550.42:546:553.067/.068(713)

Bedrock geochemistry as a guide to areas of base-metal potential in volcano-sedimentary belts of the Canadian Shield

P. H. Davenport, PH.D.

Ian Nichol, PH.D., M.I.M.M.

Both of the Department of Geological Sciences, Queen's University, Kingston, Ontario, Canada

Synopsis

Base-metal massive sulphide deposits associated with volcanic rocks are considered by many geologists to be of volcanic-exhalative origin. As such, they constitute an intrinsic part of these volcanic rocks, and the geochemistry of any particular group of these rocks might be expected to reflect the composition of the deposits developed in them. The definition of such a relationship would be valuable in base-metal exploration in this type of environment, since it would then be possible to predict the characteristics of any deposits which might occur in any particular group of volcanic rocks. The geochemistry of two mafic to felsic cycles of volcanic rocks and the base-metal deposits of each cycle were studied in the Birch–Uchi Lakes Belt, northwest Ontario. The distributions of metals in the volcanic rocks and sulphide deposits of each cycle are discussed and compared. The felsic volcanic rocks and sulphide deposits of the upper cycle, which contains the South Bay Mines, Ltd., Zn–Cu–Ag ore deposit, are higher in Zn and lower in Cu, Co and Ni than the equivalent rocks and deposits of the lower cycle, which contains no economic deposits. The distributions of Cu and Ni vary significantly along strike within the upper cycle, but the distribution of Zn is constant over a distance of 12 miles. Thus, in the study area the geochemistry of the felsic volcanic rocks of the two cycles does, in part, reflect the composition of the sulphide deposits.

It is suggested that the high Zn contents of felsic volcanic rocks containing significant mineralization may be a useful guide in distinguishing mineralized from unmineralized regions. The high average Zn contents of felsic volcanic rocks containing economically significant mineralization may be a useful guide in distinguishing these cycles from those which are unmineralized.

The Canadian Shield has long been a source of a diversity of mineral products, collectively making a major contribution to Canada's mineral wealth. Mineral exploration in the Shield is presented with many unique problems due to paucity of outcrop, glacial history and extensive muskeg cover. Exploration hitherto has largely been based on classical prospecting, geological mapping and geophysics. More recently, attention has been given to the development of geochemical exploration methods having regard to obtaining an understanding of factors affecting metal dispersion in this environment.

The results are presented here of a study of the geochemical characteristics of massive sulphide deposits and their host rocks in the Birch–Uchi Lakes area of northwest Ontario, which was aimed at establishing a method of identifying mineralized areas on the basis of bedrock geochemistry.[3]

Massive Zn–Cu sulphide deposits of the Canadian Shield are generally associated with volcano-sedimentary belts comprising well-differentiated mafic to felsic extrusive and pyroclastic rocks. The deposits are typically intimately associated with felsic volcanic rocks, which normally occur in the vicinity of ancient centres of volcanism. This association has led to the suggestion that these deposits are of volcanic-exhalative origin and possibly represent the late products of magmatic differentiation, although not all of the known volcanic centres have associated sulphide deposits. If there is a genetic relationship between the sulphide deposits and their volcanic host rocks, it might be expected that the mineralized sequences are geochemically distinct from their apparently similar, although unmineralized, equivalents.

In 1968 Selco Exploration Co., Ltd., located, on the basis of geophysics, geological mapping and drilling, the Grit orebody—a rich massive Zn–Cu–Ag deposit[1] now being mined by South Bay Mines, Ltd. The initial phase of airborne geophysical exploration located a number of anomalies, only one of which hitherto has proved to be economic. The follow-up procedure adopted involved ground geophysics, geological mapping and drilling. The purpose of the current investigation was to establish whether exploration geochemistry could assist in the screening of the geophysical anomalies.

Description of area

Geology

The Birch–Uchi Lakes volcano-sedimentary belt, of Archaean age, lies within the Superior Province

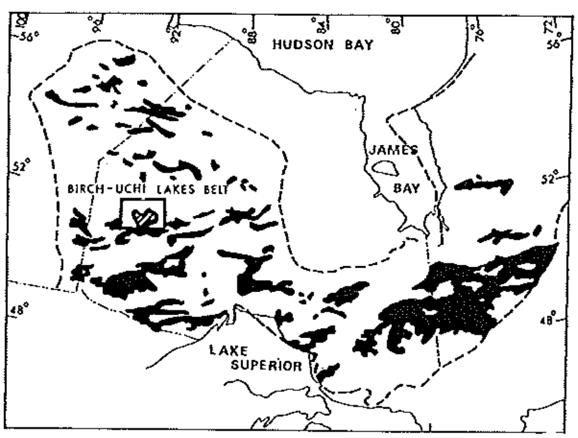

Fig. 1 Location of Birch–Uchi Lakes Belt in relation to other Archaean volcano-sedimentary belts of Superior Province of Canadian Shield

of the Canadian Shield and covers an area of some 300 square miles (Fig. 1). Geologically, the belt is typical of volcano-sedimentary belts in the Shield and is composed of predominantly volcanic rocks resting unconformably on an older predominantly sedimentary group[2, 7] and is surrounded by intrusive granites and granitic gneisses (Fig. 2).

The 72 square mile area, in Dent and Mitchell townships, on which this study was based, lies in the southwest part of the belt in an area underlain

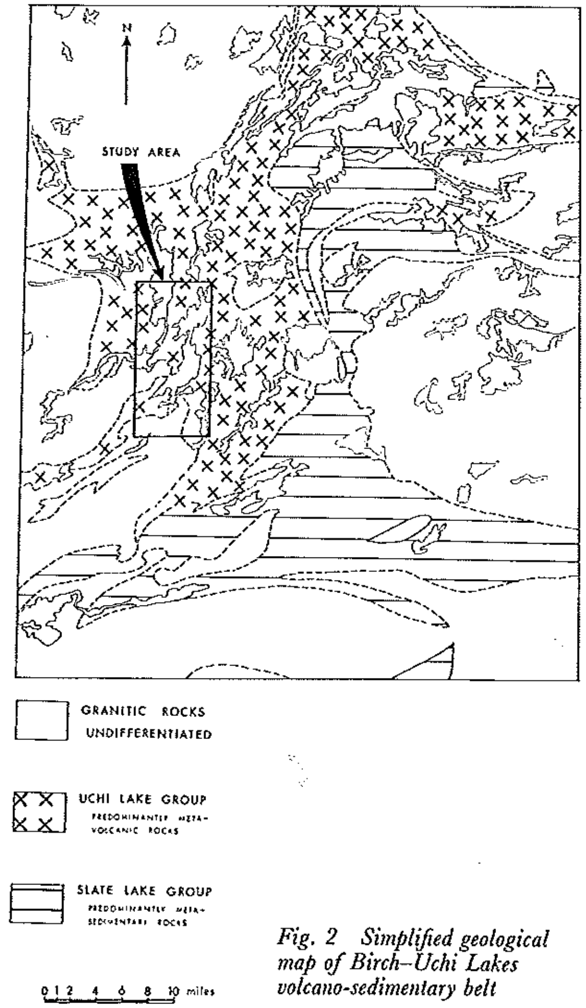

Fig. 2 Simplified geological map of Birch–Uchi Lakes volcano-sedimentary belt

by the predominantly volcanic group of rocks. The structure of this southwestern part of the belt is an isoclinal syncline or synclinorium, the study area lying mostly over the western limb and the synclinal axis lying near the eastern margin.[16]

