁾	-	+?	0	0	+	na	+	+?	+	na	m?	-	+	0	+	+	-	0
Copper Canyon ⁽⁹⁾	na	na	na	na	na	na	na	0	+	na	m	0	+	+	+	+	na	+
Bio Blanco ⁽¹⁰⁾	na	0	0	na	na	na	na	na	na	na	na	na	na	na	na	na	+	-
El Teniente ⁽¹⁰⁾	na	0	0	na	na	na	na	na	na	na	na	na	na	na	na	na	+	0

na = not analyzed; nd = not detected; + = positive halo; - = negative halo; m = positive halo at margin of deposit. Interpreted in part by the writers from the following sources: Olade and Fletcher, 1975¹, 1976a², 1976b³; Olade, 1977⁴; Gunton and Nichol, 1975⁵; Jambor, 1974⁶; Wolfe, 1974⁷; Chaffee, 1976⁸; Theodore and Nash, 1973⁹; Oyarzun, 1975¹⁰.

coincides with the known mineralization and also gives some indication of the presence of hitherto unknown mineralization.

Mineralized andesite associated with granodiorite-dacite complex of the Rio Blanco (Chile) deposit have a 3-fold Rb enrichment and an 8-fold Sr depletion relative to fresh andesite (Oyarzun, 1975); at El Teniente a 2-fold to 4-fold enhancement of Rb is characteristic of the alteration zone relative to unaltered andesite (Oyarzun, 1971). No significant variation in Sr content was noted, probably due to the abundant anhydrite present in the potassic zone. At the El Abra porphyry deposit in Chile, no significant anomalous rubidium dispersion is associated with mineralization probably due to lack of chemical contrast between intrusive and intruded rocks (Page and Conn, 1973). At Chuquicamata highly anomalous rubidium contents have been reported (Oyarzun, 1975).

Vein deposits associated with intrusive rocks represent the smallest target for exploration; geochemical halos are also correspondingly small, although narrow wall-rock halos are commonly well defined. Au and Ag anomalies occur in whole rock and ferromagnesian minerals in the Marysville (Montana, U.S.A.) quartz diorite-granodiorite up to 300 m from gold and silver vein deposits within and adjacent to the stock (Mantei and Brownlow, 1967; Mantei et al., 1970). The anomalous contents of Au and Ag in the mineralized areas of the stock were considered to have resulted from the penetration of the wall rock by mineralizing solutions. The presence of Au and Ag and lack of base metal anomalies is possibly related to a higher mobility of Au and Ag or higher contrast in content of Au and Ag of the mineralizing fluids and the adjacent rock than in the case of base metals.

An even more extensive anomalous halo of Mn in biotite in the granodiorite-quartz monzonite Philipsburg Batholith (Montana, U.S.A.) has been described by Mohsen and Brownlow (1971); the Mn content of biotite increases two-fold over 1500 m towards the margins of the intrusion where manganese deposits occur in adjacent sedimentary rocks.

The general feature of geochemical halos around vein-type deposits is illustrated in Figure 15.6 based on the

Table 15.4
Comparison of anomaly extent and contrast for selected elements (from Olade and Fletcher, 1976a)

Element	Bethlehem JA		Valley Copper		Lornex		Highmount	
	E ¹	C ²	E	C	E	C	E	C
Cu	***	5	***	5	***	5	***	5
S	***	5	***	5	nd	nd	nd	nd
Mo	*	2-5	*	2-5	*	5	*	5
B	*	1-2	0		***	2-5	***	2-5
Hg	**	5	0		nd	nd	nd	nd
Rb	**	1-2	**	1-2	nd	nd	nd	nd
Sr ³	**	1-2	**	1-2	**	1-2	**	1-2

nd: Not determined
¹Extent: 0: No anomaly
*: Anomaly confined to ore zone
**: Anomaly within alteration envelope
***: Anomaly beyond alteration envelope
²Contrast: Approximate anomaly to background ratio
³Negative anomaly

collection and analyses of chip samples, which shows the distribution of Cu, Pb, Zn, Ag, and Mn in sandstone adjacent to lead-zinc-silver and copper lode deposits in the Park City District of Utah (Bailey and McCormick, 1974). The decay pattern in metal values in wall rock away from the veins is approximately logarithmic - a common pattern that has led most observers to regard this type of dispersion as diffusion-controlled migration of mineralizing fluids from the vein. The anomalous halo has a restricted extent; anomalous Cu and Mn contents are detectable for about 10 m, and anomalous Pb, Zn, and Ag contents are detectable for about 20 m from the vein.

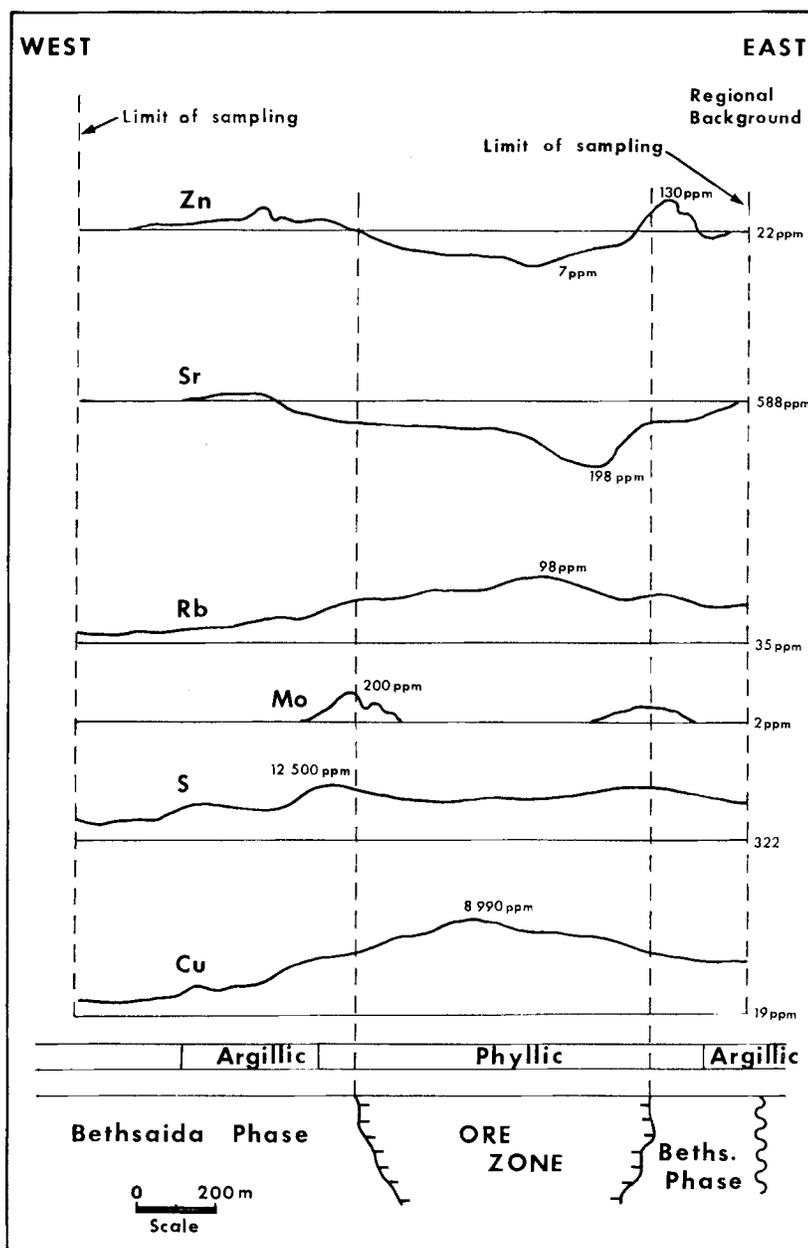


Figure 15.5. Distribution of Cu, S, Mo, Rb, Sr, and Zn in granitic rocks along a traverse over the Valley Copper porphyry copper deposit, British Columbia, Canada (redrawn from Olade and Fletcher, 1976a).

GEOCHEMICAL RESPONSE TO MINERAL DEPOSITS IN EXTRUSIVE AND SEDIMENTARY ROCKS

In this section, the lithogeochemical characteristics of the economically important stratabound sulphide occurrences – variously referred to as "massive", "volcanogenic", or "volcanic-sedimentary" – are considered. Included in this category are deposits that appear to have formed in a subaqueous environment, probably from ascending hot, metalliferous brines, and that lie conformably within mafic volcanic sequences (e.g., Cyprus), felsic volcanic sequences (e.g., Bathurst, New Brunswick, Canada), or in predominantly sedimentary sequences (e.g., McArthur River, Australia). Stratabound deposits of an apparently sedimentary origin (e.g., the Zambian Copperbelt, Kupferschiefer) and vein-type deposits of volcanic association (e.g. Kirkland Lake, Kalgoorlie, Australia) are specifically excluded.

Regional Scale

Attention has been focused by Coope (1977) on the composition of exhalative horizons as a regional indicator of mineralization. Exhalative horizons (i.e., essentially chemical precipitates) commonly occur over a wide area at the same broad stratigraphic horizon as volcanic-sedimentary sulphide deposits. The metalliferous sediments being deposited in the Red Sea represent a sedimentary hydrothermal deposit in the process of formation and show anomalous contents of Hg, Cu, Zn, and Mn in the exhalite sediments extending up to 10 km from the Atlantis II Deep with 6-fold contrasts between mean metal contents in samples adjacent to the deep relative to mean background contents in samples remote from the deep. Anomalous contents of Cu, Zn, and Mn also extend 9 km from the Nereus Deep (Bignell et al., 1976). In both cases the anomalous elements show a gradient of increasing concentration towards the exhalative centres located in the Deeps.

