

Distribution of Ore Elements in Rocks for Evaluating Ore Potential: Nickel, Copper, Cobalt and Sulphur in Ultramafic Rocks of the Canadian Shield

E. M. CAMERON, G. SIDDELEY and C. C. DURHAM
Geological Survey of Canada, Ottawa

ABSTRACT

For large deposits of nickel-copper sulphides to separate from an ultrabasic magma, the sulphur content of that magma must be relatively high at an early stage in its crystallization history. If the sulphur content is high, the solubility products of metal sulphides will be exceeded and sulphide liquid or crystals will separate and have the opportunity to coalesce before they can be trapped and diluted by crystallizing silicate minerals. The purpose of this study was to discover whether there was indeed enrichment of sulphur or sulphides of copper, nickel and cobalt in ultramafic rocks associated with copper-nickel deposits and, if this were so, to determine the best combination of chemical variables for predicting the ore potential of an ultramafic body.

A total of 1,079 samples of ultramafic rock were collected from 61 widely scattered localities across the Canadian Shield and the Eastern Townships of Quebec — 372 of these samples come from ultramafic bodies associated with moderate to large deposits of nickel-copper sulphides; 91 are from bodies associated with small deposits or significant showings of sulphides; and the remaining 616 samples come from barren ultramafics or those containing only minor quantities of sulphides. Copper, nickel and cobalt, present as sulphides, were determined from these samples by atomic absorption spectrometry, following leaching with a mixture of ascorbic acid and hydrogen peroxide. Sulphur was determined by a combustion method.

Sulphur and leachable copper, nickel and, to a lesser extent, cobalt are considerably enriched in the ore group of ultramafic rocks compared to the barren samples. Discriminant equations have been derived to best distinguish between the ore and the barren groups. Copper and sulphur contribute the most information to these discriminant equations, with nickel less and the contribution of cobalt negligible. Differences in the ratios of the above elements between the different groups of ultramafic rocks and between these rocks and the associated mineral deposits contribute to an understanding of the processes of chemical adjustment between sulphides and silicates that take place after crystallization of the primary minerals.

INTRODUCTION

IN A PAPER BY CAMERON AND BARAGAR (this volume), the frequency distribution of copper in two volcanic groups is compared. One of these groups contains copper mineralization that appears to have been derived by the segregation of copper sulphides within the basaltic magma. The other group is barren of such mineralization. Another type of mineral deposit that is considered by many to have been derived by the segregation of sulphides within a magma is represented by the nickel-copper ores that are associated with ultramafic rocks. These form an economically important class of mineral deposits. In this present paper,

the distribution of the elements forming the sulphide component are compared for ore-associated and barren ultramafic rocks.

The approach taken in the investigations reported in the two papers has been quite different. In the case of the study of volcanic rocks by Cameron and Baragar, three areas of volcanic rock were sampled with a moderate to high degree of intensity. For the study described below, a very large number of ultramafic bodies scattered across much of the Canadian Shield and adjoining areas have been sampled in reconnaissance fashion. This approach has, in part, been determined by geological considerations. Within the Coppermine River and Yellowknife volcanic belts, those rocks that are now exposed at the surface probably form a fairly representative sample of the original magma. In turn, the samples collected for analysis are reasonably representative of the rocks exposed at the surface. In contrast, many of the ultramafic bodies of the Canadian Shield are small in extent and poorly exposed. There are, for instance, over two hundred ultramafic bodies along the Waboden - Moak Lake portion of the Thompson Belt, of which only three outcrop (Kilburn *et al.*, 1969). Thus, the samples that we can collect without great expense from these bodies are unlikely to be representative of the original magma. We cannot, therefore, hope to construct distribution curves as we did for the Coppermine Group and expect to find a depletion of the sulphide component in some parts of the magma, compensated by an enrichment in others. The questions posed in this study cannot therefore be strictly quantitative. Rather, we have broadly compared the sulphide content of ultramafic bodies which appear either to have or not have an association with nickel-copper ores.

There has been a substantial amount of work carried out in the Soviet Union on the geochemical differentiation of nickel-bearing mafic and ultramafic sequences from barren ones. The results reported by Godlevskiy (1959), Polferov (1962), Polferov *et al.* (1965), Polferov and Suslova (1966) and Volkov (1963), particularly in the enrichment of trace metals within the mineralized sequences, have encouraged the writers to undertake this work in Canada.

Copper, nickel, cobalt and sulphur were determined in the samples. As the purpose of the study was to examine the frequency distribution of the sulphide component of the magma, particular emphasis was given to employing an analytical method that separated the fraction of the copper, nickel and cobalt present as sulphide from the silicate component of these elements.

NICKEL-COPPER DEPOSITS IN ULTRAMAFIC ROCKS OF THE CANADIAN SHIELD

Because of their economic importance, nickel-copper sulphide ores associated with ultramafic bodies within the Canadian Shield have received a considerable amount of study, much of which is unfortunately not published. Recent summary reports have been given by MacKenzie (1968) and by Kilburn *et al.* (1969). A report covering all North American deposits was written by Cornwall (1966).

Deposits of nickel-copper sulphides within the Shield show all stages of segregation and migration of their sulphide component. In some, the sulphide remains thinly disseminated through parts of its ultramafic host. In other deposits, the sulphides have been segregated into zones of high-grade ore and in some cases the sulphide has moved away from its original ultramafic host to be intruded into the adjoining country rocks. The degree of segregation and migration experienced by the sulphides is, of course, influenced by the type of ultramafic body and its geological history. Kilburn *et al.* (1969) have grouped ultramafic host rocks into three broad types, two of which are of importance in Canada. In the first type, the ultramafic rocks are intruded along belts of major crustal faulting. The Thompson Belt, running for 100 miles along the boundary between the Churchill and Superior sub-provinces of the Canadian Shield, is a good example of this *orogenic* type. The second or *volcanic* type consists of concordant sills or dikes distributed through volcanic belts. There is an extensive development of this type of ultramafic rock through the Archean greenstone belts of northeastern Ontario and adjacent parts of Quebec. Nickel-copper sulphides in the ultrabasic sills of the Shield have commonly settled by gravity as bands and lenses along the base of the sill and in some cases may have penetrated the wall rock of this lower contact. Segregation in this form is less common for the bodies that have been intruded along orogenic belts. These bodies more often tend to contain disseminated ore, although the Thompson orebody is a prime example of an orebody that has been injected into the wall rock. Further reflecting the relative minimization of segregation processes within the bodies of the orogenic belts, the ultramafic host rock is more homogeneous than that of the bodies intruded along volcanic belts. These latter bodies may often be differentiated into mafic as well as ultramafic rock types. The ultramafic rocks of both associations have usually been serpentinized to a greater or lesser extent.

Although a magmatic segregation hypothesis cannot be doubted for many of the nickel-copper deposits of the Canadian Shield, evidence has been presented by Sullivan (1959), Wilson and Brisbin (1961), Kullerud and Yoder (1965), and by Naldrett (1966) that some deposits may have formed by sulphurization of ultramafic rocks. In understanding this process, it is important to consider the chalcophile character of the elements involved. Goldschmidt (1954, p. 19, Table 5) lists these elements in the following order of increasing chalcophile character: iron, nickel, cobalt, copper. During the crystallization of the ultramafic rock, the iron, nickel and the cobalt may enter both the silicate and sulphide minerals; in the absence of sulphur, they can be entirely contained within the silicate components. In contrast, copper is so strongly chalcophile that it shows little tendency to enter the ferromagnesian silicates and it may persist after crystallization of the basic magma as a residual copper sulphide liquid (Wager *et al.*, 1957). If sulphur is introduced into a partly or completely crystallized ultramafic rock that previously contained little sulphur, sulphides are derived by the reaction of sulphur with the iron-, nickel- and cobalt-bearing silicates, principally olivine. In the presence of limited quantities of sul-

phur, the nickel and cobalt sulphides will tend to dominate the iron sulphides because of the more chalcophile character of these metals. After formation of the nickel-rich sulphides, which are dispersed through the ultramafic rock, there must be a mechanism for their concentration to ore grade. These ores, if such exist, will tend to have a low copper-nickel ratio, a character which they are likely to share with the earliest precipitated magmatic sulphides (Wager *et al.*, 1957; Chamberlain, 1967).

SAMPLING OF ULTRAMAFIC ROCKS

The samples utilized for this study were collected by G. Siddeley for a broader study of the total major and trace-element content of ultramafic rocks from the Shield and adjoining areas. For this study, 1,079 rock samples have been grouped into 61 locations. Some of these locations contain samples from but one ultramafic body; others are composed of samples from several bodies. Thus, some locations represent a few hundreds or thousands of feet of section of ultramafic rock; others may represent bodies scattered over several tens of miles. An estimate of the maximum distance between samples for each location is given, along with other data on the nature and sampling of the bodies, in Table I. The geographic locations of the samples are shown on Figure 1.

Because of the often limited exposure of these bodies, all possible types of sample had to be utilized. Thus, the total sample is a mixture of outcrop hand specimens, hand specimens from mine workings and drill core. In all cases, close to ½ lb of sample was crushed and ground by the same procedures given by Cameron and Baragar (this volume).

For mineralized intrusions, the ore zone itself was strictly avoided during the sampling, as the purpose of the work was to discover whether significant mineralization was scattered through the rest of the rock body. The samples are as representative as was possible of the total population of the ultramafic rock in the body. For inhomogeneous bodies, the different parts of the body were usually sampled.

CLASSIFICATION OF NICKEL OR NICKEL-COPPER DEPOSITS BY SIZE

An attempt has been made to discover the quantity of nickel and copper sulphides associated with each of the ultramafic localities that have been sampled. Unfortunately, the resulting data can only be an approximation of the truth, because the different bodies have been explored with a varying degree of thoroughness and the cut-off grades for ore vary from company to company and from locality to locality. Further, ore reserves are considered by some companies to be confidential information and are not published.

In Table I, mineralization that is known to be associated with the different bodies has been noted. In Table II, those localities that contain workable, potentially workable or significant showings of nickel and copper sulphides are examined in more detail. Those localities that are not included in Table II are classed as *BARREN*, even though they may contain minor amounts of sulphide.

In order to have a non-subjective judgment as to which localities should be classed as *ORE*, all those which have produced, or have known reserves containing greater than 5,000 tons of nickel-copper, have been placed in this category. The remainder, with less than 5,000 tons of nickel-copper, have been classed as *MINORE* (mineralized to minor amounts of ore grade material). Note that apart from important showings of sulphides, this group contains one former producer (the Alexo mine), so that inclusion within this group does not necessarily preclude commercial

exploitation. The Preissac Township locality is classed as *MINORE* because these samples were collected several miles from the Marbridge mine in what appears to be the same band of ultramafic rocks.

ANALYTICAL CONSIDERATIONS

Copper, Nickel, Cobalt

As the purpose of this study was to examine the distribution of the sulphide fraction of certain metals in ultramafic rocks, it was important to use an analytical method

that is specific for sulphides. This is of particular importance for nickel and cobalt, because these elements may be several times more abundant in the silicate-plus-oxide component of a sample than in the sulphide component. The method used for copper, nickel and cobalt employs a cold leach with a mixture of ascorbic acid and hydrogen peroxide to selectively dissolve the sulphides. This method has been extensively used in the Soviet Union (Yegorova, 1938; Dolivo-Dobrovolskiy and Klimenko, 1947; Dodin, 1963; and Smirnova *et al.*, 1968). The details of this method are given in an Appendix by John J. Lynch.

