

# COPPER AND ZINC IN PROTEROZOIC ACID VOLCANICS AS A GUIDE TO EXPLORATION IN THE BEAR PROVINCE\*

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## ABSTRACT

A lithogeochemical survey of the acid porphyry rocks of the Proterozoic Bear province has been undertaken. The data reveal patterns of copper and zinc which are relatable to known mineral occurrences. Additional areas of anomalous metal patterns are outlined which are possibly related to as yet undiscovered mineral occurrences. The behaviour of copper is essentially that of a chalcophile element whilst zinc behaves in an oxyphile manner, on average some 60% of the copper is in a sulphide form whilst only some 20% of the zinc is in that form. The use of a partial sulphide-selective leach is recommended for mineral exploration programmes and shown to be particularly important in the case of zinc. Significant regional patterns of zinc distribution are described which are believed to be related to the metallogenetic development of the Proterozoic acid volcano-sedimentary belts, and in particular their potential for stratabound volcanogenic sulphide deposits.

## INTRODUCTION

During the summer of 1973 a bedrock geochemical sampling programme was undertaken in the southern half of the Wopmay subprovince of the Bear structural province of the Canadian Shield. The geochemical study was undertaken to assess the applicability of lithogeochemical techniques developed for use in the much younger granitoid terrane of the Canadian Cordillera (Garrett, 1971, 1973a, 1974a) to the more complex Proterozoic Shield terrane. The particular test area was chosen as it overlaps part of the Operation Bear-Slave lake sediment geochemical survey area' (Allan et al., 1973) and is currently undergoing a mapping and geological revision programme (Garrett, 1974b; Hoffman, 1974; McGlynn, 1974). Additionally, it was known that a variety of mineral occurrences were present in the field area ranging from the typical Bear province Ag-U association, through porphyry copper like occurrences to stratabound copper sulphides.

The general geology of the field area has been reviewed by Stockwell and McGlynn (1970) and Fraser et al. (1972). The study area lies in Wopmay subprovince of the Bear province, which lies to the west of the Wopmay fault (a meridional fault at approximately 116°30'W) along the western margin of

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the Shield. This area west of the Wopmay fault is also known as the Great Bear batholith which forms an element of Fraser's Wopmay Orogen (Wopmay Belt of Stockwell and McGlynn, 1970). The complex of the Great Bear batholith, of Late Aphebian age, consists mainly of high-level granites and granodiorites. The roof of the batholith is best preserved in the north where great thicknesses of ignibritic tuffs and some acid flows are found. The volcano-sedimentary pile also includes basalts, andesites, conglomerates and red bed sediments. These rocks are most common in the Echo Bay and Camsell River areas in the west around the shores of Great Bear Lake.

The acid flows and pyroclastics make up some 30% of the batholith and compositions vary from dacite to rhyolite; however, in the past they have been grouped and mapped as quartz-feldspar porphyries. These porphyries

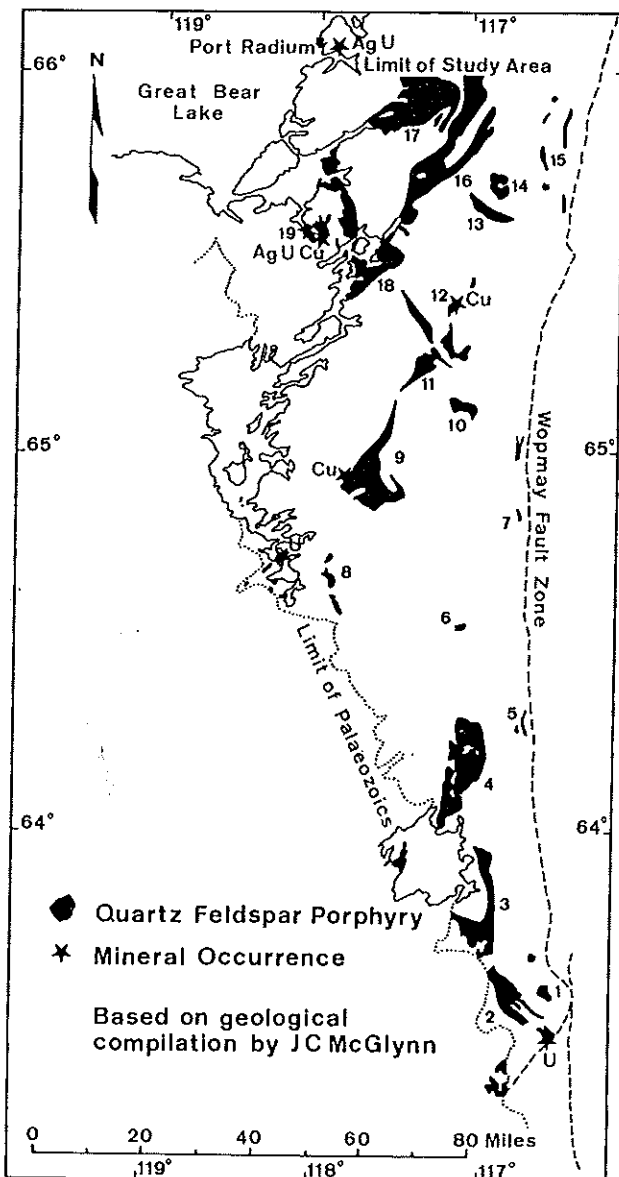


Fig.1. General geology and location map. Numbers refer to the numbers in square brackets in text. (Based on geological compilation by McGlynn, 1974.)

are both extrusive and intrusive, and in the southern part of the study area gradational phases are found between fine-grained intrusive porphyries and the granitoid rocks. It seems likely that the entire assemblage forms a comagmatic pile with acid volcanics being outpoured onto a basement, possibly similar to the Hepburn batholith on the east side of the Wopmay fault. Great thicknesses of volcanics were extruded and younger granitoid rocks, possibly parts of the feeder system, were intruded into the pile. Locally, sedimentary rocks, shales, cherts and sandstones accumulated in transitory lakes.

The most important mineral occurrences lie in the Camsell River area where silver and copper are currently produced from the Terra mine ([19], see Fig.1). The silver occurs in cross-cutting veins with associated Cu, Co, Ni and U minerals. The major source of copper is from stratabound bodies within the mine which are related to iron formation units within the volcano-sedimentary pile. Nearby on the Norex property is a large area of altered andesites where there is pervasive pyrite and chalcopyrite mineralization. The general Calder River area also contains sulphide occurrences related to magnetite iron formation and cherts, and breccia pipes in the porphyries. At Tommie Lake [12] 25 miles to the southeast chalcopyrite is found associated with magnetite, chert and jaspilite horizons as well as in coarse-grained vein deposits which are interpreted by the author as gash veins into which quartz and chalcopyrite have been mobilized. Similar occurrences characterized by cobalt and arsenous minerals occur some 120 miles to the south near Lou Lake [2] (Shegelski and Thorpe, 1972). In the central part of the field area at Bode Lake [9] occurs copper mineralization which is interpreted by R.V. Kirkham (personal communication, 1973) as having many of the attributes of a porphyry copper. Other mineral occurrences are known to occur near Mazenod [3], DeVries [5], Hardisty [8] and Blackjack Lakes [15].

