

TRACE ELEMENT PARTITION IN SULPHIDES,
NORANDA, QUEBEC

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by

William Douglas Beaton

A thesis submitted for the degree Doctor of Philosophy, to the
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ABSTRACT

The four major sulphides of the Lake Dufault orebody, pyrite, pyrrhotite, sphalerite and chalcopyrite, were analysed for cobalt and nickel using electron microprobe and atomic absorption procedures. These elements are preferentially concentrated in pyrite with respect to pyrrhotite and in the octahedrally co-ordinated minerals, pyrite and pyrrhotite, with respect to the tetrahedrally co-ordinated minerals, sphalerite and chalcopyrite.

Cobalt zoning in some pyrite grains, irregular high cobalt distribution in some pyrite grains, and cobalt minerals were related to pyrrhotite formation. Pyrrhotite is a metamorphic mineral formed by the breakdown of pyrite at low temperatures. Pyrrhotite contains less than 1000 ppm cobalt. Cobalt in excess of this amount enters adjacent pyrite grains or forms cobalt minerals.

Cobalt is homogeneously distributed throughout individual grains of pyrrhotite, sphalerite, and chalcopyrite although the concentration may vary between adjacent grains of the same phase. This indicates equilibrium is local, only in the range of 300 microns.

Trace Element Range		
	Co ppm	Ni ppm
pyrite	ND*- 38,500	ND - 297
pyrrhotite	ND - 1,000	ND - 97
sphalerite	ND - 900	ND - 40
chalcopyrite	ND - 290	ND - 63

*ND - non detectable

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in partial fulfillment of the requirements for the degree of
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Department of Geological Sciences
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PREFACE

The intention of this research was to investigate the occurrence of trace amounts of cobalt and nickel that are present in the Noranda - type massive sulphide deposit. The presentation is as follows:

- Chapter I - The Noranda Area - synopsis of regional geology and general aspects of the massive sulphide occurrences;
- Chapter II - The Lake Dufault Mine Area - summary of geology of the mine area and description of the ore zone, largely based on previous work;
- Chapter III - Cobalt and Nickel as Trace Elements - review of previous work pertinent to this study;
- Chapter IV - Cobalt and Nickel Associated with the Lake Dufault Orezone - results and discussion of work performed for this study; and
- Chapter V - Summary and Conclusions

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CHAPTER I

THE NORANDA AREA

INTRODUCTION

In 1920 Ed Horne staked a series of claims in northwestern Quebec over a copper - gold showing on the shore of Osisko Lake. This subsequently became the now famous Horne Mine. Since this discovery, the Noranda area, which is primarily limited to the four townships of Rouyn, Beauchastel, Duprat and Dufresnoy, has become one of the world's major copper, gold and zinc mining areas. Noranda is located approximately 400 miles north of both Toronto and Montreal, 40 miles east of the Quebec-Ontario boundary. It is readily accessible by plane, rail and road (Figure 1).

At the present time there are four active producers: Noranda (Horne), Quemont, Lake Dufault, all of which are primarily copper-gold and zinc producers, and the Wasamac, which is a gold producer. However, since Horne's discovery almost 30 mines have produced over 1,800,000 tons of copper, 700,000 tons of zinc and 12,000,000 ounces of gold as well as significant amounts of pyrite, silver, tellurium, selenium and cadmium (Spence, 1967).

PREVIOUS WORK

The initial reports on the Noranda area were produced by Wilson (1908, 1910, 1913) and Cooke, James and Mawdsley (1931). The most comprehensive report is Wilson's (1941) memoir. Further reports by several writers including Wilson (1948, 1962) and Robinson (1951) added to the general knowledge of the Noranda

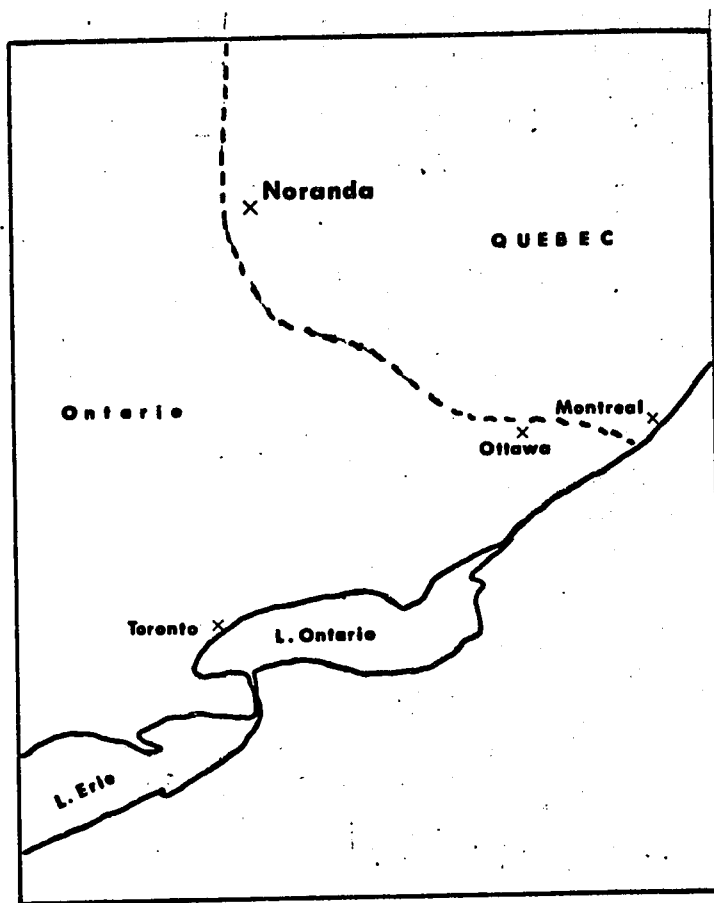


Figure 1 Noranda location map

district. Gill and Schindler (1932), Price (1933, 1934, 1948, 1949), Denis (1933), Schindler (1934), Hall (1939), Hawley (1948), Price and Bancroft (1948), Suffel (1948), Riddell (1952), Taylor (1957) and Campbell (1962, 1963) published more detailed accounts of the massive sulphide occurrences and their surrounding environments. The above authors when discussing the genesis of the massive sulphides relied strongly on an epigenetic massive hydrothermal replacement theory.

More recently many authors such as Dugas and Hogg (1962), Gilmour (1965), Goodwin (1965), Roscoe (1965), Dugas (1966), Sharpe (1967) and Spence (1967) when discussing the Noranda area are inclined to use a syngenetic model to explain the emplacement of the massive sulphides. These more recent authors have directly or indirectly used as guides the theories proposed by Oftedahl (1958) and Stanton (1960). Individual mine studies by Lickus (1965), Johnson (1966), Sakrison (1966) and Boldy (1968) support the contemporaneous stratabound theories for the emplacement of the massive ore.

REGIONAL GEOLOGY

The Noranda area lies within one of the classic Archean greenstone belts of the Canadian Shield. Various authors differ on the actual extent of the belt. Goodwin (1965) suggests that the belt extends for 175 miles from Timmins on the west to about 60 miles east of Noranda and contains the three mining camps of

Porcupine, Kirkland Lake and Noranda. He would have each of the three mining camps as a distinct mineralized volcanic complex about 25 miles in diameter within the greenstone belt as a whole.

A moderately high soda content and a distinctly low potash content (Sakrison, 1966), especially in the rocks of rhyolitic composition in the Noranda area, suggest that the rocks do not belong to the alkaline or spilite suites but rather to the basalt-andesite-rhyolite association typical of continental and island arc areas (Wilson, 1965). Engel (1965) proposes that the potash deficient rhyolitic suite is one of the end products of an extreme differentiation of a relatively uncontaminated oceanic tholeiitic magma.

The succession in ascending order of the Noranda type volcanic complex after Goodwin (1965):

- 1) 10,000-30,000 feet of mafic to intermediate flows and pyroclastics with minor felsic flows.
- 2) 5,000 - 10,000 feet of felsic flows and fragmentals with substantial but decreasing proportions of mafic extrusives;
- 3) 2,000 - 10,000 feet of predominantly felsic pyroclastics; and finally,
- 4) 2,000 - 6,000 feet of greywacks, shale and conglomerate with subordinate amounts of intercalated volcanic rocks.

The predominant structural features of this greenstone belt are the complex anticlinal structures at Porcupine, Kirkland Lake and Noranda separated by synclinal structures.

LOCAL GEOLOGY

The geology of the Noranda area has been described and discussed at great length by many authors. It is not the purpose of this study to reiterate many of the details of these descriptions and discussions but rather to review briefly the general aspects.

Volcanic Rocks

The volcanic rocks of the Noranda area very closely follow the model suggested by Goodwin (1965). They appear to be an extension of the Blake River group proposed by Gunning (1941). Extrusive rocks of basaltic to dacitic composition intercalated with lesser amounts of rhyolitic material make up the bulk of the non-intrusive rocks in the central and northern portions of the Noranda area (Figure 2 - in pocket).

The felsic flows which are locally termed rhyolites are actually for the most part acid pyroclastics. True rhyolite lavas are relatively scarce and of a very limited nature. The rhyolitic material is relatively thin, although local thickenings do occur, with respect to their areal extent. Recently Spence (1967) has subdivided the "rhyolites" into five successive periods of volcanic activity in which the massive sulphide ores occur in the third and fourth periods. The lenticular nature of the pyroclastics suggests a fissure type origin although a limited number of circular structures have been identified.

The basaltic to dacitic flows, locally termed andesites, are usually quite uniform and can be correlated with more ease

and certainty than the more acid units. The intermediate to basic units may be massive or pillowed. The pillowed nature of many of the "andesites" and the scarcity of vesiculation as well as the layering in the pyroclastic units indicate at least a partial subaqueous environment for the deposition of the extrusive rocks.

Intrusive Rocks

Approximately 25 percent of the Noranda area is underlain by granite and granodiorite occurring in three large masses. These are the Flavrian and Powell granites and the Lake Dufault granodiorite (Fig. 2). These large acid intrusives show crosscutting characteristics and are outward dipping (Spence, 1967). The two granites have identical compositions and are chemically similar to the rhyolites they cut. (Sakrison, 1966). Lickus (1965) analysed a dacite at the Vauze mine and found that it had the same chemical composition as the Lake Dufault granodiorite. These analyses support the contention of a definite relationship between the intrusives and the surrounding volcanics.

An extensive diorite to gabbro dyke and sill system occurs around the Flavrian and Powell masses. The steep dips in the dyke portion of the system lie along faults and are possibly the reflection of large fractures caused by the subsidence in the area of the granite masses (Sakrison, 1966).

Keweenaw diabase dykes cut all the volcanics, intrusives, and sediments of the Noranda area. As with the steeply dipping diorite dykes, the diabases represent the location of pre-existing faults.

Sedimentary Rocks

The southern portion of the Noranda area is overlain by sedimentary rocks that consist mainly of conglomerates and greywackes. Although separated from the volcanics by an unconformity and in places by a major east-west fault, these sedimentary rocks appear to be generally conformable with the underlying volcanics to the north. They are thought of as an extension of the Cadillac group to the east (Gunning and Ambrose, 1941) and would correspond to the top of Goodwin's (1965) succession.

The Pontiac group to the south underlies the Cadillac group and is separated from it by an unconformity. The Pontiac group which can be traced from Larder to Malartic is composed mainly of mica schist and amphibolites with minor volcanics.

In Beauchastel township the Black River, Cadillac, and Pontiac groups are all unconformably overlain by a younger series of Cobalt sediments.

Structure

The Noranda area lies in the center of what Goodwin (1965) has termed a doubly plunging complex anticline and Spence (1967) has termed a large anticlinorium. The axis of this complex fold system is east-west. The three large acidic intrusives in the central region of the Noranda area form the core of this structure.

A major fault, the Cadillac-Bouzan Break, striking east-west passes through the southern part of the area. This fault can be traced for about 100 miles from Larder Lake east to

Malartic. In the Noranda area it is located on and near the contact of the Cadillac and the Blake River groups.

Additional faulting is widespread but on a much smaller scale. In the volcanics there are three major trends: northeast, north-south and northwest.

ORE DEPOSITS

Gold Deposits

The gold deposits of the Noranda area are of epigenetic origin. They occur in shear zones or fracture zones and are associated with quartz veins, silicified and/or carbonated zones. The host rock may be an intrusive, volcanic or sedimentary rock.

Production figures are given in Table 1 and the distribution of deposits shown in Figure 2.

Base Metal Deposits

Description

It is the massive sulphide ore zones that have made Noranda one of the classic mining areas in North America. Various ore zones have been described by many authors, however, Roscoe (1965) proposed a model (Figure 3) for the "Noranda type" massive sulphide deposit that fits very well although in certain situations minor adjustments must be made. The massive ore lenses have major and

TABLE 1

PRODUCTION FROM MINES IN NORANDA AREA

Base Metal and Gold Mines

Property	Years	Tons	Copper Tons	Zinc Tons	Gold Ozs.	Silver Ozs.	Remarks
Base Metal and Gold Mines							
Aldermac	1931-43	2,057,101	30,845	-	10,750	389,100	
D'Eldona	1950-52	90,000	14	4,542	10,990	68,645	
Home *	1927-66	52,633,600	1,150,590	-	8,012,820	-	
Joliet *	1949-66	896,400	-	-	-	-	flux ore
Lake Dufault*	1964-66	1,076,500	54,446	74,042	34,631	1,946,329	
Queмонт *	1949-66	13,508,900	170,992	251,838	1,747,000	7,068,000	
Vauze	1961-65	385,000	11,150	3,600	7,435	266,600	
Waite Amulet	1930-62	9,658,000	404,009	352,921	261,448	7,692,690	
A		(5,872,000					
B, C, D, E, Bluff		(596,000					
F		(290,000					
Old Waite		(1,245,000					
East Waite		(1,655,000					
West MacDon-							
ald	1955-59	1,030,000	125	30,000	2,000	5,300	estimated
Gold Mines							
Anglo Rouyn	1948-51	145,708	-	-	34,192	-	
Arntfield	1935-42	529,989	-	-	55,662	-	
Donalds	1948-56	694,752	-	-	113,669	-	
Elder	1947-66	2,375,485	-	-	348,338	-	flux ore
Eldrich	1955-62	717,655	-	-	99,890	-	flux ore
Francoeur	1938-47	572,152	-	-	92,589	-	
Granada	1930-35	181,744	-	-	51,447	-	
McWatters	1934-44	356,609	-	-	108,317	-	
New Marlon	1947-49	108,188	-	-	19,170	-	
New-Senator							
Rouyn	1940-55	1,739,798	-	-	235,969	-	
Powell-Rouyn	1938-56	3,084,647	-	-	351,790	-	
Quesabe	1949-52	98,182	-	-	30,000	-	ozs. estimated
Stadacona	1936-58	3,023,400	-	-	465,956	-	
Wasamac *	1965-66	651,761	-	-	80,682	-	

95,615,571 1,822,171 716,943 12,174,745

*Current Producer

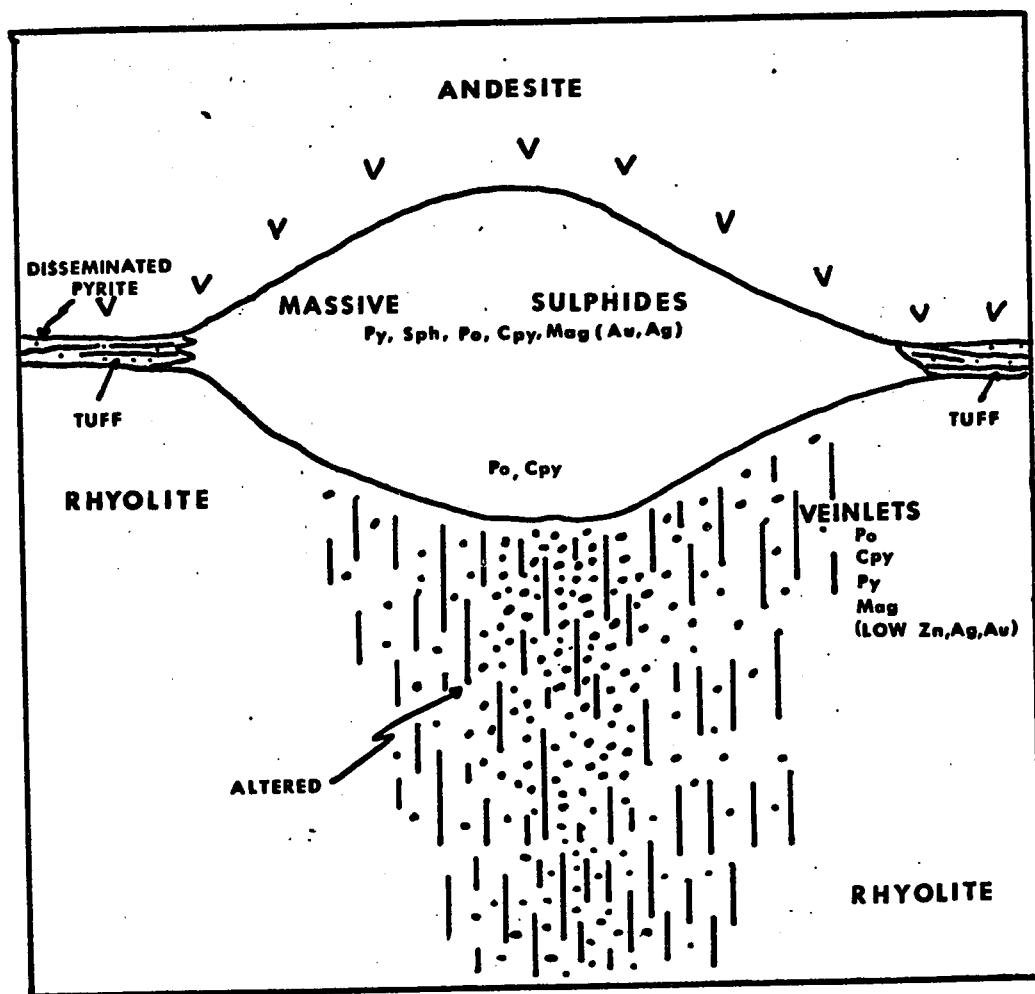


Figure 3 Features common to many Noranda-area sulphide deposits
(After Roscoe, 1965)

intermediate axes that are concordant with the enclosing rocks. On the footwall side and normal to the massive lenses are the mineralized alteration pipes.

The gross aspects of the mineralogy of the massive sulphide lenses are relatively simple. The four major sulphide minerals in order of decreasing abundance are pyrite, pyrrhotite, sphalerite and chalcopyrite. Magnetite is usually present. In addition to the major sulphide minerals many other metallic minerals have been identified. These include: bornite, linnaeite, (Lickus, 1965 - Vauze Mine); gold and many assorted tellurides (Price, 1948 - Horne Mine); galena, argentian tetrahedrite, native silver, arsenopyrite and electrum (Boldy, 1968 - Delbridge); argentite, chalcocite, cubanite, dycrasite, mackinawite, neodigenite and stannite (Johnson, 1966 - Lake Dufault Mine).

The massive sulphide lenses may be classified into two mineralogical and economic groups. The mineralogical classification is 1) pyrite - sphalerite ore and 2) pyrite - chalcopyrite - pyrrhotite ore with or without sphalerite. The northern group, which includes the mines from the old Amulet to the Vauze, are the richest zinc - copper masses with average grades between \$30.50 and \$46.14 per ton (Sharpe, 1967). The southern group containing the Horne, Quemont, Delbridge deposits which are considerably richer in gold and silver (the major northern mines assay 0.015 to 0.053 ounces gold per ton while the southern mines average 0.165 ounces of gold per ton) but do not have as high copper values and an over all grade between \$19.00 and \$21.30 per ton (Sharpe, 1967).

A definite copper and zinc zoning has been recognized in the massive sulphide lenses (Roscoe, 1965; Johnson, 1966; and Sakrison, 1966). Sphalerite tends to be concentrated at the top and the edges of the massive sulphide lens. Chalcopyrite tends to be concentrated in the footwall portions.

Alteration Associated With the Massive Sulphides

Alteration associated with the Noranda massive sulphide deposits has been discussed by many authors. The most comprehensive treatment has been the work of Riddell (1952). More recent work by Lickus (1965) on the Vauze mine area and by Sakrison on the Lake Dufault mine host rocks have contributed substantially to the chemical knowledge of the Noranda area.

The alteration associated with the massive sulphide ore bodies is confined mainly to the stratigraphic footwall portion of the rocks around the ore zones. Hanging wall alteration when present is very irregular and is usually confined to the base of the unit which may or may not be contaminated with the ore zone elements (Sakrison, 1966).

The footwall alteration can be one of two styles. The ore lenses in the northern portion of the area, which include the ore bodies from the Amulet to the Vauze, are characterized by a distinct fractured pipe-like alteration zone normal to the stratigraphic sequence. Under several lenses this pipe-like zone has been traced down for many hundreds of feet. This pipe-like zone, locally termed "Dalmatianite", is a reflection of magnesium

and iron metasomatism. It is identified as a mineral zoning from the center outwards of: anthophyllite (gedrite) - biotite; cordierite - anthophyllite (gedrite) - biotite; cordierite - biotite; and finally biotite. In some of the mines limited portions of the alteration pipes contain sufficient amounts of chalcopyrite in the fractures that mining becomes feasible. The intensity and the size of the fractures decrease going away from the massive lenses.

The alteration associated with the southern ore zones, although chemically similar to the "Dalmatianite" pipes is mainly a chlorite - sericite type zone (Riddell, 1952). The chlorite - sericite zones are associated with ore zones that have a somewhat lower copper content and are primarily massive pyrite and sphalerite bodies.

Stratigraphic Location

The ore deposits in the Noranda area occur on or very close to lithologic contacts and with one exception, the Amulet Upper 'A', the footwall is a felsic pyroclastic unit. The stratigraphic location of the massive sulphides can, as in the case with the sulphide mineralogy and the associated footwall alteration, be broken down into very similar although somewhat differing situations.

The southern group lie within felsic pyroclastic sequences. In the case of the Noranda and Quemont ore zones, the hanging wall

has been identified as a massive "rhyolite", whereas at Delbridge it is a coarse rhyolite breccia. Correlation in the southern area is quite difficult because of extensive faulting. Whether or not the ore zones lie on or close to the same stratigraphic horizon is a difficult point to make, however the distinct possibility is mentioned by Dugas (1966).

The stratigraphy of the Amulet - Vauze area has been tentatively worked out by several workers. The most recent interpretations are by Edwards (1960), Dugas and Hogg (1962), Gilmour (1965), Dugas (1966), and Spence (1967). A generalized model is given in Figure 4 (after Gilmour, 1965).

With the exception of the Amulet Upper 'A' orebody all of the massive sulphide lenses lie on the top of locally thickened felsic pyroclastics. The hanging wall in each case is andesite. Separating the two distinct units is a thin cherty horizon, which usually thickens when approaching ore. It is not unusual for the footwall pyroclastics to contain sulphide fragments. Sakrison (1966) and Lickus (1965) noticed increased metal content in both the cherty tuff and the footwall pyroclastics when approaching ore.