A number of anomalous dispersion patterns in sedimentary rocks around massive sulphides in predominantly sedimentary environments have also been reported. In the limestone overlying the Tynagh base metal deposit in Ireland there is a Mn anomaly in limestone, identifiable in surface and core samples, extending at least 7 km, with up to a 20-fold contrast (Fig. 15.7) (Russell, 1974). Up to a 20-fold range in Mn content exists in samples near mineralization requiring that an adequate number of samples are taken for representative information to be obtained. It is considered that the anomalous concentrations result from deposition of metal from "spent" mineralizing solutions following their escape into the sea subsequent to the major phase of deposition of ore metals in the underlying rocks. High Ba, Pb, Zn contents also occur in the iron formation associated with the mineralization (Russell, 1975). At the Meggen lead-zinc-barium deposit in Germany there is a Mn anomaly in limestone with up to 7-fold contents extending at least 5 km from the deposit (Gwosdz and Krebs, 1977) (Fig. 15.8). The observations based on the analyses of 342 samples again display a 3 to 4-fold range in manganese concentration (particularly near the mineralization). Peak Mn contents lie lateral to, and not immediately over the deposit which is consistent with the model for Mn dispersion in an aqueous environment around an active brine source as predicted by Whithead (1973).

At the McArthur River (Australia) Zn, Pb, Ag deposit, based on the analyses of samples from six drill holes, anomalous contents of Zn, Pb, As, and Hg extend at least 20 km from the deposit in shale which is the lateral equivalent of the unit hosting the deposit (Lambert and Scott, 1973). Anomalous zinc contents in metasediments in the region of the Kidd Creek deposit have also been recorded (Cameron, 1975). These types of extensive anomalies (Tynagh, Meggen and McArthur River) are interpreted as syngenetic with the deposits and to have resulted from deposition from solutions in euxinic basins in nearshore regions of shallow seas.

The cupriferous pyrite massive sulphides of Cyprus occur in a sequence dominated by theoleiitic basaltic pillow lavas with only minor local sedimentary rocks associated with the deposits. From 20 traverses across the strike of the Troodos volcanic belt 2000 samples were collected and were

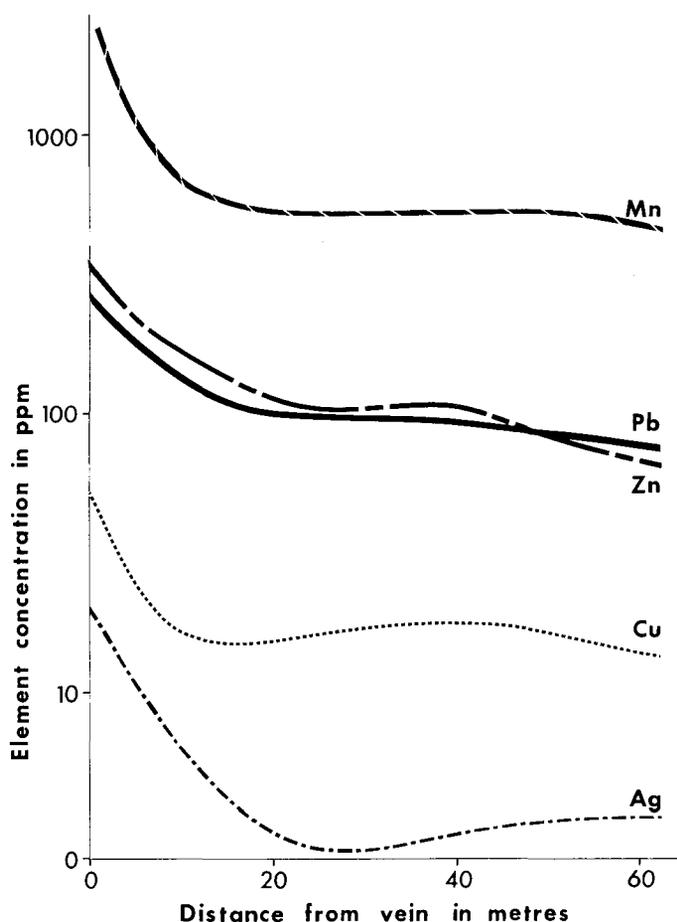


Figure 15.6. Smoothed average distribution of Ag, Cu, Pb, Zn, and Mn in sandstone adjacent to mercury-copper-lead-zinc vein mineralization, Park City District, Utah, U.S.A. (redrawn from Bailey and McCormick, 1974).

analyzed for up to eleven elements (Govett and Pantazis, 1971). As virtually no fresh surface rocks occur in Cyprus, all the samples have undergone weathering to various degrees, although attention was given to obtaining samples as unweathered as possible. The data indicated that the contents of Cu, Zn, Ni, and Co vary as a function of proximity to mineralization, stratigraphic position, petrology, rock type, and secondary processes. Mineralization occurs characteristically in areas of low Cu and high Zn and Co. No sulphide deposit occurs in a region with a Cu/Zn ratio in basalt which exceeds 1.2; all but two of the deposits occur in zones where the Cu/Zn ratio is less than 1.0, as shown in Figure 15.9 (Govett, 1976).

The salient features of Precambrian volcanogenic massive sulphide deposits in Canada have been described by Sangster (1972). Regional-scale lithogeochemical studies of massive sulphide deposits in the Canadian Shield indicate that they occur in calc-alkaline rather than tholeiitic mafic to felsic volcanic sequences, and that they generally occur in felsic rather than mafic differentiation sequences (Descarreaux, 1973; Cameron, 1975; Wolfe, 1975). The massive sulphide deposits in the Bathurst district of New Brunswick (Canada) similarly occur in calc-alkaline felsic volcanic rocks (Pwa, 1977). Distinctive geochemical features of productive and nonproductive cycles of volcanism have been noted in various areas of the Canadian Shield (Davenport and Nichol, 1973; Cameron, 1975; Nichol et al., 1975; Wolfe, 1975). Productive cycles of volcanism are generally characterized by slightly higher contents of Fe, Mg, and Zn and by lower Na₂O and CaO contents as illustrated in histograms of Fe₂O₃ and Zn contents from the productive and nonproductive cycles at Uchi Lake (Fig. 15.10) (Davenport and Nichol, 1973). These data are based on the analyses of 1 kg composite chip samples collected at a frequency of 4 samples per square mile over an area of 72 square miles. There is an almost complete overlap in the two populations for Fe₂O₃ and Zn, but the form of the frequency distributions is quite different and the mean contents for Fe₂O₃ and Zn are higher in the productive cycle. The differences between the two cycles are more clearly seen if the degree of fractionation, as represented by the SiO₂ content is taken into account (Fig. 15.11, 15.12) (Nichol, 1975). The Fe₂O₃ and Zn contents of rocks from the productive cycle are clearly higher than those from the nonproductive cycle for equivalent SiO₂ contents. In the latter case these data relate to 1 kg samples of individual

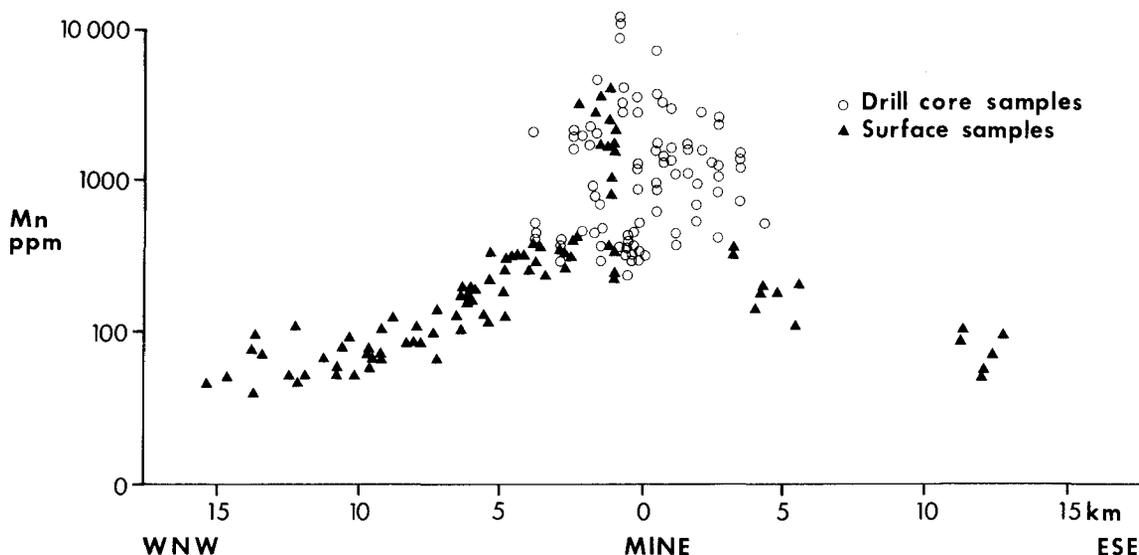


Figure 15.7. Distribution of 0.2 m acetic acid-soluble Mn in limestone that is host to the Tynagh deposit (Pb-Zn-Cu-Ag-BaSO₄) deposit, Ireland (redrawn from Russell, 1974).