#### FIELD PROGRAMME

The quartz-feldspar porphyries were systematically sampled with aid of a helicopter and boat and foot traverses. 669 sites in the volcano-sedimentary rocks were sampled, only about 3% of these sites were obviously sedimentary and the remainder were either extrusive or intrusive porphyries. Differentiating between the intrusive and extrusive phases was often difficult due to the general fine grain and lack of small-scale structures in the rocks. In no case was material included in the data analysis if it was collected directly from the mineral occurrences described, only peripheral material was included for the data analysis. Field data was recorded on field cards which served as keypunch documents and computer technology was used extensively in the compilation and interpretation of the data. At each sample site two separate samples were collected with the aid of a sledgehammer. Care was taken to collect the freshest material available, discarding outer lichen-covered chips, from two points some 20 ft apart. The two samples from each site were bagged separately and shipped to the Geochemistry Section of the Geological Survey of Canada in Ottawa for sample preparation and analysis.

TABLE I

Summary of data statistics ( $n = 1338$ )

	Range		Arithmetic		Geometric mean	Log <sub>10</sub> units		F				
	min	max	$\bar{X}$	$\sigma$		C.V. (%)	$\bar{X}$	$\sigma^2$	$\sigma^2_1$	$\sigma^2_2$	$\sigma^2_{SA}$	$(\sigma^2/\sigma^2_{SA})$
Cu	1.0	60000.0	155	2093	1350	11	1.031	0.345	0.351	0.339	0.104	4.30
Cu px	1.0	50984.0	84	656	781	6	0.774	0.485	0.490	0.480	0.164	2.96
Zn	3.0	9500.0	124	424	342	72	1.857	0.142	0.137	0.147	0.024	5.91
Zn px	1.0	8200.0	47	340	723	16	1.209	0.172	0.167	0.178	0.043	4.02
Cu px/Cu	0.012	1.0	0.61	0.24	40							
Zn px/Zn	0.032	1.0	0.26	0.15	58							

Note:  $\sigma^2_1$  is log<sub>10</sub> variance of the first samples of each site pair and  $\sigma^2_2$  is the variance of the second samples.  $\sigma^2$  is the associated total data variance and  $\sigma^2_{SA}$  is the combined sampling and analytical variance.

## SAMPLE PREPARATION AND ANALYSIS

The samples, weighing between 2 and 3 lbs. each, were reduced to minus 60 mesh, all the sample was crushed except for a hand specimen large enough for thin-section work. A split of this crushed material was ground in a ceramic ball mill to minus 100 mesh (Laverigne, 1965).

Total copper and zinc were determined by atomic absorption spectrophotometry after a  $\text{HF}/\text{HClO}_4$  decomposition. A 400-mg sample was fumed to dryness three times and the residue taken up in 2M HCl and diluted to 20 ml to yield a 1M HCl concentration. Partial copper and zinc were also determined by atomic absorption spectrophotometry after a sulphide selective leach. This attack uses  $\text{H}_2\text{O}_2$  in the presence of ascorbic acid and is identical to that described by Lynch (1971) for the ultramafic litho-geochemical study carried out by Cameron et al. (1971). A 100-mg sample was attacked in 10 ml of the leach solution, where results were in excess of the top standard, equivalent to 400 ppm in the rock, a 1/10 dilution was effected by using a 10-mg sample weight for attack.

## DESCRIPTION OF DATA STATISTICS AND DATA PRESENTATION

The summary statistics of the total and partial copper and zinc determinations are given in Table I. As the sampling was of a replicate nature it is possible to carry out an analysis of variance to determine if the combined sampling and analytical variance is significantly smaller than the overall regional variability (Garrett, 1973b).

In all cases the standard deviations of the data are greater than their associated means, leading to coefficients of variation in excess of 100%; this indicates a skewness in the data which can be deduced as being positive from an inspection of the means and ranges. Therefore, a logarithmic transform was applied to the data before further computations in order to render the data into a more normal distribution. Additionally, the logarithmic transform can be justified on theoretical grounds. The analytical method is based on an atomic absorption spectrophotometric determination which like all spectrographic methods is based on Beer's Law which is a logarithmic relationship. Thus the overall distribution of the errors inherent in the determinations are log distributed and a transform should be applied to the data.

In Table I  $\sigma^2$  is the total data variance of the 1338 samples and  $\sigma^2_1$  and  $\sigma^2_2$  are respective variances of the first and second samples from each of the 669 sampling sites. The combined sampling and analytical variance  $\sigma^2_{SA}$  is estimated from 669 paired samples and is used in computing an  $F$  ratio,  $\sigma^2/\sigma^2_{SA}$ . With so large a number of degrees of freedom,  $N - 1$  and  $N$ , and also with the two degrees of freedom being numerically close it is difficult to accurately evaluate the critical value of Fisher's  $F$ ; however, at the 99% confidence level and 668 and 669 degrees of freedom it is approximately 1.2. In all cases the calculated value of  $F$  is in excess of this critical value from

which we can deduce that the sampling and analytical variability is significantly less than the regional variability. This leads to the conclusion that the displayed elemental patterns are real and not due to local sampling or analytical variability.

The arithmetic data for the copper and zinc ratios of partial to total contents of the element are presented in arithmetic form, the means showing the different behaviour of these two elements.

Geochemical data are characterized by two features, level and relief. For any one group the level is easily expressed by the mean, and in the case of apparently lognormally distributed data the geometric mean. The appropriate parameter with which to describe the relief poses more of a problem and no one is generally accepted. In the present study the arithmetic coefficient of variation has been used. As data from the positive skew section of a distribution is included in the computation for standard deviation the computed value rises very steeply. This raw standard deviation could be used; however, the standard deviation generally increases with increasing mean so the coefficient of variation, i.e.  $\sigma/\bar{X}$ , has been used. Thus, for each of the 4 determinations two maps are presented, one depicting the geometric means of the 40 groups of volcano-sedimentary rocks and the other their arithmetic coefficients of variation, these maps of statistical parameters are considered analogous to the geochemical concepts of level and relief.

Two additional maps are presented each showing the average proportion of sulphide-selective leach metal to total metal for copper and zinc in each group.

The 1338 samples from the 669 sampling sites were divided in 40 groups. Each group contains an average of some 17 sites. In some instances the groups represent several small outcrop areas of porphyry all geographically close, and in others a much larger contiguous area of porphyry was divided up into convenient subareas. The 17 sites lead to 34 samples which are sufficient to estimate the mean metal content with a reasonable degree of confidence and also define the general nature of the frequency distribution. The relief of geochemical data is considered to be a more important criterion in interpretation than absolute level as mineralized areas are ideally reflected by high relief due to local erratic high values related to metal concentration processes. Thus, in interpreting the present data the two maps for each determination should be studied simultaneously and in the writer's opinion more weight should be given to groups exhibiting high coefficients of variation (relief) and lower means (levels) than groups having high means (levels) but low coefficients of variation (relief) which indicate uniform enrichment but no local concentration processes.