Similarities Between the Massive Sulphide Deposits

Each base metal deposit in the Noranda area has many features that are common to the other deposits. These features are listed as follows:

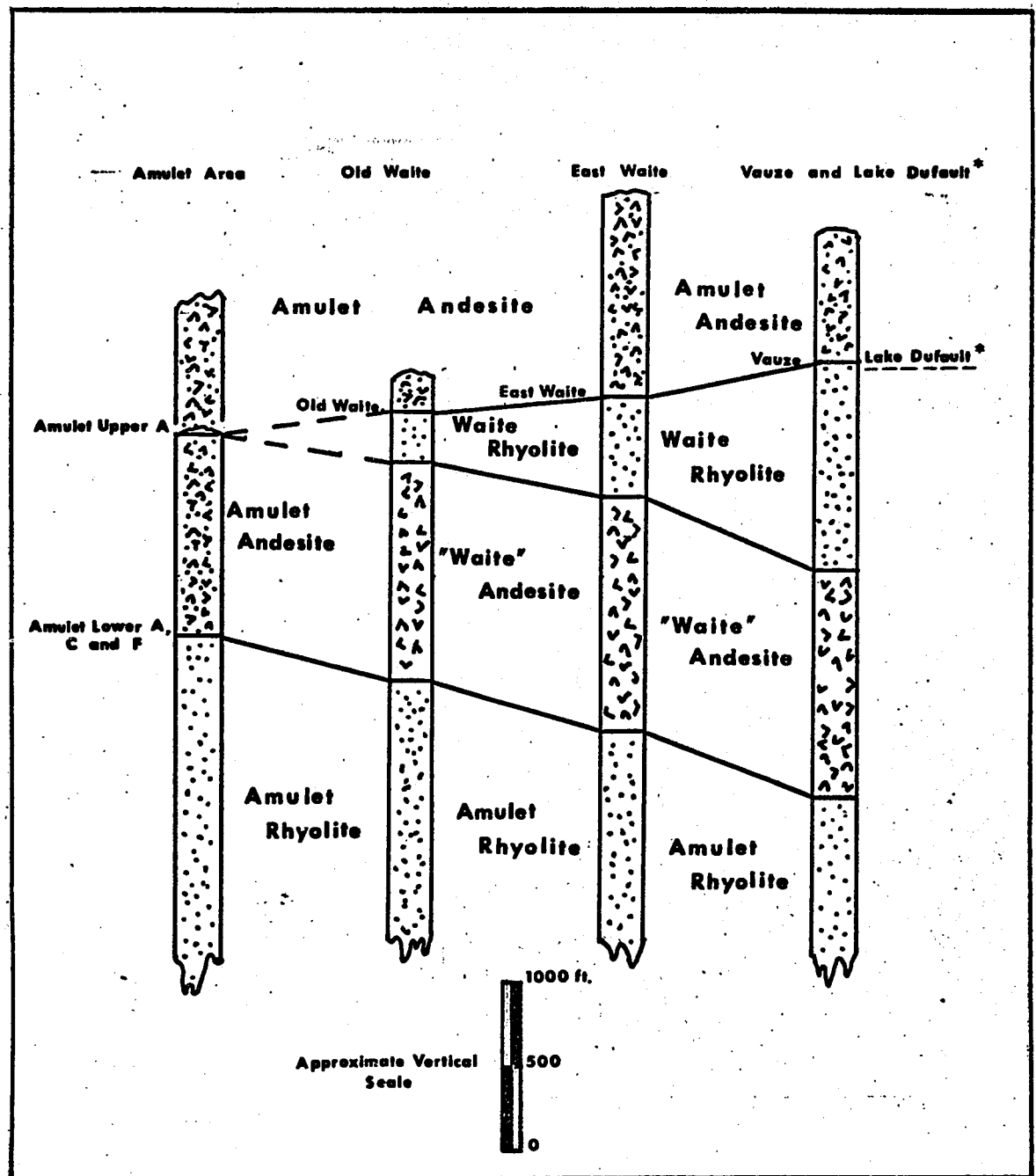


Figure 4 Generalized stratigraphic sections of the rocks in the vicinity of the massive sulphide deposits of Waite-Amulet and Vauze Mines, Ltd. (After Gilmour, 1965)

Beaton

- 1) all the massive sulphide ore lenses occur in volcanic rocks;
- 2) the footwall rocks are breccias, most commonly felsic breccias;
- 3) the orebodies occur at lithologic contacts;
- 4) the orebodies show very little hangingwall alteration that can be attributed to the ore;
- 5) the orebodies are quite commonly associated with thin mineralized laminated cherts that thicken when approaching ore;
- 6) the majority of the orebodies are located on the flanks or top of coarse "rhyolitic" pyroclastic domes;
- 7) a mineral zoning occurs within single orebodies and within groups or clusters of orebodies, chalcopyrite is more abundant at the stratigraphic bottom and sphalerite is more abundant at the stratigraphic top;
- 8) a banding, which is conformable to the hangingwall contact, between pyrite and sphalerite is found at the top of some of the ore zones;
- 9) all of the orebodies lie within 3 miles of a sizable intrusion of granite or granodiorite, most within one mile;
- 10) the orebodies are tabular and conformable with the enclosing rocks; and
- 11) the massive sulphides are located at the top of fractured pipe - shaped zones of alteration.

Genesis of the Massive Sulphide Deposits

The features enumerated in the previous section suggest a similar origin for the base metal deposits in the Noranda area. At the present time there are two distinct interpretations of the series of events relating the time and method of emplacement of the sulphides in the geological sequence at Noranda.

Until recently the interpretation was generally agreed to have been that the orebodies were the result of epigenetic replacement of a favourable horizon by deep seated solutions of unknown origin. Many of the proponents of the epigenetic model differ quite widely on the actual time of emplacement of the sulphides (Hodge, 1967). Campbell (1962) and Ryznar, Campbell and Krouse (1967) list the following sequence of events:

- 1) deposition of non-porphyritic rhyolite breccia and rhyolite;
- 2) deposition of porphyritic rhyolite and andesite;
- 3) folding of volcanics, then fracturing and minor faulting;
- 4) sericitic and chloritic alteration of the fracture zones;
- 5) sulphide ores emplaced in the fracture zones;
- 6) some movement along fault zones;
- 7) intrusion of diorites;
- 8) granite bodies emplaced and may have remobilized sulphides in places;
- 9) diabase intrusion; and
- 10) movement on faults which displaced diorite dykes.

Campbell (1963) gives the paragenetic sequence as pyrite, pyrrhotite, sphalerite and finally chalcopyrite. He does not believe this to be a sequence of introduction but rather an apparent order of deposition from a melt.

Hodge (1967), in a discussion on the theories of ore deposition in the Horne mine, summed up the epigenetic position as follows:

"Deposition took place along lithologic and intrusive contacts which acted as solution barriers. Faulting and shearing controlled the localization of these solutions. Mineralization was in three separate stages. First pyrite with sphalerite was deposited. This was followed by a period of magnetite - pyrrhotite - chalcopyrite, and finally a late period of gold associated tellurides. The second and third stages of mineralization are considered very late, probably later than the late Keweenaw diabase dykes".

Recently an alternative theory has gained many supporters (see Hutchinson, 1965, Roscoe, 1965, Sakrison, 1966 and Boldy, 1968). This theory has been variously described as syngenetic, volcanogenic, stratabound and sedimentary exhalative. Proponents of this approach relate the deposition of the sulphides to a particular cycle of acid volcanic activity. The ore is envisaged as having been deposited from epithermal or fumarolic solutions under the influence of a steep pressure - temperature gradient at or very near to the existing surface. All hangingwall rocks would then be post ore deposition. Faulting, folding and any intrusions that

cut ore and/or hangingwall rocks would be post ore. Because of pillowed lavas and layering in the tuffs and cherts associated with the ore as well as the layered sequence in the upper portions of some of the massive lenses deposition is thought to have taken place under water.

Comparable Occurrences

The "Noranda type" massive sulphide association is recognized in many different places in rocks ranging in age from Precambrian to recent. Massive sulphide lenses with very similar volcanic conditions occur at such places as: Timmins, Mattagami, Bathurst, Buch^aans, Manitou^{wd}age, North Coldstream, Snow Lake and Joutel in Canada; the Shasta and Jerome areas in the United States; Rio Tinto in Spain; pyrite deposits of Cyprus; "kuroko" type in Japan; and the Caledonides in Norway and Sweden. (see Hutchinson, 1965; Roberts, 1966; Sakrison, 1966).

CHAPTER II

LAKE DUFAULT MINE AREA

INTRODUCTION

The company, Lake Dufault Mines Limited, has an extensive holding in the Noranda area comprising 6,708 acres of ground which lie in Dufresnoy, Duprat, Beauchastel and Rouyn townships. The property can be broken down into two areas, one south and one north of the Dufault granodiorite. The northern area, referred to as the Norbec area, contains the mine area of interest in this study. This area consists of three faulted blocks of andesite and rhyolite. The Lake Dufault orebody is located in the central block.

The massive sulphide ore lens was discovered in September 1961 by surface diamond drilling. Subsequent diamond drilling and underground development proved up an orebody containing 2,369,000 tons of massive and stringer ore grading 4% Cu, 7.2% Zn, 2.2 oz/ton Ag and 0.03 oz/ton Au (Purdie, 1967). Full production at a rate of 1300 tons per day began in October, 1964.

PREVIOUS WORK

The Lake Dufault ore zone and the associated host rocks have already received a substantial amount of attention. Johnson (1966)

comprehensively compiled information on the mineralogy and the textural relationships of the ore. Sakrison (1966) extensively studied the chemistry of the host rocks in the Norbec area concentrating mainly on the alteration attributable to the sulphides. Both of the above studies explore the genetic implications encountered in the course of their work and strongly support the syngenetic model.

Roscoe (1965) has published data on trace element content in the massive sulphides and lead isotope measurements. His model (Figure 3) of the Noranda type of massive sulphide occurrence is based on the geometry of the Lake Dufault orebody. He used this as a model because very little has happened to it compared with several other known occurrences which appear to have been folded, faulted and/or intruded by later dykes and sills.

Purdie (1967) described the general geology, the structure and mineralogy of the orebody, wallrock alteration, and the genetic sequence of events.

GEOLOGICAL SETTING

Stratigraphy

The Lake Dufault orebody lies on the contact between the Waite rhyolite and the Amulet andesite. The orebodies of the Old Waite, East Waite and Vauze mines (Figure 4) lie on the same contact. These two units lie within what Edwards (1960) termed the Mine

Series which consists of the Amulet andesite, the Waite rhyolite, the Waite andesite and the oldest unit the Amulet rhyolite.

Purdie (1967) lists the sequence in the Lake Dufault mine area as follows:

Amulet andesite (1600'+)	pillowed and massive lavas; occasional thin tuff beds.
Brown tuff (2' - 10')	massive to bedded tuff with banded chert at the base; local thin bands or lenses of sulphides in the chert.
Waite rhyolite (500')	assemblage of siliceous pyroclastic breccia, tuff, rhyolitic flow rock. (Ignimbrite sheet?)
Norbec andesite (150' - 500')	pillowed massive andesitic to dacitic lavas similar to the Waite andesite types. (Upper Waite andesite?)
Norbec rhyolite (50' - 400')	siliceous pyroclastic breccia; tuff; agglomerate. Similar in part to the Waite rhyolite. (Lower Waite rhyolite?)
Transition Zone (150' - 200')	mafic lavas intercalated with agglomerate.
Waite andesite (2500'+)	pillowed massive andesitic to dacitic lavas.

Amulet Andesite

This unit forms the hangingwall of the orebody. It has massive, pillowed and amygdaloidal sections. Sakrison (1966) describes three types of alteration occurring throughout the unit. He did not find any systematic alteration that he could ascribe to the massive ore. His analyses show high cobalt and normal nickel in the Amulet andesite compared to world averages (Figure 5).

Brown Tuff

The Brown tuff separates the Amulet andesite from the Waite rhyolite in the mine area. It thickens as it approaches the massive sulphide lens. The unit is characterized by many thin alternating layers of light to dark grey chert and green chlorite. Thin layers of sulphides, mainly pyrite and pyrrhotite with minor chalcopyrite and sphalerite are common.

Waite Rhyolite

The Waite rhyolite which consists of a sequence of felsic pyroclastics including breccia, tuffs, and agglomerate forms the footwall of the massive lens. Sakrison when discussing the chemistry of the host rocks and especially the Waite rhyolite observes that Noranda area rocks are potassium deficient. This deficiency is consistent with identical situations in Mattagami, Buchans, North Coldstream, Shasta and Jerome. Young volcanic

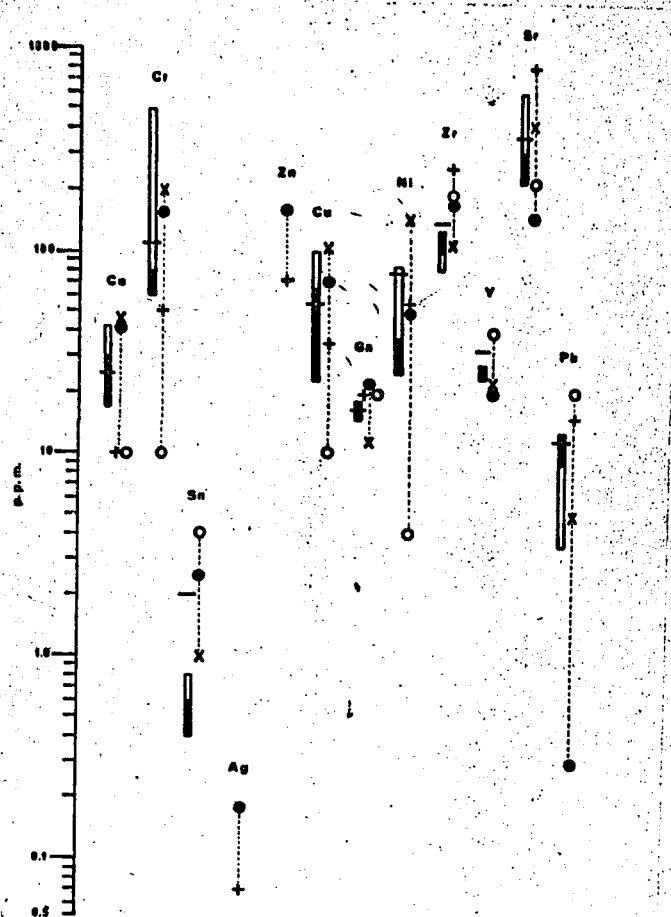


Figure 5 . COMPARISON OF THE TRACE ELEMENT COMPOSITION OF ANDESITES, BASALT, GRANITE AND CONTINENTAL CRUST. Filled rectangles, andesite from Japan and New Zealand; unfilled rectangles, mafic andesite from Japan and New Zealand; \bigcirc , Amulet andesite; +, Vinogradov's (1962) average andesite and intermediate rock; \bigcirc , granite; X, basalt; -, continental crust (after Taylor and White, 1965).

Analyses of New Zealand and Japanese andesite are by Taylor and White (1965).

The data for granite and basalt were compiled by Taylor and White from Daly (1933), Kolbe (1965)¹ and Turekian and Wedepohl (1961).

The data for continental crust are based on a 1:1 ratio of mafic and siliceous rocks and were compiled by Taylor and White from Poldervaart (1955), Taylor (1964).

1. Kolbe, P., Ph.D. thesis, Australian National University, 1965.

suites with potassium deficiencies are virtually restricted to the Circum-Pacific region, most notably on the ocean side of island arcs (Sakrison, 1966).

The "Dalmatianite" pipe is found in this unit directly under and normal to the massive sulphide lens.

Compared to world averages the Waite rhyolite contains low amounts of cobalt and nickel (Figure 6). Sakrison observes that small amounts of these metals have been added to the top of the Waite rhyolite.

Structure

The rocks of the Lake Dufault mine area show very little evidence of deformation. Evidence of folding has not been observed. The only major structures are large northwest striking steep faults which have been intruded by diorite dykes (Figure 2). No tilting of the fault blocks has been observed (Sarkison, 1966). The volcanics strike north and dip 30 degrees to the west.

In the immediate area of the orebody two low angle thrust faults have been identified. Both show quite small offsets somewhere in the order of 100 feet (Purdie, 1967, personal communication).

OREBODY

Structure

The Lake Dufault orebody may be divided into two parts,

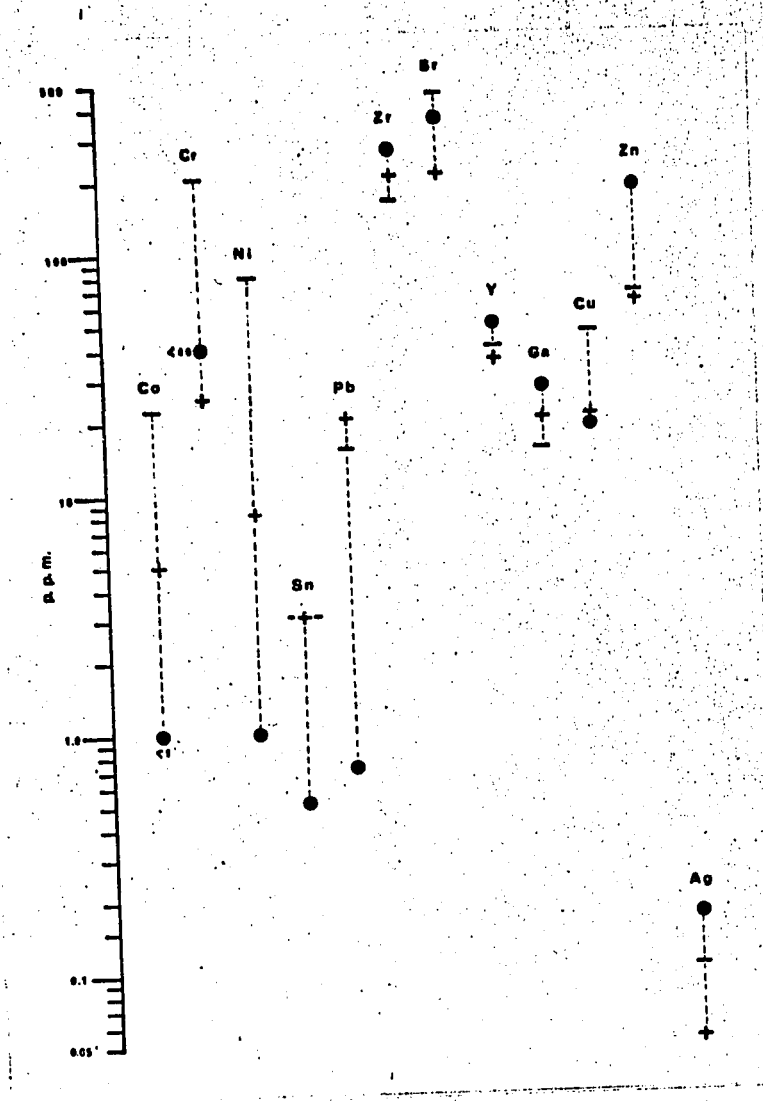
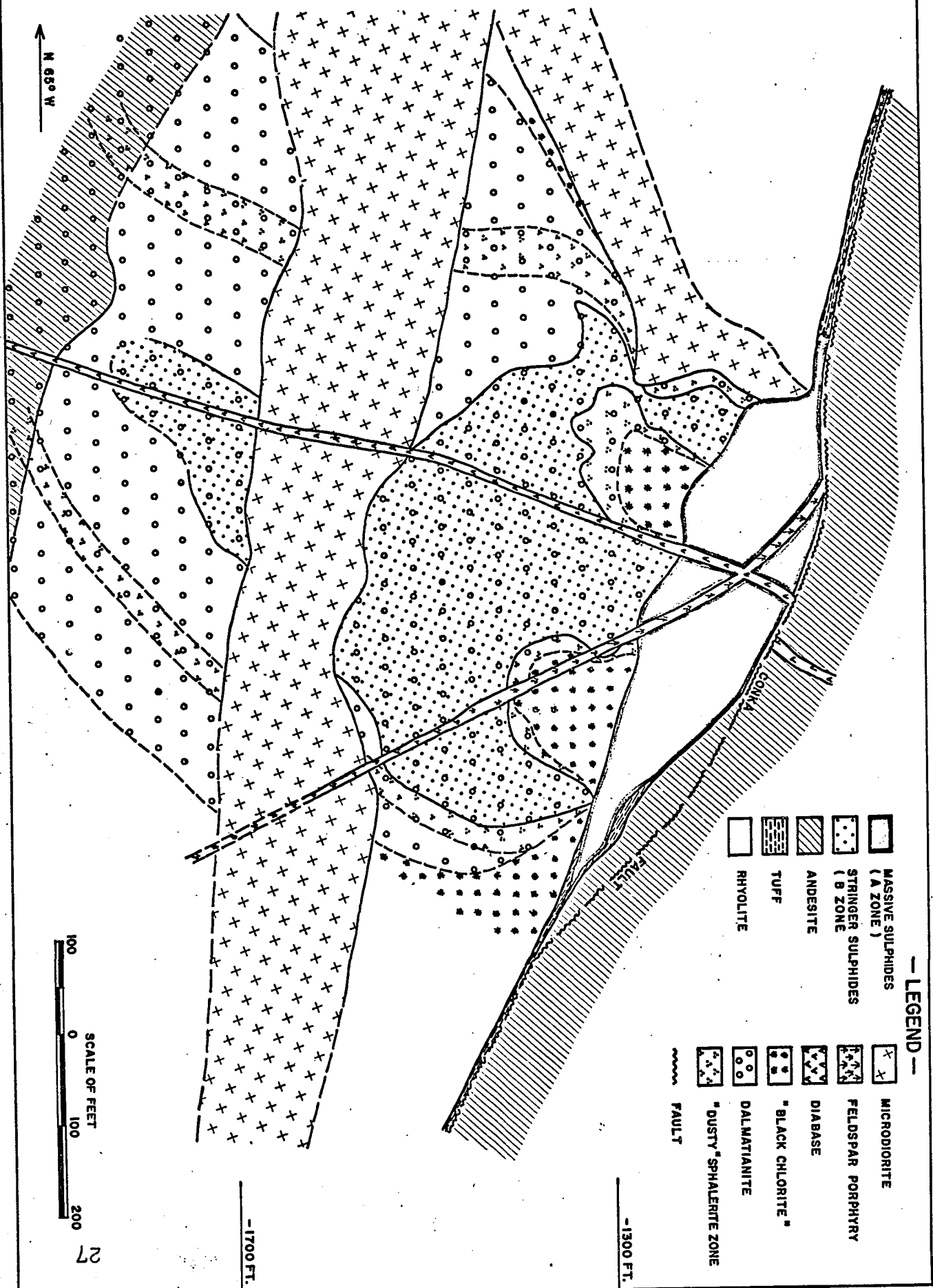


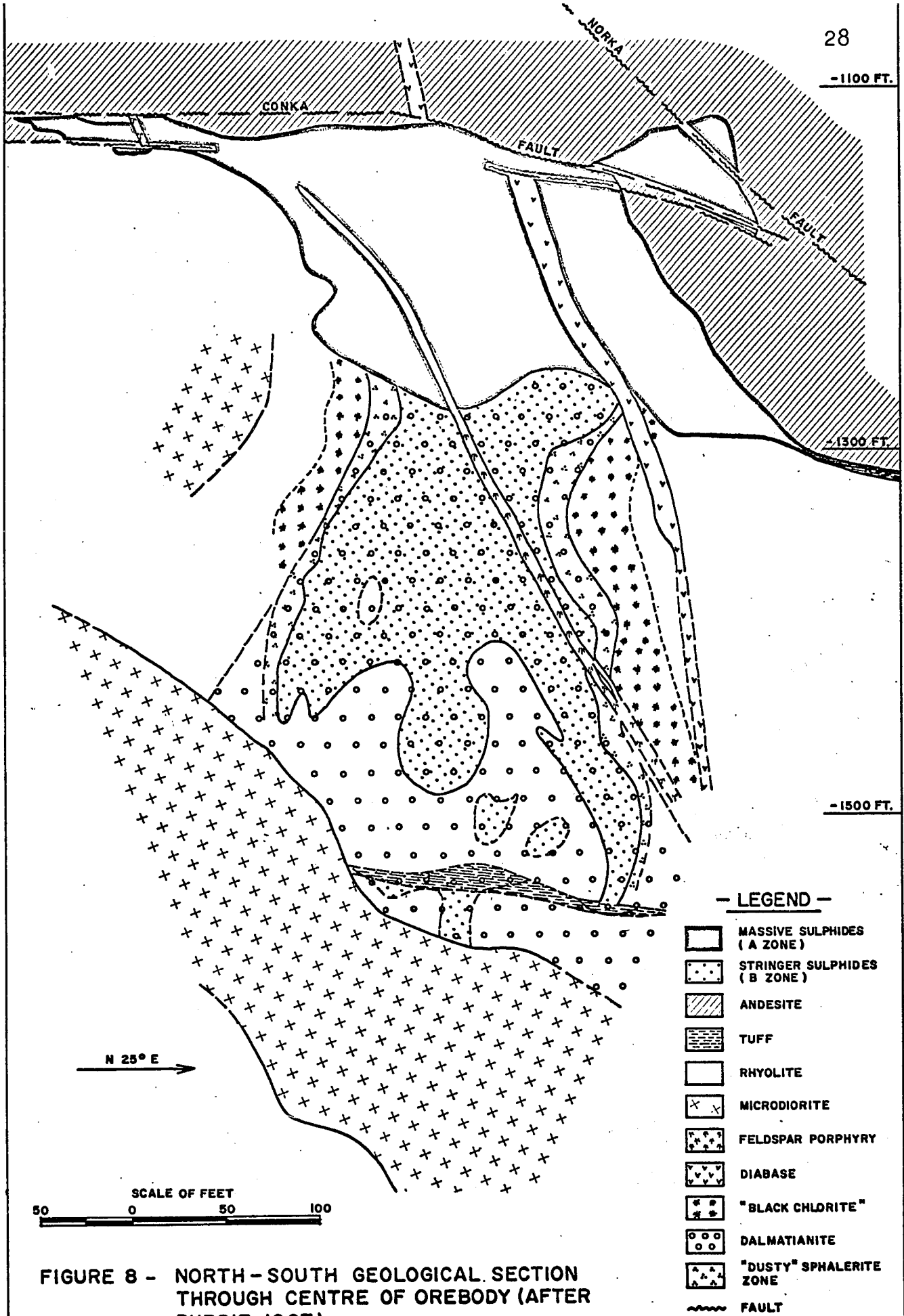
Figure 6 . COMPARISON OF THE WAITE RHYOLITE WITH THE CONTINENTAL CRUST AND THE AVERAGE FELSIC ROCK. ●, Waite rhyolite; +, average felsic rock; -, continental crust.

The data for the average felsic rock are from Vinogradov (1962).

The data for continental crust are based on a 1:1 ratio of mafic and siliceous rock and are from Mason (1960) (cf. figs. 9 and 11).

FIGURE 7 - GENERALIZED EAST-WEST SECTION (AFTER PURDIE 1967) -





the massive sulphide lens referred to as the 'A' zone and the underlying fracture zone referred to as the 'B' zone. The relative positions of the two zones are shown in Figures 7 and 8.