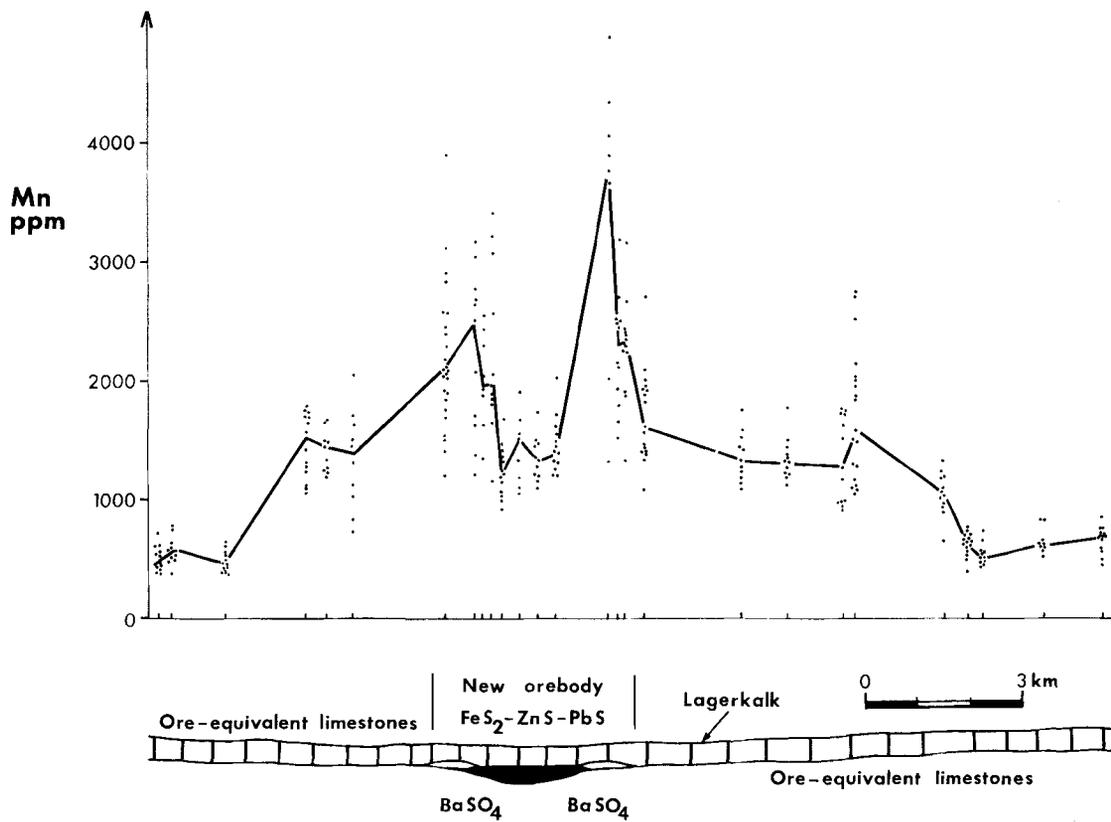


Figure 15.8. Distribution of total Mn in limestone that is host to the Meggan lead-zinc-barium deposit, Germany (redrawn from Gwosdz and Krebs, 1977).

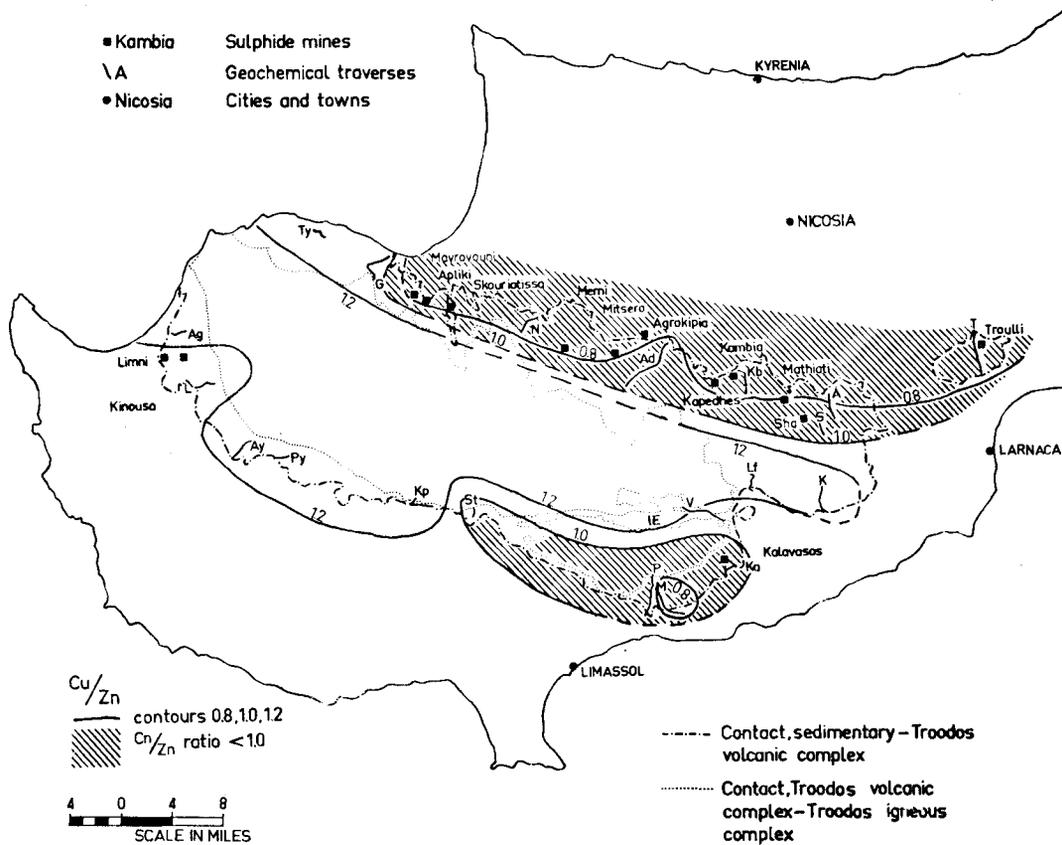


Figure 15.9. Distribution of Cu/Zn ratio in basaltic pillow lava, Cyprus (reproduced from Govett, 1976).

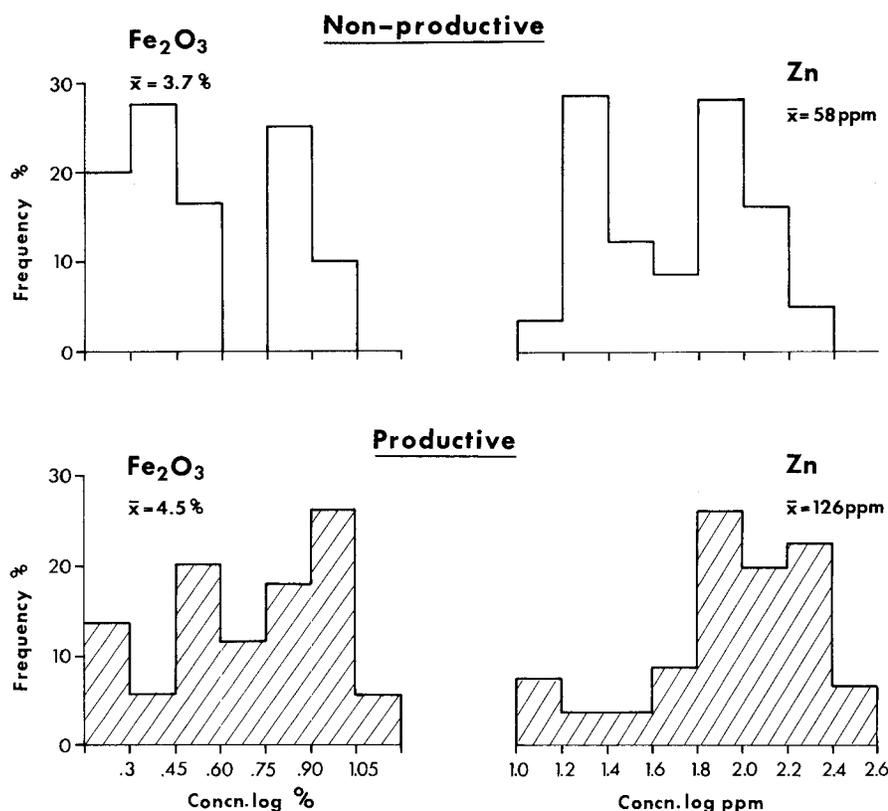


Figure 15.10. Frequency distributions of Zn and Fe_2O_3 contents in productive and nonproductive cycles of volcanism, Uchi Lake (Davenport and Nichol, 1973).

textural types rather than composite chip samples. Largely similar differences have been shown to exist between productive and nonproductive cycles of volcanism in a number of mining areas within the Superior Province of the Canadian Shield (Lavin, 1976; Nichol et al., 1975, 1977; and Sopuck, 1977). However, the geochemical distinction of productive cycles is not apparent in all textural types. For example, at Noranda a relatively high Zn content is apparent only in spheroidal flows of the productive cycle and does not appear to exist in the presumably less permeable massive flows (Fig. 15.13) (Sopuck, 1977). Similarly variations in chemical composition with textural type give rise to significant variations in composition. In pyroclastic units of the nonproductive Kakagi Lake area the fragments are more siliceous and soda-rich than the matrix whereas the matrix is enriched in MgO , Fe_2O_3 (3-fold), and Zn (5-fold) (Fig. 15.14) (Sopuck, 1977). Since these are some of the most useful elements indicative of mineralization the nature of the sample needs to be considered during interpretation.

Local and Mine Scale

Investigations of geochemical variations in rocks associated with individual massive sulphide deposits are far more numerous than regional studies (Tables 15.5 and 15.6). Again trace element anomalies are typically quite subtle and are generally most readily detected as population differences. Comparison of the distribution of Zn and Co in background basaltic pillow lavas with that in similar rocks within about 1 km of the Skouriotissa (Cyprus) cupriferous pyrite deposit shows an almost complete overlap in the range of

distribution, although the mean value and also the modal value of the anomalous group is higher, as seen in Figure 15.15 (Govett and Pantazis, 1971; Govett, 1972). This type of overlap in element content between background and anomalous populations of rock samples has led to the use of computer-based statistical techniques of data interpretation in an attempt to clarify any differences between populations. The application of discriminant analysis to this type of problem is illustrated with reference to data from a traverse across the Mathiati Mine in Cyprus (Fig. 15.16) (Govett, 1972; Pantazis and Govett, 1973; Govett and Goodfellow, 1975). The difference between a background and an anomalous population has been maximized by calculating the discriminant score that expresses the combined effect of increasing Zn and Co content and decreasing Cu content in pillow lava with proximity to mineralization. Anomalous discriminant scores extend about 2 km from the deposit.