The study area includes portions of two cycles of volcanism, which vary from basic to acid composition (Fig. 3). The older of the two cycles, the Woman Lake cycle, lies on the west side of the area and comprises predominantly basic volcanic flows, succeeded upwards by a series of predominantly intermediate pyroclastic rocks with minor flows, which, in turn, pass up into acidic tuffs and a thin sedimentary horizon. This cycle is cut by a granodioritic body towards the south.

The uppermost horizons of the Woman Lake cycle are overlain concordantly by the basic volcanic flows and minor interbedded greywackes of the Confederation Lake cycle. These basic volcanic rocks include minor intercalations of intermediate and acid units. A narrow formation of intermediate volcanic rocks overlies the basic volcanic formation in the southern part of the area, but apparently dies out to the north; thus, the acid volcanic rocks overlie the intermediate formation in the southern part of the area, and the basic volcanic rocks directly in the north. The acid volcanic rocks are cut by two major fault zones of unknown displacement. The acid volcanic rocks lying to the north of the northeast–southwest-

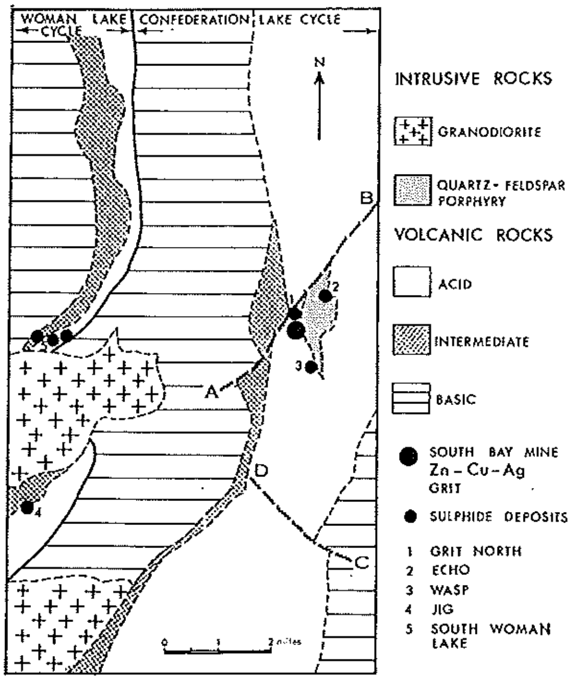

Fig. 3 Simplified geological map of study area, Dent and Mitchell townships, showing distribution of volcanic rocks and locations of base-metal deposits

trending fault are for the most part rhyodacite flows, with minor tuff units. Those in the central area are both pyroclastic rocks and flows of rhyodacitic composition, together with tuffs and agglomerates of rhyolitic composition. This central area is also characterized by bodies of quartz–feldspar porphyry, of which only the most extensive is shown in Fig. 3. These bodies are probably largely intrusive, but locally have the appearance of flows. These very high-level intrusive bodies, together with the widespread presence of agglomerates and volcanic breccias, suggest that this area is the site of a volcanic centre. The southern portion of acid volcanics, which occupies the area to the south of the southeast–northwest-trending fault, contains pyroclastic rocks predominantly of rhyolitic composition.

Gabbroic and dioritic intrusive bodies occur throughout the area, mainly as sills (not shown in Fig. 3). Similarly, several fingers of later intrusive granodiorite and minor sedimentary units have also been omitted.

Mineralization

Detailed investigations into the nature of the conductors revealed by the initial electromagnetic survey have located a number of discrete mineralizations. The deposits in the Confederation Lake cycle are associated with acid tuffs, in some places accompanied by minor argillitic units, and in many places with bodies of quartz–feldspar porphyry, whereas the deposits of the Woman Lake cycle are associated with acid to intermediate tuffs and clastic sediments. The form of the mineralization varies from pod-like lenses of massive sulphides in the Grit orebody to stringers and disseminations of sulphides in other occurrences. The mineralogy of the sulphides similarly varies from pyrite, sphalerite, chalcopyrite and minor galena at Grit to pyrite and pyrrhotite in the South Woman Lake occurrences. The mineralogy, form of mineralization and host rocks of the six individual deposits studied from the Confederation Lake cycle and the Woman Lake cycle, which are representative of the types of mineralization present in each cycle, are summarized in Table 1.

Sampling and analysis

Sampling

In order to determine the nature of the metal associations of the deposits of each cycle, samples of mineralization were collected from drill core. Sixty samples were collected from three drill cores from the ore zone of the Grit deposit, 29 samples from one core from the Wasp deposit, 9 from one core from the Grit North deposit, 6 from one core from the Echo deposit, 18 from one core from the Jig deposit and 5 from two cores from the South Woman Lake area. The drill core sampled was selected on the basis of available information to be as representative as possible of the individual deposits. This sampling is certainly not adequate as an indicator of the grade of the deposits, but it should suffice to identify characteristic metal associations of the deposits.

In order to identify any geochemical relationship between the base-metal sulphide deposits and the volcanic rocks, bedrock samples were collected from the entire succession of volcanic rocks in each cycle; 300 samples were taken from an area of 72 square miles, giving an average density of some 4 samples per square mile. Sample sites were preselected from available geological maps. The majority of the samples were taken along the shores of lakes, which provided easy accessibility and aided accurate location of the sample sites. Elsewhere, where additional samples were neces-

Table 1 Mineralogy and host rocks of the deposits

Deposits*	Nature of sulphides	Host rocks
1, Grit	Pod-like lenses of massive sulphides: pyrite, sphalerite, chalcopyrite, minor galena	Rhyolitic tuffs, tuff breccias, agglomerates and porphyritic flows; marginal to quartz–feldspar porphyry body
2, Wasp	Zone, up to 30 ft wide, consisting of stringers of sulphides: pyrrhotite, pyrite, sphalerite, minor chalcopyrite	Interbanded rhyolitic tuffs, with graphitic and argillaceous members present in the mineralized zone; marginal to quartz–feldspar porphyry body
3, Grit North	Zone, 10–20 ft in width, of stringers of sulphides: pyrrhotite, pyrite, minor sphalerite	Rhyolitic tuffs, sill or flow of quartz–feldspar porphyry
4, Echo	Zone about 10 ft in width of stringers and disseminations of sulphides: pyrrhotite, pyrite, minor sphalerite	Rhyolitic tuffs, marginal to quartz–feldspar porphyry body
5, Jig	Zone, up to 150 ft in width, of stringers and pods of massive sulphides: pyrrhotite, pyrite, chalcopyrite, minor sphalerite	Felsic tuffs and sediments (in places calcareous)
6, South Woman Lake	Number of thin zones, ½–10 ft in thickness, containing disseminated to massive sulphides: pyrite, pyrrhotite	Sediments, calcareous and graphitic argillites