The 'A' zone is a conformable lens 650 feet long by 400 feet wide with a thickness that varies from 5 feet on the edges to 150 feet in the central portion. The flanks of the lens grade very rapidly into the Brown tuff and the edge of the lens is sheathed in the chert unit.

The 'B' zone, which is situated in the central portion of the "Dalmatianite" pipe (Figure 7), has a roughly oval shape. In plan the long axis, 650 feet, coincides with the long axis of the 'A' zone both of which strike north 65 degrees west. The 'B' zone is 250 feet wide and is connected to the 'A' zone by three chalcopyrite - pyrite filled stringer pipes located on the long axis. The middle pipe, the largest, has a diameter of 100 feet (Purdie, 1967).

Mineralogy

The massive 'A' zone as appraised by the Lake Dufault staff contains 30 percent pyrite, 20 percent sphalerite, 15 percent chalcopyrite, 11 percent pyrrhotite, 20 percent disseminated silicate and carbonate gangue and 4 percent magnetite. Johnson (1966) differs somewhat in his estimates of the relative abundance of the major sulphides and although he does not assign specific percentages he lists the sulphides in decreasing order of abundance as pyrite, pyrrhotite, sphalerite and chalcopyrite.

Johnson (1966) identifies 17 metallic minerals (Table 2) which include two types of pyrite and three types of pyrrhotite. The differentiation of the types of pyrite and pyrrhotite is based on etching characteristics and not on X-ray patterns or chemical determinations. The present study encountered cobalt sulphides and one unidentified nickel occurrence which are discussed in a later section.

Distribution of the Major Sulphides

Massive Sulphide Lens

The four major sulphides which are pyrite, pyrrhotite, chalcopyrite, and sphalerite occur throughout the massive 'A' zone but exhibit a distinct zoning characteristic.

Pyrite - The abundance of pyrite relative to that of chalcopyrite and pyrrhotite increases upwards and towards the periphery of the 'A' zone.

Sphalerite - The abundance of sphalerite to that of chalcopyrite and pyrrhotite parallels that of pyrite as it also increases upwards and outwards.

Chalcopyrite - The abundance of chalcopyrite relative to pyrite and sphalerite increases with depth and towards the central portion of the base. There exists what is locally referred to as a "copper keel" at the base of the middle of the 'A' zone and assays of up to 28 percent copper are not unusual in this area.

TABLE 2
MINERALOGY

<u>Mineral Name</u>	<u>Composition</u>	<u>Abundance</u>
Argentite	Ag_2S	X
Chalcocite	Cu_2S	X
Chalcopyrite	CuFeS_2	XXX
Cubanite	CuFe_2S_3	X
Dycrasite	Ag_3Sb	X
Galena	PbS	X
Mackinawite	FeS_2	X
Neodigenite ^(a)	$\text{Cu}_{(2-x)}\text{S}$	X
Pyrite 1	FeS_2	XX
Pyrite 11	FeS_2	XXX
Pyrrhotite 1 ^(b)	$\text{Fe}_{(1-x)}\text{S}$	XXX
Pyrrhotite 11 ^(b)	$\text{Fe}_{(1-x)}\text{S}$	XXX
Pyrrhotite 111 ^(b)	$\text{Fe}_{(1-x)}\text{S}$	XX
Sphalerite	Zn(Fe)S	XXX
Silver antimonial	Ag(Sb)	X
Stannite	$\text{Cu}_2\text{FeSnS}_4$	X

XXX - major XX - minor X - trace

(a) identification inferred

(b) Fe/S ration not determined but three distinct types

Distinguished. Po 111 may just be a subtype of Po 11

(after Johnson, 1966)

Pyrrhotite - The abundance relative to pyrite and sphalerite increases towards the base of footwall.

Alteration Pipe

The alteration pipe also exhibits a mineral zoning. The 'B' zone has chalcopyrite as the major disseminated sulphide with minor pyrite and pyrrhotite and no sphalerite. However, outside of the 'B' zone there is a 20 foot zone locally called the "dusty sphalerite zone" that contains very finely disseminated sphalerite and pyrite (Figures 8 & 7).

CHAPTER III

COBALT AND NICKEL AS TRACE ELEMENTS

INTRODUCTION

Trace elements occur in minerals in several ways. They may be incorporated by surface adsorption, in which case the foreign ions are held in a loose layer at the surface of the mineral because of attraction of surface atoms whose bonding requirements have not been completely satisfied. Trace elements may also occur as occlusions. In this instance impurities adsorbed at the mineral surface become trapped as additional layers grow on the crystal. This is a significant type of occurrence as it indicates that the mineral has grown rapidly or that there have been successive periods of mineralization (McIntire - 1963).

Solid solution provides another vehicle for the occurrence of trace elements in minerals. This situation may develop in two ways as well as a combination of both. The occurrence may be interstitial solid solution and/or diadochic substitution solid solution.

Trace elements may also occur as trace minerals exsolved during cooling.

TRACE COBALT AND NICKEL IN ROCKS

The presence of cobalt and nickel as trace elements in rocks has been confirmed by many workers, all of whom have noted

decreasing concentrations with increasing silica content. In the course of magmatic differentiation nickel is extracted from silicate melt much more rapidly than cobalt and thus cobalt appears to be relatively more concentrated in residual fluids (Wager and Mitchell, 1951; Curtis, 1964; Loftus-Hills and Solomon, 1967). Wilson (1953) states: "Like nickel, cobalt appears to decrease in amount progressively from ultra-basic to granitic rocks; the rate of decrease of cobalt, however, is very much less than that of nickel. In basic, intermediate and acid rocks the distribution of cobalt is actually closer to that of copper than to that of nickel."

As may be seen from Table 3, nickel is the most abundant of the two elements in rocks.

TABLE 3

Abundance of Cobalt and Nickel in Rocks

Source	Rock Type	Co ppm	Ni ppm
Turekian and Carr (1960)	Ultra-mafic	110	2,000
	Basaltic	48	130
	High-calcium granite	6	14
	Low-calcium granite	0.6	0.4
	Shales	19	71
	Sandstones	0.5	1
	Limestones	2	27
	Deep-sea carbonate	8	30
	Deep-sea clay	100	200
	Schists	40	114
Vinogradov (1962)	Stony meteorites	800	13,500
	Ultra-mafic rocks	200	2,000
	Mafic rocks	45	160
	Intermediate rocks	10	55
	Felsic rocks	5	8
	Sedimentary rocks	20	95
Taylor (1964)	Crustal average	25	75
	Basalt average	48	150
	Granite average	1	0.5
Shaw et al. (1967)	Overall average ¹⁾	21	23
	QF ²⁾ - Northern Quebec	8.7	20
Sakrison (1966)	Waite rhyolite	<1	7.8
	Amulet andesite	53.8	104
	Brown tuff	71.3	77.9

1) Precambrian Shield

2) Quartzofeldspathic rocks including granite, granite gneiss, pegmatites, rhyolite, arkose and sandstone.

COBALT AND NICKEL AS TRACE ELEMENTS IN SULPHIDES

Sulphide Structures

Pyrite

Pyrite crystallizes in the isometric system. It exhibits a modification of the NaCl structure which is referred to as the pyrites structure (Figure 9). The co-ordination is not 6:6 as it is in the normal NaCl structure. The S-S distance within the S_2 group is such that each iron atom is surrounded by six sulphur atoms at the corner of a nearly regular octahedron, while each sulphur atom is ^{bonded} to one other sulphur atom and to three iron atoms (Evans, 1964). The co-ordination is then 6:4.

The bravoite series, the end members of which are pyrite (FeS_2), cattierite (CoS_2) and vaesite (NiS_2), have the same structure throughout (Vaughan, 1969). It is important to note that the cations or metals all have six-fold or octahedral co-ordination.

Pyrrhotite

This mineral has a defect lattice structure which is iron deficient. The iron content varies and pyrrhotite can crystallize in both hexagonal and monoclinic forms. The monoclinic form is the most iron deficient. Berry and Mason (1959) say that pyrrhotite has the hexagonal closepacked structure (Figure 10). Each of the iron atoms is octahedrally co-ordinated by six sulphur atoms, whereas each sulphur atom is surrounded by six neighbouring iron atoms at the corner of a trigonal prism. As in

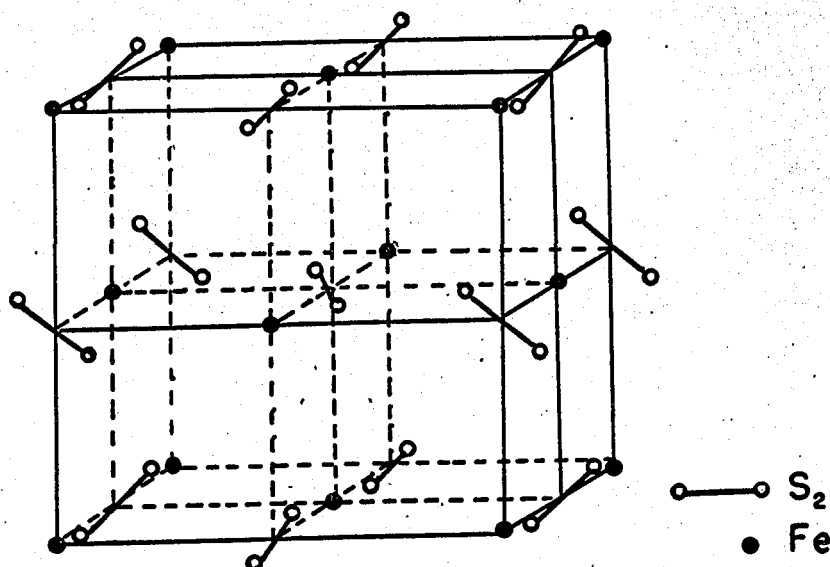


Figure 9 The pyrite (FeS_2) structure containing the dumbbell-shaped S_2^{--} anion. (After Fyfe, 1964, p.107)

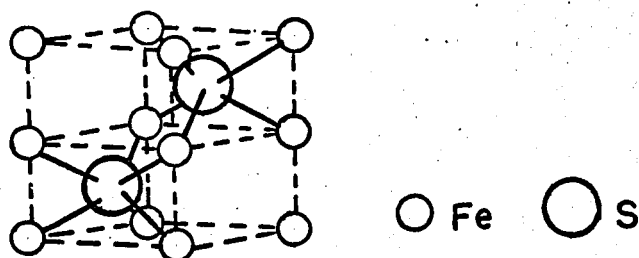


Figure 10 The nickel arsenide hexagonal closepacked structure (After Berry and Mason, 1959, p. 318)

the case of the bravoite series, FeS, CoS, and NiS all have the same structure (Evans, 1964).

Sphalerite

Sphalerite crystallizes in the isometric system. The lattice is a distinct structural type referred to as the zinc-blende structure (Figure 11). This is a cubic closepacked structure which exhibits tetragonal or 4:4 co-ordination. ZnS is polymorphous and thus may also occur in the hexagonal wurtzite form which is a high temperature inversion.

The sphalerite structure may contain up to 26 percent iron (Einaudi, 1968), however, this does not appear to change the structural state.

Chalcopyrite

The mineral chalcopyrite has 4:4 tetrahedral co-ordination (Evans, 1964) and crystallizes in the tetragonal system below 547°C and in the isometric system above this temperature, at one atmosphere pressure (Yund and Kullerud, 1966). Ignoring the difference between the copper and the iron, the structure (Figure 12) is seen to be identical to that of sphalerite. The unit cell consists of two zincblende cells stacked one upon the other. This is an example of polymeric isomorphism.

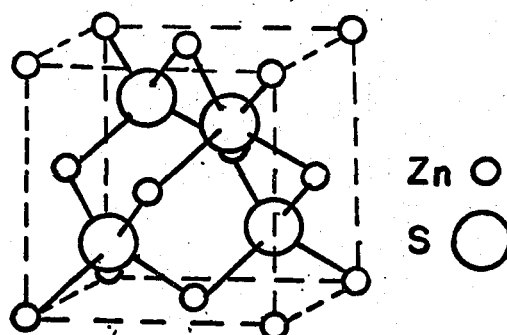


Figure 11. Zincblende structure
(After Berry and Mason, 1959, p. 312)

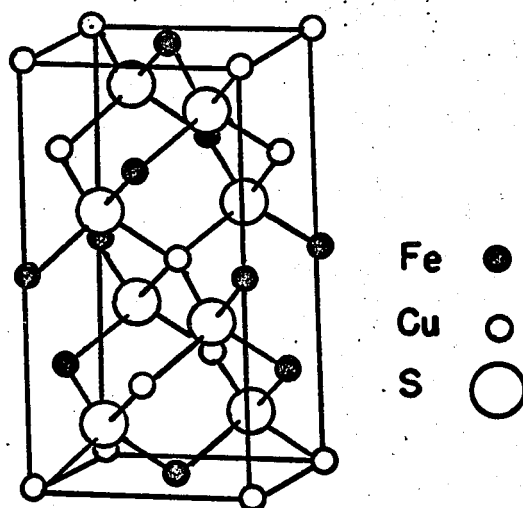


Figure 12 Chalcopyrite structure
(After Berry and Mason, 1959, p. 315)

Crystallochemical and Physical Constants and Properties of Iron

Cobalt and Nickel

The three elements iron, cobalt and nickel are very similar in many ways. They are transition elements and occur in the fourth period and Group VIII of the Periodic Table. Table 4 tabulates the constants and properties of the three elements.

TABLE 4

Properties and Constants for Iron, Cobalt and Nickel
(Data from Evans, 1964 & Serykh, 1964)

<u>Constant or Property</u>	<u>Fe or Fe⁺⁺</u>	<u>Co or Co⁺⁺</u>	<u>Ni or Ni⁺⁺</u>
Atomic number	26	27	28
Atomic weight	55.847	58.933	58.71
Ionic radius in sixfold co-ordination	0.74Å	0.72Å	0.69Å
Radius in covalent & metallic bonding	1.27Å	1.25Å	1.24Å
Electronegativity, arbitrary units	1.7	1.8	1.8
Relative total bonding energy	178	183	197
2nd ionization potential eV	16.25	17.4	18.20
Atomic radius	1.23Å	1.25Å	1.24Å
No. of d shell electrons	6	7	8

Crystal field stabilization energies as outlined by Curtis (1964) predict that divalent iron, cobalt and nickel ions have definite site preference energies in crystal lattices. All three prefer octahedral sites with nickel having the most positive affinity, followed by cobalt and then iron. Burns and Fyfe (1964) in discussing what they refer to as site preference energy for octahedral co-ordination for dipositive metals give the following list, nickel

having the highest site preference energy, $\text{Ni}^{++} > \text{Cu}^{++} > \text{Co}^{++} > \text{Fe}^{++} > \text{Mn}^{++} > \text{Ca}^{++} > \text{Zn}^{++}$. Curtis in developing the crystal field theory approach to this area points out that divalent Cu while it has a very high crystal field stabilization energy for octahedral co-ordination, because of its nine d electrons creates a very irregular octahedron, so irregular in fact, that a negative destabilization creates a distortive effect resulting in a negative crystal field energy for octahedral co-ordination and that the divalent copper ion then prefers tetrahedral sites. He thus gives the stability orders for divalent ions in octahedral co-ordination as Ni (29.3), Co (17.1), Fe (11.4), Cu (-ve).

Wells (1962) lists all monosulphides and disulphides of iron, cobalt and nickel as having octahedrally co-ordinated structures.

Nockolds (1966) states "when two cations of the same valency are capable of substitution in a crystal lattice, the one having the greater total bonding energy will be incorporated preferentially". According to Nockolds, nickel has the highest relative total bonding energy followed by cobalt which in turn is greater than iron (see Table 4).

Previous Work

A substantial number of workers have analysed sulphides for cobalt and nickel content. The bulk of the research has been directed towards pyrite and pyrrhotite occurrences and to a somewhat lesser extent chalcopyrite. To date sphalerite has not

received much attention with respect to its cobalt and nickel content.

The emphasis has been placed on using the cobalt and nickel contents as ratios used in determining the genetic history of the sulphides in which they are found. Variations have been employed to determine the effect of grain size, depth, proximity to intrusions, regional variations between similar and different types of deposits, epigenetic or syngenetic nature of the sulphides and equilibrium assemblage considerations.

The most comprehensive compilation of cobalt and nickel contents in pyrite, pyrrhotite, chalcopyrite and sphalerite is included in Fleischer's (1955) paper.

Partition of Cobalt and Nickel Between Pyrite, Pyrrhotite, Sphalerite and Chalcopyrite

Cobalt. Fleischer (1955) lists the only examples of cobalt partition between all four sulphides that the author was able to locate. He shows maximum cobalt content decreasing in the following order: pyrite, pyrrhotite, sphalerite and chalcopyrite. Gavelin and Gabrielson (1947), Carr and Turekian (1961) and Hawley and Nichol (1961) have cobalt content decreasing in the order from pyrite to pyrrhotite to chalcopyrite. Auger (1941) states that cobalt is concentrated in pyrite with respect to pyrrhotite and Carstens (1946) concludes that it is concentrated in pyrite with respect to chalcopyrite. Rose (1967) mentions that cobalt tends to be concentrated in sphalerite with respect to chalcopyrite.

Roscoe (1965) with five examples of cobalt in pyrite and pyrrhotite, lists four with a higher content in pyrite. His fifth, from Matagami, records the cobalt content of pyrrhotite as more than that of pyrite. This is quite unusual.

Nickel. The partition of nickel appears to be quite irregular and inconsistent between different deposits. Fleischer found the order of maximum nickel concentration to be pyrrhotite, pyrite, chalcopyrite and sphalerite. Gavelin and Gabrielson (1947) gave the order as pyrrhotite, pyrite, and chalcopyrite. Hawley and Nichol (1961), however, noted the following exceptions: in Chibougamau the order was found to be pyrrhotite, chalcopyrite and pyrite; and in Noranda, Normetal and McIntyre they found the sequence to be pyrite, pyrrhotite and chalcopyrite.

Roscoe (1965) found the nickel content to be higher in pyrite than in pyrrhotite in three out of five examples.

Relative Amounts of Cobalt and Nickel in Pyrite, Pyrrhotite, Sphalerite and Chalcopyrite

As has already been mentioned, the major portion of the literature of cobalt and nickel concentrations in sulphides has been devoted to their presence in pyrite and pyrrhotite.. Examination of Tables 5 and 6, which summarize many of the results of previous authors, confirms that not only have pyrite and pyrrhotite received more attention but also that they have relatively higher concentrations than either sphalerite or chalcopyrite. Desborough (1967) partially supports this contention

TABLE 5

Percent Cobalt Concentration

<u>Reference</u>	<u>Location</u>	<u>Pyrite</u>		<u>Pyrrhotite</u>		<u>Sphalerite</u>	<u>Chalcopyrite</u>	
		Max.	Mean	Max.	Mean	Max.	Max.	Mean
Fleischer (1955)	Lit. Compilation	2.5		0.85		0.30	0.20	
Auger (1941)	Noranda	0.5		0.01				
Hegemann (1941)	Norway	1	0.1	0.65				
Bjorlykke (1945)	Norway	1.25						
Carstens (1946)	Norway		0.005					
Hawley (1952) (Gold Mines)	Powell 200'-1400'		0.0102					
	1550'-2450'		0.0297					
	Kerr-Addisson		0.040					
	Porcupine		0.038					
Hawley and Nichol (1961)	Sudbury	1.81	1.03				0.086	0.00154
	Flin Flon	0.185	0.066	0.15	0.15		0.082	0.028
	Chibougamau	0.86	0.30	0.19	0.11		0.145	0.049
	Quemont	0.265	0.084	0.030	0.026		0.007	0.0055
	Noranda	0.285	0.116	0.076	0.038		0.020	0.0077
Rose (1967)	Bingham					0.0008	0.0050	
	Utah					0.0400	0.0900	
Loftus-Hills & Solomom (1967)	Australia	0.064						
Roscoe (1965)	Matagami		0.0600		0.1300			
	Noranda area		0.0500		0.0260			
	Horne Mine		0.0900		0.0400			
	Quemont, Vauze		0.0400		0.0200			
	Noranda granites		0.0350					

TABLE 6

Percent Nickel Concentration from Literature

Reference	Location	Pyrite		Pyrrhotite		Sphalerite		Chalcopyrite	
		Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean
Fleischer (1955)	Lit. Compilation	2.5		7.47		0.03		0.2	
Hegemann (1941)	Norway	0.55	0.15						
Hawley (1952) (Gold Mines)	Powell 200'-1400'		0.031						
	1550'-2450'		0.0556						
	Kerr-Addison		0.049						
	Porcupine		0.035						
Hawley and Nichol (1961)	Sudbury	0.90	0.10					1.03	0.037
	Flin Flon	0.012	0.0057		0.019			0.002	0.0013
	Chibougamau	0.019	0.011	0.082	0.032			0.024	0.012
	Quemont	0.004	0.0022	0.006	0.0034			0.003	0.00065
	Noranda	0.038	0.0041	0.01	0.0016			0.010	0.0014
Rose (1967)	Bingham					0.0060		0.060	
	Utah					0.0040		0.0150	
Loftus-Hills & Australia Solomom (1967)		0.0775							
Roscoe (1965)	Matagami area		0.0070		0.0035				
	Noranda area		0.0130		0.0050				
	Horne Mine		0.0070		0.0190				
	Quemont, Vauze		0.0100		0.0025				
	Noranda granites		0.0400						

by observing during studies on the differentiation of an olivine diabase that nickel enters iron sulphides more readily than it enters copper sulphides.

Rankama and Sahama (1950, p. 679) give the average content of cobalt and nickel in magmatic sulphide ores as 2,100 ppm and 31,400 ppm respectively.

The maximum concentration of either cobalt or nickel in sphalerite or chalcopyrite appears to be no more than about 1000 ppm. Only in two exceptions have been noted, both in chalcopyrite, and these were recorded by Hawley and Nichol (1961). The maximum cobalt content in nine samples of chalcopyrite from Chibougamau was 1450 ppm with a mean of 490 ppm. The high nickel reading of 10,300 ppm was obtained from one of 28 samples from Sudbury. The 28 samples had a mean of 370 ppm.

The maximum possible concentrations of cobalt and nickel in pyrite presents somewhat of a problem. The three metals involved, iron, cobalt and nickel, form disulphides, the bravoite series, which under metastable conditions may be completely miscible (Springer et al., 1964). Vaughan (1969) uses the term bravoite to include all compositions of the series in which the dominant metal present represents less than 80 percent of the total metal content. In cases where one metal constitutes more than 80 percent of the metals present he would refer to the mineral as a phase of either pyrite, cattierite, or vaesite which are the end members of the series. Clark and Kullerud (1963) in their study of the Fe-Ni-S system

found the maximum equilibrium solubility at 729°C to be 7.7 weight percent NiS_2 in FeS_2 . At low temperatures the equilibrium solubility is much less (L.A. Clark, 1969 - personal communication). Riley (1968) in a paper on the cobaltiferous pyrite series from the Copperbelt in Africa states: "Clearly all phases of the composition $(\text{Fe}, \text{Co})\text{S}_2$ extending over the whole range occur naturally (0-50 weight percent cobalt)". Riley does not comment on equilibrium associations.

Naldrett, Craig, and Kullerud (1967) established that $\text{Fe}_{(1-x)}\text{S}$ and $\text{Ni}_{(1-x)}\text{S}$ are completely miscible at all temperatures from 300°C to 1100°C. Although the author does not have similar data on $\text{Fe}_{(1-x)}\text{S}$ and $\text{Co}_{(1-x)}\text{S}$ they may be similar by analogy.

Variation of Cobalt and Nickel Content with Depth, Temperature of Deposition and Grain Size

There have been attempts to correlate the cobalt-nickel contents of sulphides with depth. Auger (1941) concluded that the cobalt content of pyrite decreased with "depth" in the Lower H orebody of the Horne Mine in Noranda, whereas pyrrhotite and chalcopyrite in the same orebody showed the opposite; i.e., an increase with "depth". The word depth is in question here as this writer believes that the Lower H has been tilted to an almost vertical position and therefore "depth" would actually refer to some orientation of the original length-width plane. Rose (1967), studying sphalerite and chalcopyrite from two areas in the

western United States, concluded that on a district scale lateral and vertical zoning were evident but that they were not evident on a local scale.

Fryklund and Harner (1955), Hawley and Nichol (1961) and Loftus-Hills and Solomon (1967) do not believe that the trace element content is related to depth. This conclusion is based on the results of work done in several areas.

The temperature of deposition of the sulphides does not appear to affect trace element content or distribution. Acknowledging the fact that sulphide minerals are usually unsaturated with respect to trace element content, it seems unlikely that concentration can be quantitatively dependent upon temperature. In theory, trace elements should partition between co-existing minerals as a predictable function of temperature. In practice, there are so many complicating factors that the theoretical distribution is seldom (if ever) realized. Some authors, notably Bjorlykke and Jarp (1950) and Carstens (1943), postulated that there is a correlation between high cobalt content and high temperature of formation of pyrite but recent studies (Loftus-Hills and Solomon, 1967) do not support this contention.

Very little has been done correlating grain size of the sulphides and cobalt-nickel content. Hawley (1952) found cobalt-nickel content to be lower in coarse grains and higher in fine grains. Bjorlykke and Jarp (1950) found cobalt content higher in coarse crystals.