#### DESCRIPTION OF RESULTS

Total copper data covers a range of 1 ppm to 6%, a group of samples from Tommie Lake [12] contain the exceptionally high values, these rocks are

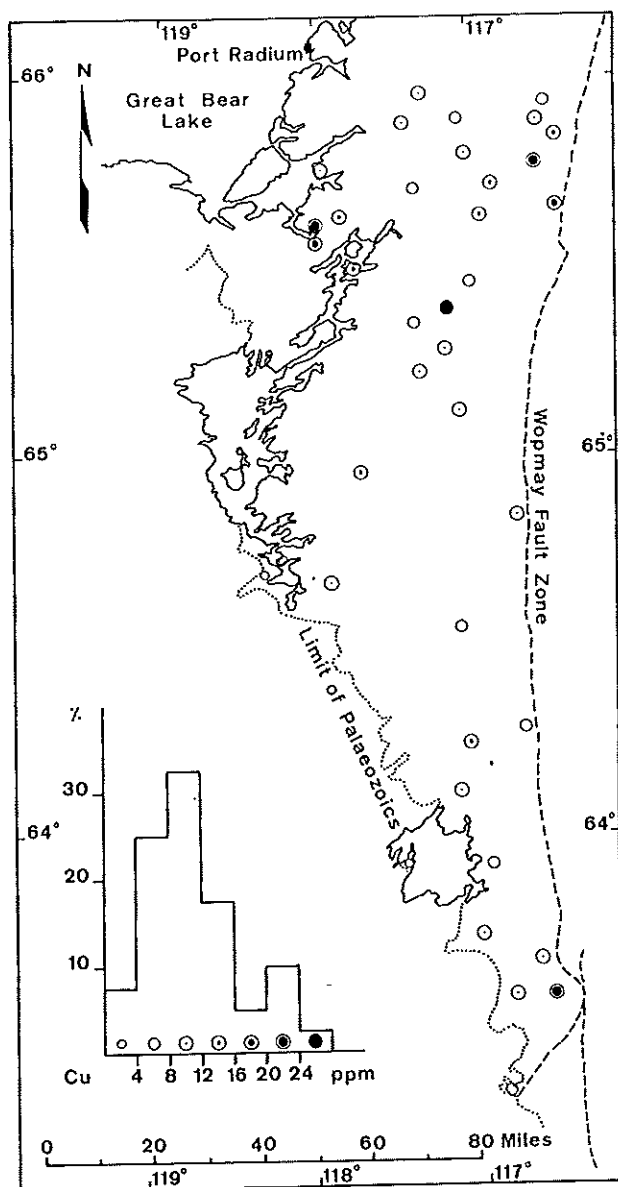


Fig.2. Geometric mean copper in volcano-sedimentary groups.

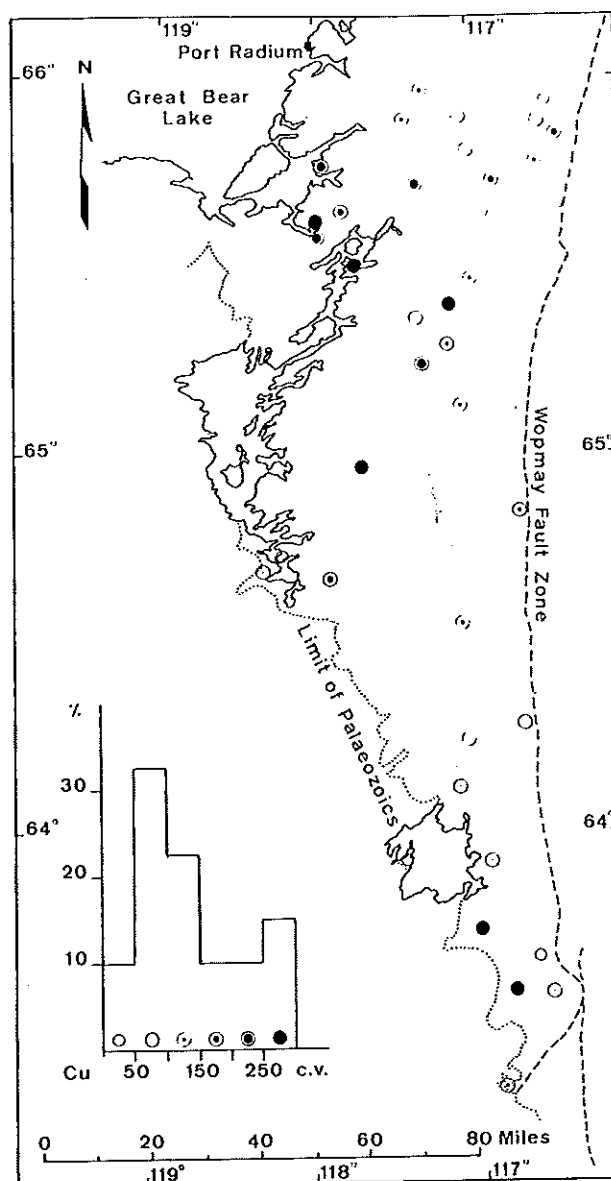


Fig.3. Arithmetic coefficient of variation for copper in volcano-sedimentary groups.

quartz-feldspar porphyries and other rocks high in magnetite which are of sedimentary origin. The overall geometric mean of 11 ppm is within the normal range of copper in acidic rocks, and 85% of the data falls between 5 and 50 ppm. The areal distributions for copper are shown in Figs.2 and 3. The data distribution shows a bimodal distribution with the second population being in excess of 20 ppm. Four groups fall into this population, three of these are known to have mineralization in the vicinity, they are Tommie Lake [12], Rainy Lake [19] and Blackjack [15]; the fourth, Hump Lake [1] near which no mineralization is known has a mean of 21 ppm. The coefficient of variation map, however, clarifies the matter. Hump Lake exhibits a normal