*1–4, Confederation Lake cycle: 5 and 6, Woman Lake cycle.

sary, these were collected along a road traverse from South Bay Mines or traverses through the bush. This sampling procedure did not give an even sample distribution over the area, but it was hoped that it would suffice to delineate the presence of any metal associations or compositional trends. At each outcrop composites of chip samples (approximately 1 kg) were collected to reduce sample variability at the outcrop scale.

Sample preparation

The samples of mineralization and bedrock were prepared for analysis in separate batches to avoid contamination. The samples were crushed to ¼-in chips in a Braun jaw crusher with steel plates. The fines produced in crushing were passed through a 6-mesh nylon sieve and discarded in order to eliminate any steel chips which might have been introduced into the samples from the steel plates. These chips were then reduced to less than 6 mesh by use of a Lemaire jaw crusher equipped with 99% alumina plates. The samples were then reduced to −80 mesh in a Lemaire pulverizer with alumina plates. Tests have shown that, in general, less than 1% alumina is introduced into the samples by this procedure.

Analytical methods

The samples of mineralization were analysed variously by assay and atomic absorption and emission spectrographic methods. The Cu and Zn data for the Grit, Wasp, Grit North, Echo and Jig deposits were obtained by assay, made available by Selco Exploration Co., Ltd. The Fe content of all samples and the Cu and Zn content of the mineralization in the South Woman Lake area were determined by atomic absorption, an aqua regia attack being employed with a 6 M hydrochloric acid leach. The accuracy of the determinations was checked by including sulphide standards in the batch, and the precision of the analyses at the 95% confidence level was ±20% for Fe, ±15% for Cu and ±20% for Zn. The compatibility of the Cu and Zn data for the mineralization in the South Woman Lake area with the assay data was checked by re-analysis of samples from previously assayed core. Ag, Pb, Sn, Co and Ni were determined spectrographically by use of a modified method from that described by Nichol and Henderson-Hamilton.[14] A 2 : 1 : 1 mixture of sample, graphite and lithium carbonate is arced for 30 sec by use of anode excitation and the element concentration is determined with Ge as an internal standard.[3] The precisions of these determinations were in the range ±40–50% at the 95% confidence level.

Silica analyses of the bedrock samples were carried out by the determination of the refractive indices of the fused samples, a slightly modified version of the method described by Mathews[13] being used. A calibration curve was established by use of secondary standards selected from the samples, the SiO_2 content of these standards being determined by X-ray fluorescence. The overall precision of the method is estimated at ±7% at the 95% confidence level. Cu, Pb, Zn, Co, Ni, Fe and Mn contents of the bedrock samples were analysed by atomic absorption. The samples were heated to dryness in 5 ml of a 4:1 perchloric–nitric acid mixture, and leached in 2·5 ml of 6 M nitric acid to dissolve the Fe, followed by the addition of 10 ml of a 5% H_2O_2 solution in deionized water to reduce the MnO_2 to Mn^{2+}. The precision of these determinations at the 95% confidence level ranges from ±25 to 40%. The elements MgO, K_2O, Cr, V and Sn were analysed spectrographically, with precisions in the range ±40–50% at the 95% confidence level.

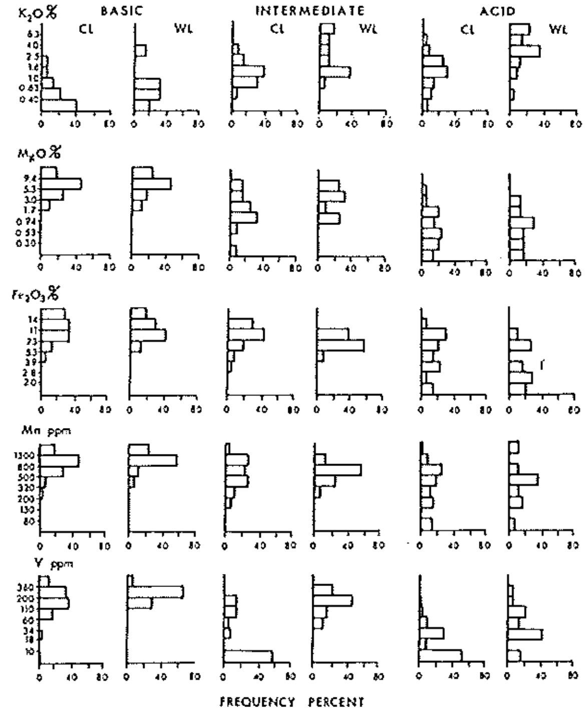

Fig. 4 Frequency distributions of K_2O, MgO, Fe_2O_3, Mn and V in basic, intermediate and acid volcanic rocks of Confederation Lake (CL) and Woman Lake (WL) cycles

Data processing

The frequency distributions of the elements in the volcanic rocks do not, in general, correspond to the Gaussian distribution (Figs. 4 and 5). The number of samples in each group is generally less than 50, and the distributions of a particular element in corresponding rock types in each cycle have markedly different variances in some cases. For these reasons, parametric statistical methods of comparison, such as Student's t test for small samples, are inappropriate, and the non-parametric Mann–Whitney U test was used for this purpose. This test requires no assumption to be made as to the shape of the distributions.