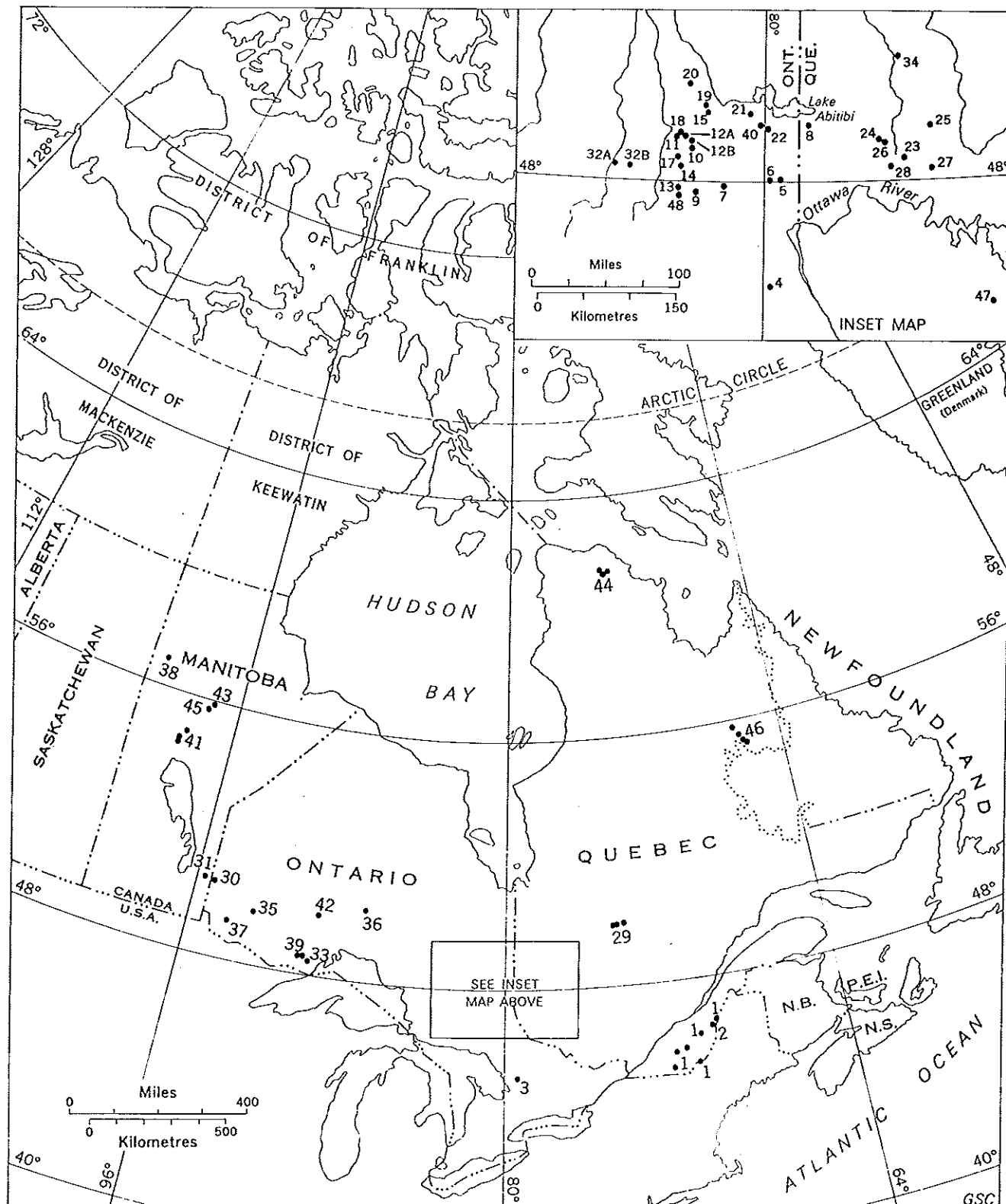


FIGURE 1 — Map showing sample locations.

TABLE I—Sampling Data and Geological Characteristics for Ultramafic Rocks

Map Code	Locality	Geological Province	Type of Intrusion	Internal Features	Rock Type Sampled	Sulphide Mineralization	Distribution of Mineralization	Samples Spread of Classified as in miles	Hand Specimen Sample (H) and/or Core Samples Sample (C)	Number of Samples	
1.	Eastern Townships (Quebec)	Appalachian	Continuous sills	Homogeneous bodies or simple differentiates	Asbestiform serpentinite derived from dunite and peridotite	None known	Planar fracture zones in country rock close to ultramafic contact	Barren	150	C	55
2.	Eastern Metals Prospect (Eastern Townships)	Appalachian	Continuous sill	Homogeneous body or simple differentiate	Serpentinized derived from dunite and peridotite	Massive chalcopyrite	Disseminated and as stockworks close to north contact in tonne of ultramafic	Ore	0.5	C	12
3.	Perry Sound — Huntsville (Ontario)	Grenville	Plugs less than ¼ mile diameter	—	Serpentinized peridotite and harzburgite	Minor sulphide mineralization	—	Barren	30	H	15
4.	Strathy Twp. (Ontario)	Superior	Elliptical plug tapering at depth	—	Serpentinized peridotite; some talcose and chloritic alteration	Chalcopyrite, pyrrhotite, pentlandite, pyrrhotite	Disseminated and as stockworks close to north contact in tonne of ultramafic	Ore	1	H and C	35
5.	McElroy and Skead Twps. (Ontario)	Superior	Continuous sills	—	Fine-grained serpentinitized peridotite	Minor Ni and Cu sulphides	Sulphides near contacts	Barren	12	H	34
6.	Facaud and Boston Twps. (Ontario)	Superior	Continuous sills	—	Serpentinized peridotite	None known	—	Barren	2	H	9
7.	Cairo and Powell Twps. (Ontario)	Superior	Lensoid sills	—	Fine-grained to aphanitic serpentinitized peridotite	None known	—	Barren	6	H	24
8.	Roquemaure Twp. (Quebec)	Superior	Lensoid sills	—	Serpentinized peridotite	None known	—	Barren	2	C	35
9.	Midlothian Twp. (Ontario)	Superior	Lensoid sills	—	Serpentinized dunite and peridotite	None known	—	Barren	2	H	31
10A.	Langmuir Ore Sill (Ontario)	Superior	Lensoid sill	Differentiated into gabbroic and ultramafic rock types	Serpentinized peridotite; talcose and carbonate alteration	Pyrite, pentlandite, pyrrhotite, millerite	Disseminated, within serpentinite close to basal contact	Ore	0.5	C	36
10B.	Langmuir Barren Sill (Ontario)	Superior	Lensoid sill	—	Serpentinized peridotite; talcose and carbonate alteration	None known	—	Barren	1	C	10
11.	Deloro Twp. (Ontario)	Superior	Lensoid sills and dikes	—	Variably serpentinitized peridotite, talc-chlorite schist	None known	—	Barren	4	H	31
12A.	Shaw Twp. (Ontario)	Superior	Lensoid sills	—	Serpentinized dunite and peridotite	None known	—	Barren	3	H	18
12B.	Carman Twp. (Ontario)	Superior	Lensoid sills	—	Serpentinized dunite and peridotite	None known	—	Barren	3	C	8
13.	Sample Twp. (Ontario)	Superior	Lensoid sills and dikes	—	Talcose, chloritic and asbestiform serpentinites and serp. peridotites	None known	—	Barren	1	C	11
14.	Texmont Mine (Ontario)	Superior	Elliptical sill-like body	Some differentiation into gabbroic and ultramafic rock types	Serpentinized peridotite with local talc alteration	Pentlandite, pyrite, rare chalcopyrite	Disseminated through vertical lenses of U.M. rock lying on schelon to strike of U.M. body	Ore	1.5	H and C	36
15.	Alexo Mine (Ontario)	Superior	Sill	Some differentiation into gabbroic and ultramafic rock types	Serpentinized peridotite	Pentlandite, pyrrhotite, chalcopyrite, heazlewoodite	Massive and disseminated ore along basal contact of ultramafic body	Minore	2	H and C	31
17.	McArthur Twp. (Ontario)	Superior	Sill	—	Very fine grained serpentinitized peridotite	None known	—	Barren	2	H	8
18.	Tisdale Twp. (Ontario)	Superior	Lensoid sill	—	Fine-grained serpentinitized peridotite; occ. talcose	None known	—	Barren	1.5	H	9
19.	McCart Twp. (Ontario)	Superior	Sill	—	Serpentinized peridotite	Very minor sulphides	—	Barren	1	H	8

Map Code	Locality	Geological Province	Type of Intrusion	Internal Features	Rock Type Sampled	Sulphide Mineralization	Distribution of Mineralization	Samples Spread of Samples as in miles	Hand Specimen Sample (H) and/or Core Sample (C)	Number of Samples
20.	Reaume Twp. (Ontario)	Superior	Sill	—	Serpentinized dunite and serpentized peridotite; occ. talcoses	None known	—	Barren	4	C
21.	Munro Twp. (Ontario)	Superior	3 sills	Homogeneous to banded; gabbro to ultramafic	Serpentinized peridotite, serpentized peridotite, pyroxenite	Minor amount nickeliferous pyrrhotite	—	Barren	5	H and C
22.	Garrison Twp. (Ontario)	Superior	Sill	Gabbroic differentiate	Asbestiform serpentized dunite and peridotite	Rare occurrences pyrrhotite	—	Barren	1.5	H and C
23.	Vassan Twp. (Quebec)	Superior	Scattered plug-like bodies	Layered in part; several outcrops homogeneous	Serpentinized peridotite and pyroxenite; local alteration to talc-chlorite-tremolite schist	None known	—	Barren	1.5	H
24.	Preissac Twp. (Quebec)	Superior	Elongate plug or sill	—	Talc-chlorite schist, sheared serpentized peridotite, and tremolitic pyroxenites	5-8 miles from Marbridge Mine within same U.M. body	See Marbridge Mine	Minor	3	H and C
25.	Carpentier Twp. (Quebec)	Superior	Sill	—	Serpentinized dunite and peridotite	None known	—	Barren	2	C
26.	Marbridge Mine (Quebec)	Superior	Elongate plug or sill	—	Serpentinized, serp. peridotite, talcoses, peridotite, talc-chlorite schist, tremolite pyroxenite	Millerite, pyrrhotite, pentlandite, pyrite	Massive in U.M. at contact and in country rock	Ore	2.5	C
27.	Louvicourt Twp. (Quebec)	Superior	Elliptical plug or sill	—	Serpentinized peridotite and dunite	None known	—	Barren	0.5	C
28.	Malartic Twp. (Quebec)	Superior	Fault-emplaced body along "Malartic Break"	Probably homogeneous; condition obscured by shearing	Talc schist, talc-chlorite schist, tremolite peridotite and carbonated var. of above	None known	—	Barren	7	C
29A.	Lac Bourbeau (Quebec)	Superior	Sills	Multiple layering: peridotite-pyroxenite-dunite	Serpentinized dunite, peridotite and pyroxenite	None known	—	Barren	1	C
29B.	Lac Antoinette (Quebec)									
29C.	Lake Chibougamau North (Quebec)									
30.	Werner and Gordon Lakes (Ontario)	Superior	Lenses and vertical pods emplaced along E-W fault zone	Originally homogeneous, some foliation and pegmatite contact alteration	Tremolite peridotite (var. amounts of amphibole), some tremolite-pyroxenite	Massive and disseminated pyrrhotite, pentlandite, chalcopyrite, some cobaltite	Disseminated through intrusion or concentrated at contact; also in fault adjacent to body	Ore	7	H and C
31.	Bird River (Manitoba)	Superior	Layered sill	Differentiated sill with peridotite and anorthositic gabbro	Chloritized, serpentized peridotite and tremolite-pyroxenite	Massive pyrrhotite, pentlandite, chalcopyrite and cubanite	In fracture zone at or below contact of sill with volcanics	Ore	3	H and C
32A.	Reeves Twp. (Ontario)	Superior	Sill	—	Serpentinized dunite and peridotite; occ. asbestiform	None known	—	Barren	1.5	H and C
32B.	Kenogaming Twp. (Ontario)	Superior	Sill	—	Serpentinized peridotite	Some disseminated pentlandite	Disseminated within ultramafic	Barren	2	H
33.	Adrian Twp. (Ontario)	Superior	Sill?	Fairly homogeneous, some pyroxenite near margin	Serpentinized peridotite	None known	—	Barren	3	H
34.	Maizerets Twp. (Quebec)	Superior	Sill?	—	Serpentinized peridotite and dunite	None known	—	Barren	12	C
35.	Dryden Twp. (Ontario)	Superior	Plug	Originally zoned? secondary alteration and shearing	Hartzburgite, serpentized peridotite and talcoses varieties of above	None known	—	Barren	1	H
36.	Nakina Area (Ontario)	Superior	Sill	—	Very fine grained serpentized peridotite	None known	—	Barren	2	H