Major element patterns in volcanic rocks around massive sulphides appear to have some common characteristics, regardless of age, economic metals, or the geological environment of the deposits (Table 15.5). Proximity to mineralization is generally indicated by an enrichment in Fe and Mg and a depletion in Na and Ca. The behaviour of K is variable; it is generally enriched relative to Na close to sulphide mineralization but in some cases it is depleted; there are also some cases where Na shows an absolute enrichment. These patterns are best developed in footwall rocks, but, in some situations, they also occur in the hanging wall. Mg enrichment and Na depletion occur adjacent to the Jay Copper Zone (Abitibi, Canada); the very distinct Na anomaly extends up to 500 m from the mineralized zone, but the Na content beyond these limits is still anomalously low (Fig. 17) (Descarreaux, 1973).

The elements that display anomalous dispersion patterns in the wall rock associated with massive sulphide deposits show some variation amongst deposits and the composition of the wall rock also reflects the effects of fractionation. In order to identify a more generally diagnostic indicator of mineralization, a function based on the Fe, Mg, Ca, and Na contents related to mineralization was determined for wall rock associated with a number of massive sulphide deposits in the Canadian Shield (McConnell, 1976). The component of the Fe, Mg, Ca, and Na content due to fractionation was estimated on the basis of the SiO_2 content and subtracted from the observed concentrations, the difference or residual content then possibly being related to mineralization. By combining the residuals of Mg, Fe, Ca, and Na in the form of a standardized net residual a more consistent reflection of proximity of mineralization was obtained. In general the strength of this factor increases towards mineralization and towards the presumable conduit of mineralizing solutions. The distribution of the "standardized net residual" at the South Bay Deposit extends beyond the mapped alteration zone (Fig. 15.18) but at the East Waite deposit it is only as extensive as the alteration zone. The variation in Mg and Ca in footwall felsic volcanic rocks with proximity to the Brunswick No. 12 deposit is shown in Figure 15.19; the Mg/Ca ratio is still three times greater than mean background 175 m from the ore zone (Govett and Goodfellow, 1975).

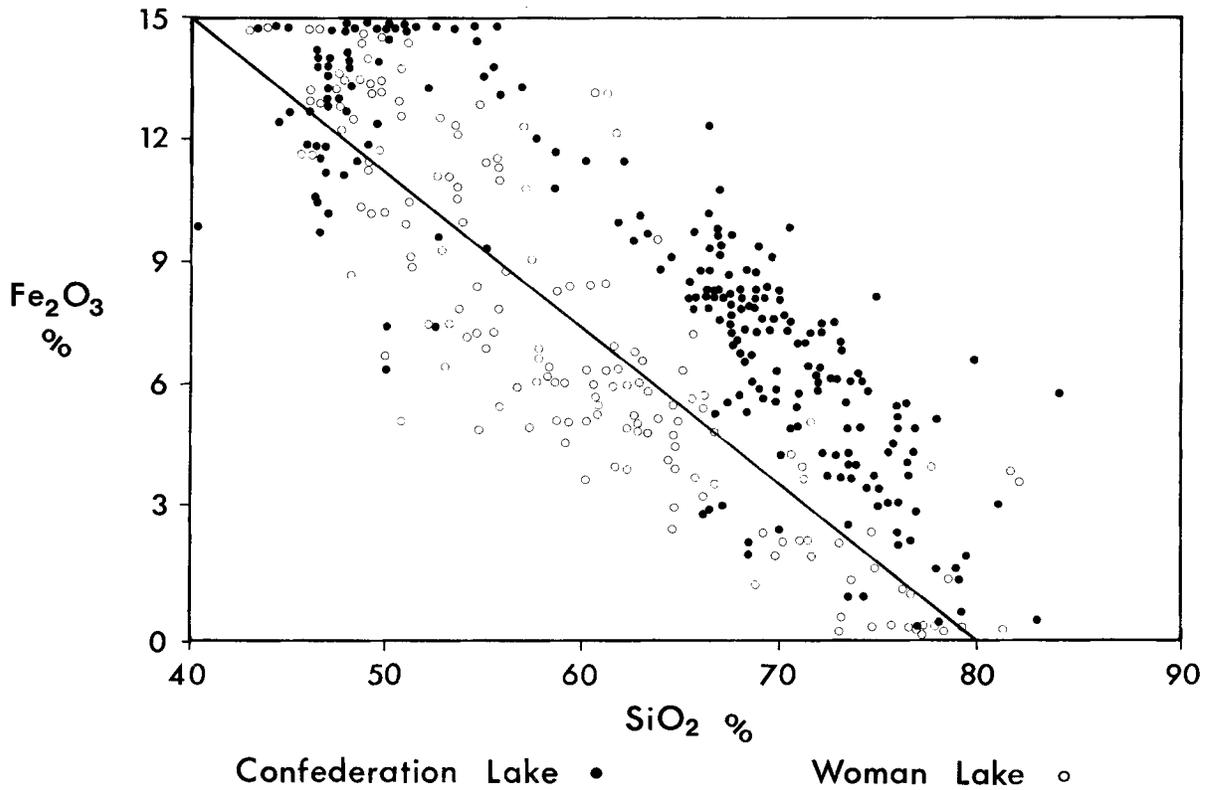


Figure 15.11. Relation between Fe_2O_3 and SiO_2 contents of productive and nonproductive cycles, Uchi Lake (Nichol, 1975).

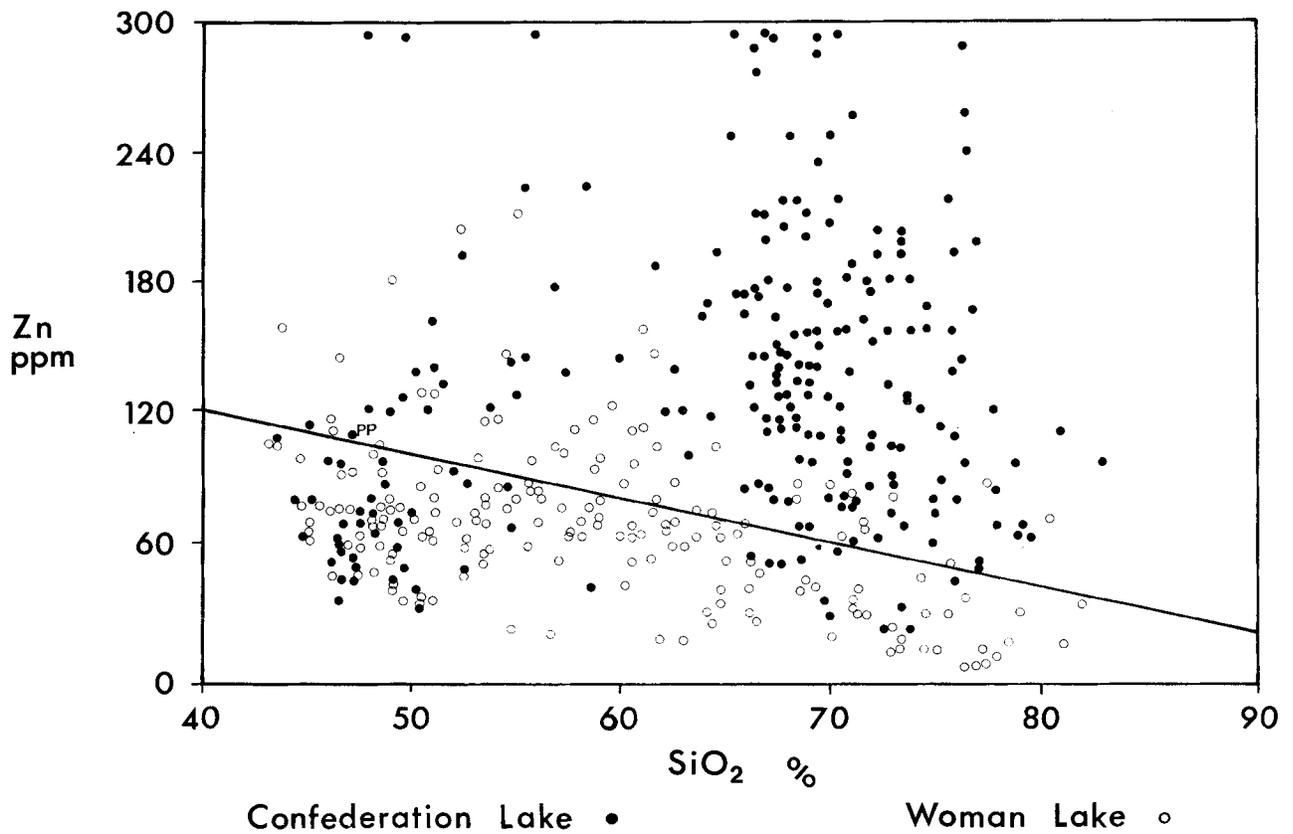


Figure 15.12. Relation between Zn and SiO_2 contents of productive and nonproductive cycles, Uchi Lake (Nichol, 1975).