Relation Between Cobalt-Nickel Concentration and Ratios to Sulphide Genesis

A great deal of emphasis has been focused on the use of cobalt-nickel ratios in determining sulphide genesis. Carstens (1945) states that the ratio Co:Ni is generally 20:1 for pyrite from hydrothermal deposits and that the ratio is much higher than 1:1 in hydrothermal deposits in which pyrite is completely replaced by pyrrhotite. He mentions also that the Co:Ni ratio of pyrite from sedimentary deposits varies from 1:10 to 1:20. In magmatic deposits the ratio is always much less than 1:1. Raychaudhuri (1959) supports these ranges and estimates.

Hawley and Nichol (1961) felt that a variation of the Co:Ni ratio in pyrite might possibly reflect a difference in the partition of elements in various types of deposits and that this may in turn be related to either different temperatures of formation or host rocks. Davidson (1962) and Wilson and Anderson (1959) are in agreement with this view and suggest that the Co:Ni ratio of the ores in effect increases with the silica content of the rock type with which they are associated.

Hegemann (1943) and Cambel and Jarkovsky (1967) found that in metamorphosed sulphide deposits the cobalt content of the sulphides increased with increasing degree of metamorphism. Carstens (1946) found that the cobalt content of pyrite in some Norwegian ore occurrences varied directly with the copper content.

CHAPTER IV

COBALT AND NICKEL ASSOCIATED WITH THE LAKE DUFALT OREZONE

INTRODUCTION

Purpose of the Present Study

This study was initiated to examine the variation in the cobalt and nickel content among the four major sulphide minerals in the Lake Dufault 'A' and 'B' orezones. Lake Dufault was chosen as it appears to be a very good example of the Noranda type sulphide deposit. This deposit shows little evidence of deformation and it was also the only one that was readily accessible of the northern group of ore deposits.

Cobalt and nickel were chosen because of the close similarity chemically and physically of their properties to those of iron. Iron is a major constituent in the four minerals that were studied.

Specifically, the object of the research was to investigate the following:

- a) the effect, if any, of the temperature of formation and/or the composition of the mineral on the value of the partition coefficient.
- b) the relative cobalt-nickel ratios between co-existing phases and the comparison of the cobalt-nickel ratios in individual phases throughout the orezone.

- c) the effect, if any, of grain size on the cobalt and nickel concentration within the major sulphide minerals;
- d) the actual position of the trace elements - whether inside or outside major mineral grains;
- e) the origin of the trace elements - whether they are derived from wallrock impurities, introduced with the sulphides or introduced later;
- f) if any of the four sulphides occur in more than one form is there any variation in the partition of the cobalt and nickel;
- g) zoning, if any, of cobalt and/or nickel within grains or crystals of the major sulphides; and
- h) can the location, relative concentration or mode of occurrence of the trace elements be used in determining or substantiating the genesis of the orezone.
- i) if the trace elements are located within grains of the major sulphides are they interstitial or in substitution positions or are they exsolved phases.

Sample Location

A total of 48 sites were sampled. These include 40 locations from eight vertical surface diamond drill holes and eight sites from within the mine workings. In most instances several samples were taken at each site.

The locations of the diamond drill holes are shown in Figure 13. The grid system used in this figure and in subsequent tables is the original one employed by the Lake Dufault staff, however it is no

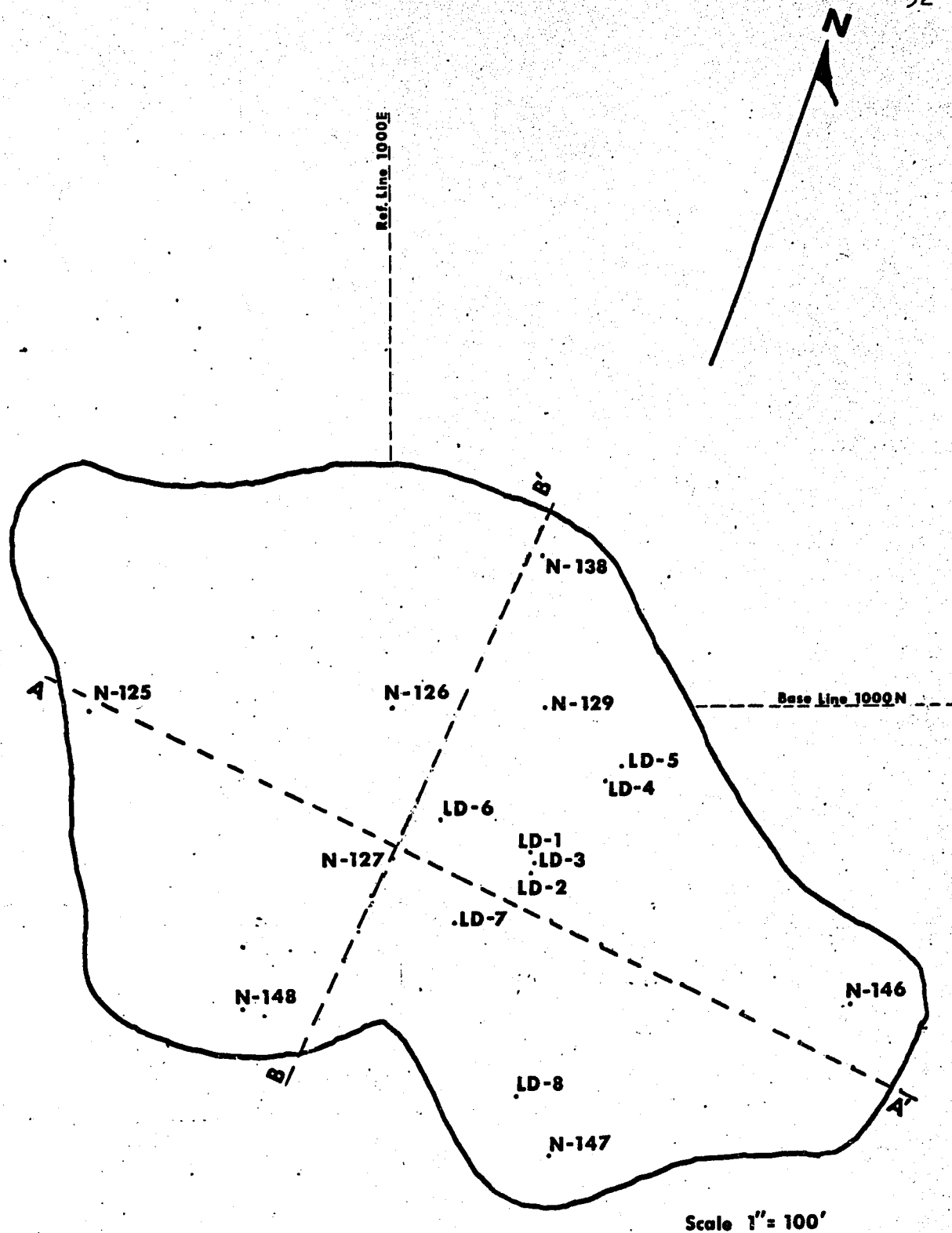


Figure 13 DDH Collar Locations and Underground (LD) Sample Locations
 (Plan showing outline of massive sulphide lens)

longer in current use at the mine. Elevations used in succeeding tables and descriptions are sea level plus 10,000 feet.

The major consideration in sample selection was to obtain specimens that contained as many of the four major sulphides as possible. The only exception to this was LD-8, a sample that is well over 95% sphalerite, which was selected for comparison with other specimens in which sphalerite was only one of two or more major sulphide phases. The sample came from a zone near the top of the 'A' zone which contains a very high proportion of sphalerite with respect to the other sulphides.

Tables 7 and 8 give the locations of the diamond drill holes and the underground samples. The massive sulphides of diamond drill hole N-129 represent a section that passes through the small pod of the massive ore that is predominately in andesite (see figure 8). This pod is believed to have been a displaced portion removed from the top of the massive 'A' zone by a low angle thrust fault. The original position of the section contained in N-129 is believed to have been above N-127 (J. Purdie, Chief Geologist, Lake Dufault - personal communication, 1967). It will therefore be treated as the upper part of N-127.

TABLE 7

Diamond Drill Hole Locations

D.D.H. No.	Co-ordinates		Collar Elevation (feet)	No. of Sample Sites	Elev. Top of 'A' Zone (feet)	of 'A' Zone length in D.D.H. (feet)	No. of 'A' Zone Sites
	N	E					
N-125	1000	800	11,170	1	10,058	8	1
N-126	1000	1000	11,157	11	10,036	140	9
N-127	900	1000	11,146	17	10,030	145	13
N-129	1000	1100	11,157	2	10,032	25	2
N-138	1100	1100	11,179	2	9,883	7	2
N-146	800	1300	11,142	3	9,801	25	3
N-147	700	1100	11,146	2	9,875	35	2
N-148	800	900	11,138	2	10,030	15	2

TABLE 8

Underground Sample Locations

Underground Sample No.	Co-ordinates		Elevation
	N	E	
LD-1	900	1090	9860
LD-2	890	1080	9865
LD-3	895	1085	9865
LD-4	950	1140	9865
LD-5	955	1150	9865
LD-6	925	1130	9915
LD-7	855	1045	10015
LD-8	740	1080	9910

Analytical Methods

Sample Preparation

The mineral specimens used in the atomic absorption procedures were prepared in the following manner. First a portion of the sample was crushed using a small jaw crusher. The crushed material was further reduced in particle size by running it through a porcelain plate pulverizer.

The material obtained from the pulverizer was then sized using silk mesh screening. The desired retainable fraction was - 140 to + 200 mesh. This range was determined by optical examination of a series of specimens. Silk screening was used in lieu of conventional metal screens so as to minimize the possibility of contamination, especially as nickel is a constituent of most solders.

The sized portion was then run through a Franz Isodynamic Separator and the pyrrhotite, sphalerite, chalcopyrite and pyrite fractions were collected. Silicates were removed from each fraction using a heavy liquid procedure with methylene iodide. In several instances hand cobbing was used, especially between sphalerite and the chalcopyrite to clean the samples. The sphalerite and the chalcopyrite fractions were often mixed as they have partially overlapping magnetic susceptibilities.

Polished sections of specimens were made for the electron microprobe analyses.

Procedures

Cobalt and nickel trace element analyses were performed using two analytical procedures: atomic absorption analysis and electron microprobe analysis.

The atomic absorption analyses were done using an EEL atomic absorption flame photometer, Model 140. To 200 mg of mineral were added:

- 1) 10 ml distilled water
- 2) 5 ml hydrochloric acid (37%)
- 3) 5 ml sulphuric acid (95%)
- 4) 5 ml nitric acid (70%)
- 5) 2 drops liquid bromine

This solution was then evaporated to dryness in a sand bath. Then 10 ml 0.1 N hydrochloric acid was added to the residue and the solution was allowed to evaporate to dryness over a steam bath. Finally 10 ml 0.1 N hydrochloric acid was added to the residue and the resulting solution was analysed for cobalt using the atomic absorption unit. The same procedure was followed for the nickel analyses. All samples were done in duplicate. Control standards of cobalt and nickel solutions, prepared by S. A. Scott, were used to calibrate the atomic absorption unit. These standards were used only to control day to day variations in instrument behaviour. Determination of concentration levels was established by synthetic sulphide standards whose preparation will be described in the next section.

The electron microprobe analyses were performed using an Acton MS-64 electron microprobe analyser. Polished sections of ore were used. The sections were made from the samples collected underground. In addition to cobalt and nickel analyses, arsenic, iron and sulphur values were also recorded in a limited number of mineral grains. In each case the $K_{\alpha 1}$ positions were used.

Standards

Two sets of cobalt and nickel standards were made for this study. Artificial FeS and CuFeS_2 were made and known amounts of synthesized CoS and NiS were added. These standards were made with the help of Dr. W. H. MacLean of McGill University who proposed and supervised their preparation.

The CuFeS_2 was prepared by combining 35.0 weight percent copper with 32.5 weight percent iron and 32.5 weight percent sulphur. The relative amounts were determined by consulting the central portion of the chalcopyrite stability field after Yund and Kullerud (1966) which is reproduced in Figure 14. Preparations of CoS and NiS were made with 61.75 weight percent metal and 38.25 weight percent sulphur. These were added to the CuFeS_2 in measured amounts so as to produce a set of chalcopyrite standards containing 50, 100, 250, 500, 1,000 and 10,000 ppm nickel and 200, 500, 1,000, 2,000 and 10,000 ppm cobalt.

A second double set was made to produce FeS by combining 61.75 weight percent iron with 38.25 weight percent sulphur (after Jensen, 1942). CoS and NiS were added to produce standards with

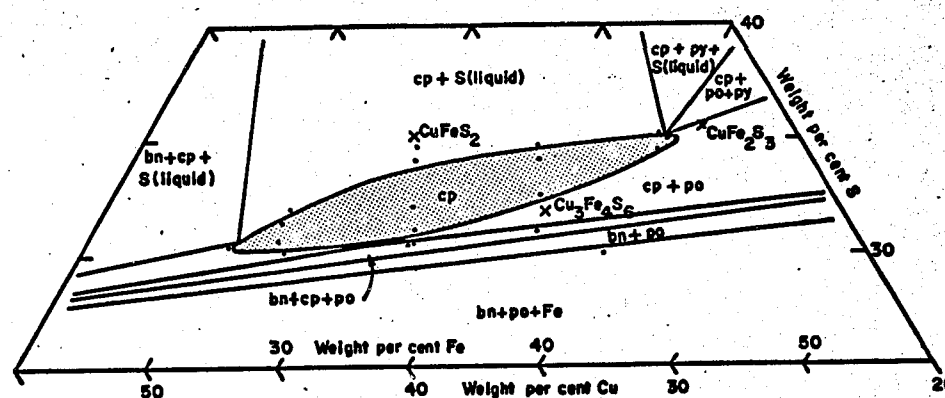


Fig.14_ Chalcopyrite solid solution at 700°C. It is noted that the CuFeS_2 , CuFe_2S_3 , and $\text{Cu}_3\text{Fe}_4\text{S}_6$ compositions lie outside the solid solution field. Only the experimental compositions situated inside or very near the solid solution field are plotted (after Yund and Kullerud, 1966).

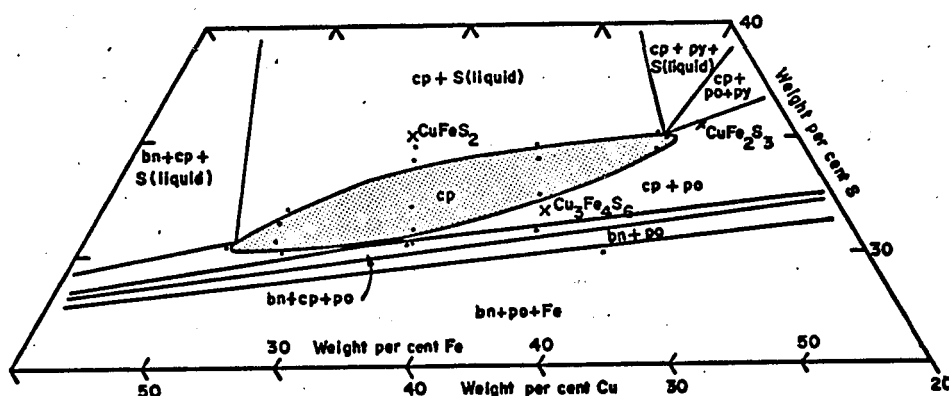


Fig.14 - Chalcopyrite solid solution at 700°C. It is noted that the CuFeS_2 , CuFe_2S_3 , and $\text{Cu}_3\text{Fe}_4\text{S}_6$ compositions lie outside the solid solution field. Only the experimental compositions situated inside or very near the solid solution field are plotted (after Yund and Kullerud, 1966).

identical cobalt and nickel concentrations to those that were produced for the chalcopyrite.

The standards were checked on the electron microprobe for homogeneity and were found to be very uniform.

PYRITE ANALYSIS

Range

Atomic Absorption

Cobalt analyses were obtained in pyrite from 24 different sample locations and nickel content was measured in 12 sample locations. The cobalt and nickel values as well as the sample locations are listed in Table 9. Under the location heading in the table the first two figures are the longitudes and latitudes (see Figure 13) in hundreds and the third figure is the elevation of the sample location.

The cobalt contents range from 170 ppm to 4540 ppm with an arithmetic average of 1570 ppm. Examination of Figure 15 shows, that although the average is 1570 ppm, 16 of the 24 samples have values of less than 1250 ppm Co. Figures 16 and 17 are sectional plots (see Figure 13) with cobalt content projected on two sections through the orezones. The center line represents the center of the 'A' zone in each diamond drill hole.

Quantitative nickel values were obtained only from atomic absorption procedures. The nickel content in the 12 pyrite analyses

TABLE 9

Co and Ni Content in Pyrite Analysed by Atomic Absorption

Sample No.	Location	Co ppm	Ni ppm
N-125-1126	10-8-10054	2450	297
N-126-1150	10-10-10007	1100	
N-126-1196	10-10-9961	810	
N-126-1257	10-10-9900	615	
N-126-1267	10-10-9890	555	
N-127-1113	9-10-10033	1420	
N-127-1134	9-10-10012	1170	
N-127-1184	9-10-9962	890	
N-127-1208	9-10-9938	570	288
N-127-1251	9-10-9895	400	
N-127-1262	9-10-9884	170	
N-127-1263	9-10-9883	300	
N-127-1293	9-10-9853	170	45
N-129-1150	10-11-10007	2650	42
N-146-1343	8-13-9797	500	64
N-146-1352	8-13-9790	4540	30
N-146-1366	8-13-9776	2450	73
N-147-1283	7-11-9863	215	187
N-147-1294	7-11-9852	4000	53
N-148-1120	8-9-10018	4450	97
LD-2	8.90-10.8-9865	4100	155
LD-4	9.50-11.4-9865	725	
LD-5	9.55-11.5-9865	3000	
LD-6	9.25-11.3-9915	420	105

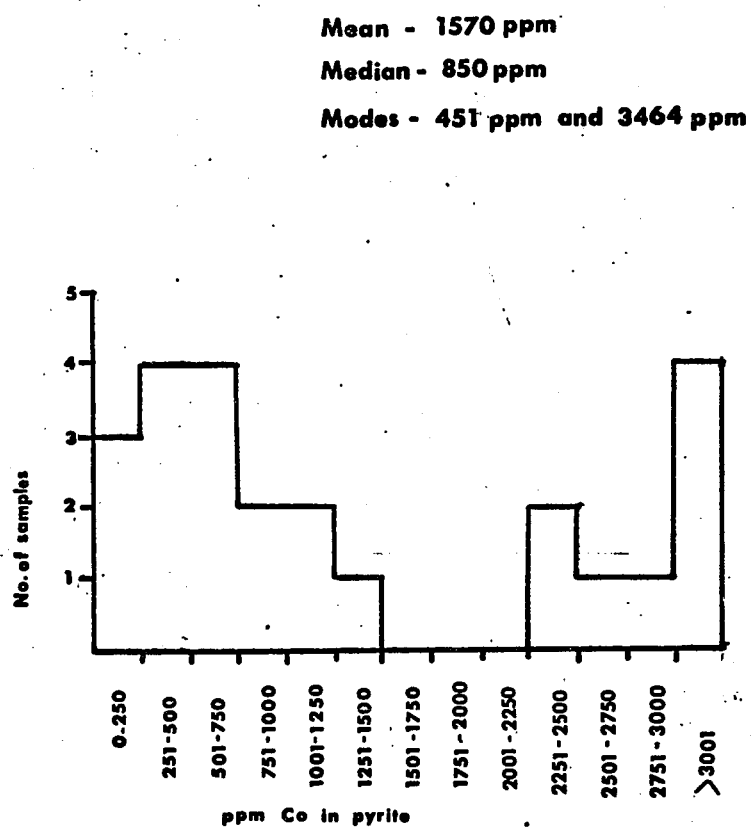


Figure 15 Co content from atomic absorption analyses of pyrite

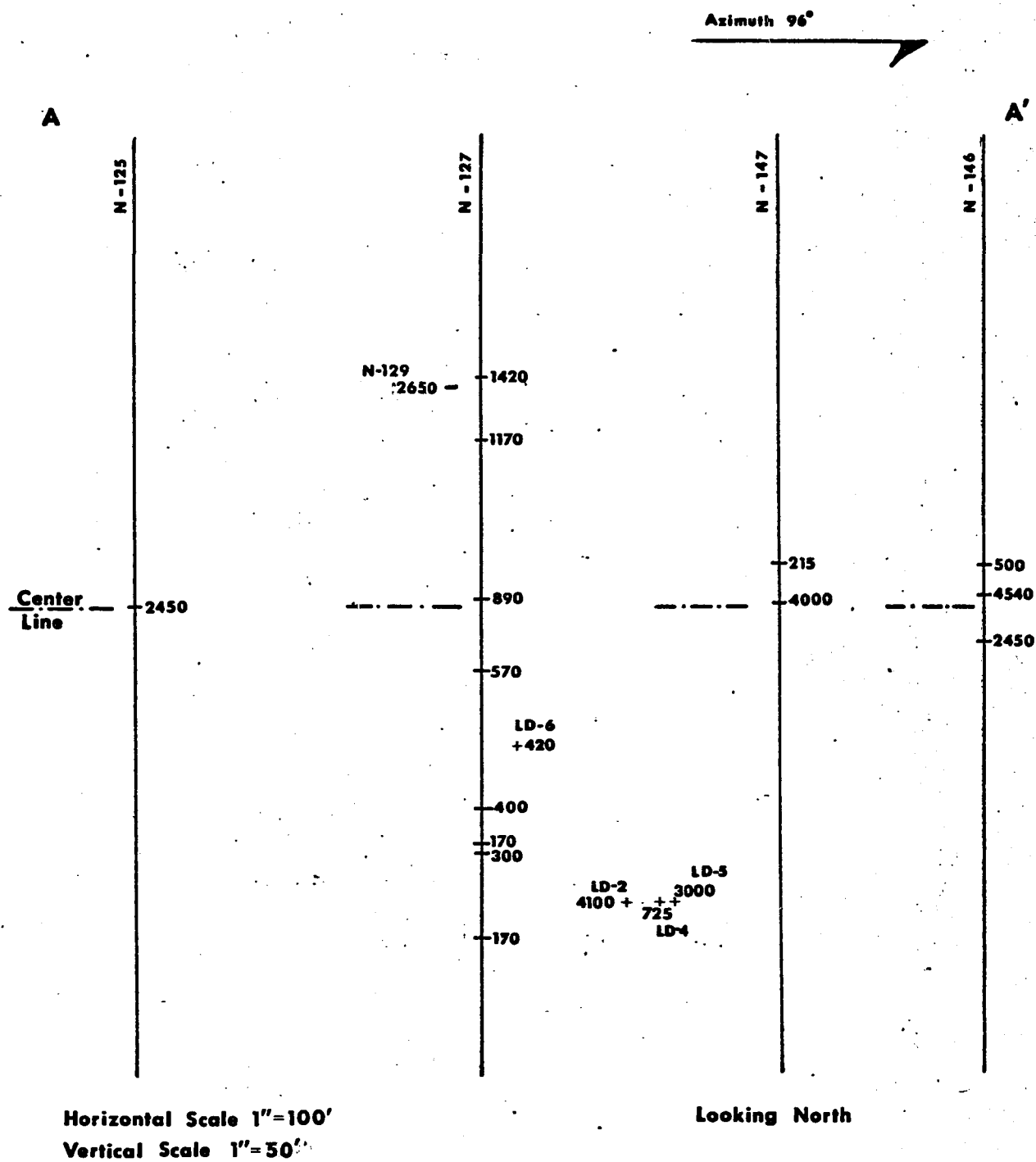


Figure 16 Section A-A' Co content in pyrite (ppm)

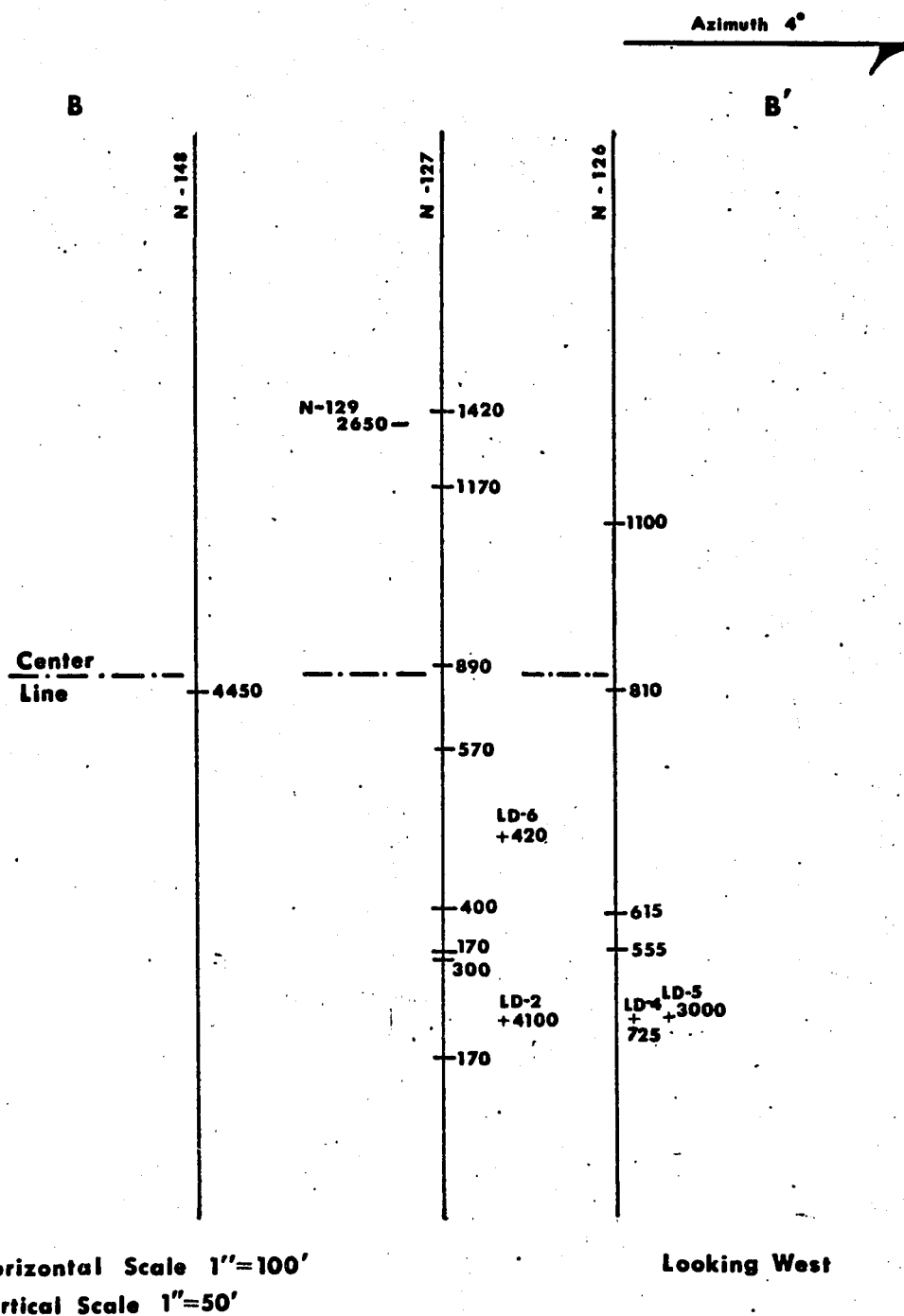


Figure 17 Section B-B' Co content in pyrite (ppm)

ranged between 30 ppm and 297 ppm with an arithmetic average of 131 ppm and eight of the values were less than the average. Table 9 indicates that there is no correlation between cobalt and nickel content.