37.	Kakagi Lake (Ontario)	Superior	Sill	—	Serpentinized dunite and peridotite, subordinate pyroxenite and talc-chlorite schist	None known	—	Barren	4	H	16
38.	Lynn Lake (Manitoba)	Churchill	Plugs	—	Gabbro body with ultramafic facies—apparently a layered intrusion	Tremolite-pyroxenite, tremolite-peridotite, serpentinized dunite	Massive and disseminated pyrrhotite, pentlandite, chalcopyrite and pyrite	Ore	1	C	25
39A.	Shebandowan Lake North Sill (Ontario)	Superior	Sill	—	—	Serpentinized peridotite, variably carbonated	Massive, some disseminated pentlandite, pyrrhotite, chalcopyrite, pyrite and pyroxenite	Ore	1.5	H and C	13
39B.	Shebandowan Lake Central and South Sills	Superior	Sills	—	—	Serpentinized peridotite, variably carbonated	None known?	Barren	4	H	16
40.	McCool Twp. (Ontario)	Superior	Sill	—	Gabbro differentiates, layered?	Serpentinized dunite and peridotite	None known	Barren	5.5	C	16
41A.	Hargrave River (Manitoba)	Churchill/Superior boundary	Lensoid sill	—	—	Serpentinized, serpentinized dunite and peridotite	None known	Barren	6	C	12
41B.	Resting Lake (Manitoba)	Churchill/Superior boundary	Lensoid sill	—	—	Serpentinized, serpentinized dunite and peridotite	None known	Barren	2	C	12
41C.	Bucko Ore Sill (Manitoba)	Churchill/Superior boundary	Discordant sill-like body	—	—	Serpentinized, talc schist	Disseminated pentlandite and pyrrhotite	Ore	<1	C	7
41D.	Bucko Barren Sill (Manitoba)	Churchill/Superior boundary	Discordant sill	—	—	Serpentinized	None known	Barren	<1	C	7
42.	Puddy Lake (Ontario)	Superior	Lensoid sill	—	—	Serpentinized, talc-chlorite schist, serpentinized pyroxenite	Irregular disseminations of millerite, chalcocopyrite, pentlandite. Also nickeliferous magnetite	Minor	2	H and C	23
43.	Moak Lake (Manitoba)	Churchill/Superior boundary	Sill	—	—	Serpentinized dunite and peridotite	Disseminated pyrrhotite and pentlandite	Ore	1	H and C	27
44A.	Katina (Quebec)						No regular pattern to disseminated sulphides in U.M.; some massive sulphides in fractures	Ore	1	C	16
44B.	Raglan (Quebec)	Churchill/Superior boundary	Sill	—	—	Serpentinized peridotite	Disseminated and massive pentlandite, pyrrhotite and chalcocopyrite	Ore	1	H and C	28
44C.	Expo (Quebec)							Ore	1	H and C	20
45.	Pipe Lake (Manitoba)	Churchill/Superior boundary	Unknown	—	—	Serpentinized peridotite	Sulphides	Ore	>1	C	4
46A.	Retty Lake (Quebec)						None known	Barren	1	H	14
46B.	Thompson Lake (Quebec)	Churchill/Superior boundary (Laborator Trough)	Sills	—	Ultramafic sills; usually have a gabbroic upper phase	Serpentinized peridotite, tremolite pyroxenite, rare serpentinized dunite	None known	Barren	>1	H	10
46C.	Asbestos Lake (Quebec)						None known	Barren	>1	H	10
46D.	Glance Lake (Quebec)						Disseminated pyrrhotite, pentlandite and chalcocopyrite	Concentrated at base of sill	1	H	10
47.	Renzy Lake (Quebec)	Grenville	Sill	—	—	Serpentinized and tremolitic peridotite, foliated	Massive and disseminated pyrrhotite, pentlandite, chalcocopyrite	Ore	1	H and C	16
48.	Sothman Twp. (Ontario)	Superior	Sill	—	Some differentiation into gabbroic and ultramafic rock types	Serpentinized dunite, serpentinized peridotite, tremolitic peridotite	Massive and disseminated pyrrhotite and chalcocopyrite	Minor	2.5	C	18

TABLE II — Size of Nickel or Nickel/Copper Ore Deposits Within or Adjoining Sampled Ultramafic Rocks. Upper five localities with less than 5,000 tons Ni + Cu classified as "MINORE"; all others classified as "ORE"

Map Code	Deposit or Locality	Thousands of Tons Ore	Ore Grade Ni %	Thousands of Tons Ni	Ore Grade Cu %	Thousands of Tons Cu	Thousands of Tons Ni+Cu	Reference	Remarks
15	Alexo Mine	56.8 ^p	(3.94)	2.2 ^p	(0.71)	0.4	2.6	1	Past producer
24	Preissac Twp.	—	—	—	—	—	—		5-8 miles from Mar- bridge mine within same ultramafic body
42	Puddy Lake	?							Nickeliferous magnetites and Ni, Cu and Co sul- phides
46D	Glance Lake	?							Pyrrhotite, pentlandite and chalcopyrite at base of sill
48	Sothman Twp. (Kirkland Minerals)	210	1.29	2.7	—	—	2.7	2 ⁶⁹	
2	Eastern Metals Prospect (St. Fabien Copper Mines)	956 389	0.15 0.91	1.4 3.5	1.52 —	14.5	19.4	2 ⁷⁰	
4	Strathy Twp. (Ajax Minerals)	732	0.38	2.8	0.65	4.8	7.6	2 ⁷⁰	Cuniptau mine — past producer
10A	Langmuir Ore Sill (McWatters Gold Mines)	166 478	1.92 0.77	3.2 3.7	— —		6.9	2 ⁷⁰	
14	Texmont Mine	3,516	1.06	37	—		37	3	Texmont Mines, Fatima nickel prospect
26	Marbridge Mine	775 ^p	(1.9)	14.5 ^p	—	—	14.5 ^p	4	Ceased production July, 1968
30	Werner-Gordon Lks. (Con. Canadian Faraday)	593 ^{r68}	1.10	6.5 8.4 ^{p68}	0.52	3.1 4.5 ^{p68}	22.5	4	Producer
31	Bird River (Dumbarton Mine)	1,350	1.06	14.3	0.34	4.6	18.9	2 ⁷⁰	Producer
38	Lynn Lake (Sherritt Gordon)	12,600	0.81	102 185 ^{p68}	0.43	54 81 ^{p68}	422	2 ⁷⁰	Producer
39A	Shebandowan N. Sill (International Nickel)	?							Production planned for 1972 at 2,900 tons ore per day
41C	Bucko Ore Sill (Bowden Lake Nickel Mines)	40,000	0.8	320	—		326	2 ⁷⁰	
43	Moak Lake (International Nickel)	?							Reserves probably greater than 5,000 tons Ni + Cu
44A	Katiniq (New Quebec Raglan)	3,392	3.06	104	0.80	27	131	5	
44B	Raglan (New Quebec Raglan)	2,621	4.43	116	0.99	26	142	5	
44C	Expo (Expo Ungava)	4,000	0.96	38	1.04	42	80	5	
45	Pipe Lake (International Nickel)	?							Reserves probably greater than 5,000 tons Ni + Cu
47	Lac Renzy (Renzy Mines)	1,012	0.72	7.3	0.70	7.1	14.4	5	Producer

Sources of Data: 1. Shankla (1969)

2. *Canadian Mines Handbook* for 1968-69(2⁶⁸) or 1969-70(2⁷⁰)

3. *Northern Miner*, January 1, 1970

4. *Financial Post Survey of Mines*, 1970

5. Laurin and Dugas (1970)

Abbreviations: p, total production

p⁶⁸, total production to end 1968

r⁶⁸, reserves to end 1968

Smirnova *et al.* (1968) have stated that the common sulphide minerals of ultramafic rocks are soluble in an ascorbic acid - hydrogen peroxide mixture within a few hours. In this study, we have confirmed that pyrite, pyrrhotite, pentlandite, chalcopyrite, tetrahedrite, sphalerite, galena and arsenopyrite are soluble when present in the amounts commonly encountered in a mineralized rock sample.

Testing of the other facet of leaching efficiency — the extent to which these metals remain within the silicate and oxide minerals of the rock — is more complex. Leaching of a monomineralic concentrate of a silicate or oxide mineral may give misleading results because of possible sulphide inclusions within these minerals. By leaching samples of olivine, clinopyroxene and titanomagnetite with ascorbic acid - hydrogen peroxide, Smirnova *et al.* (1968) found quite substantial amounts of nickel and cobalt to be dissolved. For olivines, the average percentage dissolved was 41.7 per cent nickel and 51.8 per cent cobalt; for clinopyroxenes, 34.8 per cent nickel and 38.8 per cent cobalt; and for titanomagnetites, 54.9 per cent nickel and 60.0 per cent cobalt. They attributed these soluble amounts to sulphide inclusions. For this study, we have tested two samples of olivine, a clinopyroxene and an orthopyroxene. The resulting data (Table III) are very satisfactory, as they indicate that the amounts of nickel and cobalt leached from the silicates are quite minor, in every case being less than 5 per cent of the total. For all samples but the orthopyroxene, the total copper contents are quite trivial. The orthopyroxene contains 33 ppm Cu, which is due to copper as sulphide (T. N. Irvine, personal communication). This amount has been almost totally leached from the powder.

For ultramafic rocks which have been serpentinized or altered in other ways, the matter is less clear. Are the metals bonded within silicate alteration products also stable to ascorbic acid - hydrogen peroxide attack? Changes that accompany serpentinization include the reduction of metal sulphides or of metals bound within the primary silicates (Ramdohr, 1967) to metal alloys such as awaruite, Ni_3Fe . A sample of josephenite, composed of a mixture of awaruite and native copper, tested by Mr. Lynch decomposed when attacked for several hours with ascorbic acid - hydrogen peroxide. However, does this hold for other alloys and other mixtures?

The detection limit of the analytical method is 1 ppm for copper, 2 ppm for cobalt and 3 ppm for nickel. Copper and cobalt could not be detected in some samples. For the purposes of calculation, values of 1 ppm Cu or 2 ppm Co were given to these samples. The productivity of the analytical method for copper, nickel and cobalt was 100 samples per man-day, using an automatic sampling attachment, punch-tape output and calculation of the ppm values by computer.

Sulphur

Sulphur was determined by a rapid combustion method described by Sen Gupta (1970). The detection limit of the method is 100 ppm S. Quite a considerable number of the

samples contained less than this amount and again, for purposes of calculation, a value of 100 ppm S has been given to these samples. The productivity of the method is 18 samples per man-day.*

INTERPRETATION OF THE DATA

In Table IV, statistical data for the 1,079 samples classified into 61 localities and three groups are given. For each locality and for each group, the mean, standard deviation and geometric mean are given for copper, nickel, cobalt and sulphur. Correlation coefficients for all possible combinations of these variables are also given. The correlation coefficients have been computed from logarithmically transformed data. Values for the discriminant equation best separating the barren from the ore ultramafics have been computed from the logarithmically transformed values of copper, nickel and cobalt. This will be discussed in some detail later.

The data for each element at every locality are plotted in Figures 2-5. The plots are on a logarithmic scale, with the interval for each 10^1 increment being constant from figure to figure. This allows the relative dispersion of the different elements to be visually compared. The geometric means of the elements at each locality are shown by an upward-facing arrow. If two or more samples from one locality have the identical content of a given element, the '+' signs marking the second and succeeding samples with this element content have been successively incremented to the right of the figure. Thus, a number of samples with the same content of an element (for example at the 0.01 per cent detection limit for sulphur) appear as a band stretching to the right of the given value. In Figure 6, the following ratios are plotted for each locality: $(\bar{\text{Cu}} + \bar{\text{Ni}} + \bar{\text{Co}}) / \bar{\text{S}}$; $\bar{\text{Cu}}/\bar{\text{Ni}}$; $\bar{\text{Co}}/\bar{\text{Ni}}$; where $\bar{\text{Cu}}$, $\bar{\text{Ni}}$, $\bar{\text{Co}}$ and $\bar{\text{S}}$ are the arithmetic mean contents of these elements at each locality.

It is at once apparent from the data listed in Table IV and shown in Figures 2-5 that there is a distinct enrichment of copper, nickel and sulphur, and to a lesser extent cobalt, in the ultramafic rocks associated with ore deposits, compared to barren ultramafic rocks. On each of Figures 2-5, a line has been drawn at an arbitrary position which best appears to separate the distribution of the sulphide component of the barren ultramafics from that of the ore-bearing ultramafics. For the barren ultramafics, few samples contain a greater concentration than the value represented by this line. Conversely, for the ore-bearing ultramafics, a substantial proportion of the samples contain a greater amount of one or more of these elements. For copper, the line is drawn at $\log_{10} 2.00$ (100 ppm Cu); for nickel, it is at $\log_{10} 3.25$ (1780 ppm Ni); for cobalt, it is at $\log_{10} 2.20$ (158 ppm Co); and for sulphur, the line is at $\log_{10} 1.25$ (0.178 per cent S).

*The Geological Survey of Canada will make available, in early 1971, a limited quantity of three ultramafic standards. These standards will have values for sulphur and for ascorbic acid - hydrogen peroxide soluble copper, nickel and cobalt.