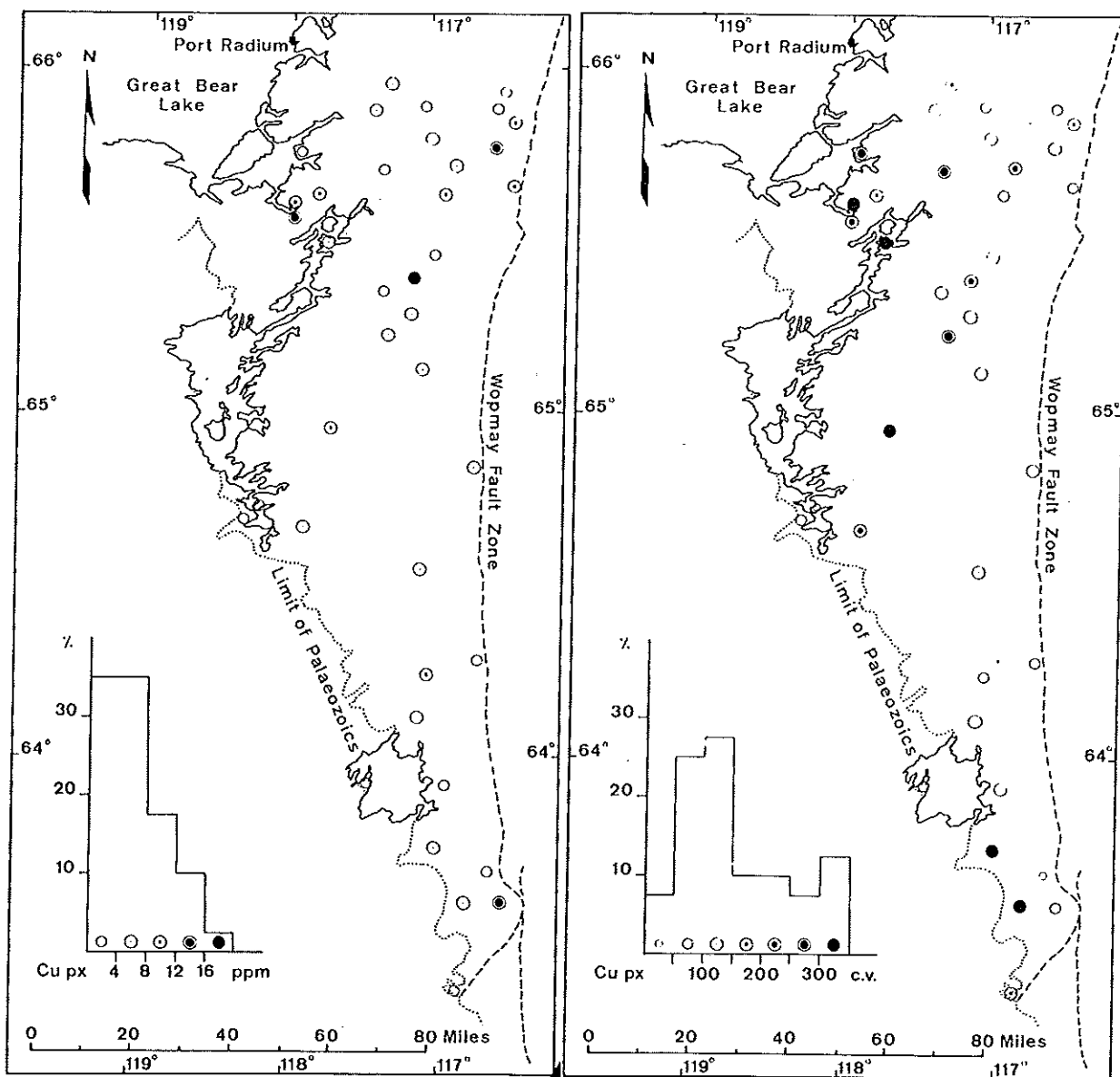


Fig. 4. Geometric mean partial copper in volcano-sedimentary groups.

Fig. 5. Arithmetic coefficient of variation for partial copper in volcano-sedimentary groups.

coefficient and on checking the range of the data there it lies between 7 and 56 ppm. Blackjack also reveals a somewhat unimportant coefficient. Thirteen groups show coefficients in excess of 150% and of these eight are known to be associated with mineralization; the Lou [2], Mazenod [3], Hardisty [8], Bode [9], Tommie [12], and Clut [18] Lakes and three groups in the Rainy Lake—Dinosaur Lake area [19]. The remaining five groups all have low associated means except Hansen Lake [14] and one group northeast of Blackjack. The group some 10 miles north of Rainy Lake on the shore of Conjuror Bay and the group on the Calder River [16] have high coefficients of variation but modal and low means, respectively, with respective maximum



values of 322 and 400 ppm. These two groups lie in volcano-sedimentary belts extending from Rainy Lake and Clut Lake, and thus may be of interest.

The data for partial copper have a unimodal J-type distribution and the maps of the data (Figs.4 and 5) show that the regional patterns exhibited by the geometric means are essentially identical to those discussed for total copper. The coefficients of variation show a modified pattern in comparison and attention is drawn to the eleven groups with coefficients in excess of 250%. Five of these coefficients are in excess of 300% and these groups are all known to have sulphide mineralization associated with them. Of the remaining six, three are known to be associated with mineralization, Hardisty Lake [8], Tommie Lake [12] and one of the Rainy Lake groups [19]. The three remaining groups, Hansen Lake [14], Calder River [16] and Conjuror Bay were also outlined by total copper coefficients of variation but the author has no knowledge of mineralization reported in these areas.

The total zinc distribution is bimodal, with the second mode having a marked positive skew. This distribution was studied using a technique and algorithm for linear clustering described by Spath (1973). This method allows a decomposition of the distribution into a specified number of clusters using the criteria of minimizing the sum of the sums of squared deviations from the cluster mean for each cluster. A three-cluster model leads to boundaries at 60 and 110 ppm with respective frequencies and cluster means of 40%, 42 ppm; 42.5%, 85 ppm; and 17.5%, 128 ppm. In contrast the overall geometric mean is 72 ppm. The generally accepted levels for zinc in acid rocks are 60 ppm for granodioritic types and 40 ppm for granites (Levinson, 1974). The two low clusters with means of 42 and 85 ppm correspond reasonably with the means for acidic and intermediate acidic rocks. The third is believed related to mineralized rocks. The data range from 3 to 9500 ppm with some 85% falling between 20 and 200 ppm. The areal distribution of the zinc data is presented in Figs.6 and 7. The most noticeable feature of the total zinc areal distribution is the very marked gradient towards higher levels in the north and northwest of the field area. The groups corresponding to the third suggested population lie in the Rainy Lake [19], Conjuror Bay, Clut Lake [18], Cruikshank River [17] and Wylie Lake [13] areas. The last two of these plot into the 100–120-ppm histogram interval on Fig.6. Only the Rainy Lake and Clut Lake groups are known to contain mineralization. The coefficients of variation reveal six groups with variations in excess of 100%. Half of these exceed 200% and are all related to areas of mineralization, they are the Tommie [12], Clut [18] and Rainy [19] Lakes. The remaining three are more enigmatic and only the first of these is in an area of known mineralization, they are the Lou [2], Rae [4] and Hansen [14] Lakes.