An excellent description of the U test has been given by Siegel.[19] Briefly stated, the test determines the probability that the bulk of two observed distributions were drawn from the same population. The procedure for carrying out the test may be summarized as follows: (1) consider two distributions, containing n_1 and n_2 samples, respectively, where $n_1 < n_2$, and $n_2 > 20$; (2) rank all the observations, from both distributions, from the lowest to the highest; (3) sum the ranks of the smaller data set to obtain R_1; (4) calculate the U statistic from the equation

$$U = n_1 n_2 + \frac{n_1 (n_1 + 1)}{2} - R_1$$

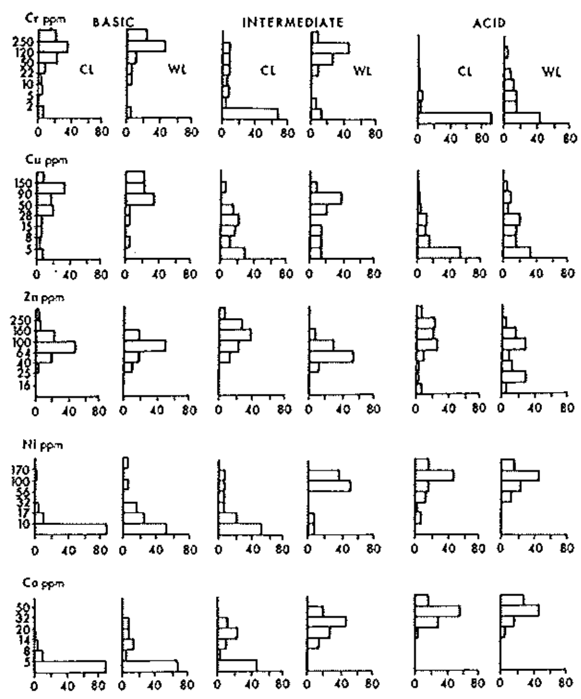

Fig. 5 Frequency distributions of Cr, Cu, Zn, Ni and Co in basic, intermediate and acid volcanic rocks of Confederation Lake (CL) and Woman Lake (WL) cycles

(5) calculate the z statistic from the equation

$$z = \frac{U - \frac{n_1 n_2}{2}}{\sqrt{\frac{(n_1)\ (n_2)\ (n_1+n_2+1)}{12}}}$$

(6) Determine the probability, p, that the two distributions are drawn from the same population from standard tables of z values.

If the two distributions are identical, the probability value would be unity. The greater the difference between the two observed distributions, the lower would be the probability that they were drawn from the same population. Three arbitrary significance levels were chosen, $\alpha_1 = 0{\cdot}05$, $\alpha_2 = 0{\cdot}01$, $\alpha_3 = 0{\cdot}002$, which correspond to the 95, 99 and 99·8% confidence levels, respectively.

When the probability, p, that two observed distributions were drawn from the same population is less than $\alpha_1 = 0{\cdot}05$, the distributions are significantly different at the 95% confidence level. If $p < \alpha_2 = 0{\cdot}01$, the distributions are significantly different at the 99% confidence level; and if $p < \alpha_3 = 0{\cdot}002$, they are significantly different at the 99·9% confidence level. A qualitative idea of the power of this test may be obtained by comparing the statistically significant differences in Fig. 9 with the frequency distributions in Figs. 4 and 5.

This test does not indicate which population is, on average, higher, since it is being used to determine the significance of differences between populations; but when the distributions differ significantly at the 95% confidence level, the population which is, on average, higher may be determined from the frequency distribution diagrams by inspection.

Metal associations of mineralizations

The mean metal contents of mineralized samples from the six deposits taken as being representative of deposits associated with the Woman Lake and Confederation Lake cycles show marked variations in level (Table 2). These differences, undoubtedly in large part, are due to variations in the proportions of sulphide minerals to silicate gangue present in the different deposits. From a consideration of the mean metal contents it is not possible to

Table 2 Mean metal content of mineralized material (ppm) from sulphide deposits

	Number of samples	Fe, %	Zn	Cu	Ag	Pb	Sn	Co	Ni
Grit	60	30·4	165 000	28 600	28	530	650	150	<5
Wasp	29	11·1	27 000	2 100	3·0	140	130	27	35
Grit North	9	8·9	14 000	1 500	2·6	71	61	22	26
Echo	6	7·5	2 600	340	<1·0	31	14	11	17
Jig	18	19·7	2 300	8 600	6·0	99	<10	75	390
South Woman Lake	5	16·0	124	167	3·0	55	<10	34	92

Table 3 Cation proportions (%) of Fe, Zn, Cu, Pb, Sn, Co, Ag and Ni in sulphide deposits

Deposit	Fe	Zn	Cu	Pb	Sn	Co	Ag	Ni
Grit	64	30	5·4	0·031	0·066	0·030	0·0031	‡
Wasp	82	17	1·4	0·028	0·045	0·019	0·0012	0·025
Grit North	87	12	1·3	0·019	0·028	0·020	0·0013	0·024
Echo	97	2·9	0·39	0·011	0·0087	0·014	†	0·021
Jig	95	0·95	3·7	0·013	*	0·034	0·0015	0·19
South Woman Lake	99·8	0·066	0·092	0·0094	*	0·020	0·0010	0·055

*Sn not detected in these deposits.

†Ag too low in this deposit to be reliably estimated.

‡Trace Ni (<5 ppm) only in this deposit.

identify differences in metal associations of the deposits.

Assuming that these elements Fe, Zn, Cu, Pb, Sn, Ag, Co and Ni will be strongly concentrated in the sulphide relative to the silicate phases, the variations caused by differing proportions of sulphides to silicate gangue will be largely eliminated by ratioing the mean content of each of these metals to the total content of these metals of each deposit. Table 3 gives the ratios of the atomic proportions of each metal (i.e. mean content divided by atomic weight) to the sum of atomic proportions of these metals for each deposit. In the deposits of the Confederation Lake

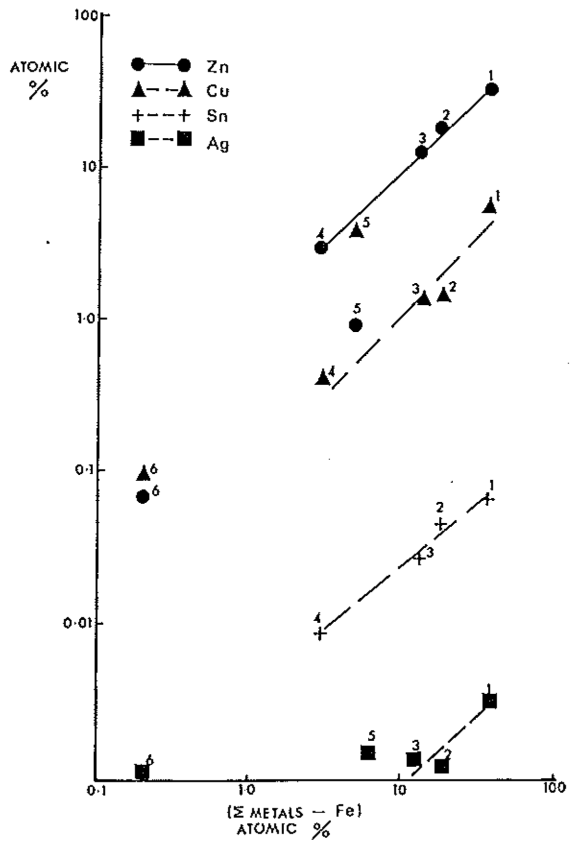

Fig. 6 Variations of atomic proportions of Zn, Cu, Sn and Ag in sulphide deposits

cycle there is a negative correlation between the atomic proportions of Zn, Cu, Ag, Pb, Sn and Co with Fe. This feature is further illustrated in Figs. 6 and 7, where, for each deposit, the atomic proportions (from Table 3) of these elements are plotted as a percentage against the sum of the atomic proportions of all the elements less the atomic proportion of Fe. On this basis the deposits of the Confederation Lake cycle are higher in Zn and Sn and lower in Cu, Co, Ni and Ag than those of the Woman Lake cycle.