TABLE III — Ascorbic Acid - Hydrogen Peroxide Leaching of Silicate Minerals

Minerals	Complete Decomposition (HF)			Ascorbic Acid - H_2O_2 Leach		
	Cu ppm	Ni ppm	Co ppm	Cu ppm	Ni ppm	Co ppm
Olivine, Duke Island, Alaska.....	3	695	173	2	26	7
Olivine, Aiken Lake, B.C.....	9	2,000	125	5	66	5
Clinopyroxene, Muskox, N.W.T.....	7	246	38	3	12	1
Orthopyroxene, Muskox, N.W.T.....	33	493	83	30	12	0

TABLE IV — Chemical Data for Localities and Groups of Ultramafic Rocks. Data for copper, nickel and cobalt as ascorbic acid - hydrogen peroxide soluble metal (\bar{X} = Mean, S = Standard Deviation, G = Geometric Mean)

Map Code	Locality	Number of Samples	Copper ppm			Nickel ppm			Cobalt ppm			Sulphur per cent			Dis- criminant score	Correlation Coefficients for Log-Transformed Data				
			\bar{X}	S	G	\bar{X}	S	G	\bar{X}	S	G	\bar{X}	S	G		Cu/Co	Cu/S	Ni/Co	Ni/S	Co/S
1	Eastern Townships	55	3.7	3.8	2.5	527	395	389	30.9	29.8	22.8	0.28	0.32	0.18	2.6	38	28	53	59	52
2	Forty-Six-Townships	15	62.3	64.7	39.3	140	139	87.9	99.1	49.7	82.1	327	358	112	2.5	17	38	53	59	52
3	McIntyre-St. Lawrence	34	10.1	15.2	3.8	861	469	38.7	57.4	32.0	44.2	0.39	0.40	0.12	3.1	84	84	53	59	52
5	Pacific-Boston Twp.	9	104	79.6	87.1	198	349	38.7	43.8	37.3	15.6	0.98	0.92	0.25	3.1	0.99	37	37	37	37
6	Carro-Fowling Twp.	24	23.7	29.1	8.3	876	796	355	54.3	35.2	39.3	0.77	0.75	0.15	3.4	1.0	101	101	101	101
7	Midchuan Twp.	35	6.3	9.1	2.8	479	345	402	36.3	35.8	37.9	0.77	0.75	0.15	3.4	1.0	101	101	101	101
8	Midchuan Twp.	31	18.1	34.8	6.1	561	490	333	32.9	22.3	27.0	0.42	0.34	0.28	3.2	0.87	25	25	25	25
10B	Lanmuir Barren Sill	30	3.4	4.4	1.9	638	571	371	44.3	26.2	38.8	0.43	0.33	0.31	2.4	0.93	25	25	25	25
11	Deloro Twp.	31	31.2	64.4	3.5	646	519	371	45.8	26.5	38.3	0.43	0.33	0.31	2.4	0.93	25	25	25	25
12A	Shaw Twp.	18	16.9	8.3	3.5	211	242	111	20.6	16.7	16.4	0.11	0.03	0.11	2.5	0.89	27	27	27	27
12B	Carman Twp.	13	16.7	40.2	12.4	827	538	668	24.2	16.7	16.6	0.32	0.27	0.20	2.9	0.94	27	27	27	27
17	McArthur Twp.	11	22.7	25.1	10.5	816	259	780	22.6	23.4	16.6	0.38	0.27	0.20	2.9	0.94	27	27	27	27
18	Tisdale Twp.	8	12.4	16.7	3.3	554	106	545	45.5	10.2	44.4	0.19	0.17	0.15	3.3	0.85	27	27	27	27
19	McCart Twp.	9	10.7	10.7	9.0	863	335	807	50.6	27.9	64.2	0.35	0.27	0.22	3.3	0.85	27	27	27	27
20	Reame Twp.	10	13.8	13.8	15.8	504	331	263	54.7	32.0	42.9	0.35	0.27	0.22	3.3	0.85	27	27	27	27
21	Munro Twp.	28	62.8	65.1	5.6	1,030	705	880	58.2	30.2	49.0	0.41	0.29	0.23	3.3	0.85	27	27	27	27
22	Garrison Twp.	12	32.2	40.4	22.9	437	252	350	36.6	43.9	21.7	0.54	0.39	0.23	3.3	0.85	27	27	27	27
23	Vassan Twp.	11	15.7	40.4	4.4	523	362	300	64.2	26.3	20.8	0.17	0.17	0.12	3.3	0.85	27	27	27	27
25	Leicester Twp.	11	10.8	17.9	12.0	329	331	211	29.4	26.3	20.8	0.17	0.17	0.12	3.3	0.85	27	27	27	27
27	Louisa Twp.	16	58.1	123.5	54.6	278	362	128	38.8	26.3	20.8	0.17	0.17	0.12	3.3	0.85	27	27	27	27
28A	Lac Beauport	12	66.3	109.5	17.1	842	537	317	34.3	35.7	21.5	0.52	0.47	0.37	3.4	0.85	27	27	27	27
28B	Lac Beauport	12	66.3	109.5	17.1	842	537	317	34.3	35.7	21.5	0.52	0.47	0.37	3.4	0.85	27	27	27	27
29C	Lac Beauport	12	66.3	109.5	17.1	842	537	317	34.3	35.7	21.5	0.52	0.47	0.37	3.4	0.85	27	27	27	27
32A	Lac Beauport	16	126	285	10.1	823	503	631	42.8	16.5	39.8	0.50	0.33	0.39	3.4	0.85	27	27	27	27
32B	Reeves Twp.	9	117	305	16.9	1,330	662	1,205	66.4	12.3	65.6	0.46	0.20	0.23	3.4	0.85	27	27	27	27
33	Kenora Twp.	8	8.9	9.6	5.1	509	303	348	42.4	25.2	35.9	0.45	0.20	0.23	3.4	0.85	27	27	27	27
34	Adrian Twp.	18	6.5	6.5	3.7	442	315	193	24.5	21.1	20.1	0.30	0.09	0.09	3.4	0.85	27	27	27	27
35	Malzer's Twp.	18	26.0	34.0	14.5	304	222	133	27.9	18.6	21.2	0.31	0.09	0.09	3.4	0.85	27	27	27	27
36	Nakina Twp.	16	20.2	31.1	2.9	147	70.5	121	35.5	13.4	32.1	0.46	0.11	0.11	3.4	0.85	27	27	27	27
37	Kakagi Lake	16	20.2	31.1	2.9	147	70.5	121	35.5	13.4	32.1	0.46	0.11	0.11	3.4	0.85	27	27	27	27
39B	Shebandowan C+S Sills	16	14.8	15.7	9.9	267	227	179	28.6	13.8	20.8	0.30	0.13	0.13	3.4	0.85	27	27	27	27
40	McCool Twp.	16	15.3	35.0	3.8	503	200	469	25.1	20.0	17.3	0.48	0.21	0.21	3.4	0.85	27	27	27	27
41A	Hargrave River	15	22.3	16.0	13.2	1,149	377	1,106	61.5	19.9	39.8	0.48	0.21	0.21	3.4	0.85	27	27	27	27
41B	Resting Lake	12	75.0	117.2	18.9	791	458	586	54.9	32.1	20.0	1.07	0.72	0.55	4.2	0.87	27	27	27	27
41D	Bucko Barren Sill	17	6.7	6.2	4.7	928	411	1,066	61.5	19.9	39.8	0.48	0.21	0.21	3.4	0.85	27	27	27	27
46A	Retty Lake	14	22.4	44.6	7.5	322	302	199	41.6	26.3	34.2	0.32	0.33	0.23	3.2	0.87	27	27	27	27
46B	Thompson Lake	10	9.7	13.9	5.3	494	96.1	484	41.6	26.3	34.2	0.32	0.33	0.23	3.2	0.87	27	27	27	27
46C	Asbestos Lake	10	13.2	17.4	7.1	696	134	685	60.7	22.9	55.6	0.55	0.25	0.25	3.5	0.87	27	27	27	27
TOTAL	BARREN ULTRAMAFICS	616	25.9	74.5	6.9	579	483	354	43.9	33.3	31.3	0.59	0.36	0.36	3.3	0.87	27	27	27	27
15	Alexo Mine	31	15.2	16.6	6.2	1,208	786	1,014	55.9	36.0	45.7	0.59	0.36	0.36	3.3	0.87	27	27	27	27
24	Preissac Twp.	9	33.8	33.2	38.0	546	358	317	38.4	23.4	25.9	1.49	0.99	0.61	3.5	0.87	27	27	27	27
42	Puddy Lake	23	33.1	41.6	3.7	351	361	218	23.5	30.1	9.3	0.53	0.79	0.25	4.5	0.87	27	27	27	27
46D	Glance Lake	10	29.6	41.6	38.4	1,024	806	698	87.4	90.9	57.8	1.39	0.79	0.25	2.7	0.87	27	27	27	27
48	Sethman Twp.	18	6.3	11.9	2.7	884	448	789	25.6	22.4	20.4	0.29	0.36	0.19	4.8	0.87	27	27	27	27
TOTAL	MINORE ULTRAMAFICS	91	52.2	166	6.8	842	687	560	43.5	45.4	25.2	1.77	0.59	0.36	3.4	0.87	27	27	27	27
2	Eastern Metals Prosp.	12	2.5	1.7	2.2	1,225	454	863	68.7	23.6	56.5	1.43	0.96	0.14	2.8	0.87	27	27	27	27
4	Strath Twp.	35	25.1	30.7	12.9	587	481	268	66.7	42.6	47.4	1.14	0.55	0.55	5.3	0.87	27	27	27	27
10A	Langmuir Ore Sill	14	40.0	89.5	16.3	742	823	319	51.6	32.3	41.3	1.20	0.90	0.87	3.9	0.87	27	27	27	27
14	Temont Mine	36	43.5	89.4	12.7	988	823	470	49.6	26.1	41.3	1.28	0.87	0.87	3.9	0.87	27	27	27	27
26	Werner-Gordon Mines	36	57.5	166	15.4	1,370	1,900	1,130	77.6	51.4	65.7	1.20	0.87	0.87	3.9	0.87	27	27	27	27
30	Werner-Gordon Mines	29	25.0	25.0	17.0	1,370	1,900	1,130	77.6	51.4	65.7	1.20	0.87	0.87	3.9	0.87	27	27	27	27
31	Bird River	32	26.3	26.3	17.0	1,370	1,900	1,130	77.6	51.4	65.7	1.20	0.87	0.87	3.9	0.87	27	27	27	27
32	Lynn Lake	32	26.3	26.3	17.0	1,370	1,900	1,130	77.6	51.4	65.7	1.20	0.87	0.87	3.9	0.87	27	27	27	27
33	Shebandowan N. Sill	25	26.3	26.3	17.0	1,370	1,900	1,130	77.6	51.4	65.7	1.20	0.87	0.87	3.9	0.87	27	27	27	27
39A	Bucko Ore Sill	13	38.0	58.1	10.9	996	1,233	376	57.6	95.4	24.4	1.39	0.96	0.14	2.8	0.87	27	27	27	27
41C	Moak Lake	43	31.0	58.1	11.8	996	1,233	376	57.6	95.4	24.4	1.39	0.96	0.14	2.8	0.87	27			

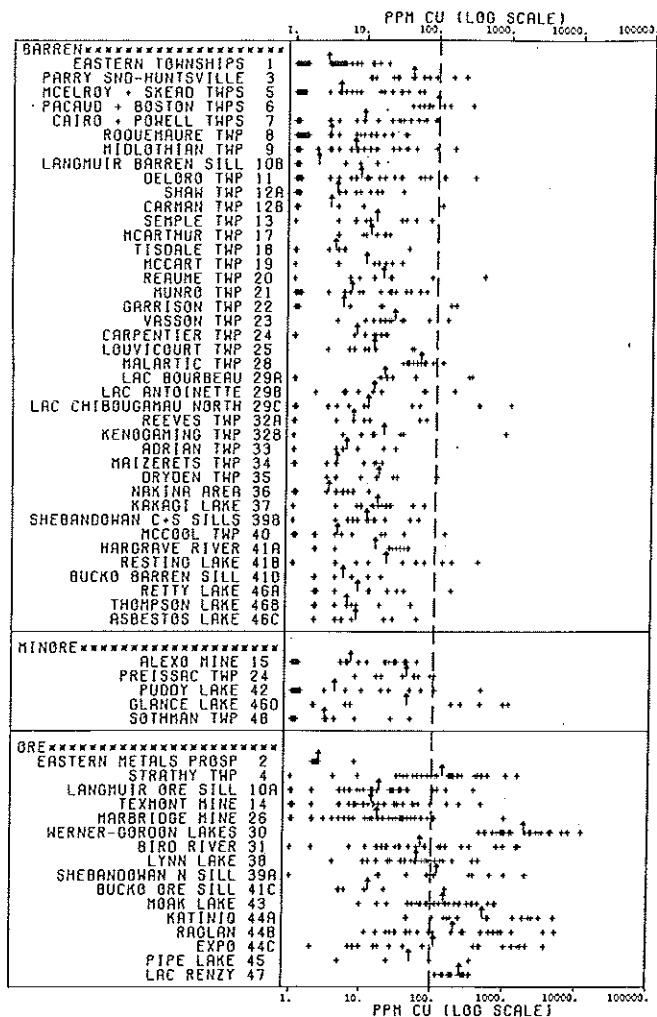


FIGURE 2—Distribution of copper as ascorbic acid - hydrogen peroxide soluble metal.