The data for partial zinc are presented in Figs.8 and 9. The overall distribution of partial zinc, unlike that of total zinc, is unimodal, but is somewhat positively skewed. The tail of the distribution starts around 20 ppm and 10 groups have geometric means in excess of 20 ppm. Only three of these have known mineralization nearby, Tommie Lake [12], Clut Lake [18] and

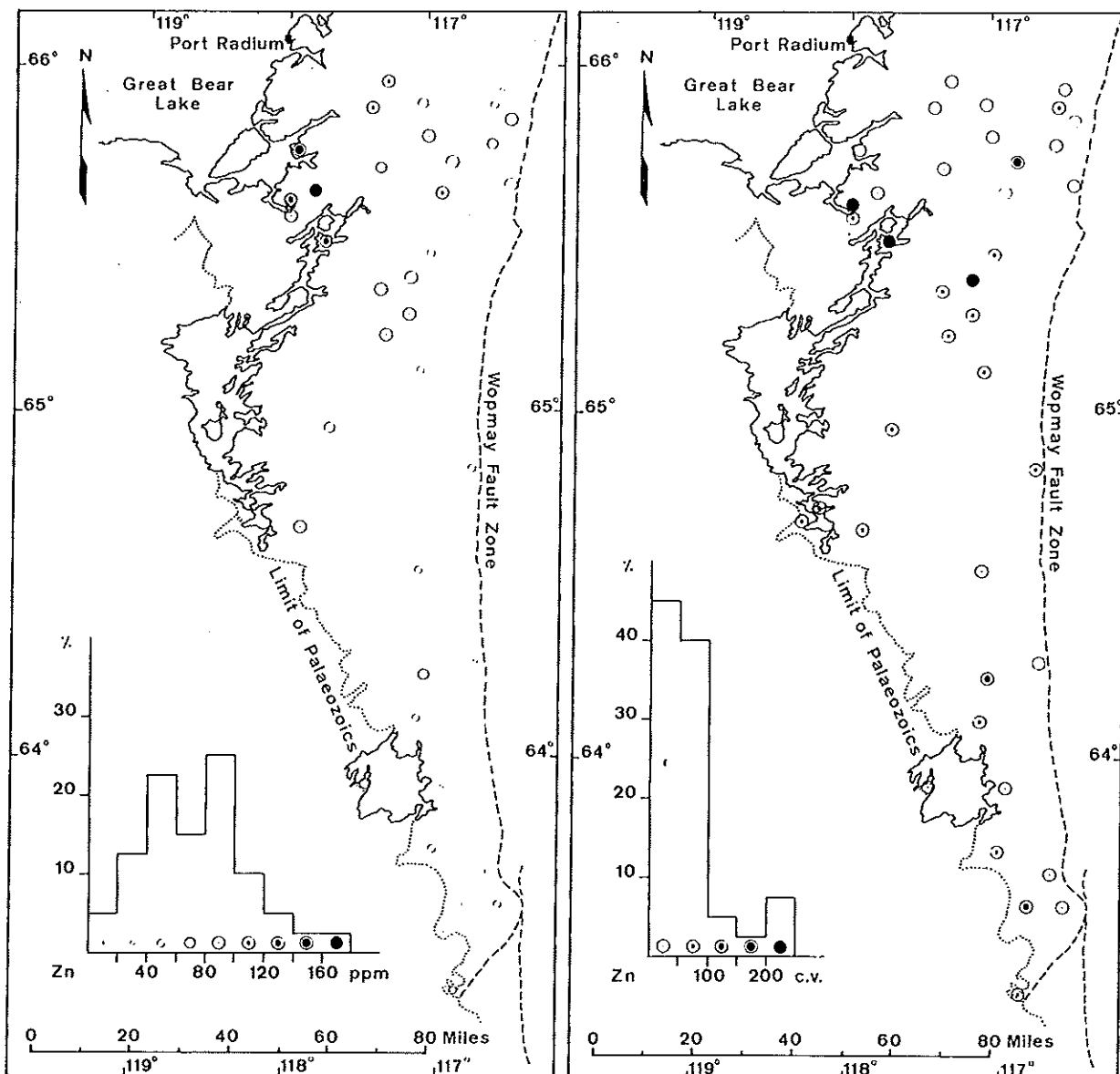


Fig. 6. Geometric mean zinc in volcano-sedimentary groups.

Fig. 7. Arithmetic coefficient of variation for zinc in volcano-sedimentary groups.

Rainy Lake [19], three others are of particular interest as they have means in excess of 25 ppm but are not associated with known mineralization, Wylie Lake [13], Hansen Lake [14] and Cruikshank River [17]. The coefficients of variation reveal 11 groups with variations in excess of 100%, seven of these are known to have mineralization in the area, Lou Lake [2], Hardisty Lake [8], Bode Lake [9], Tommie Lake [12], Clut Lake [18] and two from the Rainy Lake area [19]. The remaining four are at Rae Lake [4], Angle Lake [10], Hansen Lake [14] and Cruikshank River [17]. The general regional trend to higher levels of zinc in the north and northwest is also revealed in the partial zinc data; however, the steady increase from the south is not as well depicted by the partial data.