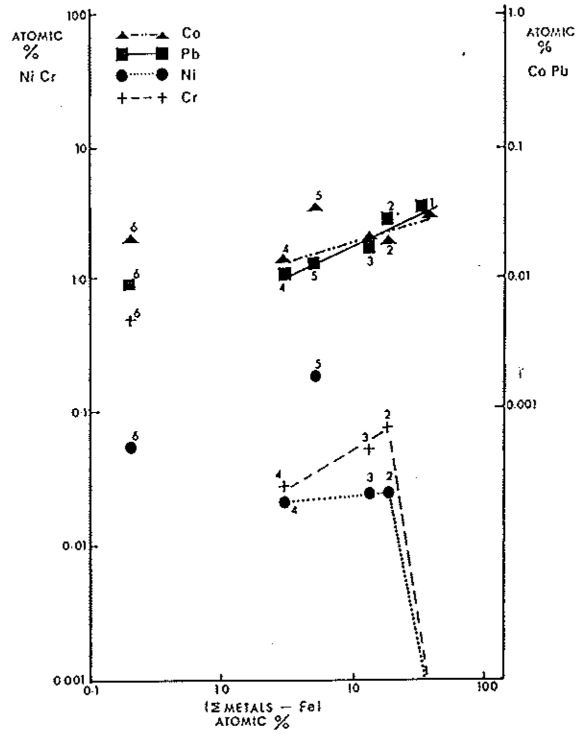

Fig. 7 Variations of atomic proportions of Co, Pb and Ni in sulphide deposits, and variations of Cr content of gangue material

Metal associations of volcanic rocks

Classification of rocks

The concentrations of a number of elements show variations through the basic to acid differentiation sequence of the volcanic rocks. From this it is clearly important, when considering variations in minor-element composition of rocks, to consider only comparable rock types. The bedrock samples have, therefore, been classified on the basis of their silica content. In this way it is possible to consider variations in metal contents of rocks which display only limited ranges of SiO_2 content.

The data have been divided into three arbitrary groups: <56% SiO_2 basic volcanics; 56–64% SiO_2 intermediate volcanics; and >64% SiO_2 acid volcanics. From a consideration of the frequency distribution of SiO_2 in rocks from the two cycles it is clear that basic, intermediate and acid varieties are not equally represented (Fig. 8). In the Confederation Lake cycle the small number of intermediate types reflects their paucity of occurrence, but the predominance of acid over basic varieties reflects a sampling bias conditioned by a greater accessibility of acid volcanics and the fact that they crop out over a proportionately greater area as they occupy the core of the syncline

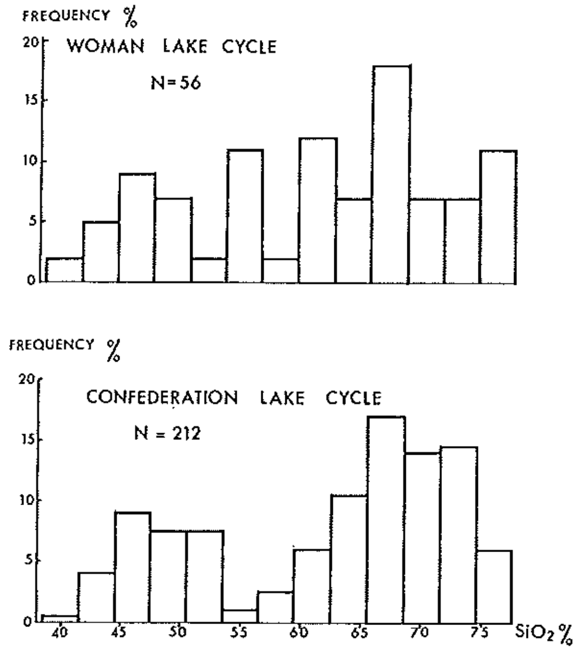

Fig. 8 Frequency distributions of silica in volcanic rocks of Confederation Lake and Woman Lake cycles

(Fig. 3). The samples from the Woman Lake cycle are more representative of the actual proportions of the three volcanic units.

Variation in geochemistry between volcanic cycles

The frequency distributions of K_2O, MgO, total Fe as Fe_2O_3, Mn, V, Cr, Co, Ni, Cu and Zn in the basic intermediate and acid volcanic rocks of each cycle are shown in Figs. 4 and 5. For some elements their distributions in certain rock types are obviously different, but in other cases the variance of the data precludes the identification of differences by casual inspection. Zinc is generally higher in the intermediate and acid rocks of the Confederation Lake cycle relative to similar rocks of the Woman Lake cycle. In addition, the Zn distribution within the Confederation Lake cycle displays a much higher variance than that in the Woman Lake cycle. K_2O appears to be generally higher in the intermediate and acid rocks of the Woman Lake cycle. Cu, Ni, Cr and V are generally higher in the intermediate volcanics of the Woman Lake cycle and Co is higher in the acid volcanics relative to the corresponding rocks of the Confederation Lake cycle. No variations in the distribution of MgO, Fe_2O_3 or Mn are apparent between comparable rocks of the two cycles. Pb and Sn are below the detection limits (10 ppm) of the analytical method for all samples.

These differences between the distributions of various elements between the two cycles of volcanism are qualitative observations and unavoidably subjective. In order to compare these distributions more objectively, the data were analysed statistically by the Mann–Whitney *U* test to determine the probability that the distributions of each particular element in corresponding bedrock types from each cycle were drawn from the same population.

As the distributions of many elements vary with the silica content, it is essential in any comparison of element distributions of rock units to ensure that their silica distributions are as similar as possible.

The probabilities that the SiO_2 distributions of the basic, intermediate and acid volcanics of the Woman Lake and Confederation Lake cycles are drawn from the same populations are 0·91, 0·13 and 0·21, respectively. The low values obtained for the intermediate and acid volcanics suggests that the SiO_2 contents for the intermediate and acid varieties are not entirely comparable. An

ELEMENT	BASIC	INTERMEDIATE	ACID
SiO_2			
K_2O		>>>	>>>
MgO		>	
Fe_2O_3		<<	
Mn			>
V	>	>>>	>>>
Cr		>>>	>>>
Co		>>>	>>
Ni		>>>	>>>
Cu		>	>
Zn		<<<	<<<

> >> >>> Woman Lake Cycle significantly higher at the 95%, 99% and 99.8% confidence levels, respectively

< << <<< Confederation Lake Cycle significantly higher at the 95%, 99% and 99.8% confidence levels, respectively

Fig. 9 Comparison of distributions of elements in corresponding volcanic rock types between Confederation Lake and Woman Lake cycles by Mann–Whitney U test

improved correspondence in populations was achieved by restricting the SiO_2 range of the intermediate volcanics to 57–64% and the acid volcanics to greater than 66%: the probabilities that the populations are the same are then, respectively, 0·65 and 0·84. Some of the data have, therefore, been neglected in the interests of achieving a comparison between rock units that contain SiO_2 contents that are as comparable as possible.