At this point, it is necessary to digress in order to discuss the physicochemical mechanisms which may have given rise to the above element values. In a basic or ultrabasic magma, an immiscible sulphide liquid and/or sulphide crystals will separate when the solubility product of one or more of the different metal-sulphide combinations is exceeded. Until this occurs, all of the metals and the sulphur are held in solution within the silicate liquid. The point at which sulphide separates from the silicate liquid is dependent on the relative amount of metals which are available to enter the sulphide fraction, on the content of other components within the silicate melt, and on temperature and pressure. However, the dominant gross control of the separation of sulphide is the sulphur content of the magma. For magmatic segregation nickel-copper ore deposits to form, an immiscible sulphide liquid or crystalline sulphides must separate at an early stage in the crystallization of the silicate liquid, so that these sulphides are not trapped between silicate crystals. This implies a high sulphur content for the silicate liquid, whether it be the original magma or a differentiate of this magma. After the initial separation of sulphides, the silicate liquid will still contain sulphur which will continue to separate as sulphide liquid or crystals from the silicate liquid as the latter crystallizes. These later sulphides will tend to be dispersed through the resulting ultramafic rock because they are precipitated with, and thus trapped and diluted by, silicate crystals.

Limited data are available on the solubility of sulphides in basic magmas. Wager *et al.* (1957), in a study of the Skaergaard intrusion, estimate that copper-rich sulphides were separating at different times when the sulphur content

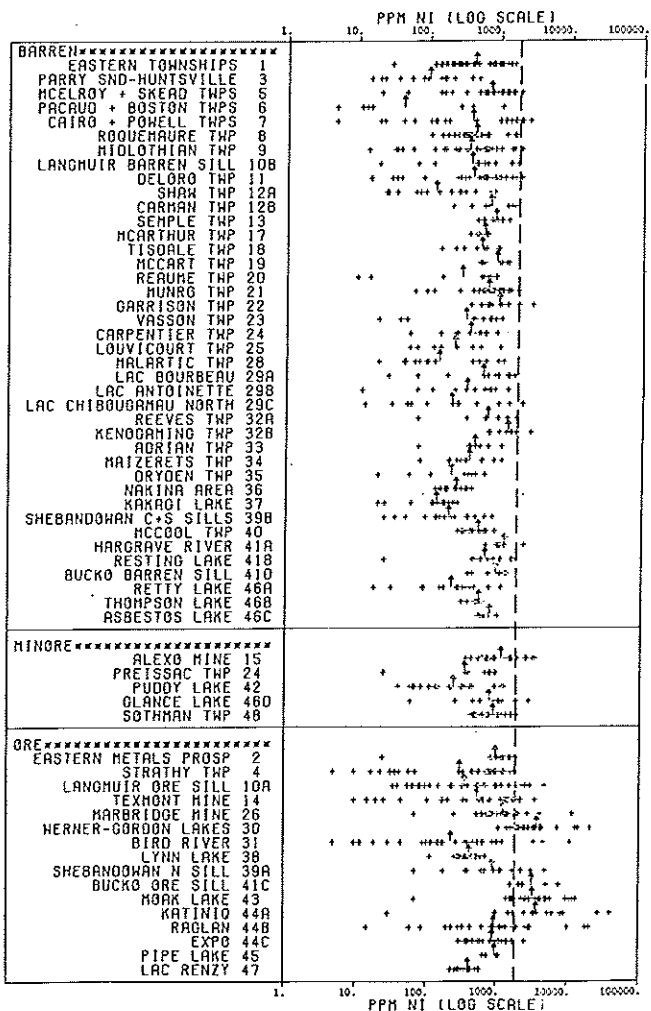


FIGURE 3 — Distribution of nickel as ascorbic acid - hydrogen peroxide soluble metal.

of the magma ranged between approximately 100 to 300 ppm S. Later, iron sulphide separated when the silicate liquid contained approximately 600 ppm S. Skinner and Peck (1969) found that liquid and crystalline sulphides separated from a basaltic magma when that magma reached a content of 380 ppm S at a temperature of 1,065°C.

Examining the data for sulphur given in Table IV and in Figure 5, it may be seen that the mean content of sulphur in the *BARREN* class of ultramafic localities is mostly in the range of 0.01-0.1 per cent S. The mean sulphur content of the 616 samples from this group is .059 per cent S and the geometric mean content 0.031 per cent S. Relating these data to the above values for sulphide solubility in basic magmas, it appears that the majority of bodies classed as *BARREN* may have been too low in sulphur to allow early separation and segregation of sulphide crystals or liquid. For most of the bodies or localities classed as *ORE* the converse is true. Here, the range in mean sulphur values is in the range of 0.11-1.92 per cent and the mean content for the 372 samples is 0.582 per cent S, almost exactly an order of magnitude higher than for the *BARREN* group.

It is pertinent here to ask how representative of the ultramafic bodies these mean sulphur values are, particularly for the *ORE* group. Fortunately, some of the bodies that are richest in sulphides are also among the most representatively sampled. For the Werner - Gordon Lake belt, the mean value of 1.92 per cent S and geometric mean of 1.09 per cent S are derived from 29 samples spaced along the

7-mile length of the belt. The values for the three ORE localities in Ungava (Katiniq, Raglan and Expo) are derived from drill core or outcrop specimens that representatively sample these ultramafic sills from top to bottom, avoiding of course the ore zone at the base. In the case of the Katiniq locality, based on 16 drill-core samples, we may compare our results — an arithmetic mean of 1.92 per cent S and a geometric mean of 0.71 per cent S — with a mean of 1.21 per cent S and a geometric mean of 1.01 per cent S for 37 serpentinite samples listed by Wilson *et al.* (1969, Table 2). The latter samples come from a complete drill-core section through the sill, but its location relative to the core that we have sampled is not known. In compiling these data, the basal massive sulphide zone has also been omitted. The mean values derived from Wilson *et al.*'s data are likely to be more precise than those for the data reported here, as they have analysed the entire length of the core as composite samples of each 10 feet. It is therefore not surprising to find a much lower variance for their data — expressed as a smaller difference between the geometric and arithmetic means — compared to our analysis of ½-lb samples taken at intervals of approximately 20 vertical feet. Considering that the different parts of the sill were sampled by quite different sampling methods, the agreement for the two sets of data from Katiniq is excellent.

We may conclude that those ultramafic bodies associated with nickel-copper deposits are enriched in sulphur, often very considerably. For those deposits that have formed by magmatic segregation processes, this enrichment of sulphur in the parent ultramafic magma will have caused early sepa-

ration and concentration of sulphides. It may be of significance that the small nickel deposits of the Porcupine area (Alexo, Texmont, Langmuir), where Naldrett (1966) has suggested the formation of the nickel sulphides by sulphurization, together with other deposits from this general region (Sothman township, Marbridge), are lower in sulphur than the average for the ORE group. The 157 samples that were taken from these five locations average 0.161 per cent S, with a geometric mean of 0.064 per cent S.

Enrichment of sulphur in the ORE group of samples is, of course, paralleled by an enrichment in one or more of the elements copper, nickel and cobalt in the same samples. For most of the ORE localities, the enrichment in nickel and cobalt is not very high in relation to the total nickel and cobalt content of typical ultramafic rocks (Turekian and Wedepohl, 1961; 2,000 ppm Ni, 150 ppm Co, 10 ppm Cu). For copper, this enrichment is often very considerable. This observation poses some interesting questions. Was this copper introduced with the sulphur either from an external source or by concentration from other parts of the primary magma? If it were not introduced with the sulphur, what occurs during the crystallization of sulphur-deficient but copper-enriched ultrabasic magmas? Can considerable volumes of copper-rich residual solution result, which then can migrate to deposit copper ores apparently unrelated to the ultramafic material? For the total set of samples, the correlation between copper and sulphur is, at 0.65 (Table IV), higher than the correlation of nickel or cobalt with sulphur (0.49 and 0.59 respectively).

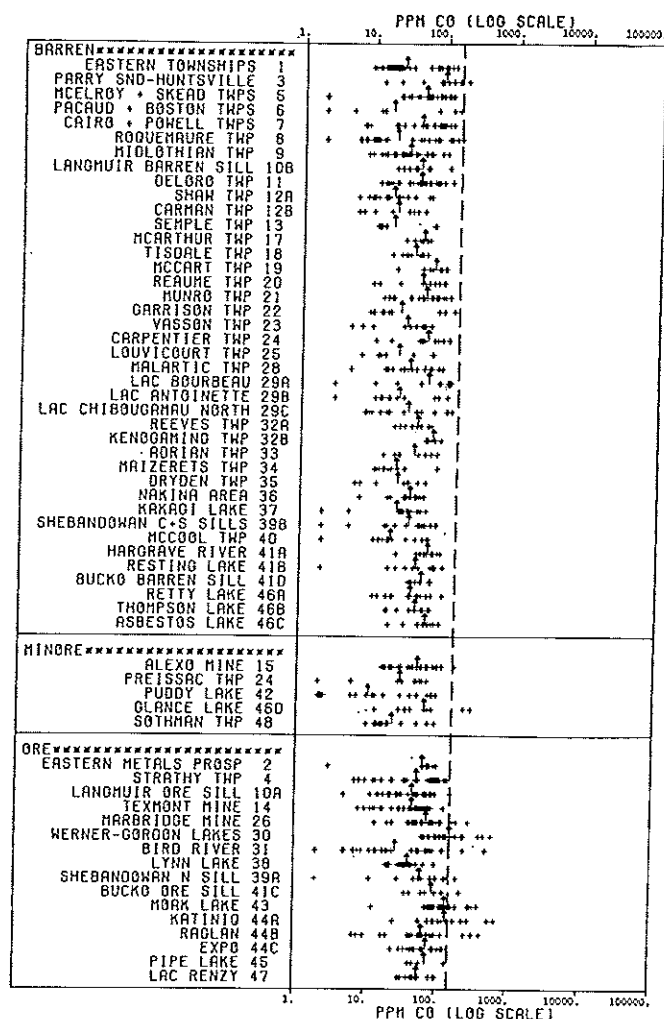


FIGURE 4 — Distribution of cobalt as ascorbic acid - hydrogen peroxide soluble metal.

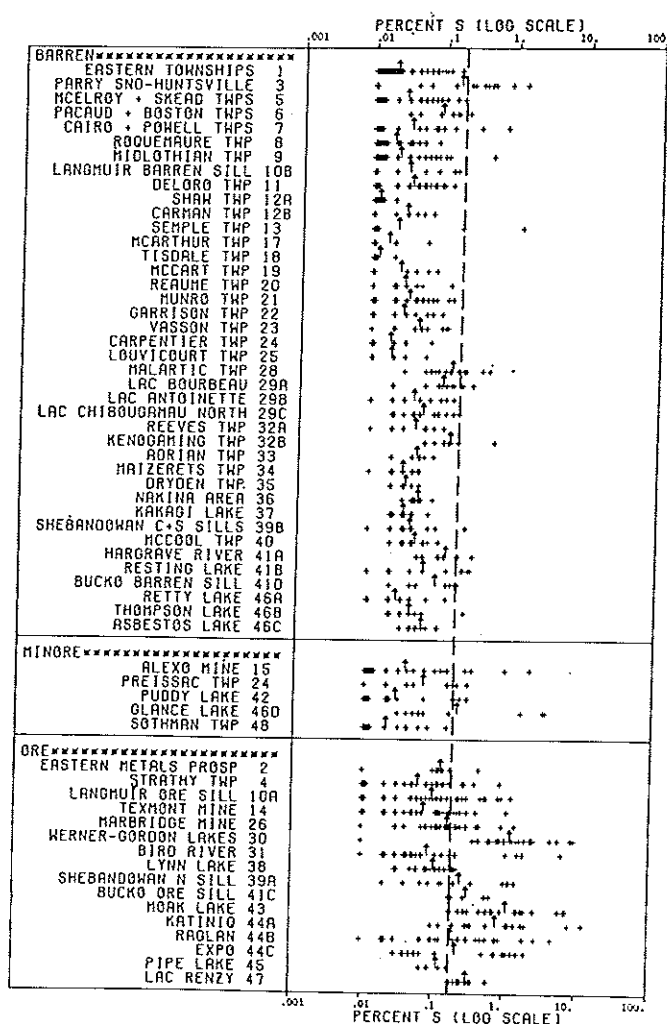


FIGURE 5 — Distribution of sulphur.