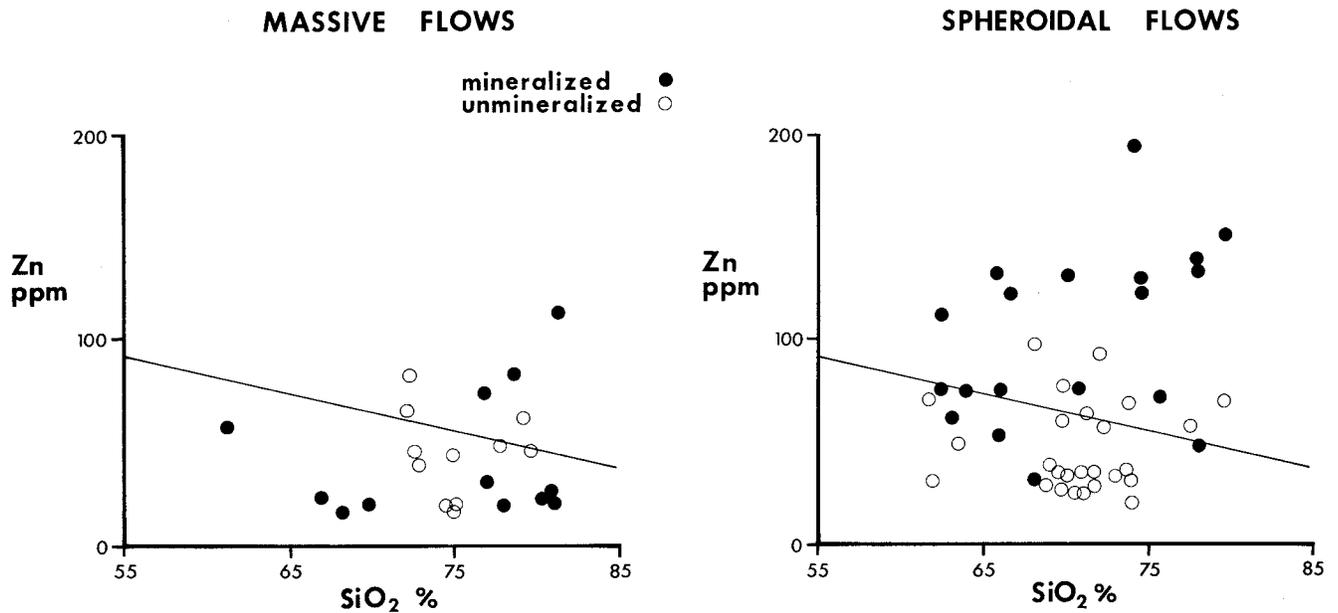


Figure 15.13. Relation between the composition and texture of productive and nonproductive cycles, Noranda (Nichol, 1975).

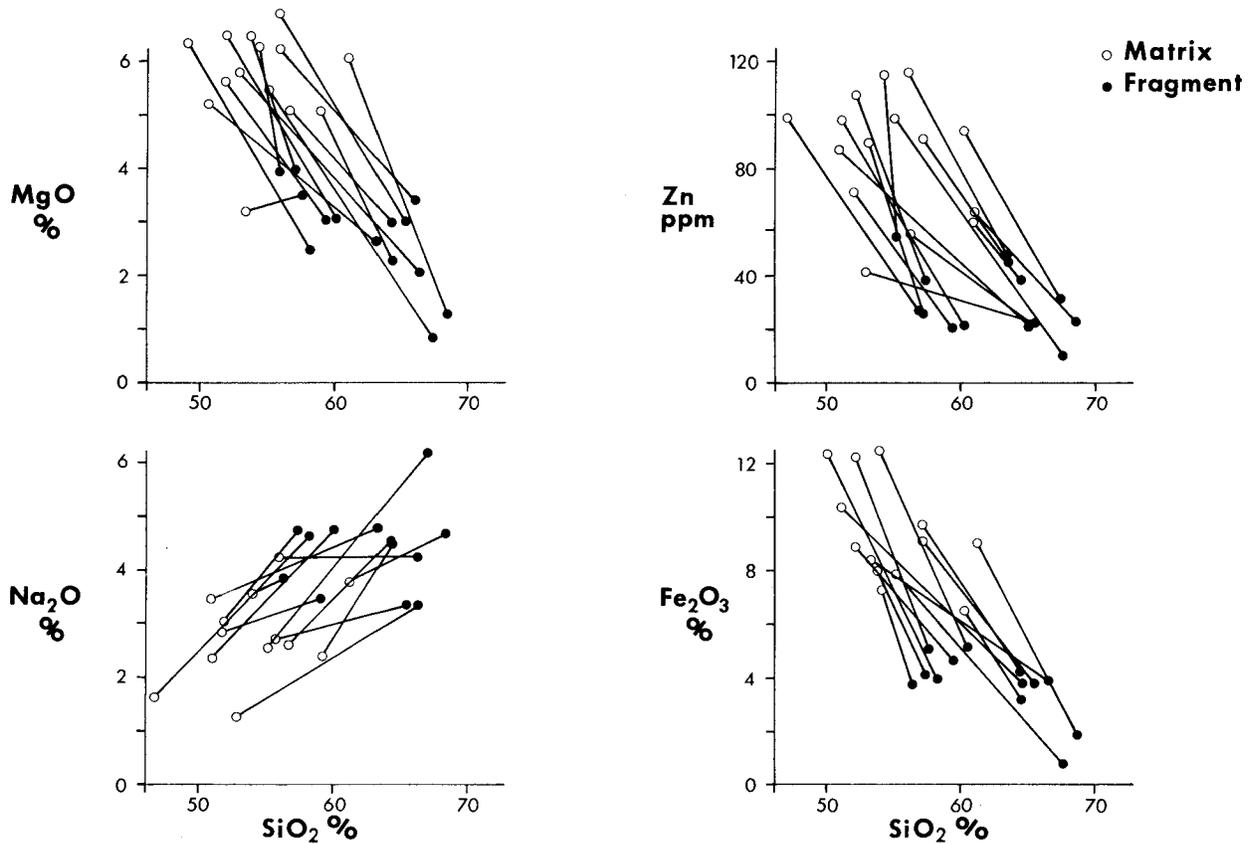


Figure 15.14. Relation in composition of fragment and matrix of pyroclastics at Kakagi Lake (Sopuck, 1977).

Table 15.5
Summary of major element dispersions in relation to
volcanogenic massive sulphide deposits

Deposit	Alteration mineralogy	Elements enriched	Elements depleted	Elements unchanged	Age
Kuroko, Japan Lambert & Sato (1974)	Mon, Ser, Chl, Kaol	K, Mg, Fe, Si	Ca		Cenozoic
Kuroko, Japan Tatsumi & Clark (1972)	Ser, Qtz, Cal	Mg, K	Na, Ca, Fe	Al	Cenozoic
Hitachi, Japan Kuroda (1961)	Cord, Anthoph.	Mg, Fe, Ba	Na, Ca, Sr		Cenozoic
Buchans, Canada Thurlow et al. (1975)	Chl, Ser, Qtz	Mg, Fe, Si	Na, Ca, K		Paleozoic
Heath Steele, Canada Wahl et al. (1975)	Chl, Ser	Mg	Na, Ca		Paleozoic
Brunswick No. 12 Canada Goodfellow (1975)	Chl, Ser, Qtz	Mg, Fe, (Mn), (K)	Na, Ca (Mn), (K)	Al	Paleozoic
Killingdal, Norway Rui (1973)	Chl, Bio, Qtz	Mg, K, Mn	Na, Ca, Si	Al, Ti, Fe (total)	Paleozoic
Skorovass, Norway Gjelsvik (1968)	Chl, Ser	Mg	Na, Ca		Paleozoic
Boliden, Sweden Nilsson (1968)	Chl, Ser, Qtz, Andal	Mg, K, Al	Na, Ca		Proterozoic
Mattabi, Canada Franklin et al. (1975)	Qtz, Carb, Ser, Chld, Chl, Andal, Gar, Kyan, Bio	Fe, Mg	Na, Ca		Archean
Millenbach, Canada Simmons et al. (1973)	Chl, Ser, Anthoph, Cord.	Mg, Fe	Na, Ca, Si		Archean
Mines de Poirier Canada Descarreaux (1973)	Chl, Ser,	Mg, K	Na, Ca	Si	Archean
Lac Dufault, Canada Sakrison (1966)	Chl, Ser	Mg, Fe, Mn	Na, Ca	Al, Ti K, Si	Archean
East Waite, Mobern, Joutel, Poirier, Agnico-Eagle, Mattabi, Sturgeon Lake, South Bay McConnell (1976)	Qtz, Ser, Chl, Carb, Sauss, Lpidote	Mg, Fe	Na, Ca	Si, Al	Archean

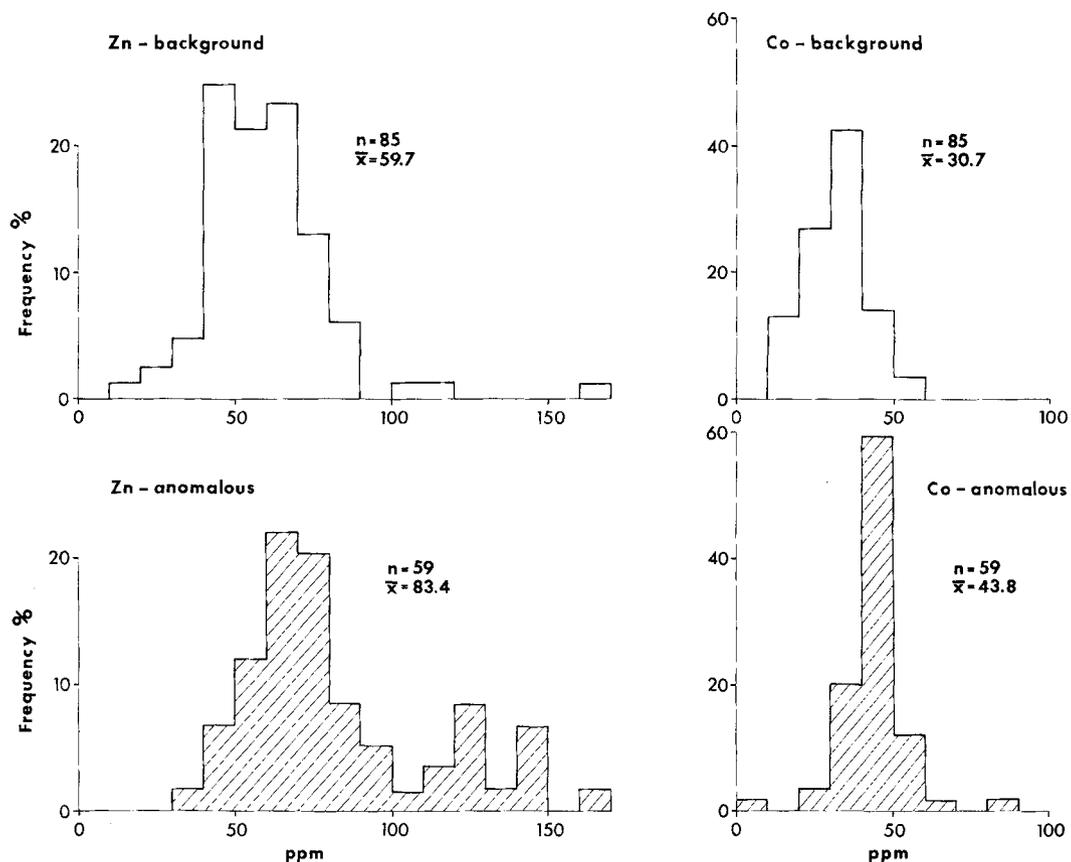


Figure 15.15. Frequency distributions of Zn and Co in basaltic pillow lava from background and anomalous areas within 1 km of the Skouriotissa cupriferous pyrite deposit, Cyprus (data from Govett and Pantazis, 1971; Govett, 1972).