Electron Microprobe Analyser

In addition to the atomic absorption analyses the LD series or the underground series were subjected to quantitative analysis using the electron microprobe. These analyses were for cobalt content only as the nickel content was never found to be above background with very few exceptions. Six of the eight samples contained pyrite. Table 10 lists the cobalt content measured in unzoned pyrites. No pyrite was analysed in either LD-8 or LD-3.

The cobalt content ranges from non-detectable (ND) in LD-4 to 38,448 ppm in LD-1. The average cobalt content in LD-2, LD-4, LD-5 and LD-6 compared to the results obtained from the atomic absorption procedures (Table 9) are given in Table 11.

Variation

The variation within a given specimen is quite extensive. Using the field of view ($\approx 500\mu$) of the binocular eyepiece which is a part of the electron microprobe as a gauge, Figure 18 shows an inverse correlation between the percent pyrite in the field versus the cobalt content of the unzoned pyrite. There is also a direct relationship between cobalt content and actual grain size.

TABLE 10

Co. Content in Unzoned Pyrite - Electron Microprobe

Sample No.	Location	Co ppm	No. of Grains Analysed
LD-1	9.00-10.9-9860	38066 37111 38448 30617 898 2044	6
LD-2	8.90-10.8-9865	6245 5692 1680 4259 5405 5978 8385 5692 4355 7029 5405	11
LD-4	9.50-11.4-9865	19 898 973 ND ND ND ND	7
LD-5	9.55-11.5-9865	3017 4106 898	3
LD-6	9.25-11.3-9915	4594	1
LD-7	8.55-10.4-10015	497 8327 8499	3

TABLE 11

Comparison of Results Obtained by Electron Microprobe Analyser with
Those Obtained from Atomic Absorption Procedures for Cobalt Content
in Pyrite

Sample No	A. A.	E-Probe Av.	No. of Grains
LD-2.	4100 ppm	5466 ppm	11
LD-4	725 "	630 "	3
LD-5	3000 "	2674 "	3
LD-6	420 "	4594	1

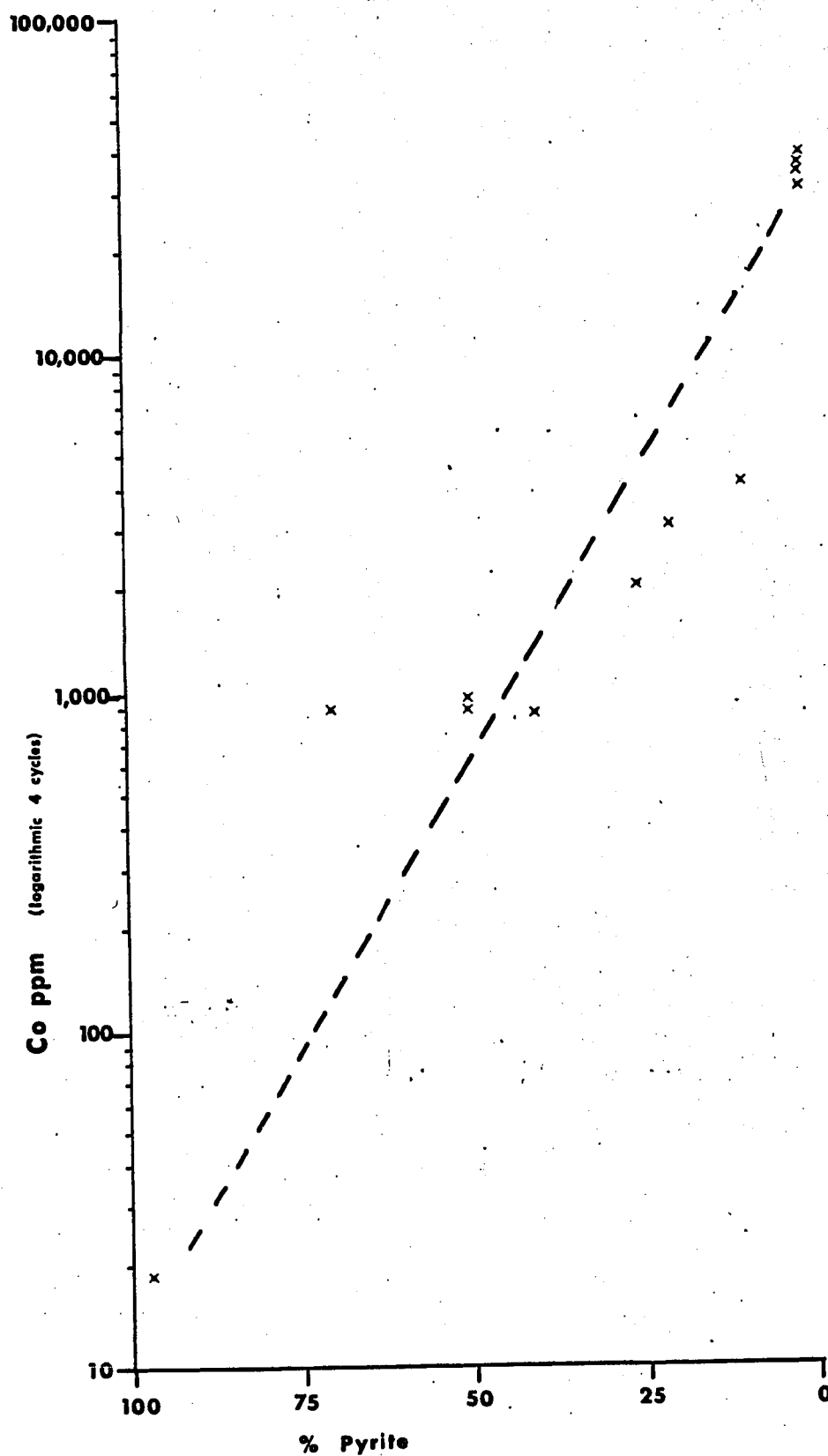


Figure 18 Graph of Co (ppm) in pyrite vs percent pyrite in field of view of electron microprobe binocular

The smaller grains (less than 40 μ) always contain the higher amounts of cobalt. The four very high analyses in LD-1 (Table 10) were found in grains that ranged in size from 10 μ to 15 μ .

The four samples taken from the 'B' zone (N-126-1257, N-126-1267, N-127-1263, N-127-1293) and N-127-1262, which is less than six inches from the bottom of the 'A' zone are low in cobalt content.

PYRRHOTITE ANALYSIS

Range

Atomic Absorption

A total of 35 analyses for cobalt content were obtained for 30 samples (Table 12). The amount of cobalt present ranges from 95 ppm in N-147-1283 to 2450 ppm in N-129-1150. The arithmetic average cobalt content was 741 ppm. The depth or the sample location does not appear to influence the cobalt content. The only exceptions would be the two 'B' zone samples, N-126-1267 and N-127-1293 which are well below the average content.

In five samples the pyrrhotite was separated into two fractions using the Franz Isodynamic Separator. This separation was based strictly on magnetic properties, Po-1 is the most magnetic fraction and Po-2 the least. The results show that Co does not appear to concentrate preferentially in either fraction.

Nickel analyses were determined in 18 pyrrhotite samples. The nickel concentrations are not noticeably affected by depth,

TABLE 12

Co and Ni Content in Pyrrhotite Analysed by Atomic Absorption

Sample No.	Location	Co ppm	Ni ppm	Po - 1		Po - 2	
				Co ppm	Ni ppm	Co ppm	Ni ppm
N-126-1076	10-10-10081	1645					
N-126-1166	10-10-9991	370					
N-126-1196	10-10-9961	1495					
N-126-1197	10-10-9960	575					
N-126-1217	10-10-9940	740					
N-126-1237	10-10-9925	675	86				
N-126-1257	10-10-9900	1170					
N-126-1267	10-10-9890	345					
N-127-1116	9-10-10030	660					
N-127-1128	9-10-10018	570	80				
N-127-1154	9-10-9992	680					
N-127-1173	9-10-9973	285					
N-127-1176	9-10-9970	735					
N-127-1203	9-10-9938	50					
N-127-1251	9-10-9895	370					
N-127-1293	9-10-9853	110					
N-129-1125	10-11-10032			440	62	280	69
N-129-1150	10-11-10007	2450	47				

TABLE 12 (con't)

Sample No.	Location	Co ppm	Ni ppm	Po - 1		Po - 2	
				Co ppm	Ni ppm	Co ppm	Ni ppm
N-138-1297	11-11-9882			1250	43	1225	97
N-138-1303	11-11-9876	1110	42				
N-146-1343	8-13-9799			335	38	420	39
N-146-1352	8-13-9790	500	45				
N-146-1366	8-13-9776			525	41	700	43
N-147-1238	7-11-9863	95	38				
N-147-1294	7-11-9852			1660	52	770	27
LD-1	9.00-10.9-9860	310					
LD-2	8.90-10-8-9865	950	80				
LD-6	9.25-11.3-9915	250	25				
LD-7	8.55-10.4-10015	650					

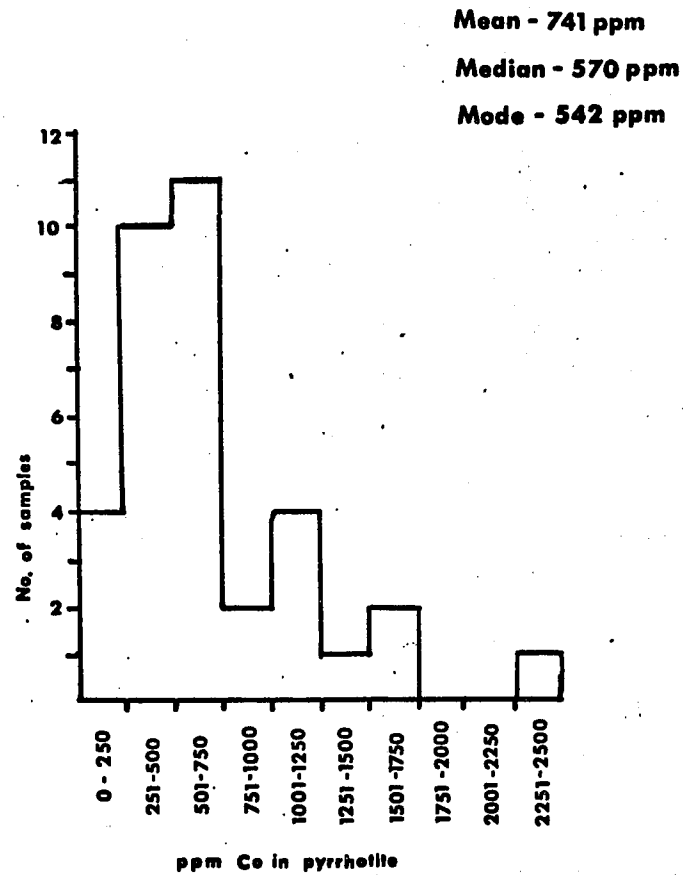


Figure 19 Co content from atomic absorption analyses of pyrrhotite

location or cobalt concentration. The nickel values range from 25 ppm to 97 ppm with an average content of 53 ppm.

Electron Microprobe Analyser

There were 25 cobalt analyses measured from seven sample locations in the LD series (Table 13). The range in concentration was from 898 ppm in LD-2 to 59 ppm in LD-6. The average cobalt content was 373 ppm. The range in a given sample was greatest in LD-1, 176 ppm to 666 ppm, and in LD-4, 117 ppm to 780 ppm. The composition of individual grains appears to be very uniform and no evidence of zoning was encountered.

The sample averages compare quite well with the results obtained by atomic absorption procedures (Table 14).

SPHALERITE AND CHALCOPYRITE ANALYSES

Range

Atomic Absorption

The cobalt content in sphalerite from 26 samples ranges from non detectable to 900 ppm (Table 15) and has an arithmetic average of 239 ppm. The nickel concentration in 16 samples ranges from 3 ppm to 40 ppm with an average content of 11 ppm. The relative positions of the different sample locations show no correlation with either cobalt or nickel concentration. Figure 20 shows the relative concentrational distribution of cobalt in sphalerite.

TABLE 13

Co Content in Pyrrhotite - Electron Microprobe

Sample No.	Location	Co ppm	No. of grains analysed
LD-1	9.00-10.9-9860	666 254 176	3
LD-2	8.90-10.8-9865	898	1
LD-3	8.95-10.8-9865	722 702 468 449 566	5
LD-4	9.50-11.4-9865	780 176 117	3
LD-5	9.55-11.5-9865	176 215 254 176 176 215 137	7
LD-6	9.25-11.3-9915	59 117 254	3
LD-7	8.55-10.4-10015	741 605 605	3

TABLE 14

Comparison of Results Obtained by Electron Microprobe Analyser
with those Obtained from Atomic Absorption Procedures for
Cobalt Content in Pyrrhotite

Sample No.	A. A.	E-Probe Av.	No. of Grains
LD-1	310 ppm	365 ppm	3
LD-2	950 ppm	898 ppm	1
LD-6	250 ppm	143 ppm	3
LD-7	650 ppm	650 ppm	3

TABLE 15

Co and Ni Content in Sphalerite and Chalcopyrite Analysed by Atomic
Absorption

Sample No.	Location	Sphalerite		Chalcopyrite	
		Co ppm	Ni ppm	Co ppm	Ni ppm
N-125-1126	10-8-10054	105	21		
N-126-1150	10-10-10007	130			
1193	9964	60			
1196	9961			70	
1197	9960			55	
1217	9940	70			
1232	9925			65	
1257	9990			290	
1267	9890			245	
N-127-1116	9-10-10030			175	
1128	10018	460		125	
1134	10012	640		170	
1154	9992			40	
1173	9973			40	
1176	9970	560		220	
1184	9962			165	
1221	9925	50	5		
1233	9913	320		210	
1251	9895	ND			
1262	9884			20	26
1263	9883			10	
1293	9853	50			
N-129-1125	10-11-10032	200	4	70	12
1150	10007	155	5	140	11
N-138-1297	11-11-9882	330	3		
1303	9876	235	13	100	34
N-146-1343	8-13-9799	200	4	165	20
1352	9790	165	10	135	12
1366	9776	225	37	130	18
N-147-1238	7-11-9863	ND	7		
1294	9852	500	40	155	17

TABLE 15 (con't)

Sample No.	Location	Sphalerite		Chalcopyrite	
		Co ppm	Ni ppm	Co ppm	Ni ppm
N-148-1107	8-9-10031			130	41
1120	10018	275	4	160	46
LD-1	9.00-10.9-9860			50	
LD-2	8.90-10.8-9865			140	26
LD-3	8.95-10.8-9865	215	5	70	63
LD-4	9.50-11.4-9865	40	4		
LD-5	9.55-11.5-9865	215			
LD-6	9.25-11.3-9915	125	3		
LD-7	8.55-10.4-10015			140	32
LD-8	7.40-10.8-9910	900	10		

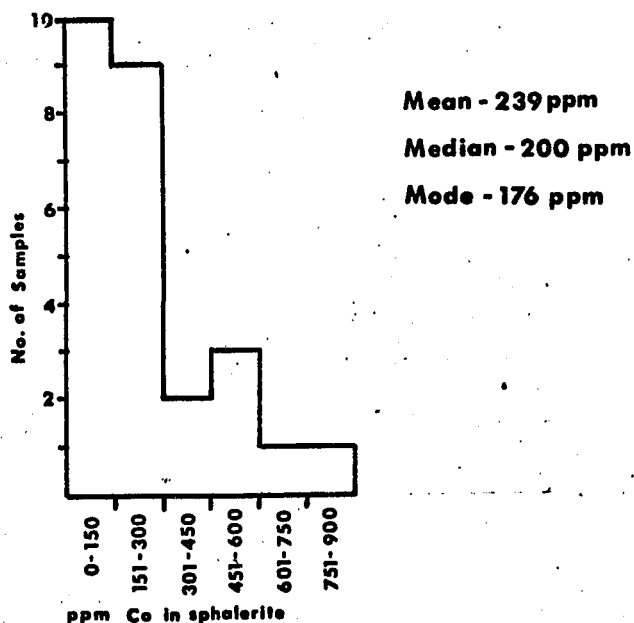


Figure 20 Co content from atomic absorption analyses of sphalerite

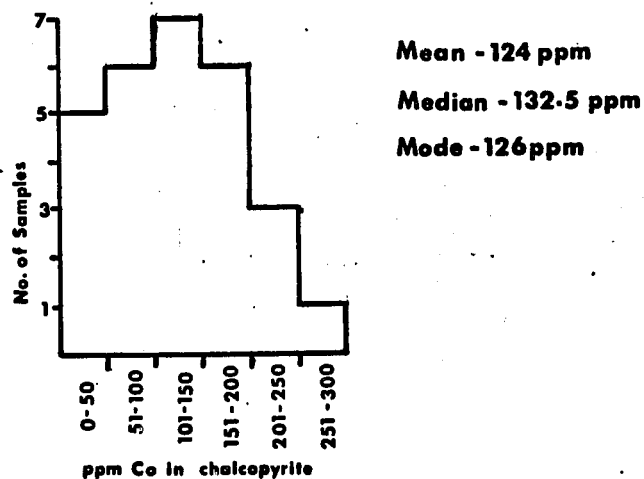


Figure 21 Co content from atomic absorption analyses of chalcopyrite

The cobalt content in chalcopyrite from 28 samples has a range of 10 ppm to 290 ppm (Table 15). The average concentration is 124 ppm. The nickel concentration determined from the analyses of 13 samples ranges from 11 ppm to 63 ppm with an average concentration of 27 ppm. Figure 21 shows the relative concentrational distribution of cobalt in chalcopyrite.

Electron Microprobe Analyser

The range of cobalt concentration in sphalerite for 24 analyses from the first seven samples of the LD series is from non detectable to 718 ppm with an arithmetic average of 242 ppm (Table 16). The cobalt content in chalcopyrite from the same samples is from non detectable to 187 ppm with an average of 101 ppm.

Table 17 compares the microprobe results with those obtained by atomic absorption procedures.

The range of cobalt in sphalerite is greatest in LD-1, from 94 ppm to 699 ppm. Cobalt in chalcopyrite has the greatest range in LD-5, 56 ppm to 187 ppm. A total of eight grains of sphalerite were tested in samples LD-4 and LD-5 and in each case the cobalt content was below the detection limit of the electron microprobe. The specimen LD-4 in which all four sulphides are present is mainly sphalerite and pyrite, not mixed but ^{eg}segregated into two distinct zones, a pyrite zone and a sphalerite zone.

TABLE 16

Co Content in Sphalerite and Chalcopyrite - Electron Probe

Sample No.	Location	Sphalerite Co ppm	Chalcopyrite Co ppm
LD-1	9.00-10.9-9860	699 699 94	75 ND 57
LD-2	8.90-10.8-9865	624 718	149 112
LD-3	8.95-10.8-9865	176 416 435 416 265	56 94 94 56
LD-4	9.50-11.4-9865	ND ND	150 150
LD-5	9.55-11.5-9865	ND ND ND ND ND ND	131 187 112 56 131 131 150
LD-6	9.25-11.3-9915	ND 75 ND	75 75 19
LD-7	8.55-10.4-10015	397 416 378	112 131 112

TABLE 17

Comparison of Results Obtained by Electron Microprobe Analyser
with those Obtained from Atomic Absorption Procedures for
Cobalt Content in Chalcopyrite and Sphalerite

Sample No.	A. A.		E-Probe Av.	
	Sphalerite	Chalcopyrite	Sphalerite	Chalcopyrite
LD-1		50 ppm	497 ppm	44 ppm
LD-2		140 ppm	671 ppm	130 ppm
LD-3	215 ppm	70 ppm	342 ppm	75 ppm
LD-4	40 ppm		ND	150 ppm
LD-5	215 ppm		ND	128 ppm
LD-6	125 ppm		25 ppm	58 ppm
LD-7		140 ppm	397 ppm	118 ppm

PARTITION BETWEEN SULPHIDES

Cobalt Content in Co-existing Phases

The variation of cobalt content between co-existing phases was measured in several locations with the electron microprobe analyser. The results of the measurements are tabulated in Table 18. The sixth column in the table shows the relative amount of cobalt in pyrite, pyrrhotite and sphalerite which occurs in each particular occurrence. Examination of Table 18 shows that for the measured examples, the cobalt content of chalcopyrite never exceeds or is equal to the cobalt content of pyrrhotite. The cobalt content of sphalerite is greater than the cobalt content chalcopyrite in 10 of the 17 measured sites.

The cobalt content of pyrrhotite varies over a moderately wide range, from 117 ppm to 898 ppm. The same is true of sphalerite, from non detectable to 624 ppm. The cobalt content of any mineral does not seem to be influenced by the relative amounts in co-existing phases.

Cobalt-Nickel Ratios

A total of 56 Co:Ni ratios were determined and Table 19 lists the results. The pyrrhotite analyses are split into two groups. The first column of pyrrhotite results contain samples from which only one pyrrhotite fraction was collected and as well the most magnetic fraction of the five fractions that were split into two groups. The fourth column, labeled Po-2, contains the least

TABLE 18

Co Content in Co-existing Phases

Sample No.	Pyrite	Co ppm			Co content normalized to Cp
		Pyrrhotite	Sphalerite	Chalcopyrite	
LD-1		176	94	57	3.1/1.6/1
LD-2		898	624	149	6/4.2/1
LD-3		712	170	56	12.7/3/1
		468	425	94	5/4.5/1
		449	416	94	4.8/4.4/1
		566	265	56	10.1/4.7/1
LD-4		780	ND	150	5.2/0/1
LD-5		176	ND	131	1.3/0/1
		215	ND	187	1.1/0/1
		254	ND	112	2.4/0/1
		176	ND	56	3.1/0/1
LD-6	4594	254	ND	19	241/13.4/0/1
		117	75	75	1.6/1/1
LD-7		741	397	112	6.6/3.5/1
		605	416	131	4.6/3.2/1
		605	378	112	5.4/3.4/1

TABLE 19
Cobalt/Nickel Ratios

Sample No.	Pyrite			Pyrrhotite			Po-2			Sphalerite			Chalcopyrite		
	Co	Ni	Co/Ni	Co	Ni	Co/Ni	Co	Ni	Co/Ni	Co	Ni	Co/Ni	Co	Ni	Co/Ni
N-125-1126	2450	197	12.4/1							105	21	5/1			
N-126-1232				675	86	7.8/1									
N-127-1128				570	80	7.1/1									
N-127-1208	570	288	1.9/1							50	4	12.5/1			
N-127-1221													60	27	2.2/1
N-127	170	45	3.8/1												
N-129-1125				440	62	7.1/1	280	69	4.1/1	200	4	50/1	70	12	5.8/1
N-129-1150	2650	42	63.1/1	2450	47	52.1/1					5		140	11	12.7/1
N-138-1297				1250	43	29.1/1	1225	97	12.9/1	330	4	82.5/1			
N-138-1303				1110	42	26.4/1				235	13	18.1/1	103	34	3/1
N-146-1343	500	64	7.8/1	335	38	8.8/1	420	39	10.8/1	200	4	50/1	165	20	8.2/1
N-146-1352	4540	30	151.3/1	500	45	11.1/1				165	11	15/1	135	13	10.4/1
N-146-1366	2450	73	33.6/1	525	41	12.8/1	700	42	16.7/1	225	36	7.4/1	130	18	7.2/1
N-147-1283	215	187	1.1/1	95	38	2.5/1				ND	7				
N-147-1294	4000	53	75.5/1	1660	52	31.9/1	770	27	28.5/1	512	40	12.8/1	155	17	9.1/1
N-148-1107													130	41	3.2/1
N-148-1120	4450	97	45.9/1							275	4	68.7/1	160	46	3.5/1
LD-2	4100	155	26.5/1	950	80	11.9/1							140	26	5.4/1
LD-3										215	5	43/1	70	63	1.1/1
LD-4										ND	4				
LD-6	420	105	4/1	250	25	10/1				125	3	41.7/1			
LD-7													140	32	4.4/1
LD-8										900	9	100/1			

magnetic fraction of the five samples. All of the values in Table 16 are based on analyses obtained from the atomic absorption procedures.