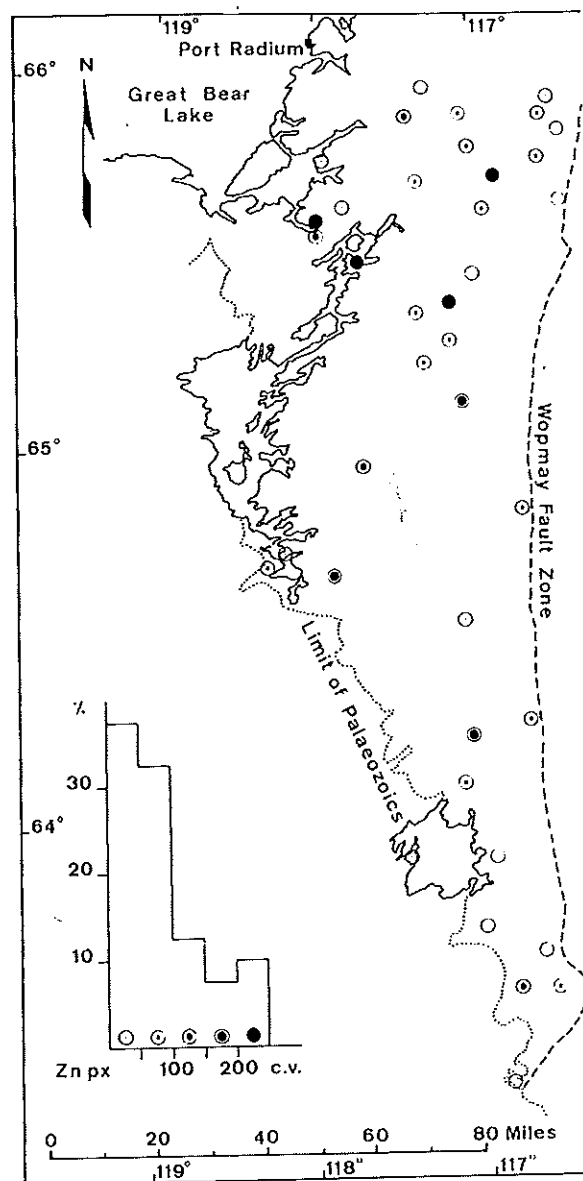
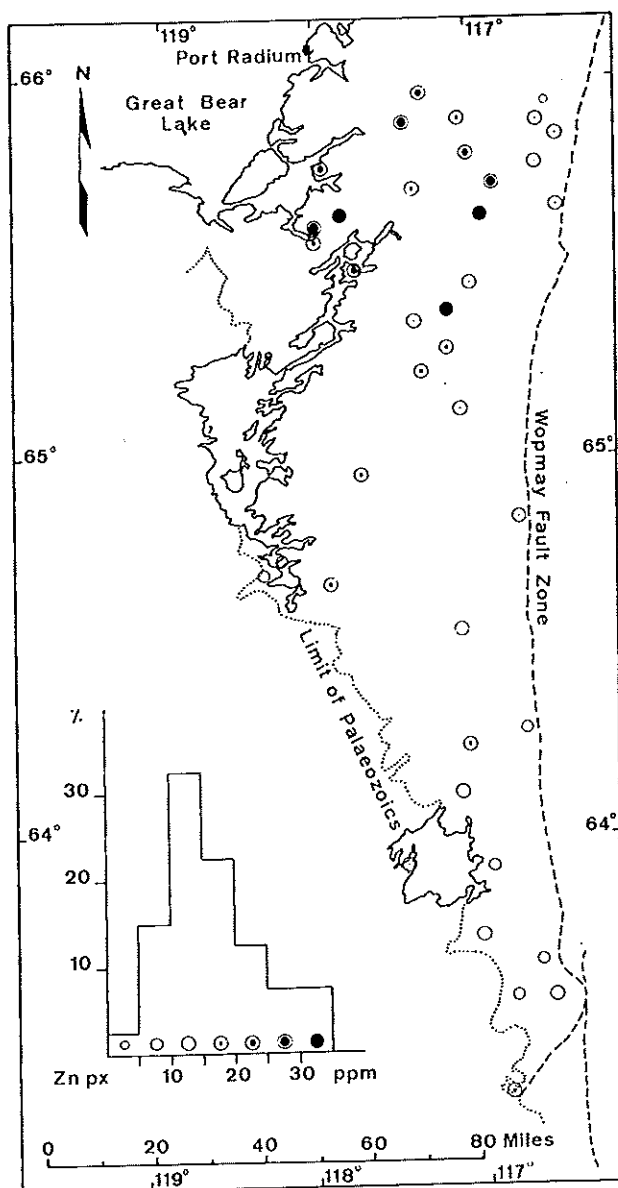


Fig.8. Geometric mean partial zinc in volcano-sedimentary groups.

Fig.9. Arithmetic coefficient of variation for partial zinc in volcano-sedimentary groups.

Summarizing the conclusions for both copper and zinc, seven groups show anomalous patterns, these are ordered in a general decreasing order of prominence; the Rainy [19], Tommie [12], Clut [18], Lou [2], Hansen [14], Hardisty [8] and Bode [9] Lakes. Only at Hansen Lake is there no known mineralization. Anomalous copper patterns were observed at four groups, Mazenod Lake [3], Self Lake [11], Blackjack [15] and Calder River [16], only at two of these, Mazenod Lake and Blackjack is mineralization known. Lastly, anomalous zinc patterns were found in four groups where mineralization is unknown at present, Rae Lake [4], Angle Lake [10], Wylie Lake [13] and Cruikshank River [17].

## DISCUSSION OF RESULTS

Additional plots have been made of the areal distribution of the partial to total metal ratios and also of the relationship of these ratios to total metals to aid interpretation (Figs.10—13).

Copper is on average divided in the molar proportion 61/39 between partially extractable and total forms. This would indicate that 61% of the copper in the quartz-feldspar porphyry volcano-sedimentary belts is in a sulphide form. The distribution of the ratios reveal a negative skew with only a very small group of data falling above the mode; these data are for the

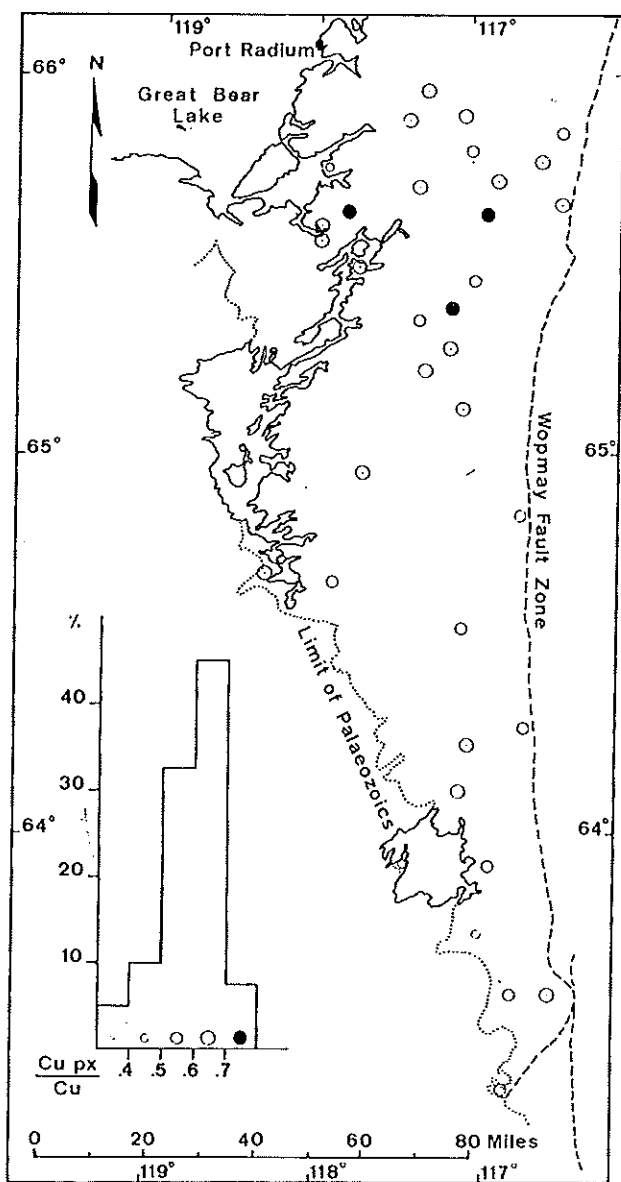


Fig.10. Average partial copper to total copper in volcano-sedimentary groups.

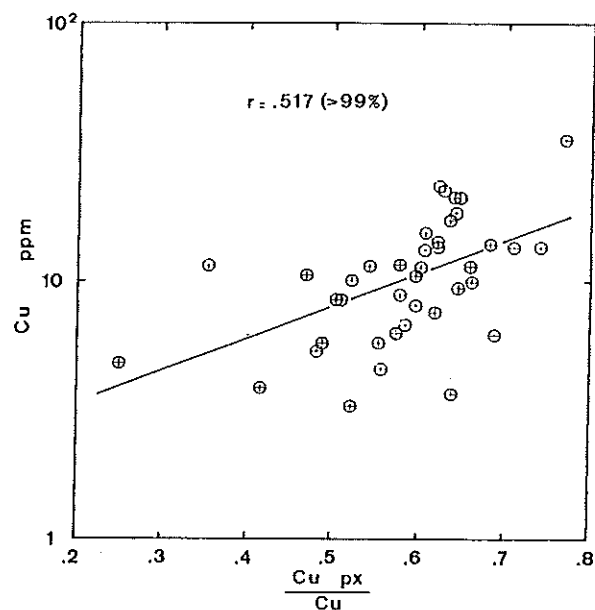


Fig.11. Plot of partial copper to total copper ratio versus total copper.