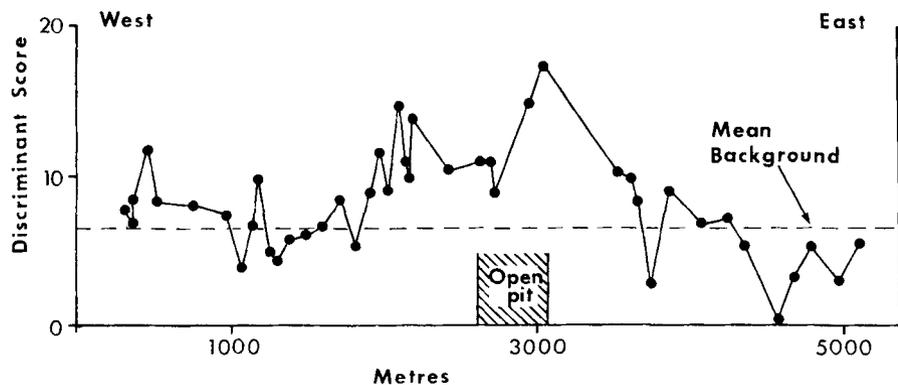


Figure 15.16. Distribution of anomalous discriminant scores for Cu, Zn, and Co across the Mathiati cupriferous pyrite deposit, Cyprus (Govett and Goodfellow, 1975).

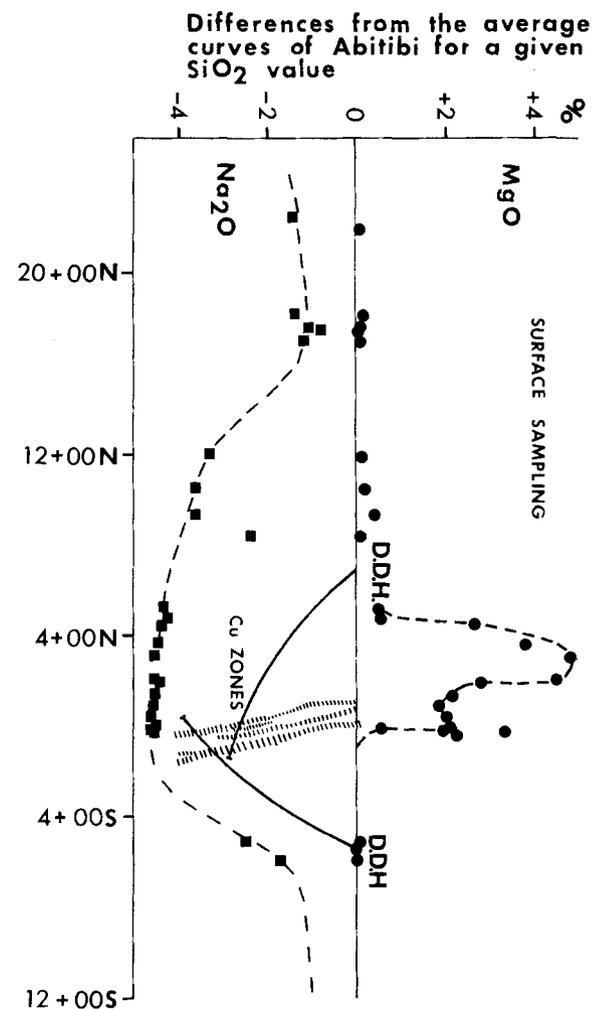


Figure 15.17. Distribution of "residual" MgO and Na₂O in felsic volcanic rocks across the Jay copper deposit, Abitibi District, Canada. "Residual" represents the difference between analyzed content and average value in the Abitibi District for corresponding SiO₂ content (redrawn from Descarreaux, 1973).

Table 15.6

Summary of trace-element dispersion in relation to volcanogenic massive sulphide deposits

Deposit	Ore mineralogy	Metal dispersion	Age
Kuroko type, Japan Lambert & Sato (1974)	py, cpy, sph, ga, bar	Zn, Cu, Pb	Cenozoic
Buchans, Canada Thurlow et al. (1975)	sph, ga, cpy, (py, tet, bo, cov)	Zn, Pb, Ba, (Ag) (Cu)	Paleozoic
Brunswick No. 12, Canada Goodfellow (1975)	py, sph, ga, po, cpy, tet, bo	Zn, Pb	Paleozoic
Heath Steele, Canada Whitehead and Govett (1974)	py, sph, ga, cpy	Pb, Zn	Paleozoic
Killingdal, Norway Rui (1973)	py, sph, cpy	Cu, Zn	Paleozoic
Mattabi, Canada Franklin et al. (1975)	cpy, py, sph	Cu, Zn, S	Archean
Millenbach, Canada Simmons et al. (1973)	cpy, py, sph	Zn	Archean
East Waite Mobern, Joutel, Poirier, Agnico-Eagle, Mattabi, Sturgeon Lake, South Bay Mines, McConnell (1976)	ph, sph, cpy (po)	Zn, Cu, S	Archean

Variations in the nature of footwall and hanging wall anomalies have been noted according to the spatial relation of the deposit to the vent (Wahl, 1978). Extensive Ca and Mg halos occur in both the footwall and hanging wall of deposits located proximal to the vent (A) (Fig. 15.20) whereas a deposit located distal to the vent (B) has an associated footwall anomaly but only a very restricted hanging wall anomaly. The extensive dispersion associated with the proximal deposit is attributed to deposition from acidic fumarolic brines whereas the more restricted dispersion associated with the distal deposit is related to deposition from metal-rich brines that have flowed down the slope from the vent.

The same elements show the same types of trends on both a regional and a local and mine scale in an Archean massive sulphide environment. At the Joutel-Poirier area in the Canadian Shield, relative enrichment of Fe, Mg, and Zn with depletion of Ca, Na, and K, occurs around the deposit on a scale of hundreds of metres; these element distribution patterns also occur regionally on a kilometre scale (Fig. 15.21, Sopuck, 1977). The same situation is evident in the Bathurst district of New Brunswick, where enrichment of Zn and Mg and depletion of Ca and Mn occur both regionally and in the immediate vicinity of individual deposits (Whitehead and Govett, 1974; Goodfellow, 1975; Pwa, 1977; Wahl, 1978). It is reasonable to suppose that similar processes were operative at both the local and regional scale.

SOVIET LITHOGEOCHEMISTRY

It may be surmised from translated articles and other Soviet contributions over the past decade that geochemists in the U.S.S.R. have developed techniques that enable them to successfully detect blind orebodies at depths of hundreds of metres; moreover, they appear to be able to assess whether halos reflect probable economic mineralization or merely the root zone of deposits that have had the economic portion eroded away. The basis of the technique is the establishment of zoning patterns of different elements in halos (Fig. 15.22). Investigations of hydrothermal orebodies have shown that, despite a marked variation in composition and in local geological conditions, the halos conform essentially to a general zoning pattern (Grigoryan, 1974); for steeply dipping bodies the sequence from top to bottom (supra-ore elements to sub-ore elements) is:

Ba-(Sb,As,Hg)-Cd-Ag-Pb-Zn-Au-Cu-Bi-Ni-Co-Mo-U-Sn-Be-W.

Ovchinnikov and Baranov (1972) reported a general zonal sequence in halos around a subvolcanic hydrothermal copper-pyrite deposit of Ba, Ag, Pb, and Zn in the upper zones, and Cu, Mo, Co, and Bi in the lower zones; this is consistent with Grigoryan's sequence.

Soviet geochemists generally use multi-element ratios to reduce the effects of local reversals in zoning sequences, and also to reduce analytical variations (most of their analyses are semi-quantitative spectrographic). Additive halos (addition of different element values standardized to respective background), multiplicative halos (multiplication of element values), and ratios of supra-ore to sub-ore elements are favoured rather than some of the techniques such as regression and discriminant analyses that have found wider use in the Western world. Western geochemists are more concerned with interpreting the absolute content of an element in a halo to the exclusion of its other defining parameter – dimension. Soviet geochemists, on the other hand, use the dimension of halos as an effective interpretive aid by calculating the linear productivity of a halo; this is simply the product of the average content of an element and the width of an anomaly (areal productivities are also used). It has been stated (Grigoryan, 1974) that not only do different deposits have similar zoning patterns, but that their extent, as defined by the change in linear productivity with depth, is also similar.