The 12 pyrite Co:Ni ratios have an average value of 35.6:1, with a high of 151.3:1 and a low of 1.1:1. The 13 pyrrhotites in column three have an average Co:Ni ratio of 16.8:1, with a high of 52.1:1 and a low of 2.5:1. The five Co:Ni ratios from the least magnetic pyrrhotite fraction have an average value of 16.1:1, with a high of 28.5:1 and a low of 4.1:1. The 13 ratios from sphalerite have an average of 39:1, with a high of 100:1 and a low of 5:1. The results of 13 ratios for chalcopyrite gave an average of 5.7:1, with a high of 12.7:1 and a low of 1:1.

It is interesting to note that the averages for the two pyrrhotite groups are almost identical. The high average ratio for sphalerite is due more to very low nickel content rather than high cobalt content.

Variation Between Grains and Within a Grain of the Same Phase

The cobalt distribution in unzoned pyrites, pyrrhotites, sphalerites and in chalcopyrites appeared to be extremely uniform for a given grain and no areas of high or low concentration were observed in individual grains during electron microprobe analysis or scanning. Within a sample, the cobalt content could vary between co-existing grains of the same species. This was especially true in the case of the unzoned pyrites (Table 10).

A series of cobalt analyses, using the electron microprobe,

was performed on pyrrhotite and chalcopyrite grains in sample LD-5 to determine the uniformity of the cobalt distribution within single grains as well as the difference in concentration between co-existing grains of the same phase. Five grains of each mineral were analysed. Each grain was analysed at five different points and at each point five repetitions were recorded. The results are listed in Table 20 (pyrrhotite) and Table 21 (chalcopyrite).

The readings from Tables 20 and 21 were then subjected to a standard hierarchical design statistical model (see Appendix B) used by Krumbein and Slack (1956).

Table 22 shows the results of the analysis of variance and variance components for the pyrrhotite grains and Table 23 the similar information for the chalcopyrite grains. The (a) part of Tables 22 and 23 list the mean squares in the last column. These values are used as a basis for the estimates of the variance components listed in the last column of the (b) part of each table (see Appendix B).

The data found in Tables 22 and 23 suggests that the main variance contribution occurs at the grain level, that no real variance contribution occurs at the point level and that a minor variance contribution occurs at the repetition level. The relatively short counting time, 10 seconds, would quite likely account for a substantial portion of the variance at the repetition level. This test sustains the contention that the cobalt is distributed

TABLE 20

Co in Pyrrhotite from LD - 5

Values are recorded as 10 second counts from electron microprobe

Point	Repetitions per point	Grain No.				
		1	2	3	4	5
1	1	654	664	603	721	644
	2	622	679	604	700	649
	3	622	674	590	697	652
	4	645	654	631	717	664
	5	656	672	615	717	662
2	1	620	641	584	695	651
	2	649	687	613	709	671
	3	617	649	627	709	660
	4	623	664	621	711	616
	5	643	650	609	721	677
3	1	628	677	619	715	642
	2	630	650	627	719	675
	3	648	670	609	695	645
	4	650	656	615	700	632
	5	663	641	600	711	618
4	1	624	629	640	699	644
	2	636	647	607	695	632
	3	661	645	597	701	636
	4	640	672	613	693	644
	5	630	677	628	711	658
5	1	660	645	612	711	631
	2	639	657	635	713	648
	3	660	651	617	705	629
	4	624	668	614	721	652
	5	611	659	623	716	650

TABLE 21

Co in Chalcopyrite from LD-5

Values are recorded as 10 second counts from electron microprobe

Point	Repetitions per point	Grain No.				
		1	2	3	4	5
1	1	509	516	484	527	464
	2	483	516	481	523	432
	3	470	474	468	499	462
	4	522	456	516	513	451
	5	494	483	446	527	411
2	1	452	463	515	520	443
	2	460	480	483	527	451
	3	487	504	484	506	430
	4	482	470	444	519	440
	5	455	514	477	531	471
3	1	500	503	493	531	460
	2	474	483	518	517	449
	3	492	497	482	511	458
	4	500	469	474	526	460
	5	446	493	496	531	437
4	1	476	500	461	527	439
	2	443	461	502	523	467
	3	498	499	507	499	474
	4	517	509	491	516	444
	5	465	515	475	521	454
5	1	514	522	484	506	432
	2	484	483	485	504	434
	3	493	472	488	499	459
	4	497	509	482	519	466
	5	513	453	496	516	462

TABLE 22

Analysis of Variance and Variance Components

(Co in Pyrrhotite)

(a) Analysis of Variance

Source	Sum of Squares	Degrees of Freedom	Mean Square
Between grains	120909.0	4	30227.25
Between points within a grain	3043.4	20	152.17
Between repetitions per point	20753.6	100	207.54

(b) Variance Components

Level	Difference	Sample Size	Components
Grains	30075.08	25	1203.00
Points	-55.37	5	0.00
Repetitions	207.54	1	207.54

TABLE 23

Analysis of Variance and Variance Components

(Co in Chalcopyrite)

(a) Analysis of Variance

Source	Sum of Squares	Degrees of Freedom	Mean Square
Between grains	251486.2	4	62871.5
Between points within a grain	5426.8	20	271.34
Between repetitions per point	34312.0	100	343.12

(b) Variance Components

Level	Difference	Sample Size	Components
Grains	62600.16	25	2504.01
Points	-71.78	5	0.00
Repetitions	343.12	1	343.12

homogeneously throughout individual grains, but that the concentration may vary between co-existing grains of the same phase.

COBALT ZONING IN PYRITE

During the course of analysing pyrite grains with the electron microprobe, it was noticed that many of the pyrites did not appear to have a homogenous cobalt content. When examined in greater detail certain grains were found to have a rim or zone around the outer edge (this rim may or may not wholly encompass the grain) that contained appreciably higher cobalt values than the central portion. The reverse was never encountered.

The grains are usually located away from large masses of pyrite, and if near large masses are always on the edge and never in the central portions. The zoned grains encountered were quite small, in the order of 150 microns or less, and for the most part were located on the edges of or adjacent to pyrrhotite masses or grains. Table 24 lists 12 examples of zoned pyrite grains.

The fifth column in Table 24 is an estimation of the total amount of pyrite present in the field of view of the microscope that is part of the electron probe unit. This field is about 500 microns on a side. The electron beam or the area in which the analysis was performed is in the exact center of the field of view.

TABLE 24
Co Zoning in Pyrite

Sample No.	Location	Co ppm		Relative Am't Pyrite
		Edge	Central Portion	
LD-5	9.55-11.5-9865	15,089	5,596	less than 5%
		3,744	2,941	50%
		1,624	993	80%
		13,618	1,489	less than 5%
LD-6	9.25-11.3-9915	1,967	57	20%
		4,221	248	30%
		3,724	2,846	50%
		96	ND	90%
		1,948	229	75%
LD-7	8.55-10.4-10015	4,908	592	15%
		7,945	2,234	5%
		6,589	458	10%

The zoned pyrite grains show a high cobalt zone, but neither the high zone, nor the central portion of the grain have uniform cobalt distribution. Table 25 lists 24 cobalt analyses from four grains. Plates 1 and 2 taken on specimen LD - 6 show the mineralogy, the points where analyses were performed, and the cobalt distribution in the pyrite grain.

Evidence of Solid Solution

The similarities in the chemical and physical properties of divalent iron, cobalt and nickel have often led to the contention that they are interchangeable in sulphide lattices in at least moderate concentrations. Therefore, a series of analyses were performed using the electron microprobe on pyrite grains and the cobalt and iron contents were measured. It was noted that the iron content decreased when the cobalt content increased and vice - versa. Table 26 (Figure 22) lists a series of these measurements performed on three zoned pyrite grains, the cobalt content is listed in both counts per second (cps) and in ppm while the iron content is listed only under counts per second.

Additional work was done, again using the electron microprobe, and in this instance the pyrite was analysed for cobalt, iron, sulphur, arsenic and nickel. The samples were also checked for copper, lead, manganese and magnesium. The only elements detected were cobalt, iron and sulphur. The microprobe results

PLATE 1



Zoned Pyrite Grain LD-6

Cobalt Analyses from Electron Microprobe Analyser

1	764 ppm Co
2	554 ppm Co
3	936 ppm Co
4	8,710 ppm Co
5	3,514 ppm Co
6	5,253 ppm Co
7	10,658 ppm Co

PLATE 1



Zoned Pyrite Grain LD-6

Cobalt Analyses from Electron Microprobe Analyser

1	764 ppm Co
2	554 ppm Co
3	936 ppm Co
4	8,710 ppm Co
5	3,514 ppm Co
6	5,253 ppm Co
7	10,658 ppm Co

PLATE 2



Electron Probe Scanning Micrograph

CoK α scan of zoned pyrite grain in Plate 1 from LD-6

PLATE 2



Electron Probe Scanning Micrograph

CoK α_1 scan of zoned pyrite grain in Plate 1 from LD-6

TABLE 25

Cobalt Analyses from 4 Pyrite Grains

Sample No.	Grain No.	Edge	Co ppm
			Central Portion
LD-5	1	20,265	4,278
		14,898	3,342
	2	15,796	2,139
		19,291	2,273
		18,680	2,005
		22,404	
	3	14,278	3,954
		14,592	2,445
		22,595	4,450
LD-6*	1	8,710	764
		3,514	554
		5,253	936
		10,658	

* See Plates 1, and 2.

TABLE 26
Co-Variation of Iron & Cobalt in Zoned
Pyrite LD-5

Grain No.	Co		Fe
	cps	ppm	cps
1	29.1	4,278	1,275.9
	112.8	20,265	1,222.3
	24.2	3,342	1,284.4
	84.7	14,898	1,239.4
2	89.4	15,796	1,239.4
	17.9	2,139	1,292.3
	107.7	19,291	1,239.5
	18.6	2,273	1,277.3
	104.6	18,680	1,244.6
	17.2	2,005	1,296.5
	124.0	22,407	1,232.5
3	81.5	14,287	1,242.3
	27.4	3,954	1,257.6
	19.5	2,445	1,263.6
	83.1	14,592	1,218.2
	30.0	4,450	1,285.5
	125.0	22,595	1,196.2

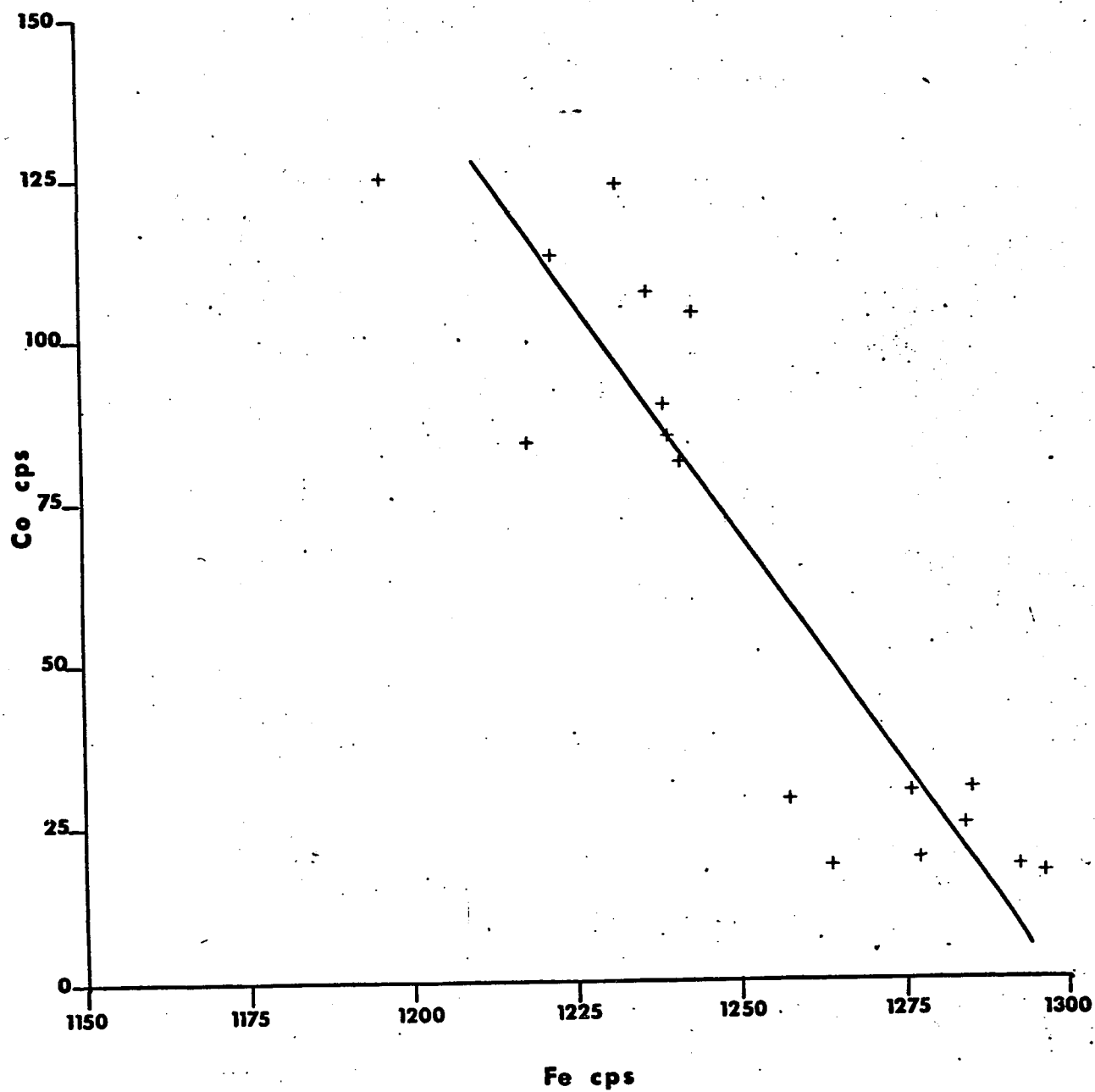


Figure 22 Plot of Table 26 showing covariation of iron and cobalt in zoned pyrite

were corrected for background, drift, deadtime and matrix effects using the McGill version of the EMPADR V computer program written by J. Rucklidge and E. L. Gasparrini of the University of Toronto. The program utilizes the fluorescence correction of Reed (1965), the Philbert absorption correction as revised by Duncumb and Shields (1966) and the atomic number correction of Duncumb and daCasa (1967). The results of this work are given in Table 27.

COBALT MINERALS

Location

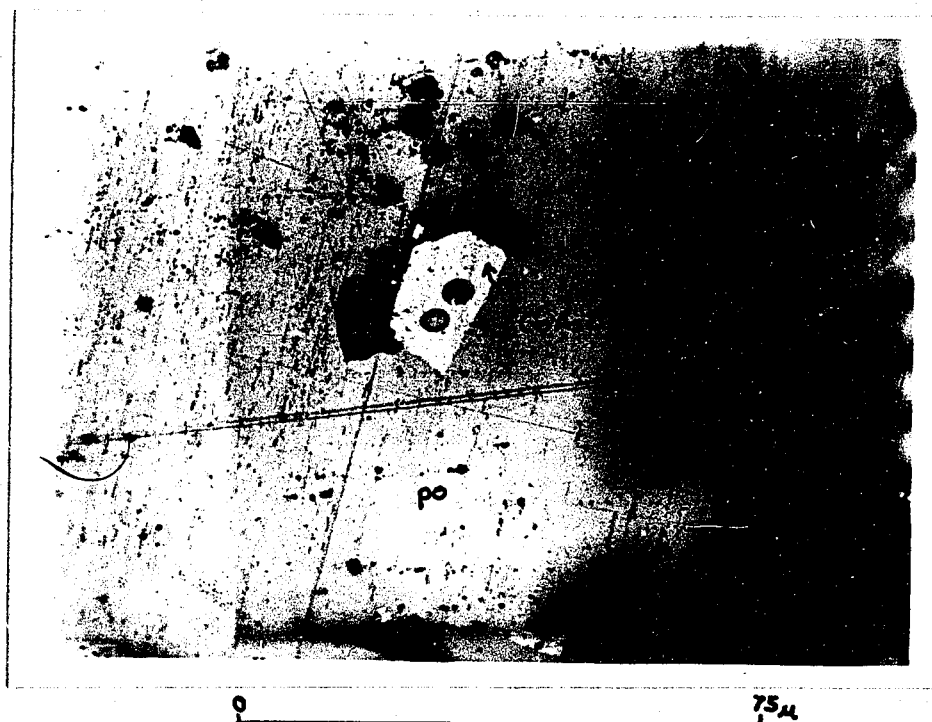
During the course of scanning samples LD-1 to LD-7 with the electron microprobe microphone, a number of mineral species with a high cobalt content were encountered in the samples LD-1 and LD-3. When examining these mineral grains through the microscope on the electron microprobe, there seemed to be two distinct types. The most common type appeared to be not unlike pyrite in appearance with a corresponding high relief. The second type looked also somewhat like pyrite but exhibited a much lower relief. These mineral grains ranged in size from 5 - 15 microns. Both types occurred together or singly, as groups or as single grains, in fractures and on grain boundaries. They occur either in large masses of pyrrhotite or on the edge of pyrrhotite grains in contact with either sphalerite or chalcopyrite. In no observed instance were

TABLE 27

Cobalt, Iron and Sulphur Content in 4 Pyrite Grains
LD-3

Grain No.	Element	Weight Percent	Sigma	No. of Moles	Wt.% to 100%
1A	Co	3.55	0.150	0.060	3.69
	Fe	42.96	0.631	0.769	44.60
	S	49.82	0.570	1.554	51.71
	total	96.34			
1B	Co	0.44	0.043	0.008	0.45
	Fe	45.75	0.416	0.819	46.31
	S	52.60	1.162	1.641	53.25
	total	98.79			
2A	Co	2.47	0.063	0.042	2.55
	Fe	43.65	0.490	0.782	45.03
	S	50.82	0.879	1.585	52.42
	total	96.94			
2B	Co	0.53	0.049	0.009	0.53
	Fe	45.99	0.550	0.824	46.00
	S	53.46	1.015	1.667	53.47
	total	99.98			
2C	Co	1.54	0.112	0.026	1.56
	Fe	45.03	0.362	0.806	45.44
	S	52.52	0.823	1.638	53.00
	total				
2D	Co	1.12	0.111	0.019	1.12
	Fe	45.53	0.399	0.815	45.63
	S	53.13	0.990	1.657	53.25
	total	99.77			
3A	Co	3.91	0.194	0.066	4.12
	Fe	41.62	0.447	0.745	43.87
	S	49.34	0.989	1.539	52.01
	total				
3B	Co	2.20	0.119	0.037	2.25
	Fe	44.33	0.529	0.794	45.29
	S	51.36	0.786	1.602	52.47
	total	97.90			
4A	Co	3.04	0.265	0.052	3.13
	Fe	43.37	0.493	0.777	44.66
	S	50.70	1.068	1.581	52.21
	total	97.10			
4B	Co	2.04	0.057	0.035	2.05
	Fe	44.91	0.628	0.804	45.15
	S	52.53	1.065	1.638	52.80
	total	99.49			

PLATE 3



Cobalt Mineral (cobaltite) LD-3
Analysis from Electron Microprobe Analyser
(see Table 28)

Weight Percent

Co	34.29
Fe	4.91
S	21.83
As	38.50
Ni	0.46

PLATE 3

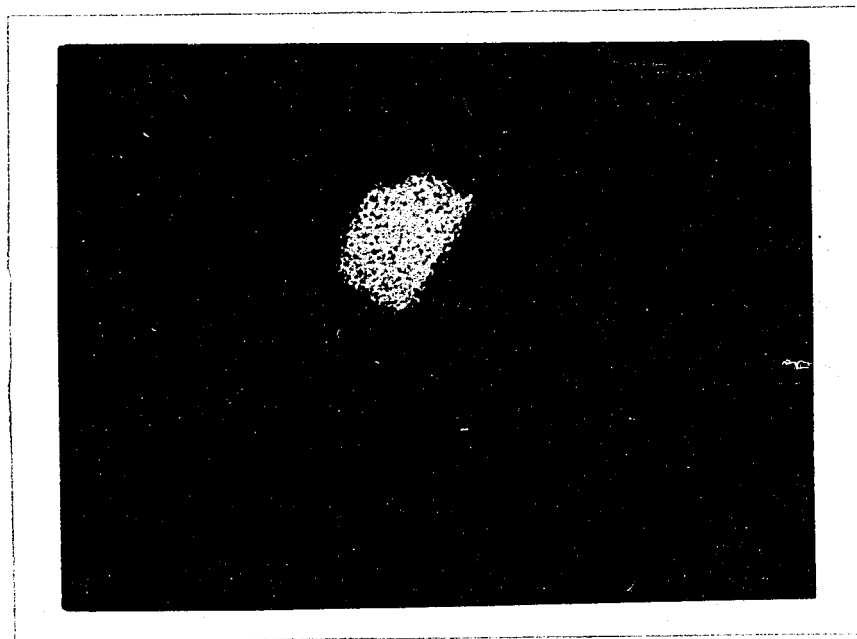


Cobalt Mineral (cobaltite) LD-3
Analysis from Electron Microprobe Analyser
(see Table 28)

Weight Percent

Co	34.29
Fe	4.91
S	21.83
As	38.50
Ni	0.46

PLATE 4



Electron Probe Scanning Micrograph of Cobalt Mineral in
Plate 3 (Co $K_{\alpha 1}$)

PLATE 4

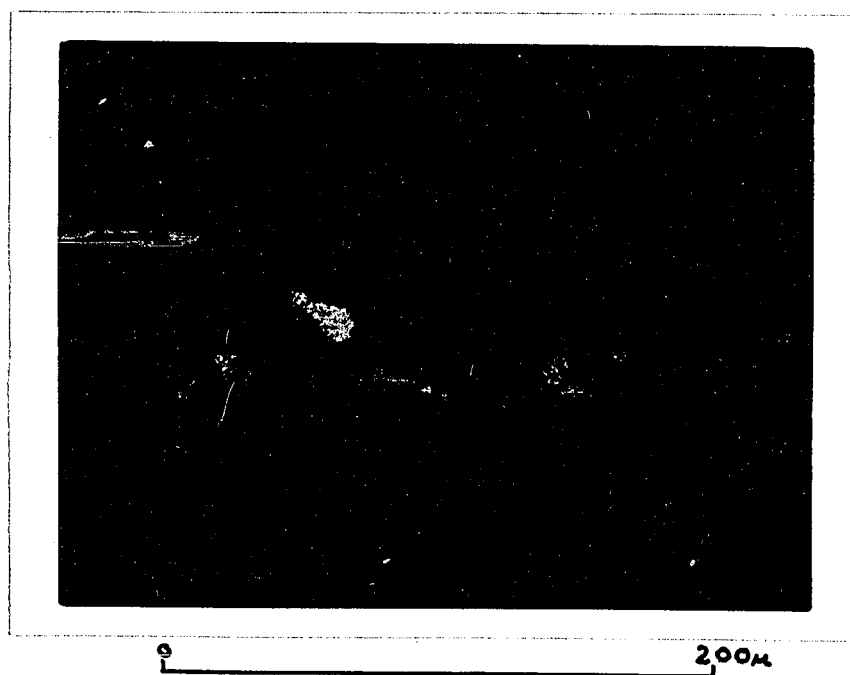


Electron Probe Scanning Micrograph of Cobalt Mineral in
Plate 3 (Co K_{α1})

PLATE 5



(a)