Fig. 9 summarizes the results of the *U* test; the direction of the significant differences is also indicated. The basic volcanic rocks of each cycle are similar in composition, with the exception of V, which is significantly higher in the Woman Lake cycle at the 95% confidence level. The intermediate rocks of the Woman Lake cycle are significantly higher in K_2O, Co, Ni, Cr and V at the 99·8% confidence level, and MgO and Cu at the 95% confidence level. The intermediate rocks of the Confederation Lake cycle are significantly higher in Zn at the 99·8% confidence level and in Fe_2O_3 at the 99% confidence level. The acid volcanic rocks of the Woman Lake cycle are significantly higher in K_2O, Ni, Cr and V at the 99·8% confidence level, and in Co at the 99% and Mn and Cu at the 95% confidence levels. The acid rocks of the Confederation Lake cycle are significantly higher in Zn at the 99·8% confidence level.

Thus, the Mann–Whitney *U* test essentially confirms the differences noted visually and, in addition, identifies as significant other differences not readily apparent before.

Variation of geochemistry within acid volcanic formation of Confederation Lake cycle

From a consideration of the areal element distribution of certain elements within the acid volcanics it is apparent that certain elements show marked changes in distribution along strike in the acid volcanic rocks of the Confederation Lake cycle. In particular, K_2O, MgO, V and possibly Ni show a general increase in level from north to south, whereas Fe_2O_3 and possibly Mn show a decrease southward. Cu, on the other hand, appears to attain maximum concentrations in the central part of the area.

The acid volcanic formation in the Confederation Lake area is cut by two major fault zones of unknown displacement. The northern area is composed predominantly of rhyodacitic flows with a silica content in the range 65–70%. The central area contains both rhyodacitic and rhyolitic rocks, with a silica content of 65–75%, and the southern area rhyolitic rocks with 70–77% silica—indicating a general increase of SiO_2 in passing from north to south. This variation in silica content precluded the direct comparison of all three areas over a single silica range by use of an analysis of variance technique. The northern segment was, therefore, compared with the central segment, samples in the range 65–69% SiO_2 being used, by the Mann–Whitney *U* test. Similarly, the central and southern segments were compared over the range 70–74% SiO_2. Thus, the two groups taken from the central portion are entirely distinct.

	NORTH		CENTRE		SOUTH
K_2O		«			
MgO		⋘		«	
Fe_2O_3					
Mn				>	
V		⋘		<	
Cr					
Co					
Ni		«			
Cu		<			
Zn					

> » ⋙ Distributions significantly different at the 95%, 99% and 99.8% confidence levels, respectively. Direction of arrows indicates direction of difference

Fig. 10 Comparison of distribution of elements between north, central and southern parts of acid volcanic rocks of Confederation Lake cycle by Mann–Whitney U test

The direction and significance level of changes in the distributions of elements in the acid volcanic rocks from north to south, after the effects of silica variation have been eliminated, are presented in Fig. 10. MgO and V increase consistently from north to south; K_2O, Ni and Cu are lower in the northern part, and have similar distributions in the central and southern parts; Mn is higher in the northern and central parts than in the southern portion. The apparent decrease in Fe_2O_3 from north to south is not statistically significant when samples of similar silica content only are compared. The apparent statistical similarity in the distributions of Cr and Co may be misleading, as the bulk of the data for these elements are below the detection limits of the analytical method used. The distribution of Zn in the three segments is very similar.

Discussion

The essential requirement for geochemistry to aid in regional mineral exploration in volcano-sedimentary belts is that the host rocks of economic deposits have some geochemically diagnostic feature that allows them to be distinguished from similar, but barren, rocks.

The Confederation Lake cycle, which contains the ore deposit, is characterized by a number of differences in the distributions of certain elements in the acid and intermediate volcanic rocks relative to the Woman Lake cycle. The mineral deposits in each cycle are also distinct on the basis of their metal content. In order to determine which of the observed differences between the volcanic rocks of each cycle are related to the differences in the metal content of the deposits of the cycles, it is necessary to consider the possible processes that affect the composition both of the volcanic rocks and the deposits.

Metal content of sulphide deposits

Variations in the compositions of sulphide deposits with increasing distance from volcanic centres have been noted in the Abitibi belt of the Canadian Shield.[10] In that belt pyritic Zn–Cu–Ag massive sulphide deposits occur adjacent to volcanic centres, whereas away from the centres the deposits are typically iron sulphides, essentially barren of base metals, commonly associated with volcanogenic clastic sediments. This spatial association of massive sulphide deposits may not be generally true, however, as is evidenced by the deposits of the Manitouwadge area of the Canadian Shield which are in metasediments.[16] Furthermore, Gilmour[5] considered massive, concordant base-metal deposits in general to be of volcanic-exhalative origin, regardless of whether volcanic rocks form a conspicuous proportion of their host rocks.

Within the deposits of the Confederation Lake cycle the elements Zn, Cu, Sn and possibly Ag show comparable relationships to one another in each of the deposits (Fig. 6). This is considered to indicate that these elements were derived from the same or similar exhalative sources. The depletion of these elements relative to iron may correlate with distance of the deposits from the original exhalative vent or vents, as is suggested for the Abitibi belt. From the present positions of the deposits, however, this is not apparent. In view of the absence of a breccia pipe in the vicinity of any of these deposits, such as that described by Roscoe,[17] the deposits may have been tectonically transported soon after their formation, as was suggested by Jenks.[11] Thus, the present positions of the deposits may be substantially different from their original positions.

The virtual absence (< 5 ppm) of Ni in the Grit deposit, which, it is assumed, was formed adjacent to the exhalative vent, suggests that this element is not of exhalative origin in the other deposits of the Confederation Lake cycle, where it is present in higher concentrations, although it may be of exhalative origin in the Jig deposit. The similar patterns shown by Ni and Cr in the deposits (Fig. 7) suggest that these elements are associated with argillaceous material in the Wasp, Grit North and Echo deposits, since Cr is not associated with the sulphides. Co and Pb are associated with the sulphides of the Grit deposit, but do not decrease in relative content as rapidly as Zn, Cu and Sn in the other deposits. It is suggested that Co and Pb are associated both with the exhalations and the argillaceous material, and possibly the processes of deposition are such as to cause enrichment of Co and Pb relative to Zn, Cu and Sn.