The application of the procedures of multiplicative and linear productivities is illustrated schematically in Figure 15.22. Elements (a) and (b) give supra-ore halos; elements (c) and (d) give sub-ore halos. The enhancement of anomalies – and the clear distinction between above-ore and below-ore halos – using multiplicative ratios of supra-ore to sub-ore halos is obvious when compared to profiles of elements. Changes in linear productivities with depth for supra-ore element (a) and sub-ore element (d) are also illustrated. The trend of linear productivities of ratios with depth is particularly striking (this schematic trend is typical of those illustrated in the Soviet literature). The practical importance of this type of approach is the apparent possibility of determining the location of blind deposits from surface samples, of predicting the likelihood of the deposits being economic or not, and of accurately locating mineralization from limited drillhole data. The size of the halos (according to Beus and Grigorian (1977), are 200-850 m) are comparable to those detected by Western geochemists, but interpretative procedures seem to be rather more advanced.

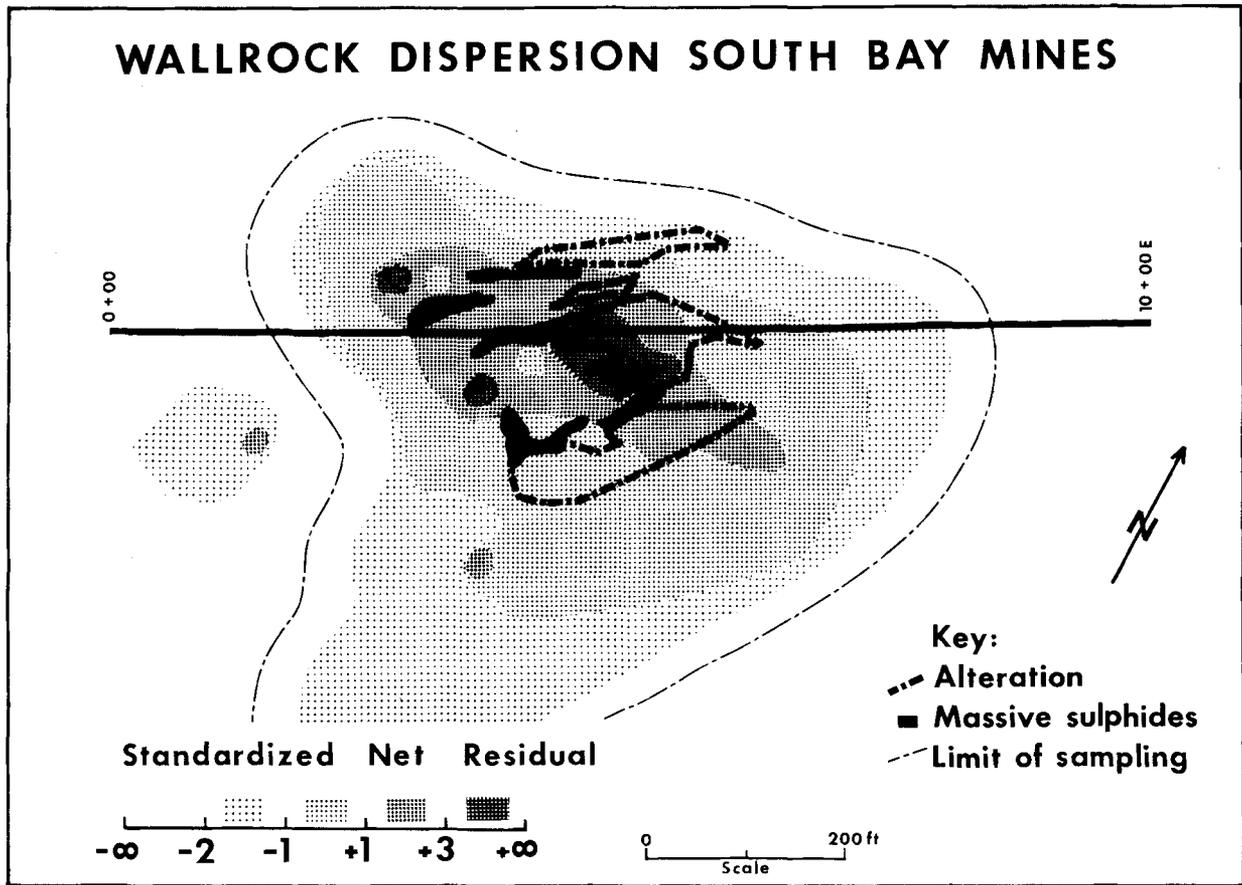


Figure 15.18. Distribution of "standardized net residual" at South Bay Mine (McConnell, 1976).

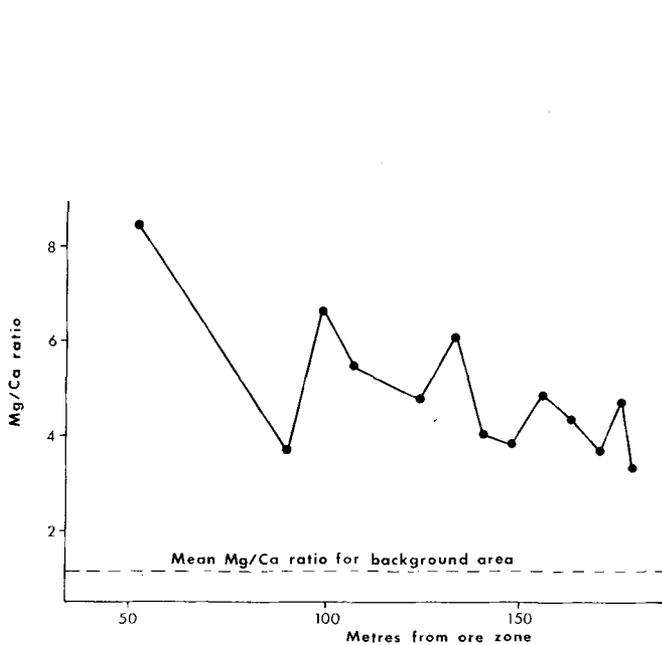


Figure 15.19. Distribution of Mg/Ca ratio in footwall felsic volcanic rocks, Brunswick No. 12 deposit, New Brunswick (reproduced from Govett and Goodfellow, 1975).

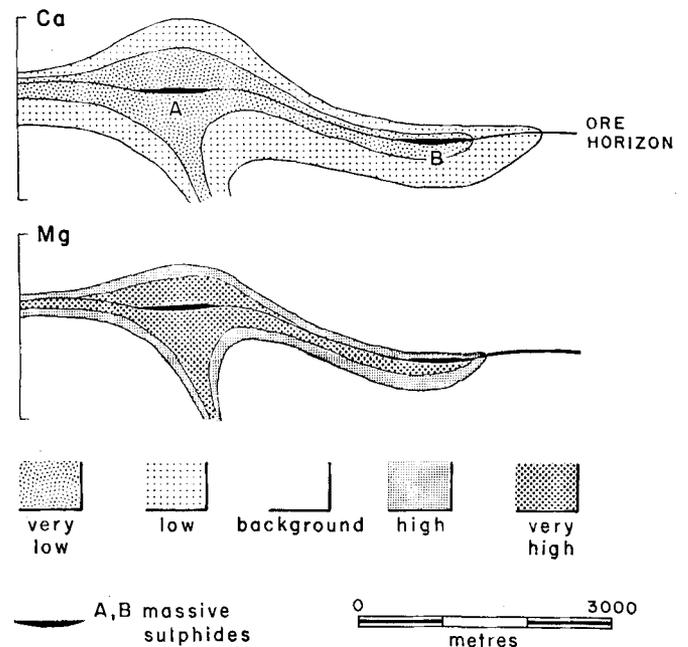


Figure 15.20. Schematic distribution of Ca and Mg in felsic volcanic rocks around proximal (A) and distal (B) massive sulphide deposits, New Brunswick (data from Wahl, 1978).

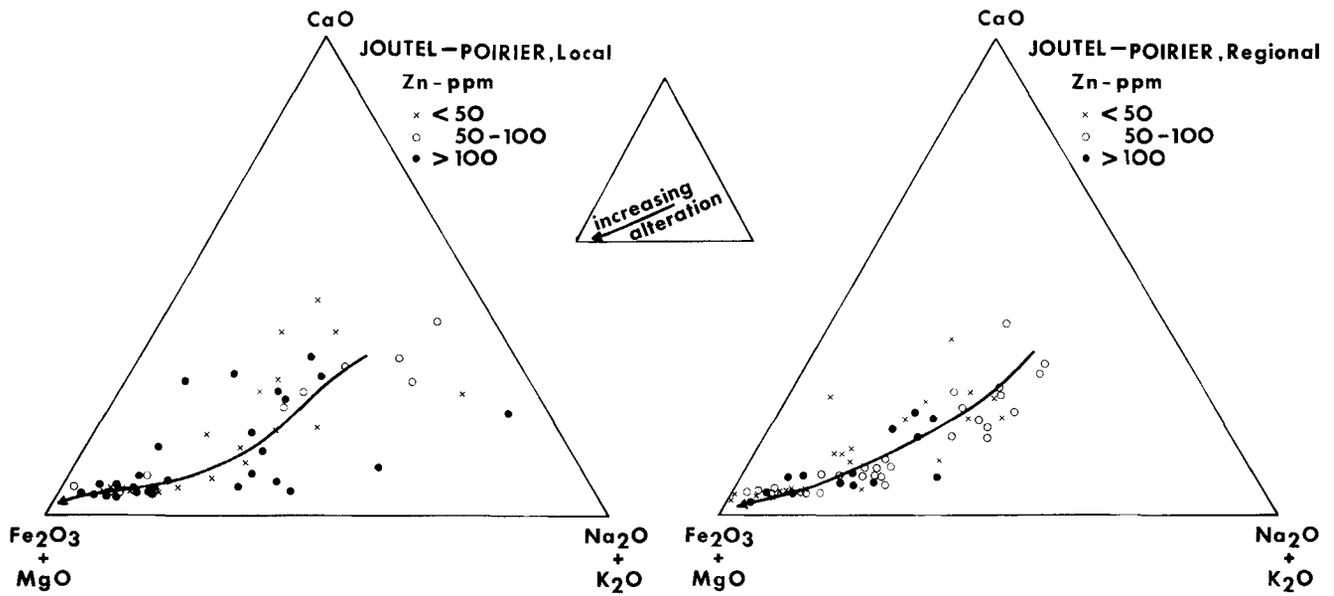


Figure 15.21. Relation between geochemistry and the degree of alteration on the local and regional scale at Joutel-Poirier (Sopuck, 1977).