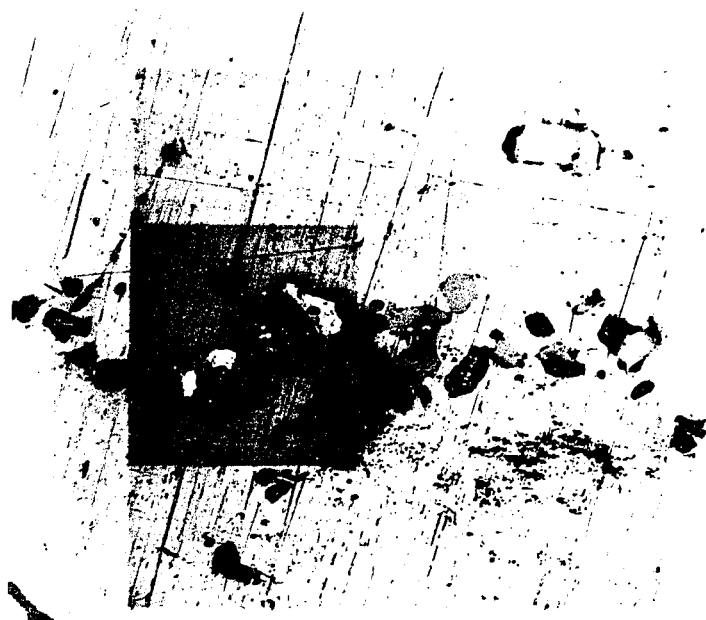


(b)

(a) Cobalt Minerals LD-3

(b) Electron Probe Scanning Micrograph ($\text{CoK}_{\alpha 1}$) of (a)

PLATE 5



(a)



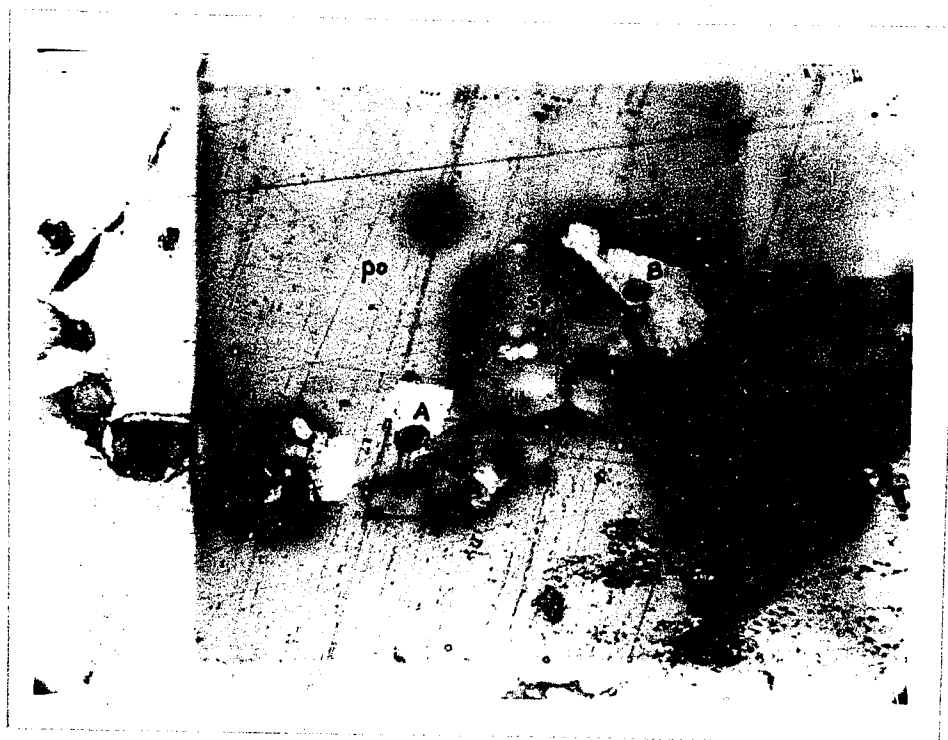
0 200μ

(b)

(a) Cobalt Minerals LD-3

(b) Electron Probe Scanning Micrograph ($\text{CoK}_{\alpha 1}$) of (a)

PLATE 6



Cobalt Minerals LD-3

Enlargement of dark portion of plate 5 (a)

Analysis from Electron Microprobe Analyser (see Table 28)

Weight Percent

A	Co	34.98	B	Co	33.39
	Fe	2.04		Fe	3.56
	S	21.32		S	21.61
	As	41.53		As	40.80
	Ni	0.12		Ni	0.65

PLATE 6



Cobalt Minerals LD-3

Enlargement of dark portion of plate 5 (a)

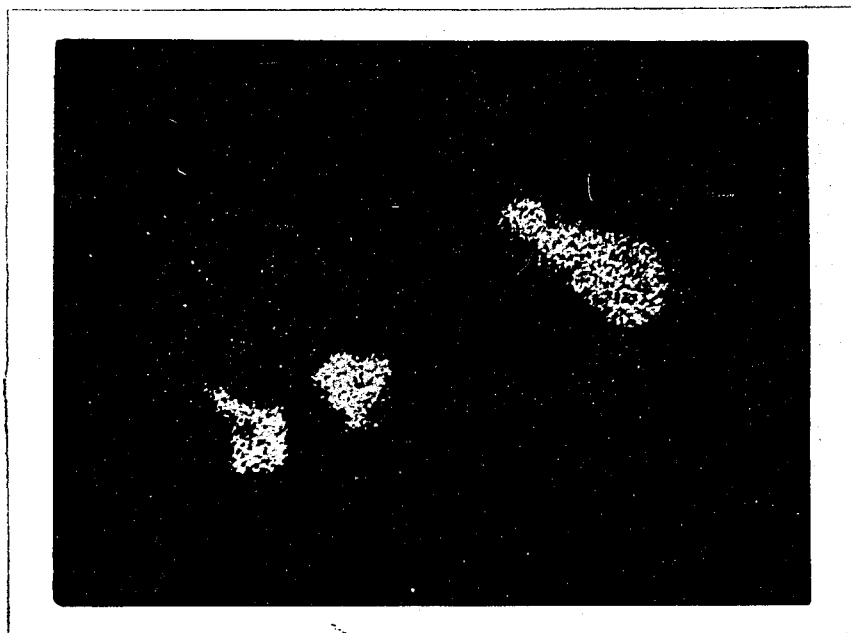
Analysis from Electron Microprobe Analyser (see Table 28)

Weight Percent

A	Co	34.98
	Fe	2.04
	S	21.32
	As	41.53
	Ni	0.12

B	Co	33.39
	Fe	3.56
	S	21.61
	As	40.80
	Ni	0.65

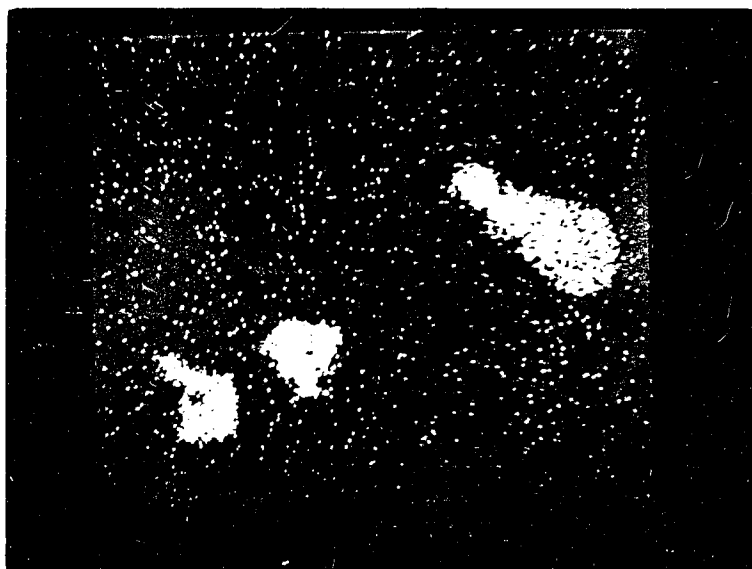
PLATE 7



Electron Probe Scanning Micrograph of Cobalt Minerals in Plate 6

(Co $K_{\alpha 1}$)

PLATE 7



Electron Probe Scanning Micrograph of Cobalt Minerals in Plate 6

(Co $K_{\alpha 1}$)

they found to occur in the vicinity of pyrite grains or masses.

Composition

The cobalt content in these minerals varies from 12-36 weight percent. Table 28 lists five occurrences found in LD-3 with the composition calculated using the EMPADR V computer program. The first four are very close to pure cobaltite with small amounts of iron and trace amounts of nickel. The fifth is an iron monosulphide solid solution bearing 12% cobalt.

DISCUSSION

Partition of Cobalt and Nickel

The results of the cobalt and nickel analyses of the pyrite, pyrrhotite, sphalerite and chalcopryrite from the Lake Dufault ore zone are in general agreement with previous workers' results from many other deposits. In the case of cobalt content pyrite has the most, followed by pyrrhotite, then sphalerite and chalcopryrite has the least. It is interesting to note that the analyses performed for the present study, however, gave significantly higher cobalt values in the major sulphides than earlier studies of Auger (1941), Hawley and Nichol (1961), and Roscoe (1965) in the Noranda area (see Tables 5, 9, 10, 12, 13, 15 and 16). The cobalt

TABLE 28
Cobalt Minerals

No.	Weight Percent				
	Co	Fe	S	As	Ni
1	34.29	4.91	21.83	38.50	0.46
2	34.98	2.04	21.32	41.53	0.12
3	35.31	3.80	21.21	39.54	0.15
4	33.39	3.56	21.61	40.80	0.65
5	12.17	51.46	36.37	ND	ND
Cobaltite (Dana)	35.5	-	19.3	45.2	-

was measured in the present study by two different analytical methods which generally were in quite close agreement.

The close agreement is most evident in the sphalerite and chalcopyrite analyses for cobalt. The average cobalt content in all the samples done by atomic absorption procedures in sphalerite and chalcopyrite is 239 ppm and 124 ppm while electron microprobe analyses give 242 ppm and 101 ppm respectively for the two minerals. The electron microprobe analyses, however, give much more interesting results and point out that the other procedure just gives sample averages and that actually in a given sample there can be a concentration range between co-existing grains of the same material. This fact is demonstrated clearly in Table 16, where in the case of sphalerite from LD-1 the cobalt content ranges from 94 ppm to 699 ppm and LD-5 shows a chalcopyrite range of 56 ppm to 187 ppm.

The nickel content in sphalerite and chalcopyrite is found to be very low, 11 ppm average for sphalerite and 27 ppm average for chalcopyrite. It has a very limited concentration range in both minerals and although it could not be analysed in distinct sulphide grains there is no reason to believe that its distribution would differ much from cobalt; i.e., each sample showing a concentration difference between co-existing grains.

In some cases the cobalt content in pyrrhotite is significantly higher in the analyses performed by the atomic absorption than in the analyses performed by the electron microprobe. It is quite possible that this is the result of the presence of cobalt minerals

in the pyrrhotite obtained by the mechanical mineral separation procedures. The particle size retrieved from these procedures was the fraction -140 mesh (102 microns) to +200 mesh (75 microns) while the cobalt minerals found in pyrrhotite were usually in the range of 5 - 15 microns and so quite likely much of this material when present would be incorporated in the pyrrhotite grains and particles and thus the somewhat higher cobalt content.

The nickel content in pyrrhotite (average 53 ppm) while not as high as that found in pyrite (average 131 ppm) is considerably more than that found in sphalerite (11 ppm) and chalcopyrite, (27 ppm).

The cobalt content of unzoned pyrite grains was very irregular, both between grains within a given sample and between samples. With two exceptions the cobalt content in pyrite was always greater than that measured in the other major sulphides, either within a given co-existing sequence or between samples. The two exceptions, N-126-1196 and N-126-1257, contain pyrrhotite that contained higher sample averages, but this may have been due to the presence of cobalt minerals.

The nickel content of pyrite was also higher than that of the other three sulphides. The average nickel content in pyrite and pyrrhotite, 131 ppm and 53 ppm respectively, is virtually identical to that recorded by Roscoe (1965) who lists 130 ppm and 50 ppm for the two minerals. Hawley and Nichol obtained slightly lower values at the Horne Mine and Quemont (see Table 6).

The relative position of either a given mineral or co-existing sulphide species within the Lake Dufault massive sulphide lens does not appear to influence the amount of cobalt or nickel present in a mineral.

The observed partition of cobalt and nickel between the four minerals, pyrite, pyrrhotite, sphalerite and chalcopyrite from the Lake Dufault ore zone certainly helps to establish the viability of using the crystal field approach in determining trace element behaviour. The high positive crystal field stabilization orders that nickel and cobalt have for octahedral sites as outlined by Curtis (1964) are clearly substantiated in the results obtained in this study. In pyrite and pyrrhotite the metallic ions are octahedrally co-ordinated while in sphalerite and chalcopyrite, they are tetrahedrally co-ordinated.

The cobalt and nickel concentration in the sulphides of the Lake Dufault ore zone show a definite preference towards pyrite and pyrrhotite as opposed to sphalerite and chalcopyrite.

The further partition within the two groups; i.e. those with octahedrally co-ordinated metal ions and those with tetrahedrally co-ordinated metal ions, is not as easily explicable. One of the major problems is the origin of the pyrrhotite, whether it was derived from authigenic or diagenic processes. It is the considered opinion of the writer that the pyrrhotite is not of primary origin. McDonald (1967) and James (1966) consider that pyrrhotite very rarely occurs as an authigenic mineral in the sedimentary and

volcanic environment. Richards (1966) in discussing mineralogical changes in fault zone sulphides of Broken Hill, N.S.W. attributed to deformation, includes the exsolution of pyrrhotite and chalcopyrite from sphalerite and also, the exsolution of sphalerite, pyrrhotite and valleriite from chalcopyrite. Several workers have mentioned the possibility of forming pyrrhotite by the breakdown of pyrite to form pyrrhotite plus sulphur and perhaps magnetite. (L.A. Clark, personal communication; McDonald, 1967; Gammon, 1966; Hutchinson, 1965; Tsusue, 1962, and Friedman, 1959). Recent volcanogenic sulphide deposits in Japan and Cyprus are essentially devoid of pyrrhotite (L.A. Clark, personal communication). The sulphides deposited in the discharge pipes connected to the wells that tap the Salton Sea geothermal brine have no pyrrhotite (Skinner, et al., 1967) and the sulphides deposited from the geothermal brines in the Red Sea contain no pyrrhotite (Ross*).

In passing it is interesting to note another observation about the occurrence of pyrrhotite. This is in connection with its seeming absence when little or no chalcopyrite is present. Price (1948) notes the absence of pyrrhotite in the pyrite-sphalerite orebody at the Horne Mine. Boldy (1968) did not identify pyrrhotite at the Delbridge deposit and this is primarily a pyrite-sphalerite ore zone that contains only very minor amounts of chalcopyrite. Doe (1968) in his study of the Balmat area, New York, noticed the absence of pyrrhotite in those ore zones in which the

* D. Ross, Woods Hole, Mass.- Geothermal Brines in the Red Sea - Lecture given at McGill in 1968.

major sulphides are pyrite and sphalerite. In the case of the massive pyritic deposits of the Caledonides in Norway, Vokes (1962) mentions the pyrite-sphalerite association and the pyrrhotite-chalcopyrite association; as previously mentioned this has been noted in the massive lens and the disseminated sulphides in the footwall at Lake Dufault.

The partition of cobalt within the two groups, those with octahedrally co-ordinated metals and those with tetrahedrally co-ordinated metals, is very predictable. Cobalt is concentrated in pyrite with respect to pyrrhotite and in sphalerite with respect to chalcopyrite. Bachinski (1969) in his discussion on bond strength and sulphur isotopic fractionation in co-existing sulphides states that the pyrite lattice has a much higher bond strength than pyrrhotite and that the bond strength of sphalerite is much higher than that of chalcopyrite. This might explain the higher cobalt concentrations in pyrite as opposed to pyrrhotite and in sphalerite as opposed to chalcopyrite.

The partition of nickel is not as predictable as that of cobalt. It was noted previously that the results of previous workers disagreed somewhat. In the major sulphides at Lake Dufault the nickel is concentrated in pyrite with respect to pyrrhotite and in chalcopyrite with respect to sphalerite although in each instance reversals occur. The pyrite-pyrrhotite partition is the same as that found with cobalt but the partition between sphalerite and chalcopyrite is reversed.

The relative size of grains of pyrrhotite, sphalerite and chalcopyrite has no noticeable influence on the cobalt concentration. The grain size of pyrite, however, shows a definite correlation with cobalt content. The smaller grains, usually less than 50 microns, contained the highest amounts of cobalt. These smaller grains that contained the high cobalt content were located either right on the edge of masses of pyrite or were the only pyrite grains visible in the field of view.

Zoned Pyrite

The cobalt zoning encountered on the edges of some pyrite grains is unique in several ways. The zoning is restricted to small pyrite grains. The rim or zone may or may not be complete. The cobalt content both within the central portions and the rim, is greatly influenced by the amount of pyrite in the immediate vicinity (Table 24). The cobalt content is not homogenous either in the rim or in the central portion (Tables 25 and 27), and this type of inhomogeneity was not detected in pyrrhotite, sphalerite, chalcopyrite or unzoned pyrite grains (see Tables 10, 20, 21, 22 and 23). Figure 23 is plot of the data from Table 27. The increasing cobalt content appears not only to be coupled with decreasing iron content but also with decreasing sulphur content and tends to suggest that rather than having a solid solution series with CoS_2 the pyrite seems to be trending towards CoS , or at least may be becoming somewhat sulphur deficient and thus the zoned pyrite may actually fall on the FeS_2 - CoS composition line.

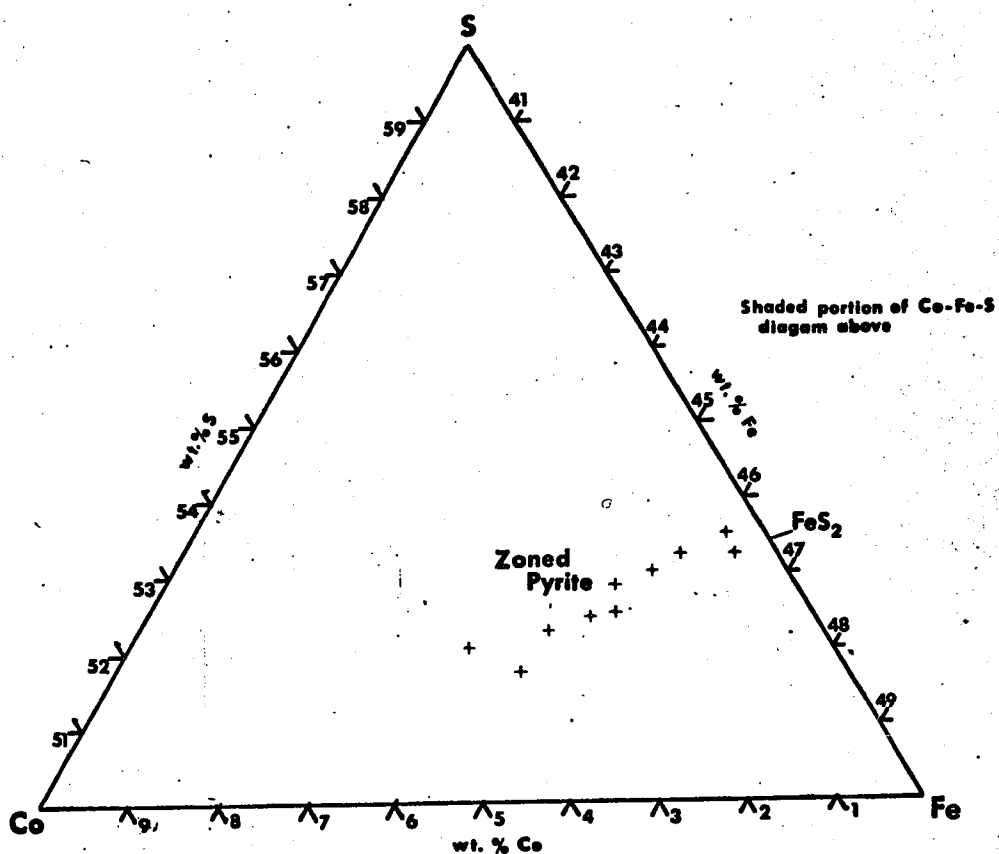
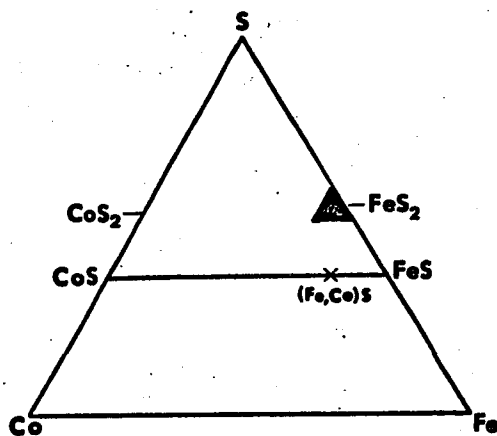


Figure 23 Plot of Table 27 showing zoned pyrite analyses

The iron (51.46 wt%) cobalt (12.17 wt%) monosulphide (36.37 wt% S) is plotted on Figure 23 and falls on the composition line between FeS and CoS.

The location of these zoned pyrite grains, as was mentioned before, is very similar to the high unzoned grains; i.e., away from or on the outer edges of pyrite zones.

Cobalt Minerals

Although cobalt was identified as a major constituent in unknown minerals and had a wide compositional range, from 12-36 weight percent, the chemical composition was often very difficult to determine. A mineral that is very close to cobaltite (Table 28) was identified several times and an iron cobalt monosulphide was analysed. The minerals with the intermediate cobalt concentrations were not analysed. Many of these proved to be very unstable phases with a varying composition. Attempting to analyse these unknowns using the electron microprobe was very difficult. The analyses were based on five or more repetitions per point for three elements simultaneously and with these unstable phases the reproducibility was extremely poor for as the electron beam burned into the grain the composition would change over wide ranges and when the results were submitted to the EMPADR V program the results were unusable. It is very significant that all cobalt minerals were found within pyrrhotite masses or on the boundaries and that pyrite was never present in the immediate vicinity. The presence of cobalt minerals in a

co-existing assemblage had no effect on the amount of cobalt present in pyrrhotite, sphalerite, or chalcopyrite. The only other reports of cobalt minerals in the Noranda massive sulphide deposits are those from the Vauze Mine (Lickus, 1965; Stumpfl and Clark, 1964).

The association between the cobalt minerals forming in or on the edges of pyrrhotite masses in the absence of pyrite suggests the following possibility. The pyrrhotite may have formed from the breakdown of pyrite over extensive periods of time at relatively low temperatures. It may also have formed by the mechanism suggested by Richards (1966); i.e., as a phase exsolved from both chalcopyrite and sphalerite. Johnson (1966) described exsolution textures involving pyrrhotite exsolving from chalcopyrite and sphalerite in his study of textures in the Lake Dufault ore zone. McDonald (1967) in his discussion on the effects of deformation of sulphides states ".... deformation introduces defects into mineral structures, thereby promoting diffusion of substitutional and interstitial ions towards these sites. It therefore acts to remove foreign ions from mineral structures. Effects of deformation can be recognized where exsolved mineral phases occur along crystallographic directions occupied by slip planes or intergranular boundaries". This mechanism can be used for not only the formation of some of the pyrrhotite, but also accounts for the occurrence of the cobalt minerals as well as the cobalt zoned pyrites, and is in fact an excellent description of their observed occurrence.

The excess cobalt that is found in the pyrite rims or that forms the cobalt minerals is believed to have originally been in pyrite. This pyrite which initially had a high cobalt content, possibly not unlike the irregular high cobalt observed in some of the pyrite grains, broke down to form pyrrhotite. This pyrrhotite is presumed to have formed at relatively low temperatures and is therefore capable of holding only 1000 ppm cobalt or less (1000 ppm cobalt is the maximum observed in this study). The excess cobalt is exsolved and migrates out of the pyrrhotite lattice possibly using the mechanism that McDonald (1967) suggests. The cobalt will then enter pyrite grains, if any are available, and if no pyrite is available will form the cobalt minerals.

Equilibrium Considerations

Within the detection limits of the analysing techniques that were used, cobalt distribution would appear to be quite uniform within individual grains of pyrrhotite, sphalerite and chalcopyrite. The distribution, however, varies between co-existing grains of the same mineral and no predictable distribution between co-existing phases was established other than the decreasing concentration through the series pyrite, pyrrhotite, sphalerite and chalcopyrite.

The concentration of cobalt plus other elements in the zoned pyrites and in some of the cobalt minerals is not uniform within given grains. These grains are in a state of disequilibrium. Bachinski (1969) notes that reactions involving pyrite are extremely sluggish

when compared to those involving pyrrhotite, sphalerite and chalcopyrite and attributes this to the very high bond energy of pyrite as opposed to the others.

Metamorphism, both dynamic and thermal, promotes the formation of equilibrium assemblages. The ore zone at Lake Dufault shows indications of disequilibrium assemblages even after the great length of time since its emplacement. The cobalt minerals and the cobalt zones in some of the pyrites are indications of a metamorphic reaction that has not reached equilibrium. Tables 23 and 24 which give the analyses of variance and variance components of cobalt content in pyrrhotite and chalcopyrite imply that equilibrium in each case has not progressed beyond the single grain stage.