Tommie Lake [12], Wylie Lake [13] and Dinosaur Lake [19]. Of these three, the first and the last are from areas already selected as anomalous for copper. Wylie Lake has slightly elevated levels of both total and partial copper but modal or low coefficients of variation. It may be concluded that the Wylie Lake group has uniformly slightly elevated levels of copper, a higher than usual proportion of which is in a sulphide form, but which also shows no local concentration features which would be indicative of mineralization.

The total copper versus partial to total ratio plot reveals a positive correlation in the data, the line is the least-squares linear regression fit. The correlation is significant and indicates that as the total amount of copper in the rock

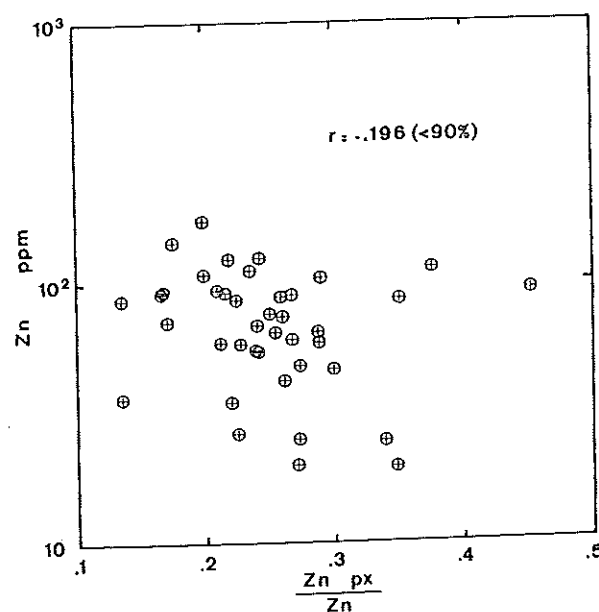
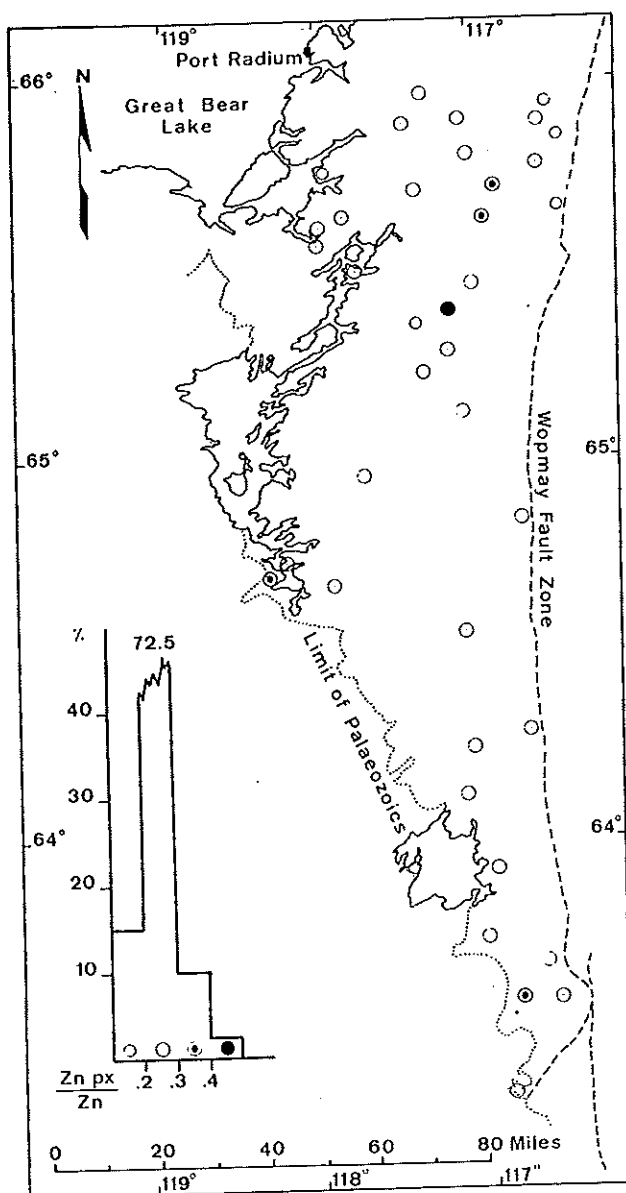


Fig.12. Average partial zinc to total zinc in volcano-sedimentary groups.

Fig.13. Plot of partial zinc to total zinc ratio versus total zinc.

increases a larger proportion goes into the sulphide phase, this could be regarded as typical behaviour for a chalcophile element.

The behaviour of zinc is in contrast to that of copper; firstly, the molar proportion of partial and total zinc is reversed and in the ratio 26/74, and secondly, the data are distributed with a positive skew. Five volcano-sedimentary groups show increased average levels of zinc in the sulphide phase, of these four are already selected as anomalous; two are from areas of known mineralization, these are respectively Lou [2] and Tommie [12] Lakes and Wylie [13] and Hansen [13] Lakes. The fifth is a group of scattered small volcano-sedimentary outcrops around Beaverlodge and Hottah Lakes 10 miles west of Hardisty Lake [8]. As with the Wylie Lake group copper data neither the means or coefficients of variation for the total and partial data are particularly unusual in the Beaverlodge group. It is concluded that the generally less than modal levels are simply associated with a uniformly higher proportion of zinc in the sulphide phase which shows no great tendency to local concentration indicative of high relief and therefore mineralization.

The plot of total zinc versus partial to total metal ratio shows that the relation between the two is random and that the effect of increasing the total zinc in the rock has an unpredictable effect on the partial to total zinc ratio. It is most probable that the increased levels of zinc are accommodated by substitution in magnetite or dark silicates such as biotite and hornblende. In this respect the behaviour of zinc in the Bear province acid volcano-sedimentary rocks is essentially oxyphile.

Thus, two particular features contrast the different behaviour of copper and zinc in the rocks of the study area. Firstly, almost two-thirds of the copper in the rocks is in the sulphide form, probably in pyrite, chalcopyrite and possibly pyrrhotite if it is present. This observation would tend to confirm the proposal made on thermodynamic grounds by Putnam (1973) that biotite at unit activity and in equilibrium with chalcopyrite should only contain 6 ppm copper. Putnam extends the 6-ppm figure to 30 ppm, allowing for the thermodynamic uncertainties, and considers it very unlikely that biotite can contain any more copper than 30 ppm in true isomorphous substitution. Secondly, the positive correlation between total copper and partial to total copper ratio indicates that increasing copper levels are accommodated in the sulphides and that either total or partial copper could be used in copper exploration programmes.