Although copper and nickel are so often associated in ore deposits derived from ultramafic rocks, their chemical properties are rather dissimilar. The very low correlation of 0.19 between copper and nickel is therefore not unexpected. Cobalt's correlation with copper of 0.40 and with nickel of 0.71 indicates that cobalt is intermediate in character between the other two elements, but more closely resembles nickel. For the *ORE* group, the copper-nickel correlation rises to 0.89.

As might be expected from their low correlation, the copper/nickel ratio varies widely from locality to locality. Where data are available, the correspondence between the copper/nickel ratio of the ore deposits and the copper/nickel ratio of the sulphides contained in the associated ultramafic rocks is generally close (Table V, Figure 7). Only for the Eastern Metals prospect and for the Strathy Township deposit are there gross differences between the pair of ratios. For these two deposits, this may be reason enough to question the genetic relationship between the sulphides of the ore and the sulphides of the adjoining ultramafic rock. It may be seen from Figure 7 and Table V that there is a general tendency for the sulphides of the ultramafic rocks to have a lower copper/nickel ratio than the associated orebody. At first sight this is surprising, because the sulphides disseminated through the ultramafic rocks should, in part, have separated later than those that went to form the ore deposit. Chamberlain (1967) has shown, for the Muskox intrusion, that nickel-rich sulphides separate before nickel-copper sulphides. A possible explanation for this anomaly is that the disseminated sulphides of the ultramafic rock will have had a greater opportunity to re-equilibrate with nickel-rich, copper-poor silicates during serpentinization than will the massive sulphides of the ore zone. During the re-equilibration processes, nickel may become enriched in these disseminated sulphides because it is more chalcophile than iron, thus decreasing the copper/nickel ratio. If this explanation is correct, one might expect the *BARREN* ultramafics to have a lower copper/nickel ratio than the *ORE* group, as enrichment of nickel by this mechanism will be relatively greater the lower the sulphide content. This is indeed the case. Based on the mean copper and nickel contents of the three groups, the copper/nickel ratio is 0.234 for the *ORE* group, 0.070 for the *MINORE* group and 0.045 for the *BARREN* group. It should be pointed out that a non-geological factor will influence this ratio. As was explained in an earlier section, some nickel — hopefully small in amount — is leached from the silicate components of each sample. On the average, this amount will remain constant over the range of sulphide contents dealt with here and will therefore contribute a built-in decrease in the copper/nickel ratio of the samples as the sulphide content of the samples decreases.

If re-equilibration processes are significant in causing the ratio changes noted above, they should also influence other metal ratios. Slightly more chalcophile cobalt should be en-

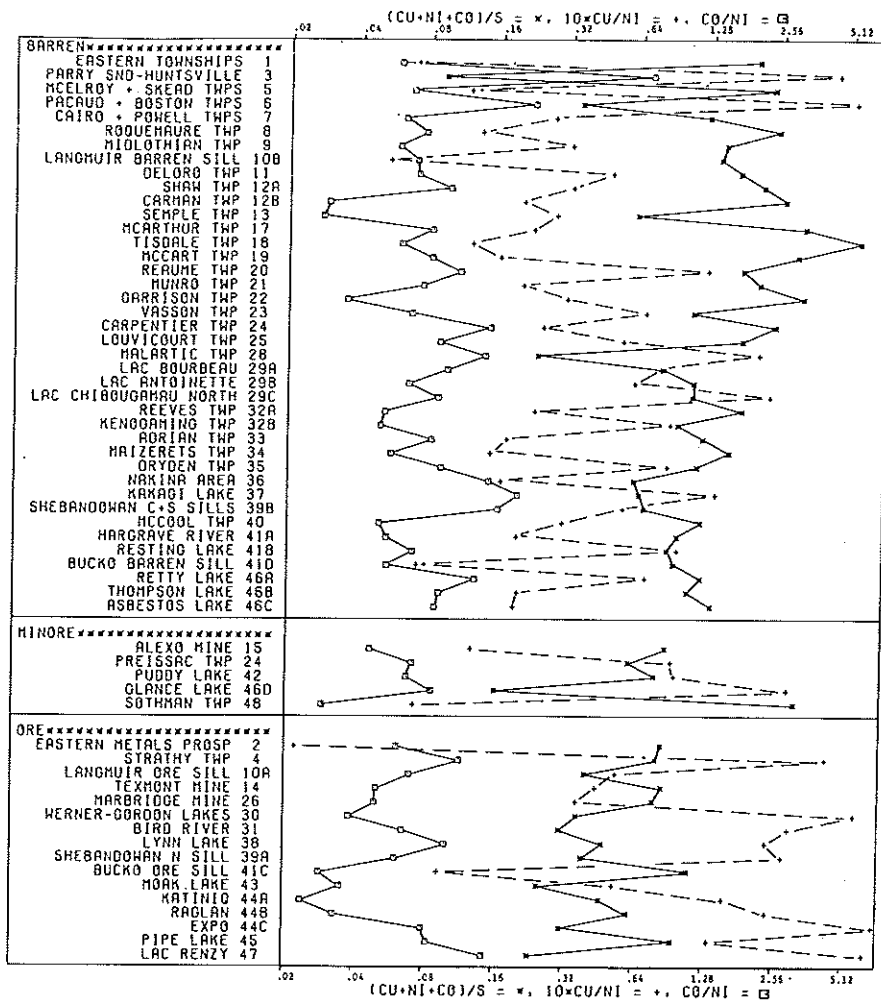


FIGURE 6 — Distribution of element ratios [$\ast = (Cu + Ni + Co)/S$; $+ = (Cu/Ni) \times 10$; $\square = Co/Ni$].

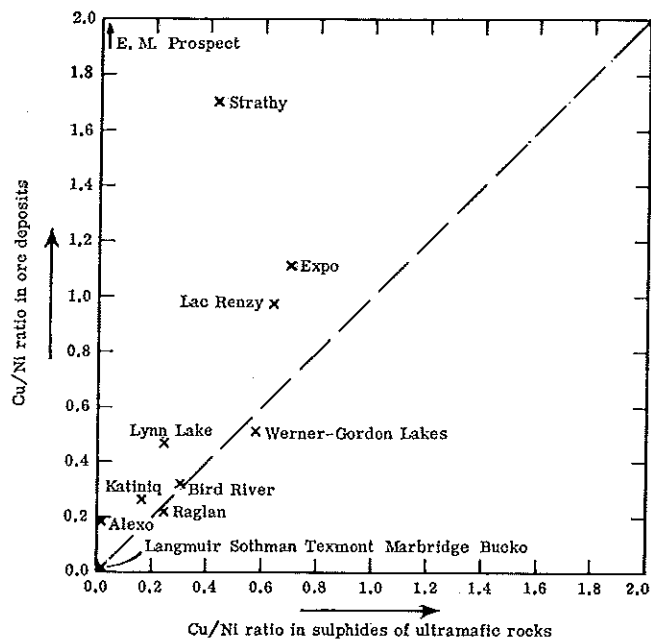


FIGURE 7 — Comparison of Cu/Ni ratio of ore deposits with the Cu/Ni ratio of sulphides in associated ultramafic rocks.

riched relative to nickel in the low-sulphide rocks. Both elements are available within silicates. Again this is the case. The cobalt/nickel ratio of the *ORE* group is 0.045, increasing to 0.052 for the *MINORE* group and to 0.075 for the *BARREN* group. Another ratio which should

change as a result of re-equilibration is the nickel/iron ratio, increasing from the *ORE* group to the *BARREN* group. Although iron has not been measured, we may examine the (Cu+Ni+Co)/S ratio. This increases from 0.41 in the *ORE* group to 0.53 in the *MINORE* group and to 1.10 in the *BARREN* group. A decrease in the amount of iron relative to copper, nickel and cobalt will, in part, explain the increase in this ratio. Other causes are a loss in sulphur and the creation of sulphur-deficient mineral species such as heazlewoodite (Ni₃S₂), or of metal alloys such as awaruite (Ni₃Fe), which are at least partially soluble in the leach solution. The metals to form these alloys may have come from either sulphides or silicates (Ramdohr, 1967).

A considerable amount of information of academic and economic interest is revealed by a comparison of the metal contents and element ratios for the different localities, as shown in Figures 2 to 6. It is not appropriate to detail such comparisons here. There are, however, some points which should be noted. For the *BARREN* group, samples with sulphur contents greater than 0.178 per cent S (Figure 5) include some from Parry Sound - Huntsville, Malartic township, Lac Bourbeau, Kenogaming township and the Thompson Belt (Hargrave River, Resting Lake, Bucko Barren Sill). The enrichment in the Thompson Belt is not surprising because of the abundance of nickel and copper sulphides in this belt. The Malartic ultramafic rocks were emplaced along a notably mineralized, major fault zone and the Lac Bourbeau samples come from an area of widespread copper mineralization. Minor pentlandite mineralization is known within the rocks sampled in Kenogaming township. The Parry Sound - Huntsville samples are peculiar in having a very high content of leachable cobalt. The mean value for this locality is 99.1 ppm Co, which is three times greater than the mean for the whole group and is exceeded only by three localities of the *ORE* group.

APPLICATION TO MINERAL EXPLORATION

As the four element components which we have studied are enriched in the ore-associated ultramafic rocks compared to barren ultramafics, we may now consider how best to use this phenomenon to predict the ore potential of any given ultramafic body.

One of the primary considerations must be the analytical productivity for measuring the different elements. For the methods used in this study, the sample productivity to determine copper, nickel and cobalt is approximately five times greater than that of the method used to determine sulphur. Thus, provided little information is lost, the practicality of this method in mineral exploration is considerably enhanced if sulphur need not be determined. We have, therefore, first examined what contribution is made by copper, nickel and cobalt to discriminating between the *ORE* and the *BARREN* groups; we have then considered what additional information is contributed by sulphur.

The primary statistical method employed in this section is discriminant analysis. Discriminant analysis finds the best combination of variables to separate two or more groups of samples. In determining which of two groups a sample most resembles, one may compare the different variables one by one. It is, however, much easier and more efficient to combine these different variables into one measure (the discriminant score) for each sample, which may then be compared with the discriminant score of every other sample. Discriminant analysis is more efficient the greater the number of variables to be compared. For the three or four variables to be compared here, the advantages to be derived from employing discriminant analysis are obviously much less than when twenty or thirty variables are to be compared.

The discriminant equations described below are computed to best distinguish the 616 samples of *BARREN* ultramafic rock from the 372 samples of the *ORE* group. The method of discriminant analysis has been particularly well described by Cooley and Lohnes (1962), and has previously been applied to multivariate geochemical data by Cameron (1969). The element values were first converted to logarithms because of the high variance of the data. The matrices *W* and *A* were then computed from the transformed data:

$$w_{ij} = \sum_{k=1}^g \left[\sum_{n=1}^{N_g} (\bar{x}_{ikn} - \bar{x}_{ik})(\bar{x}_{jkn} - \bar{x}_{jk}) \right]$$

$$a_{ij} = \sum_{k=1}^g N_g (\bar{x}_{ik} - \bar{x}_i)(\bar{x}_{jk} - \bar{x}_j)$$

TABLE V — Comparison of Cu/Ni Ratio of Ore Deposits with the Cu/Ni Ratio of Sulphides in Associated Ultramafic Rocks

Map Code	Locality	Thousands of Tons Reserves and/or Production ⁽¹⁾			Mean Content H ₂ O ₂ Soluble Element in U.M. Rocks of Locality ⁽²⁾		
		Cu	Ni	Cu/Ni	Cu	Ni	Cu/Ni
15	Alexo Mine	0.4	2.2	0.18	15.2	1208.	0.01
48	Sothman Twp.	—	2.7	Low	6.3	884.	<0.01
2	E. M. Prospect	14.5	4.9	2.96	2.5	1125.	<0.01
4	Strathy Twp.	4.8	2.8	1.71	251.	587.	0.43
10A	Langmuir Ore Sill	—	6.9	Low	40.	742.	0.05
14	Texmont Mine	—	37.	Low	43.5	988.	0.04
26	Marbridge Mine	—	14.5	Low	57.5	1570.	0.04
30	Werner-Gordon Lks.	7.6	14.9	0.51	2500.	4380.	0.57
31	Bird River	4.6	14.3	0.32	263.	882.	0.30
38	Lynn Lake	135.	287.	0.47	94.7	396.	0.24
39A	Shebandowan N.	?	?	?	380.	1350.	0.28
41C	Bucko Ore Sill	—	320.	Low	31.	3330.	<0.01
43	Moak Lake	?	?	?	221.	4180.	0.05
44A	Katiniq	27.	104.	0.26	1180.	7570.	0.16
44B	Raglan	26.	116.	0.22	651.	2690.	0.24
44C	Expo	42.	38.	1.11	669.	960.	0.70
45	Pipe Lake	?	?	?	122.	895.	0.14
47	Lac Renzy	7.1	7.3	0.97	247.	386.	0.64

(1) From Table II. (2) From Table IV

TABLE VI—Variance - Covariance Matrices for BARREN and ORE Groups of Ultramafic Rocks

	BARREN GROUP				ORE GROUP			
	Cu	Ni	Co	S	Cu	Ni	Co	S
Cu.....	.46	-.07	.05	.11	.85	.23	.16	.39
Ni.....	-.07	.27	.11	.05	.23	.46	.24	.31
Co.....	.05	.11	.15	.07	.16	.24	.16	.18
S.....	.11	.05	.07	.20	.39	.31	.18	.46

where g is the number of groups, N_g the number of samples in group 'g' and i and j run from 1 to p , with p being the number of variables.