If the exhalations were juvenile magmatic waters, the base-metal content of the late-stage magmatic liquids would, presumably, influence the base-metal concentrations present in these fluids. If, on the other hand, these fluids are recycled sea water which have leached metal from consolidated volcanic rocks, as Ferguson and Lambert[4] suggested from their study of hydrothermal spring waters associated with recent volcanism, the base-metal content of the exhalations will be controlled by the concentration of base metals in the volcanic rocks which they leach in their passage to surface. In the latter case, therefore, the presence of high concentrations of, for example, Zn in the late-stage volcanic rocks would favour Zn-rich exhalations. Thus, in either case, the composition of the exhalations might be expected to reflect, in part, the composition of the late-stage volcanic rocks.

Distributions of metals in volcanic rocks

The distribution of metals in the pyroclastic rocks will be controlled largely by magmatic processes, but may also be modified by sedimentary processes in their environment of deposition. The similarity in the geochemistry of the basic volcanic rocks, which are predominantly flows, suggests that the magma sources of the two cycles were similar and that the differences between the later differentiates, which are, in large part, pyroclastic, are due to factors such as the physico-chemical conditions of differentiation, and also to processes operating in the depositional environment of the pyroclastic rocks.

The volcanic centres occurred in sub-aerial or shallow-water environments, whereas in more remote areas deeper-water conditions prevailed. Away from volcanic centres intermediate and acid volcanics become subordinate to volcanogenic clastic sediments, and the thickness of pyroclastic rocks may decrease away from the centre. This suggests that equilibration between the volcanic material and the water may become increasingly important away from the centre in modifying trace-element distributions.

The portion of the Confederation Lake cycle sampled in the present study contains a volcanic centre with a preponderance of acid volcanics and high-level intrusives. In contrast, the area sampled within the Woman Lake cycle is apparently more remote from a centre with a smaller proportion of acid volcanics and a more extensive development of volcanogenic sediments.

The acid volcanic rocks of the northern segment of the Confederation Lake cycle are predominantly flows and, therefore, their composition will be largely unaffected by sedimentary processes during their deposition. Thus, the significant differences in the distributions of K_2O, MgO, V, Ni and Cu between these rocks and those of the central and southern segments may be caused, in part at least, by sedimentary processes which operated on the predominantly pyroclastic rocks of these two segments. The elements MgO and V are also significantly higher in the southern than in the central segment. The elements K_2O, V, Ni and Cu, together with Cr and Co, are significantly higher in the acid volcanic rocks of the Woman Lake cycle than in the Confederation Lake cycle, and it is suggested that these differences may be related, in part at least, to the greater effect of sedimentary processes in the Woman Lake cycle. This is supported by comparing the acid rocks of the southern part of the Confederation Lake cycle with those of the Woman Lake cycle. The distributions of V in the two data sets are not significantly different, and the confidence levels at which the differences in the distributions of Cr, Co, Ni and Cu are significant are lower in this case than when all of the data from the Confederation Lake cycle are used. The remaining differences may be related to initial differences in the composition of the volcanic rocks caused by magmatic processes, which have merely been exaggerated by sedimentary processes. Alternatively, by sampling areas at greater distances from the volcanic centre in the Confederation Lake cycle, the distributions of some or all of the elements may approach those in the portion of the Woman Lake cycle sampled in this study. The differences in the distributions of these elements between the intermediate volcanic rocks of the two cycles may also be due, in part, to the sampling of different segments of the two belts relative to the centres of volcanism in the two cycles.

The distribution of zinc in the acid volcanic rocks of the Confederation Lake cycle is remarkably constant: this suggests that the differences in the zinc distributions in the acid rocks of the two cycles are not a feature of the segments of the cycles, relative to the volcanic centre, which have been sampled. Rather, it is considered that the difference in the distributions of zinc between the acid and intermediate rocks of the Confederation Lake cycle from the equivalent rocks of the Woman Lake cycle is a fundamental geochemical difference between the two volcanic suites.

In the Confederation Lake cycle the mean zinc content increases from the basic rocks to the later intermediate and acid rocks, the means being 105, 134 and 128 ppm, respectively, whereas in the Woman Lake cycle the mean zinc content decreases from the basic and intermediate rocks to the later acid rocks, the means being 79, 74 and 63 ppm, respectively. The rather scanty data in the literature on the behaviour of zinc in suites of differentiated igneous rocks also indicate that in any particular suite zinc may show either an overall decrease or increase in level from the early to the late differentiates.[6,12,18,20] It is considered that the difference between the zinc distributions in the intermediate and acid rocks of the two cycles may be reflecting different physico-chemical conditions under which differentiation occurred. It is suggested, therefore, that the increase of zinc in the later fractions of the Confederation Lake cycle favoured the formation of zinc-rich base-metal deposits.

Summary and conclusions

The purpose of this study was to investigate the geochemistry of the volcanic rocks of a portion of the Birch–Uchi Lakes greenstone belt in order to determine whether it is possible to distinguish the Confederation Lake cycle, which contains the Grit ore deposit and several similar sub-economic deposits, from the Woman Lake cycle, which contains no economic deposits. Insofar as the data presented refer only to a portion of a single volcano-sedimentary belt, any conclusions reached here may apply only to this particular area, although there is evidence to believe that these conclusions may be generally applicable to the belt as a whole.[3] In view of the similarities between Archaean volcano-sedimentary belts of the Canadian Shield,[8,9] some of the conclusions may be more generally applicable, and similar studies in other belts where the volcanic stratigraphy and nature of the sulphide deposits are known would seem to be worth while on the basis of the present data.

Conclusions regarding the distributions of metals in the volcanic rocks and sulphide deposits and their interrelationships are outlined below.

(1) The relative contents of Zn, Cu, Sn and possibly Ag in the deposits are related directly to the composition of the volcanic exhalations from

which they were formed. The elements Pb and Co are related, in part, to the composition of the exhalations, but they may be also concentrated in argillaceous material. Ni is unrelated to the exhalations in the Confederation Lake cycle, and the nickel content of these deposits is due to the presence of argillaceous material. Ni in the deposits of the Woman Lake cycle may be derived, in part, from volcanic exhalations.

(2) The sulphide deposits of the Confederation Lake cycle are relatively richer in Zn and Sn, and poorer in Cu, Ag, Co and Ni, than the deposits of the Woman Lake cycle.

(3) The composition of the volcanic exhalations is considered to be related, directly or indirectly, to the composition of the late-stage volcanic rocks of each cycle. The acid and intermediate rocks of the Confederation Lake cycle contain significantly higher Zn, and lower Cu, Co and Ni, than the corresponding rocks of the Woman Lake cycle.