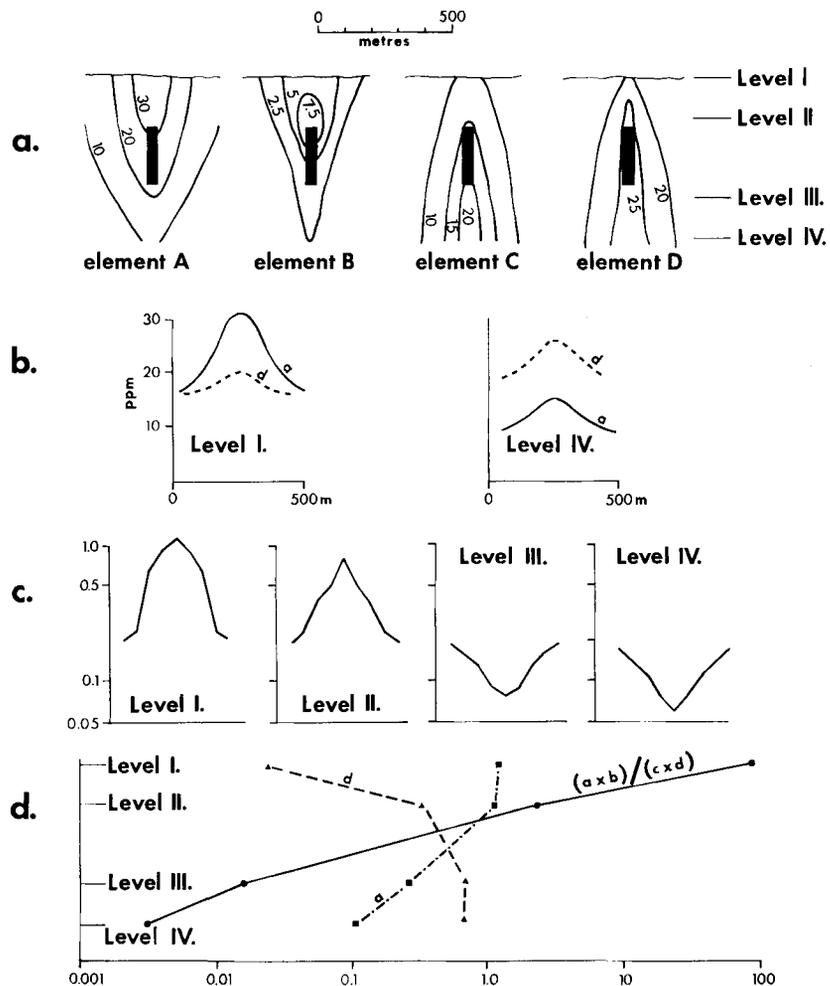


Figure 15.22. Schematic illustration of supra-ore and sub-ore litho geochemical halos, and anomaly enhancement through the use of multiplicative halos and linear productivities (after Govett, 1977).

Evaluation of State-of-the-Art and Conclusions

The existence of diagnostic lithogeochemical signatures have been recognized on a number of scales associated with different types of deposits. These have a variety of applications in exploration.

- a. anomalous metal contents of mineralized relative to unmineralized intrusions e.g., (1) Sn (Australia), W (Canada), Sn (United Kingdom) and Ni, Cu (Canada). These features are attributed to the high metal content of the parent magma that gave rise to the intrusives and the associated deposits. (2) Cu, Mo (United Kingdom) resulting from post-magma hydrothermal activity in the host intrusions.
- b. anomalous metal contents of mineralized zones of intrusions relative to unmineralized zones e.g., porphyry copper deposits in general resulting from the permeation of hydrothermal fluids into the intrusion from the centre of mineralization.
- c. localized anomalous metal contents in the wall rock adjacent to vein-type mineralization e.g., Pb, Zn, Ag mineralization in Utah as a result of mineralizing fluids diffusing into the wall rock.
- d. anomalous metal contents in favourable areas of sedimentary basins for mineralization e.g., McArthur River, Australia; Tynagh, Ireland; Meggen, Germany.

These patterns are related to the exhalation of metal-rich solutions into the sea and subsequent deposition with and decay of certain metal contents over considerable distances from the deposits.

- e. anomalous metal contents in productive relative to nonproductive cycles, and on more local scales associated in general with volcanogenic massive sulphide deposits. These features apparently result from hydrothermal activity associated with the phase of mineralization.

These diagnostic geochemical parameters have variously been identified on the basis of whole rock composition, analysis of separate mineral phases or the distinction of subtle variations in the form of populations.

Equally important in terms of drawing attention to the limitations of lithogeochemistry in exploration has been the demonstration that the composition of the whole rock or mineral phases may not be diagnostic of proximity to mineralization. Since the composition of rocks is the result of the overall geological history of the sample the composition represents the effects of a number of processes that have affected the sample. Only in cases where the mineralizing episode is the over-riding process will effects due to mineralization be readily identifiable. In other cases effects on composition due to other causes must be taken into account before any response due to mineralization can be recognized. This feature is illustrated by the need to take into account the effects of fractionation in the interpretation of data relating to igneous rocks if a variety of lithologic types are sampled in order to identify responses due to mineralization. It is thus vital at the interpretation stage to take into account those aspects of the geological history that have a bearing on the geochemistry in order to identify meaningful responses due to mineralization. The lack of general acceptance of lithogeochemistry as an aid in exploration is undoubtedly due to a lack of recognition of diagnostic patterns related to in part petrogenesis, tectonic, and overall geological history.

In many of the examples cited in the review the investigations have been carried out over areas of known mineralization where the geological knowledge is relatively high. Whilst these locations are logical focal points for

establishing the nature of dispersion associated with mineralization it may be that in view of the subtlety of many of the responses, they have only been recognized as anomalous responses because of the relatively good geological data base.

The diversity of geochemical responses related to mineralization in terms of anomalous elements, lateral extent, and contrast from different examples of the same type of deposit clearly is an adverse factor affecting the applicability of lithogeochemistry in exploration. This feature is illustrated by the diversity in elements showing anomalous responses, extent, and magnitude of the anomalous dispersions associated with four porphyry-type deposits in the Highland Valley, British Columbia.

In exploration over relatively unexplored terrain the necessary level of geological information to aid interpretation is not available or can only be obtained at considerable expense which must constitute a further constraint on the applicability of the technique. It is probable that a reconnaissance survey carried out over relatively unexplored ground will generate a multitude of subtle anomalies similar to those associated with known mineralization but in the absence of adequate geological information it will be impossible to identify those anomalies reflecting mineralization from those related to other causes.

Notwithstanding these limitations, within the past ten years in the Western World lithogeochemistry has advanced from an essentially academic involvement to a technique used sparingly by the mining industry in mineral exploration. However, we are not aware of any mineral discovery to date that can be attributed to lithogeochemistry.

The use of lithogeochemistry on pre-drilling exploration is dependent upon adequate surface outcrop or expensive surface drilling through overburden to bedrock. Sampling, therefore, is generally more costly than in stream sediment or soil geochemical surveys; crushing and grinding of samples preparatory to analysis is at least five times more expensive than sieving soil or stream sediments.

Nevertheless, there are a number of exploration situations where lithogeochemistry is useful and may be expected to become increasingly important in the future. These are:

1. Regional scale exploration to identify potentially productive plutons and volcanic or sedimentary horizons (anomalous geochemical patterns are detectable over many kilometres).
2. Local scale exploration to locate deeply-buried and blind deposits (geochemical halos have dimensions of more than 100 m and can range up to 1 km).
3. Exploration drilling to assist in drill hole location.
4. Mine scale exploration and underground mapping.

As indicated previously, the nature of geochemical responses in bedrock associated with mineralization varies considerably in terms of anomalous element associations, extent and magnitude of anomalies amongst different examples of the same type of deposit. This situation related in part to conditions in the geological environments prevents the definition of any standardized procedures. Perhaps more than in any other branch of geochemical exploration, it is essential to carry out an orientation survey over known mineralization to establish the nature of geochemical dispersion associated with known mineralization and appropriate sampling, analytical and interpretational procedures. These operational procedures may only be applicable in a precisely similar geological environment.

In terms of sampling the nature of the optimum sample should be established i.e., grab or composite chip sample, and sample interval or density to ensure adequate representivity in terms of the target population. Sample preparation procedure involving preparation of whole rock or mineral separates should be considered. With regard to analytical procedures attention should be given to identifying elements that display diagnostic distributions and ways of analyzing these in terms of obtaining the necessary sensitivity, accuracy, and precision and in some cases the metal held in particular mineral phases e.g., sulphide-held metal. In order to identify the necessary interpretational procedures it will be essential to identify those features of the geological environment that have a bearing on geochemical dispersion.

At the end of 1977 there is abundant evidence that geological events – including those that give rise to mineral deposits – are detectable by litho geochemistry, given appropriate geological interpretation. Future development and success will depend upon improved understanding of geological processes and the mechanisms of element migration and fixation. The fact that litho geochemical surveys are more costly to conduct than stream sediment or soil surveys means that the major application of rock geochemistry in the near future is likely to be restricted to areas that have already been well-prospected by more traditional techniques. Moreover, since multi-element data are generally required and interpretation is correspondingly difficult, litho geochemical techniques are likely to be limited by the availability of advanced analytical technology and highly-trained geochemists. To the extent that the mining industry is prepared to invest in renewed exploration in the well-prospected areas of North America and Europe, litho geochemistry provides a promising new technique.

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