These matrices are then formed into the following equation, I being the identity matrix, and the eigenvectors and eigenvalues are extracted:

$$[W^{-1}A - \lambda I] = 0$$

The eigenvectors are the discriminant functions; for this two-group problem, only one eigenvector is extracted. To test for a significant difference between the composition of two groups, Λ is computed:

$$\Lambda = 1/(1 + \lambda)$$

where λ is the eigenvalue associated with the eigenvector that is the discriminant function. Lambda is tested by the F approximation of Rao (1952). For a two-group problem, F is computed thus:

$$F_{v,p} = [(1 - \Lambda)/\Lambda] (v/p)$$

where $v = N - p + 1$, N is the number of samples, and p is the number of variables. Λ may also be computed as the ratio of scatter within groups to total scatter. Thus, Λ may be conveniently used to measure the discriminating power of different combinations of variables. The lower the value of Λ , the greater the discriminating power of these variables.

To show the relative contributions of the different variables to a discriminant equation, a scaled discriminant vector may be obtained by multiplying the vector of discriminant coefficients by the vector of square roots of the diagonal of the W matrix.

Discriminating between the ORE and BARREN groups of samples using the variables copper, nickel and cobalt, the following values are obtained:

Discriminant Vector (1) 0.92 Cu, 0.37 Ni, 0.08 Co
Scaled Vector (1) 22.6 Cu, 6.85 Ni, 1.01 Co

$\lambda = 0.42$, $\Lambda = 0.70$, $F_{3,93}^* = 137$, $p < 0.0001$

The F and p values indicate that there is a very high probability that the two groups are different. This information is almost superfluous, because this fact is visually observable in Figures 2 to 5. What is of more interest is that the scaled vector indicates that a considerable role is played by copper in distinguishing between the two groups; cobalt plays a very minor role. That cobalt is of little help in discriminating between the two groups is not surprising. Comparing the plots for the four elements (Figures 2-5) or the group mean values (Table IV), cobalt shows the least relative difference between the ORE and the BARREN groups. Furthermore, because it has moderate to high correlations with the other elements, much of the discriminating power of the data for cobalt is rendered redundant by these correlations.

The very considerable difference between the ORE and the BARREN groups is also reflected in differences in their variance-covariance matrices (Table VI), which can be shown, by techniques described in Cooley and Lohnes (1962), to be markedly heterogeneous. Most multivariate

analyses of variance and covariance methods and discriminant analysis methods assume a reasonable degree of homogeneity in the different variance-covariance matrices. Anderson and Bahadur (1962) have described a procedure for constructing a discriminant vector for unequal variance-covariance matrices. A Fortran coding of the procedure has been published by Reymont *et al.* (1969). Using this method, the following discriminant vector was obtained —

Discriminant Vector (2) 1.59 Cu, 0.63 Ni, 0.14 Co

Although, at first sight, this vector appears to be different than discriminant vector (1) above, converting the two vectors to percentage values shows that this is not so:

(1) 67 Cu, 27 Ni, 6 Co
(2) 66 Cu, 29 Ni, 5 Co

If we now include sulphur (as \log_{10} ppm S) in the discriminant analysis, the following values are derived:

Discriminant Vector (3) 0.51 Cu, 0.10 Ni, -0.18 Co, 0.84 S
Scaled Vector (3) 12.5 Cu, 1.87 Ni, -2.22 Co, 14.3 S
 $\lambda = 0.53$, $\Lambda = 0.65$, $F_{4,93}^* = 130$, $p < 0.0001$

The decrease in the value of Λ compared to the value associated with discriminant vector (1) indicates that a modest increase in the discriminating power of the data set is gained by including sulphur. If we again compute a discriminant vector by the method of Anderson and Bahadur (1962), the following coefficients are obtained:

Discriminant Vector (4) 1.04 Cu, 0.20 Ni, -0.37 Co, 1.75 S

Again, in terms of percentage values, there is not a great deal of difference between discriminant vectors (3) and (4).

The value Λ has been computed for all possible combinations of variables:

Ni - Co - S	0.70	Cu - Ni - Co - S	0.65
Cu - Ni	0.70	Cu - Ni - S	0.65
Ni - S	0.70	Cu - Co - S	0.65
Co - S	0.70	Cu - S	0.65
Cu - Co	0.71	Cu - Ni - Co	0.70
Ni - Co	0.91		

From this, it appears that copper and sulphur are of approximately equal value in discriminating between the ORE and the BARREN groups, that nickel is of lesser importance and that cobalt is of very little value. Copper and sulphur together are as powerful for discriminating between the groups as are all four elements combined.

The scalar discriminant score may be computed for each sample by multiplying a row discriminant vector by a column vector of element values (as \log_{10} ppm in this case). This has been done for the sample data using discriminant vector (2). The discriminant scores are plotted on Figure 8 and the locality and group means are given in Table IV. In Figure 8, a line has been drawn at an arbitrary score value of 5.5, which best appears to separate the distribution of the BARREN group from the upper part of the distribution of the ORE group. On or to the right of this line, score values are plotted as a larger cross. Mean values

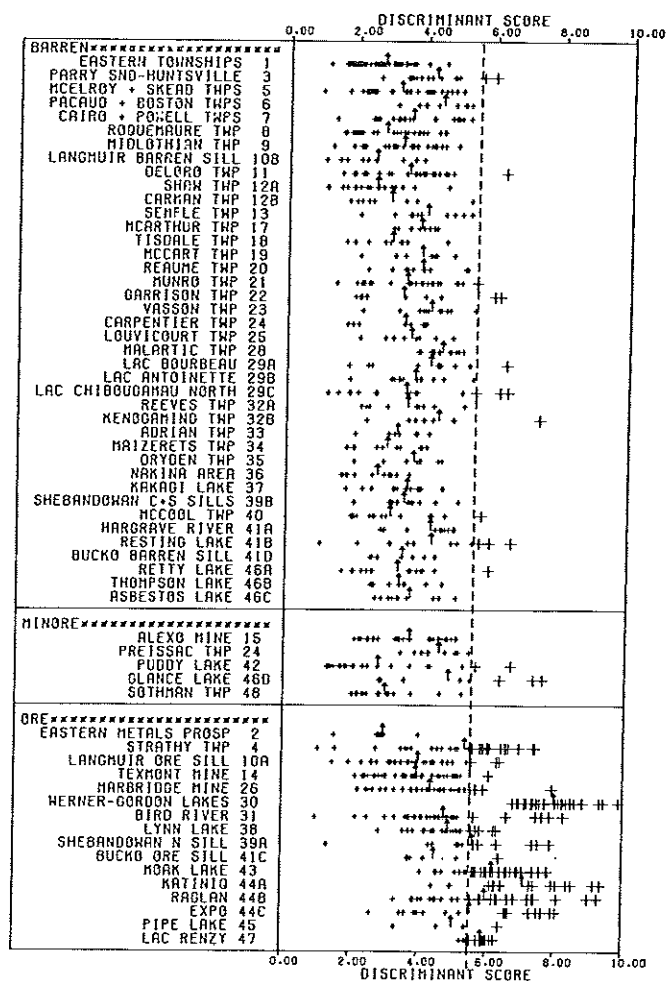


FIGURE 8 — Distribution of discriminant scores computed from copper, nickel and cobalt.

for the discriminant scores at each locality were computed and these are plotted as an upward-facing arrow. It should be recalled that Figure 8 is essentially a logarithmic plot, because the element values have been transformed to logarithms prior to the discriminant scores being computed.

Only 16 of the 616 BARREN samples have discriminant score values equal to or greater than 5.5. In contrast, a substantial proportion of the ORE group of samples have scores equal to or greater than this value. On the basis of this plot, many of the ore-associated ultramafic bodies could be identified as such, particularly those associated with greater quantities of ore-grade material. The majority of MINORE localities more closely resemble those of the BARREN group. In practical exploration, it would be worthwhile to follow-up any sample which gave a discriminant score greater than 5.5.

ACKNOWLEDGMENTS

It would not have been possible to have undertaken this study without the generous cooperation of many members of the Canadian mining fraternity. The writers are particularly indebted to the management and geological staff of the following companies for facilitating access to their properties or for providing drill-core samples:

Ajax Minerals Ltd.
Amax Exploration Inc.
Barnat Mines Ltd.
Canadian Johns-Manville Co. Ltd.
Commerce Nickel Mines Ltd.
Consolidated Canadian Faraday Ltd.
Copperfields Mining Corp. Ltd.
Daniel Mining Co. Ltd.
Falconbridge Nickel Mines Ltd.

International Nickel Co. of Canada, Ltd.
McIntyre Porcupine Mines Ltd.
McWatters Gold Mines Ltd.
M. E. M. Consultants Ltd.
Mid-Chibougamau Mines Ltd.
Norpax Nickel Mines Ltd.
Pre-Cam Explorations and Development Ltd.
Renzy Mines Ltd.
Resource Exploration and Development Co. Ltd.
Sherritt Gordon Mines Ltd.
Spirit Lake Mines Ltd.
Sullivan Mines Ltd.
Texmont Mines Ltd.

We are further indebted to members of the staff of the mines departments of the provinces of Manitoba, Ontario and Quebec for providing needed information.

At the inception of this study, Dr. J. A. Chamberlain suggested sample sites. P. Lavergne prepared the samples; atomic absorption determinations were made by G. Gauthier, Mrs. S. Lindsay and Mrs. A. MacLaurin; the sulphur determinations were made by Dr. J. Sen Gupta and S. Courville; David Hobbs carried out parts of the computer programming; and Mrs. R. Chaffey typed the manuscript. To all of these persons we express our gratitude. Our special thanks to Dr. R. Eckstrand, who generously shared his knowledge of Canadian nickel deposits and who has provided constructive criticism of the manuscript.

REFERENCES

- Anderson, T. W., and Bahadur, R. R., 1962: Classification into Two Multivariate Normal Distributions with Different Covariance Matrices; *Ann. Math. Statist.*, 33, pp. 420-431.
- Cameron, E. M., 1969: Regional Geochemical Study of the Slave Point Carbonates, Western Canada; *Can. J. Earth Sci.*, 6, pp. 247-268.
- Cameron, E. M., and Baragar, W. R. A., 1970: Distribution of Ore Elements in Rocks for Evaluating Ore Potential: frequency distribution of copper in the Coppermine River Group and Yellowknife Group volcanic rocks, N.W.T., Canada; (*this volume*).
- Chamberlain, J. A., 1967: Sulphides in the Muskox Intrusion; *Can. J. Earth Sci.*, 4, pp. 105-153.
- Cooley, W. W., and Lohnes, P. R., 1962: *Multivariate Procedures for the Behavioral Sciences*; John Wiley and Sons, New York.
- Cornwall, H. R., 1966: Nickel Deposits of North America; *U.S. Geol. Surv. Bull.* 1223, 62 p.
- Dodin, D. A., 1963: Nekotoryye Zakonomernosti raspredeleniya mikroelementov v trappakh Gory Kharaelakh; (distribution of trace elements in the Mt. Karaelakh traps); *Tr. Inst. Geol. Arkiki*, 1963, p. 168.
- Dolivo-Dobrovolskiy, V. V., and Klimenko, Yu. V., 1947: Ratsional'nyy analiz rud; (rational analysis of ores); *Metallurgizdat, Sverdlovsk*.
- Godlevskiy, M. N., 1959: Trapy i Rudonosnyye Intruzii Noril'skogo Rayona; (the traps and ore-bearing intrusives of the Noril'sk region); *Gosgeoltekhizdat, Moscow*.
- Goldschmidt, V. M., 1954: *Geochemistry*; ed., Alex Muir, Clarendon Press, Oxford, 730 p.
- Kilburn, L. C., Wilson, H. D. B., Graham, A. R., Ogura, Y., Coats, C. J. A., and Scoates, R. F. J., 1969: Nickel Sulphide Ores Related to Ultrabasic Intrusions in Canada; *Symposium: Magmatic Ore Deposits*; ed. H. D. B. Wilson, Econ. Geol. Publ. Co., pp. 276-293.
- Kullerud, G., and Yoder, H. S., Jr., 1965: Sulphide-Silicate Reactions and their Bearing on Ore Formation under Magmatic, Postmagmatic and Metamorphic Conditions; *Symposium: Problems of Postmagmatic Ore Deposition*, 2, pp. 327-331, Geol. Surv. Czechoslovakia, Prague.
- Laurin, A. F., and Dugas, J., 1970: Current Mining Exploration and Development in Quebec; *Can. Min. J.*, 91, pp. 66-69.
- MacKenzie, B. W., 1968: Nickel — Canada and the World; Mineral Rept. No. 16, Mineral Resources Div., Dept. Energy, Mines and Resources, Ottawa, 176 pp.
- Naldrett, A. J., 1966: The Role of Sulphurization in the Genesis of Iron-Nickel Sulphide Deposits of the Porcupine District, Ontario; *CIM Bulletin*, 59, pp. 489-497; *CIM Transactions*, 69, pp. 147-155.