(4) The intermediate volcanic rocks of the Confederation Lake cycle are also significantly higher in Fe_2O_3, and lower in K_2O, MgO, V and Cr, than those of the Woman Lake cycle. The acid volcanic rocks of the Confederation Lake cycle are significantly lower in K_2O, Mn, V and Cr than those of the Woman Lake cycle.

(5) The significant variations in the distributions of V, Ni and Cu within the acid volcanic formation of the Confederation Lake cycle are considered to be related to sedimentary processes operating in the environment of deposition of the pyroclastic rocks. This being so, it might be expected that these elements, and also possibly Cr and Co, would show a general increase away from the volcanic centre in rocks deposited under deeper-water conditions. It is suggested, therefore, that the differences in the distributions of V, Cr, Co, Ni and Cu between the acid and possibly the intermediate volcanic rocks of the two cycles may be related, in part at least, to the position, relative to the volcanic centres, of the portions of the cycles sampled. These sedimentary processes may, however, have accentuated differences in the compositions of the volcanic rocks which are due to magmatic processes.

(6) The significant differences between the intermediate and acid volcanic rocks in the distributions of K_2O, MgO, Fe_2O_3 and Mn may possibly be related to magmatic processes. The relationship between the distributions of these elements, and V and Cr, and the nature of the sulphide deposits present in the two cycles cannot be assessed from the present study.

(7) The differences in the distributions of Zn in the acid and intermediate rocks of the two cycles and the lack of any variation along strike in the acid volcanic rocks of the Confederation Lake cycle suggest that this element is the most reliable indicator with respect to the type of mineralization developed in each cycle. Within the Birch–Uchi Lakes the cycle containing the South Bay Mines, Ltd., Zn–Cu–Ag ore deposit may be distinguished by the higher average Zn content throughout its intermediate and acid volcanic rocks.

(8) It is suggested that the distributions of certain elements, in particular zinc, in the intermediate and acid rocks of volcano-sedimentary belts may be useful in identifying favourable areas for economic base-metal mineralization. The sampling parameters required would vary in any particular area, being dependent on the degree of geological control available. In order to define adequately the distribution of zinc in any particular volcanic formation, it is suggested that at least 20, and preferably 50, samples are required. The determination of silica in all samples is a valuable aid in comparing only similar rocks from different areas, and is essential if the metamorphic grade of the rocks make accurate field identification difficult.

Acknowledgment

Selco Exploration Co., Ltd., provided generous support for this work, which represents part of a Ph.D. research programme by P. H. Davenport at Queen's University supervised by Professor Ian Nichol. Grateful appreciation is expressed to Mr. J. S. Auston of Selco Exploration Co., Ltd., and Dr. O. W. Nicolls of Selection Trust, Ltd., for suggesting the investigations and for the benefit of their opinions throughout the study. The interest shown during the work by the geologists of Selco Exploration, their ready assistance and helpful comments are gratefully acknowledged. In particular, the authors wish to thank Dr. G. D. Pollock, Dr. I. G. Sinclair and Mr. V. Wierzbicki.

In addition, the staff of the Department of Geological Sciences, Queen's University, are thanked for assistance with analytical work and preparation of the paper.

References

1. Auston, J. S. Uchi Lake—a geophysical case history. Paper presented at Society of Exploration Geophysicists Annual Meeting, Calgary, Alberta, 1969.

2. Bateman, J. D. Geology and gold deposits of the Uchi–Slate lakes area. *Rep. Ont. Dep. Mines*, **48**, pt 8, 1939, 1–43.

3. Davenport, P. H. The application of geochemistry in base-metal exploration in the Birch–Uchi Lakes Volcano-Sedimentary Belt, northwestern On-

tario. Ph.D. thesis, Queen's University, Kingston, Ontario, 1972.

4. Ferguson, J. and Lambert, I. B. Volcanic exhalations and metal enrichments at Matupi Harbor, New Britain, T.P.N.G. *Econ. Geol.*, **67**, 1972, 25–37.

5. Gilmour, P. Strata-bound massive pyritic sulfide deposits—a review. *Econ. Geol.*, **66**, 1971, 1239–44.

6. Goldschmidt, V. M. *Geochemistry* (Oxford: Clarendon Press, 1954), 730 p.

7. Goodwin, A. M. Volcanic studies in the Birch–Uchi lakes area of Ontario. *Misc. Pap. Ont. Dep. Mines* 6, 1967, 96 p.

8. Goodwin, A. M. Evolution of the Canadian Shield. *Proc. Geol. Ass. Can.*, **19**, 1968, 1–14.

9. Goodwin, A. M. and Ridler, R. H. The Abitibi orogenic belt. In Basins and geosynclines of the Canadian Shield, Baer, A. J. ed. *Pap. geol. Surv. Can.* 70–40, 1970, 1–24.

10. Hutchinson, R. W. Ridler, R. H. and Suffel, G. G. Metallogenic relationships in the Abitibi belt, Canada: a model for Archean metallogeny. *CIM Bull.*, **64**, April 1971, 48–57.

11. Jenks, W. F. Tectonic transport of massive sulfide deposits in submarine volcanic and sedimentary host rocks. *Econ. Geol.*, **66**, 1971, 1215–24.

12. Lundegårdh, P. H. Rock composition and development in central Roslagen, Sweden. *Ark. Kemi, Miner. Geol.*, **23**, nos 4–5 1947, 160 p.

13. Mathews, W. H. A useful method for determining the approximate composition of fine grained igneous rocks. *Am. Miner.*, **36**, 1951, 92–101.

14. Nichol, I. and Henderson-Hamilton, J. C. A rapid quantitative spectrographic method for the analysis of rocks, soils and stream sediments. *Trans. Instn Min. Metall.*, **74**, 1965, 955–61.

15. Pryslak, A. P. Geology of Dent and Mitchell townships, District of Kenora (Patricia portion). *Prelim. Maps Ont. Dep. Mines* pp. 592 and 593, 1970.

16. Pye, E. G. Geology of the Manitouwadge area. *Rep. Ont. Dep. Mines*, **66**, pt 8, 1957, 114 p.

17. Roscoe, S. M. Geochemical and isotopic studies, Noranda & Matagami areas. *Trans. Can. Inst. Min. Metall.*, **68**, 1965, 279–85.

18. Sandell, E. B. and Goldich, S. S. The rarer metallic constituents of some American igneous rocks. *J. Geol.*, **51**, 1943, 167–89.

19. Siegel, S. *Nonparametric statistics for the behavioral sciences* (New York: McGraw-Hill, 1956), 330 p.

20. Wilson, H. D. B. Geology and geochemistry of base metal deposits. *Econ. Geol.*, **48**, 1953, 370–407.