In contrast only about a fifth of the zinc is present in the sulphide form, presumably in pyrite, the remainder it is suggested is accommodated in magnetite and dark silicates. The lack of correlation between total zinc and partial to total zinc ratio indicates that the total zinc in the rock is not a good predictor of the sulphide zinc content of the rock. Therefore, in contrast to copper a partial sulphide-selective leach is to be preferred for zinc if an estimate of the sulphide zinc potential of the rocks is required.

In studying the data from a broad regional geochemical viewpoint the most important feature is the gradient seen in both total and partial zinc from low

levels in the south to high levels in the north and northwest. One possible interpretation based on the bimodal nature of the total zinc data is that dacitic rocks should be more common in the north whilst rhyolitic types would predominate in the south. The partial zinc data indicate increased levels of sulphide held zinc in the north, these may be a contributory factor in the total zinc patterns. Equally well one could argue that the increased partial levels are to be expected due to the postulated prominence of intermediate dacitic rocks in the north. However, of the six groups exhibiting low partial to total zinc ratios,  $\leq 0.2$ , five lie north of  $65^{\circ}\text{N}$ . It is of interest that as one proceeds north the proportion of tuff and extrusive porphyries increases relative to intrusive phases. Thus, the northern parts of the area are represented by higher-level porphyries and the south by deeper-level rocks. The higher levels of partial zinc in the north indicate the areas of greatest sulphide zinc potential. As a generalization of the volcanogenic ore genesis model one might state that copper can occur either in high level or extrusive phases, e.g. porphyry coppers, pipe breccias and volcanogenic stratabound massive sulphides. Zinc in contrast is concentrated in the extrusive environment where zinc is found in the stratabound massive sulphides. The lack of any marked gradient in the copper patterns could correlate with lack of any exclusive site for copper deposits in the model, whereas the increased zinc levels in the north correlate with the increased abundance of extrusive rocks which are the preferred host for zinc deposits in the general volcanogenic model. This hypothesis is open to criticism as the typical Shield volcanogenic model does not truly apply to the field area. In Archean areas basic and intermediate rocks are far more common than acidic varieties. In the field area the opposite is true with basic and intermediate rocks only accounting for a small proportion of the rocks. In this respect the field area resembles more a basin and range situation (Hoffman, 1974). However, the author considers the hypothesis stimulating and therefore worthwhile.

It is also interesting to note that the regional lake sediment survey carried out by the G.S.C. in 1972 revealed a large area of elevated zinc levels in the northwest of the survey area (Allan and Cameron, 1973; Allan et al., 1973). At the time of the initial interpretation of the lake sediment data it was not clear what the source of the zinc in the sediments might be. Now it is proposed that as the areas of high partial zinc in the porphyries and areas of high zinc in lake sediments coincide that the zinc in the lake sediments has moved there in solution following the weathering of the porphyries of the volcano-sedimentary belts and the release of zinc from sulphides. This correlation and proposal, which seems very reasonable, can only increase one's faith in the applicability of low density reconnaissance geochemical programmes based on the secondary environment for delineating major geochemical features related to the bedrock.

## CONCLUSIONS

The reconnaissance lithogeochemical survey data has been presented using the statistical parameters of geometric mean and coefficient of variation which are analagous to the geochemical criteria of level and relief. The known mineral occurrences containing significant amounts of copper and zinc sulphides present in the volcano-sedimentary porphyry belts have been outlined by anomalous metal patterns in the enclosing rocks. Additionally, attention has been drawn to certain areas which exhibit similar metal patterns but where no mineral occurrences are known; these areas are considered to have an increased mineral potential.

In contrast to copper zinc is best depicted by maps of the selectively leached sulphide phase if the objective of the survey is mineral potential estimation. This is largely due to the fact that copper behaves in an essentially chalcophile manner whilst zinc behaves in an oxyphile manner. Related to this fact is that the molar ratios for sulphide held metal to total metal are 61/39 and 21/79 for copper and zinc, respectively.

From a mineral exploration viewpoint the sulphide-selective leach is recommended. Although the total metal in this study was determined after a HF/HClO<sub>4</sub> attack which is both expensive in capital and operating costs it is considered probable that a less rigorous attack based on aqua regia, which would be less expensive, would remove almost as much copper into solution and probably less zinc, due to that element's oxyphile tendencies. Work by Brabec and White (1971) on granitoid rocks from the Guichon Creek batholith indicates somewhat similar conclusions as to metal location in the rock. Using their data from 37 samples some 79% of the copper is aqua regia extractable over a range of 2–155 ppm, as the extractable copper increases from an average of 15 to 132 ppm the extractable percentage increases from 71 to 91%. Their data for zinc shows less spread with a mean extractable ratio of 51% over a range of 9–45 ppm aqua regia extractable zinc, again as extractable zinc increases from 20 to 34 ppm the extractable percent increases from 48 to 55%. However, the author of this paper is not convinced that this 7% increase is significant. Although the rock types in the present study and Guichon Creek are not identical, both are acid and igneous and some comparisons may be drawn. Aqua regia extracts some 80% of the copper from the rock, whereas the sulphide selective leach removes 60%, in the case of zinc the extractable percentages are 50% and 20%, respectively. It is quite obvious that the differences are most severe for zinc, the more problematical of the two elements. It is proposed that the aqua regia removes significant amounts of zinc from the dark silicates and magnetite. The general increase in extractable copper to total copper ratio with increasing copper levels is similar to that described for the Proterozoic volcanics and indicates the chalcophile nature of copper.

On the basis of these observations it is proposed that the method of analysis for copper is relatively unimportant. Copper is chalcophile and total,



aqua regia or  $H_2O_2$ -ascorbic acid extractable copper all yield data of use in estimating mineral potential. Ideally, the author would choose the latter, but for exploration work would settle for aqua regia due to ease of analysis and cost. In the case of zinc the aqua regia attack doubles the amount of zinc extracted relative to the  $H_2O_2$ -ascorbic acid attack. Thus the patterns of zinc distribution in sulphides are clouded by zinc from silicate and oxide sources. On these grounds it is proposed that the weak sulphide-selective attack is the preferred method of analysis if, as in exploration, the sulphide mineral potential is the major topic of interest in the survey area.

Lastly, the zinc data reveal broad regional patterns in agreement with reconnaissance lake sediment survey data. It is proposed that these patterns are related to the level of the present surface in relation to the original volcano-sedimentary pile, and that they reflect the metallogenetic development of the area, particularly the potential for massive stratabound volcanogenic sulphide deposits. One interesting aside is that if such deposits also occurred in the south they have been eroded and presumably their weathering products were dumped into the western sedimentary basin. Much of this metal would have been in solution or in a relatively soluble form. Could it have been a source for some or all of the zinc deposits now found in the sedimentary basin?

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