- Polferov, D. V., 1962: Geokhimicheskiye Poiski Mestorozhdeniy Medno-Nikelevykh Sul'fidnykh Rud; (geochemical prospecting for deposits of copper-nickel sulphide ores); *Byull. ONTI MG i ON SSSR*, 35.
- Polferov, D. V., Suslova, S. I., and Arkhipova, A. I., 1965: Opredeleyeniye Perspektiv Rudonosnosti Osnovnykh-Ultraosnovnykh Massivov na Osnovanii Zakonomernostey Pervichno-Konstitutsional'nogo Rasseyaniya; (determination of degree of mineralization of mafic-ultramafic massifs on the basis of the regularities of primary dispersion of the elements); *Tr. N. -i. Inst. Geologii Arktiki, Ser. Regional'naya*, No. 5.
- Polferov, D. V., and Suslova, S. I., 1966: Geochemical Criteria of Nickel Mineralization in the Mafic-Ultramafic Massifs; *Geochemistry International*, 3, pp. 487-496.
- Ramdohr, Paul, 1967: A Widespread Mineral Association, Connected with Serpentinization; *N. Jb. Miner. Abstr.*, 107, pp. 241-265.
- Rao, C. R., 1952: *Advanced Statistical Methods in Biometric Research*; John Wiley & Sons, New York.
- Reyment, R. A., Ramden, Hans-Ake, and Wahlstedt, W. J., 1969: Fortran IV Program for the Generalized Statistical Distance and Analysis of Covariance Matrices for the CDC 3600 Computer; Computer Contribution 39, State Geol. Surv., U. Kansas, Lawrence, 42 pp.
- Sen Gupta, Joy G., 1970: Rapid Combustion Methods for Determining Sulfur in Rocks, Ores and Stony Meteorites: a comparative study of the usefulness of resistance-type and induction furnaces; *Anal. Chim. Acta.*, 49, pp. 519-525.
- Shankla, Roman, 1969: Copper, Nickel, Lead and Zinc Deposits of Ontario; Mineral Resources Circ. 12, Ontario Dept. Mines, 394 pp.
- Skinner, Brian J., and Peck, Dallas L., 1969: An Immiscible Sulphide Melt from Hawaii; *Symposium: Magmatic Ore Deposits*; ed., H. D. B. Wilson, Econ. Geol. Publ. Co., pp. 310-322.
- Smirnova, N. P., Nesterenko, G. V., and Al'mukhamedov, A. I., 1968: The Mode of Occurrence of Nickel and Cobalt in Mafic Rocks; *Geochemistry International*, 5, pp. 363-372.
- Sullivan, C. J., 1959: The Origin of Massive Sulphide Ores, *CIM Bulletin*, 52, pp. 613-619.
- Turekian, K. K., and Wedepohl, K. H., 1961: Distribution of the Elements in Some Major Units of the Earth's Crust; *Bull. Geol. Soc. Am.*, 72, pp. 175-192.
- Volkov, I. D., 1963: Raspredeleniye Mikroelementov v Izverzhenykh Porodakh Noril'skogo Raiona; (distribution of trace elements in the igneous rocks of the Noril'skogo region); *Voprosy Magmatizma, Metamorfizma i Rudoobrazovaniya, Gosgeoltekhizdat*, Moscow.
- Wager, L. R., Vincent, E. A., and Smales, A. A., 1957: Sulphides in the Skaergaard Intrusion, East Greenland; *Econ. Geol.*, 52, pp. 855-895.
- Wilson, H. D. B., and Brisbin, W. C., 1961: Regional Structure of the Thompson - Moak Lake Nickel Belt; *CIM Bulletin*, 54, pp. 815-822; *CIM Transactions*, 64, pp. 470-477.
- Wilson, H. D. B., Kilburn, L. C., Graham, A. R., and Ramalal, K., 1959: Geochemistry of Some Canadian Nickeliferous Ultrabasic Intrusions; *Symposium: Magmatic Ore Deposits*; ed., H. D. B. Wilson, Econ. Geol. Publ. Co., pp. 294-309.
- Yegorova, Ye. N., 1938: O Nikelonosnosti Olivina; (on nickel concentrations in olivine); *Zap. Vses. Mineralog. Obshch.*, 67.

APPENDIX

The Determination of Copper, Nickel and Cobalt in Rocks by Atomic Absorption Spectrometry Using a Cold Leach

JOHN J. LYNCH

Geological Survey of Canada, Ottawa

PRELIMINARY REMARKS

THE METHOD DESCRIBED IN THIS PAPER is an application of the studies carried out by N. P. Smirnova *et al.* (1968), wherein certain trace elements occurring in rocks as sulphide minerals were preferentially dissolved by the action of hydrogen peroxide in the presence of ascorbic acid. The ascorbic acid lowers the pH of the solution to approximately 2.5 and provides a reducing medium which inhibits the oxidation of ferrous sulphate to ferric sulphate, which in turn hydrolyzes to hydrous ferric oxide. The ascorbic acid - hydrogen peroxide solution prepared as described below was found to decompose galena, arsenopyrite, chalcopyrite, pyrite, pyrrhotite, pentlandite, tetrahedrite, sphalerite and awaruite.

Mixed standard solutions for the calibration of the atomic absorption spectrophotometer were initially prepared in the same concentration of ascorbic acid - hydrogen peroxide as was used for the decomposition of the samples. These standard solutions were found to be unstable over periods longer than three or four days. A fresh set of standard solutions contained in ascorbic acid and hydrogen peroxide were compared against a set of standard solutions contained in 1N HNO₃. There was no appreciable difference in the per cent absorbance readings between the standard solutions prepared in the two media (Table I).

Standard solutions contained in 1N HNO₃ have been found to be stable for over a year, and these are used for calibration.

TABLE I — Comparison of Standard Solutions Prepared in Ascorbic Acid - Hydrogen Peroxide and in 1N HNO₃

Concentration µg/ml	Cu, % Absorption		Ni, % Absorption		Co, % Absorption	
	H ₂ O ₂ — Ascorbic Acid	1N HNO ₃	H ₂ O ₂ — Ascorbic Acid	1N HNO ₃	H ₂ O ₂ — Ascorbic Acid	1N HNO ₃
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.5	18.5	18.5	7.0	7.1	11.8	11.6
1.0	36.6	36.9	13.8	13.8	23.0	23.2
2.0	70.4	70.0	24.2	24.2	43.5	43.9
4.0	—	—	44.7	44.9	79.7	80.1

ANALYTICAL PROCEDURE

Decomposition of the Sample

1. Into a clean dry test tube (16 by 125 mm), calibrated at 10 ml, weigh a 100-mg sample of the ground rock. A larger sample weight may be used if low values are anticipated.
2. Add 7 ml of ascorbic acid - hydrogen peroxide mixture and allow to stand approximately 18 hours (overnight), with occasional mixing. Do not heat.
3. Dilute to the 10-ml mark with metal-free water. Stopper the test tube with a clean cork and shake vigorously to mix.
4. Centrifuge for 5 minutes to obtain a clear supernatant solution.

General Procedure for Calibration of Instrument

1. The operating parameters described here refer to the Perkin Elmer Model 303 atomic absorption spectrophotometer. Other makes of instruments will require changes in some of these parameters.

Parameter	Copper	Nickel	Cobalt
Meter Response	1*	1*	1*
Filter	out	out	out
Scale	x5	x2	x5
Slit	4 (7Å)	3(2Å)	3(2Å)
Source Current	15 ma	25 ma	30 ma
Range	U.V.	U.V.	U.V.
Wavelength	3,247 Å	2,320 Å	2,407 Å
Burner	10 cm single slot	Boling	Boling
Air Pressure	30 psi	30 psi	30 psi
Air Flow	9*	9*	9*
Acetylene Pressure	8 psi	8 psi	8 psi
Acetylene Flow	8*	7½*	7½*

*Arbitrary units given by Perkin-Elmer

2. Aspirate 1N HNO₃ into the flame and zero the instrument.
3. Using the parameters listed above, the following standard solutions are used for calibration:

Cu: 0.5, 1.0 and 2.0 µg/ml
 Ni: 0.5, 1.0, 2.0, 4.0, 6.0 and 8.0 µg/ml
 Co: 0.5, 1.0, 2.0 and 4.0 µg/ml

4. Calibration curves are plotted relating per cent absorption and µg/ml.

General Procedure for Analysis of Samples

1. After calibrating, aspirate 1N HNO₃ and readjust zero if necessary.
2. Aspirate sample solutions and record per cent absorp-

tion. Care should be taken not to suck any of the sediment into the burner. Aspirate 1N HNO₃ between each sample and check a calibration standard after every tenth sample. If check standard changes by more than 1 per cent absorption, recalibrate and repeat the previous ten samples.

3. Using calibration curves, interpolate per cent absorption of samples to obtain µg/ml. Calculate the concentration in parts per million using the equation:

$$\text{ppm element} = \frac{\mu\text{g/ml} \times 10}{\text{sample weight (gm)}}$$

4. Should the sample be above the top standard of the calibration curve, an aliquot of the sample solution may be diluted to 10 ml with the appropriate volume of ascorbic acid - hydrogen peroxide mixture and metal-free water. Alternatively, the sensitivity of the instrument may be lowered by reducing the scale expansion and/or using a smaller burner. This permits the use of standards up to considerably higher concentrations.

Preparation of Reagents

1. *1 per cent acid solution*: Dissolve 5.0 gm ascorbic acid in metal-free water and dilute to 500 ml with metal-free water. This solution should be prepared freshly just prior to using.
2. *Ascorbic acid - hydrogen peroxide mixture*: Add 200 ml of 30 per cent hydrogen peroxide to 500 ml of ascorbic acid and mix thoroughly. This solution is made up freshly each day.
3. *Mixed copper, nickel and cobalt standard solution*: 1000 µg/ml (Solution A). In a 1000-ml volumetric flask, dissolve 3.9297 gm of copper sulphate (CuSO₄·5H₂O), 4.0487 gm of nickelous chloride (NiCl₂·6H₂O) and 4.0372 gm of cobaltous chloride (CoCl₂·6H₂O) in about 900 ml of metal-free water. Add 6 ml of concentrated nitric acid mix and allow to cool to room temperature. Dilute to 1000 ml with metal-free water and mix well. This solution is about 0.1N with respect to nitric acid.
4. *Mixed copper, nickel and cobalt standard solution*: 100 µg/ml (Solution B). Pipette 100 ml of solution A into a 1000-ml volumetric flask. Add 5.4 ml of concentrated nitric acid, dilute to about 900 ml with metal-free water, mix and allow to cool to room temperature. Dilute to 1000 ml with metal-free water and mix well. This solution is about 0.1N with respect to nitric acid.
5. *Mixed copper, nickel and cobalt calibration solutions*: These are prepared according to the dilutions listed in Table II.
6. *1N HNO₃*: Dilute 125 ml of concentrated HNO₃ to 2,000 ml with metal-free water. Store in a polyethylene bottle.

TABLE II — Mixed Copper, Nickel and Cobalt Calibration Solutions

Concentration (µg/ml)	Volume of Solution A(ml)	Volume of Solution B(ml)	Volume of Concentrated HNO ₃ (ml)	Final Volume (ml)
0.5	—	1	12.5	200
1.0	—	2	12.5	200
2.0	—	4	12.5	200
4.0	—	8	12.5	200
6.0	—	12	12.5	200
8.0	—	16	12.5	200
10.0	—	20	12.5	200
15.0	3	—	12.5	200
20.0	4	—	12.5	200
25.0	5	—	12.5	200
30.0	6	—	12.5	200
35.0	7	—	12.5	200
40.0	8	—	12.5	200