Genetic Implications of This Study

Roscoe (1965) suggests that the sulphide ore bodies in the Noranda area were formed at or near the surface, or sea floor, under the influence of a very steep pressure-temperature gradient. Skripchenko (1967) notes that there ".... is strong evidence that submarine precipitation of sulphides at the outlets of volcanic ore solutions was the dominant method of accumulation of the large concordant massive pyritic copper deposits".

Skinner, et al., (1967) in reporting their findings pertaining to sulphides deposited in discharge pipes from the well tapping the Salton Sea geothermal brines noted the following:

- 1) the brine was concentrated, containing more than 25 percent dissolved solids;
- 2) a four inch discharge pipe deposited between five to eight tons of scale which contained about 20 percent copper and high gold and silver values over a three month period;
- 3) the samples studied were deposited at 220°C, and 170°C, and 130°C and contained sulphides in layers mixed with alternate layers of disseminated sulphides in an opaline matrix;
- 4) the deposition occurred under conditions of extreme disequilibrium; and
- 5) the material deposited represented, excluding Fe, less than 0.1 percent of the total heavy metals carried by the brine.

Barnes* in discussing the origin of the Mississippi Valley deposits, would transport the metals in a brine and deposit them in openings at 100°C. Ross notes that the Red Sea brines are depositing sulphides at 56°C.

The above examples are given in order to show that sulphide assemblages, in many ways are very similar to those found in Noranda, and may form from geothermal brines under the influence of a pressure-temperature gradient at near surface conditions.

The zoning reflected in the ore body, that of the Cu in the bottom and the Zn in the top of the massive lens as well as the position of the dusty sphalerite zone and the chalcopyrite in the central portion of the alteration pipe could very likely represent zoning

*"Mississippi Valley Type Deposits"- Lecture given at McGill in 1969.

brought on by a temperature gradient. Barnes reports the same type of zoning in the Mississippi Valley deposits. It is interesting to note that he concludes that the mineral deposition is from one ore solution.

The origin of the chert horizon that is associated with the ore zone may be accounted for by the conjecture of Skinner, et al., (1967) concerning the sulphide-bearing opaline material found in the Salton Sea discharge pipes: "It is interesting to speculate that similar opaline materials may have been progenitors of some of the fine-grained sulphide-bearing cherts found in epithermal deposits, the sulphides forming into distinct phases as the opal later broke down and recrystallized to chert".

The homogeneous distribution of cobalt within the unzoned pyrite grains and the cobalt distribution within the grains of pyrrhotite, sphalerite and chalcopyrite suggests that the trace elements were introduced at the same time as the major elements. The variations between individual co-existing grains of the same phase certainly indicates gross disequilibrium at the time of formation because metamorphism still has not brought about equilibrium beyond grain boundaries. These observations support the deposition of the ore at surface conditions from one ore solution under a steep pressure-temperature gradient possibly not unlike the conditions now existing at the Salton Sea or the Red Sea.

The irregular cobalt distribution in the zoned pyrite grains and in some of the small pyrite grains and the cobalt minerals all of which are associated with pyrrhotite indicate a later mobility of cobalt associated with metamorphism.

CHAPTER V

SUMMARY AND CONCLUSIONS

1. The analyses performed on pyrite, pyrrhotite, sphalerite, and chalcopyrite from the Lake Dufault ore zone for trace cobalt and nickel contents support the contention that these elements concentrate in octahedrally co-ordinated minerals as opposed to tetrahedrally co-ordinated minerals.

2. There is no lateral or vertical zoning or gradient of cobalt or nickel concentration in the Lake Dufault ore zone.

3. Cobalt occurs with decreasing concentration through the series pyrite, pyrrhotite, sphalerite, chalcopyrite. Nickel occurs with decreasing concentration through the series pyrite, pyrrhotite, chalcopyrite, sphalerite.

4. The cobalt partition is much more predictable on the basis of the work performed for this study than that of the nickel, especially in the tetrahedrally co-ordinated minerals.

5. Other than the predicted sequence of mineral preference, cobalt and nickel do not partition between co-existing phases in predictable ratios.

6. Grain size is only significant in the case of pyrite. The smaller pyrite grains contain the higher cobalt values.

7. The presence of cobalt minerals, cobalt zoned pyrites and the high cobalt pyrites is associated with the occurrence of pyrrhotite. It is suggested that these three different occurrences

of cobalt result from the formation of pyrrhotite as a metamorphic mineral. The pyrrhotite forming from the breakdown of pyrite and/or being exsolved from chalcopyrite and sphalerite at low temperature and not being able to retain the cobalt in any significant amounts. When there is excessive cobalt present it will enter pyrite when present and if no pyrite is present will form cobalt sulphides.

8. Equilibrium between co-existing phases of pyrrhotite and chalcopyrite has not progressed beyond the boundaries of individual grains.

9. The zoned pyrite grains and the unstable cobalt phases indicate that these assemblages have not yet reached a state of internal equilibrium and thus that metamorphic equilibrium within the ore body has not yet been attained.

CONTRIBUTIONS TO KNOWLEDGE AND CLAIM TO ORIGINAL WORK

The author claims the following:

- 1) The analyses performed for this investigation;
- 2) The established limits of cobalt and nickel in pyrite, pyrrhotite, sphalerite and chalcopyrite for the ore zones;
- 3) Other than the established mineral preference the distribution of cobalt and nickel is not predictable in these orezones;
- 4) The establishment of restricted equilibrium limits within the orezone;
- 5) The recognition, description and interpretation of the zoned pyrites and the pyrite grains with irregular high cobalt distribution;
- 6) The manner in which the cobalt minerals are formed from the breakdown of pyrite.

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APPENDIX A - STANDARDS

ELECTRON MICROPROBE

Cobalt in Chalcopyrite Standards

\bar{x} = mean in counts per second

s = standard deviation in counts per second

n = number of readings

t = Students t for 5% significance level

$$\text{Confidence interval} = \frac{ts}{n}$$

10,000 ppm Co

\bar{x} = 60.1

s = 1.3

Confidence interval = 0.7
(at 95% confidence limits)

n = 15

\bar{x} with 95% confidence limits = 60.1 ± 0.7

5,000 ppm Co

\bar{x} = 34.7

s = 0.85

Confidence interval = 0.4
(at 95% confidence limits)

n = 20

\bar{x} with 95% confidence limits = 34.7 ± 0.4

2000 ppm Co

\bar{x} = 18.3

s = 0.55

Confidence interval = 0.28

n = 18

\bar{x} with 95% confidence limits = 18.3 ± 0.28

1000 ppm

$$x = 12.7$$

$$s = 0.5$$

$$n = 17$$

Confidence interval = 0.25
(95% confidence limits)

x with 95% confidence limits = 12.7 ± 0.25

500 ppm

$$x = 10.4$$

$$s = 0.35$$

$$n = 16$$

Confidence interval = 0.19
(95% confidence limits)

x with 95% confidence limits = 10.4 ± 0.19

200 ppm

$$x = 8.2$$

$$s = 0.45$$

$$n = 18$$

Confidence interval = 0.22
(95% confidence limits)

x with 95% confidence limits = 8.2 ± 0.22

Cobalt in Pyrrhotite Standards

10,000 ppm

$$x = 58.3$$

$$s = 1.0$$

$$n = 20$$

Confidence interval = 0.44
(95% confidence limits)

x with 95% confidence limits = 58.3 ± 0.44

5000 ppm

$$x = 33.0$$

$$s = 0.85$$

$$n = 16$$

Confidence interval = 0.47
(95% confidence limits)

$$x \text{ with 95\% confidence limits} = 33.0 \pm 0.47$$

2000 ppm

$$x = 17.2$$

$$s = 0.7$$

$$n = 21$$

Confidence interval = 0.31
(95% confidence limits)

$$x \text{ with 95\% confidence limits} = 17.2 \pm 0.31$$

1000 ppm

$$x = 12.6$$

$$s = 0.55$$

$$n = 21$$

Confidence interval = 0.31
(95% confidence limits)

$$x \text{ with 95\% confidence limits} = 12.6 \pm 0.31$$

1000 ppm

$$x = 12.6$$

$$s = 0.55$$

$$n = 16$$

Confidence interval = 0.30
(95% confidence limits)

$$x \text{ with 95\% confidence limits} = 12.6 \pm 0.30$$

500 ppm

$$x = 9.2$$

$$s = 0.50$$

$$n = 16$$

Confidence interval = 0.28
(95% confidence limits)

$$x \text{ with 95\% confidence limits} = 9.2 \pm 0.28$$

200 ppm Co

$$x = 7.7$$

$$s = 0.18$$

$$n = 4$$

Confidence interval = 0.26
(95% confidence limits)

$$x \text{ with 95\% confidence limits} = 7.7 \pm 0.26$$

Background

The background effect was determined by taking readings 5° on each side of the Co $K_{\alpha 1}$ peak on each of the four minerals. The results were:

pyrite 5.0 cps

pyrrhotite 4.8 cps

chalcopyrite 4.6 cps

sphalerite 5.6 cps

In addition to the instrumental background contribution there was also a contribution from a minor Fe peak that coincides with the Co $K_{\alpha 1}$ peak. The effect of this iron peak was determined by running samples of both at the artificial standards (FeS and CuFeS_2) that contained no cobalt on the Co $K_{\alpha 1}$ peak. A linear graph was then made using weight percent iron as one axis and the cps as the other.

The weight percent iron in pyrite was plotted as 46.5 and that of sphalerite as 16.6. The total background then becomes

	Background	Fe peak	Total
pyrite	5.0 cps	1.7 cps	6.7 cps
pyrrhotite	4.8 cps	1.9 cps	6.7 cps
chalcopryite	4.6 cps	1.4 cps	6.0 cps
sphalerite	5.6 cps	1.2 cps	6.8 cps

Cobalt Conversion Factors

The cobalt content in both the chalcopryite and pyrrhotite plots as essentially a straight linear function. Because of this, the slope of the curves were used to determine the conversion factors as follows:

$$\text{chalcopryite} = \frac{10,000 \text{ ppm Co}}{(60.1 - 6.0) \text{ cps}} = 185 \text{ ppm Co/cps}$$

$$\text{pyrrhotite} = \frac{10000 \text{ ppm Co}}{(58.3 - 6.7) \text{ cps}} = 194 \text{ ppm Co/count}$$

Pyrite and sphalerite were assigned the mid point between 60.1 cps and 58.3 cps which is 59.1 cps. The conversion factors for these minerals were then:

$$\text{pyrite} = \frac{10000 \text{ ppm Co}}{(59.1 - 6.7) \text{ cps}} = 191 \text{ ppm Co/count}$$

$$\text{sphalerite} = \frac{10000 \text{ ppm Co}}{(59.1 - 6.8) \text{ cps}} = 190 \text{ ppm Co/count}$$

ATOMIC ABSORPTION

Cobalt in Pyrrhotite

Concentration	Meter Reading		
200 ppm	1.06	1.06	1.05
500 ppm	1.80	1.84	1.80
1000 ppm	2.22	2.23	2.22
2000 ppm	2.79	2.83	2.81
5000 ppm	3.87	3.85	3.85

Nickel in Pyrrhotite

Concentration	Meter Reading		
50 ppm	1.18	1.20	1.20
100 ppm	1.80	1.78	1.80
250 ppm	2.40	2.40	2.40
500 ppm	3.00	3.05	3.05
1000 ppm	3.45	3.50	3.50

Working Conditions

	Cobalt	Nickel
Slit width	0.08mm	0.08mm
Wavelength	2397A	2320A
Air	5 lbs	5 lbs
Acetylene	14.5 lbs	13 lbs

Atomic Absorption Sample Dispersion

Standard Deviation

Cobalt

N-127-1293 pyrite

repetitions in ppm = 2650, 2500, 2600, 2800, 2725

s = standard deviation = 103 ppm

N-127-1293- sphalerite

repetitions in ppm = 50, 55, 47, 48, 50

s = standard deviation = 2.8 ppm

Nickel

N-147-1295

repetitions in ppm = 47, 55, 50, 51, 47

s = standard deviation = 2.97 ppm

APPENDIX B

B-1

$$X_{ijk} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk}$$

ANALYSIS OF VARIANCE

Source	Sum of squares	Degrees Freedom	Mean Square
Between Grains	$SS_1 = \frac{\sum_i (\sum_{jk} X_{ijk})^2}{bc} - \frac{(\sum_{ijk} X_{ijk})^2}{abc = n}$	$(a - 1)$	$V_1 = \frac{SS_1}{a - 1}$
Between points within grains	$SS_2 = \frac{\sum_{ij} (\sum_k X_{ijk})^2}{c} - \frac{\sum_i (\sum_{jk} X_{ijk})^2}{bc}$	$a(b - 1)$	$V_2 = \frac{SS_2}{a(b - 1)}$
Between repetitions between points	$SS_3 = \sum_{ijk} (X_{ijk})^2 - \frac{\sum_{ij} (\sum_k X_{ijk})^2}{c}$	$ab(c - 1)$	$V_3 = \frac{SS_3}{ab(c - 1)}$
Total	$\sum_{ijk} (X_{ijk})^2 - \frac{(\sum_{ijk} X_{ijk})^2}{abc = n}$	$abc - 1$	

ESTIMATION OF VARIANCE COMPONENTS

Levels	Difference	Sample size	Variance component
Grains	$V_1 - V_2$	bc	$S_\alpha^2 = \frac{V_1 - V_2}{bc}$
Points	$V_2 - V_3$	c	$S_\beta^2 = \frac{V_2 - V_3}{c}$
Repetitions	V_3	1	$S_\gamma^2 = V_3$

EXPLANATION OF SYMBOLS

X_{ijk} = a single observation

μ = grand mean

α_i = comp. due to grain i

β_{ij} = comp. due to point, within grain i

γ_{ijk} = comp. due to repetition k , within point j , within grain i

$\alpha_i, \beta_{ij}, \gamma_{ijk}$ are independent with mean 0 and variances S_α^2, S_β^2 , and S_γ^2

i varies from 1 to a

j varies from 1 to b

k varies from 1 to c

where

a = number of grains

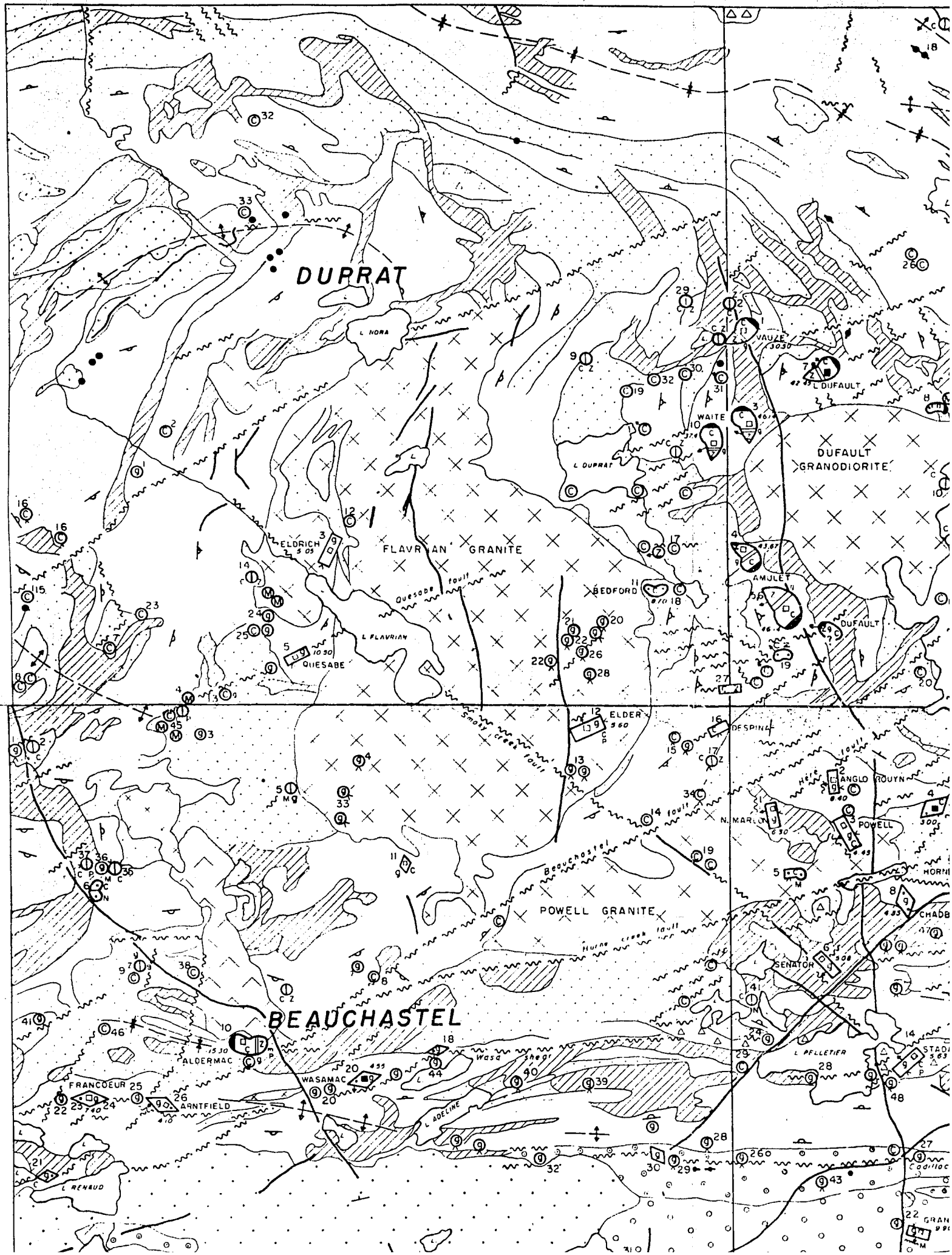
b = number of points / grain

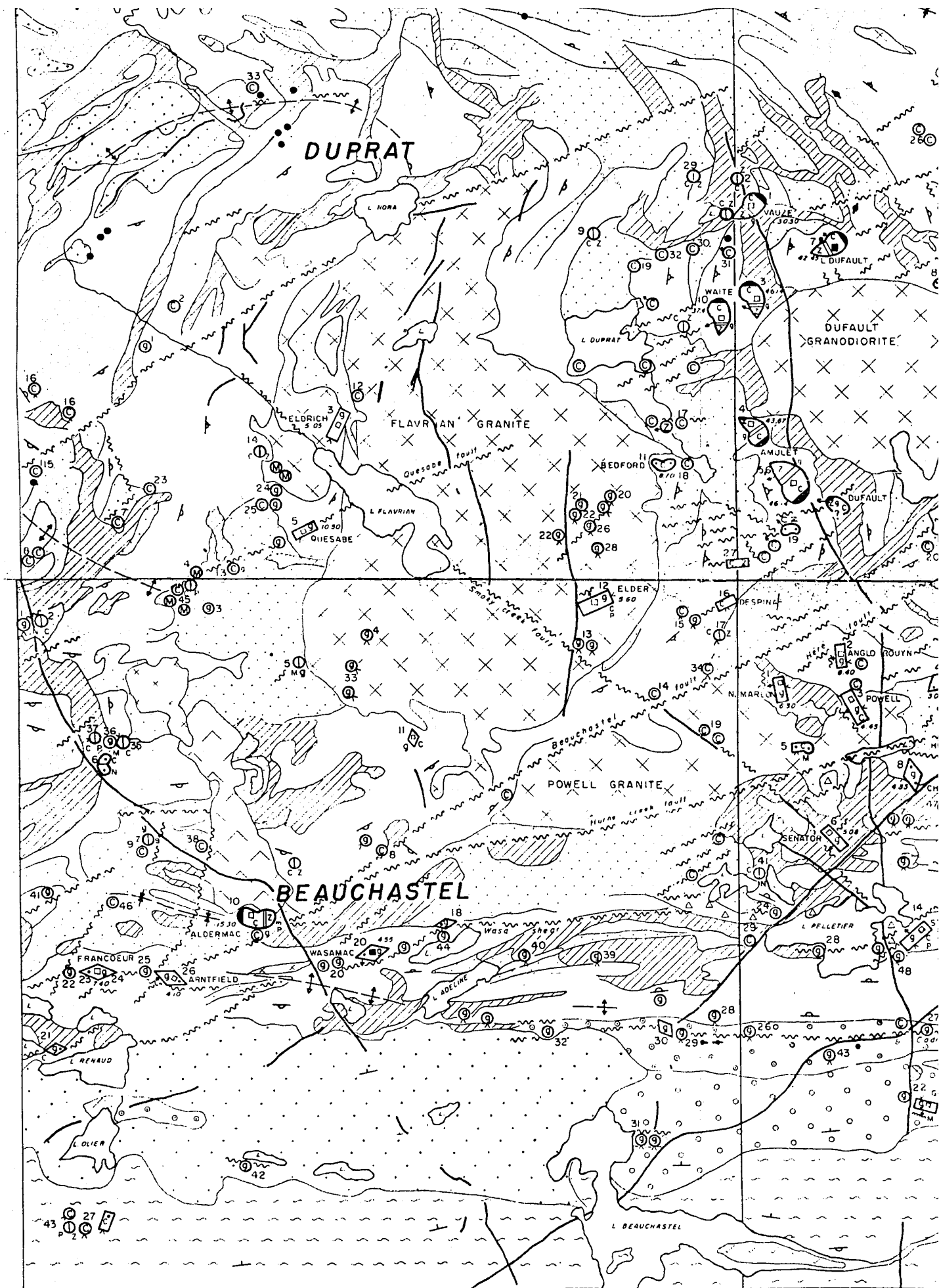
c = number of repetitions / point

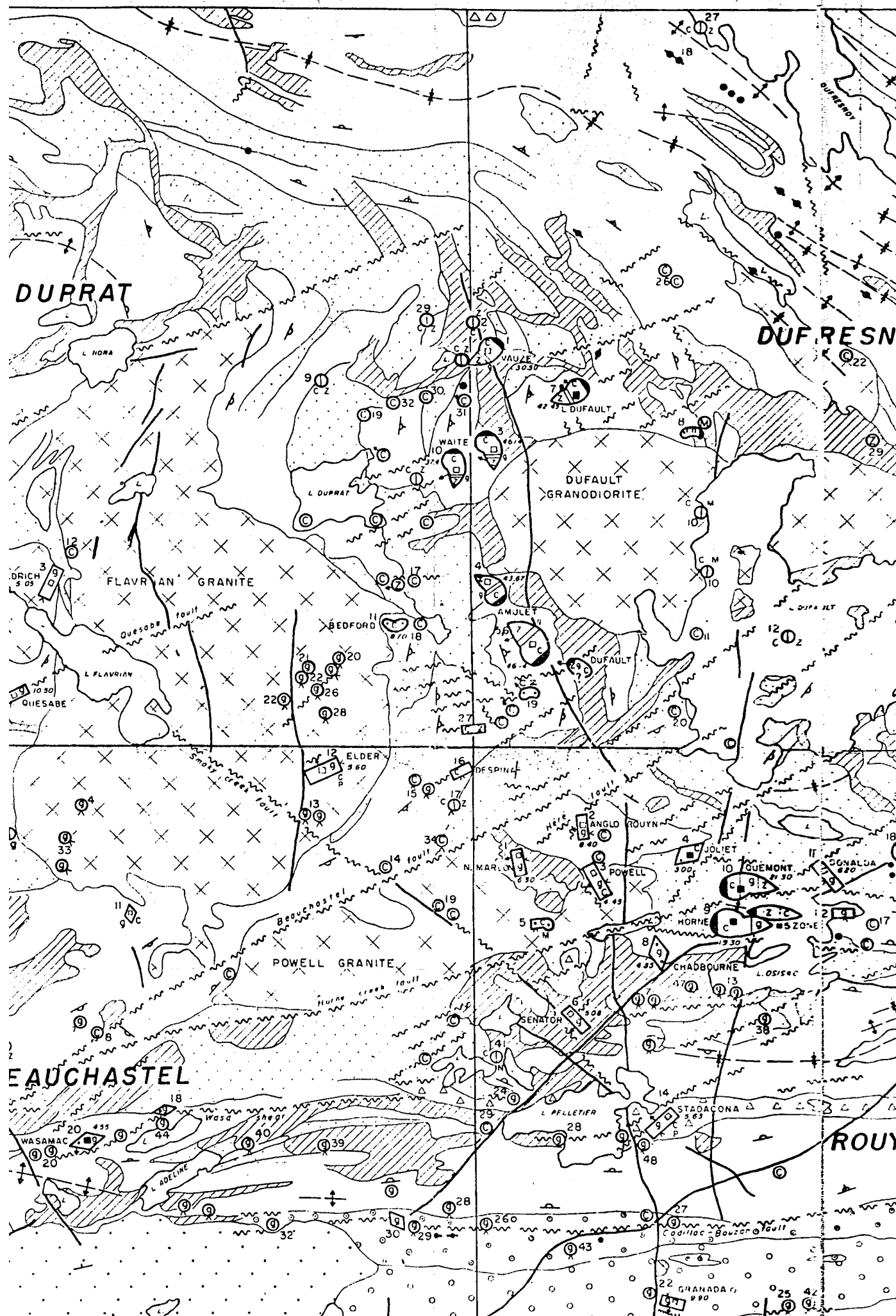
$n = abc$ = total repetitions recorded

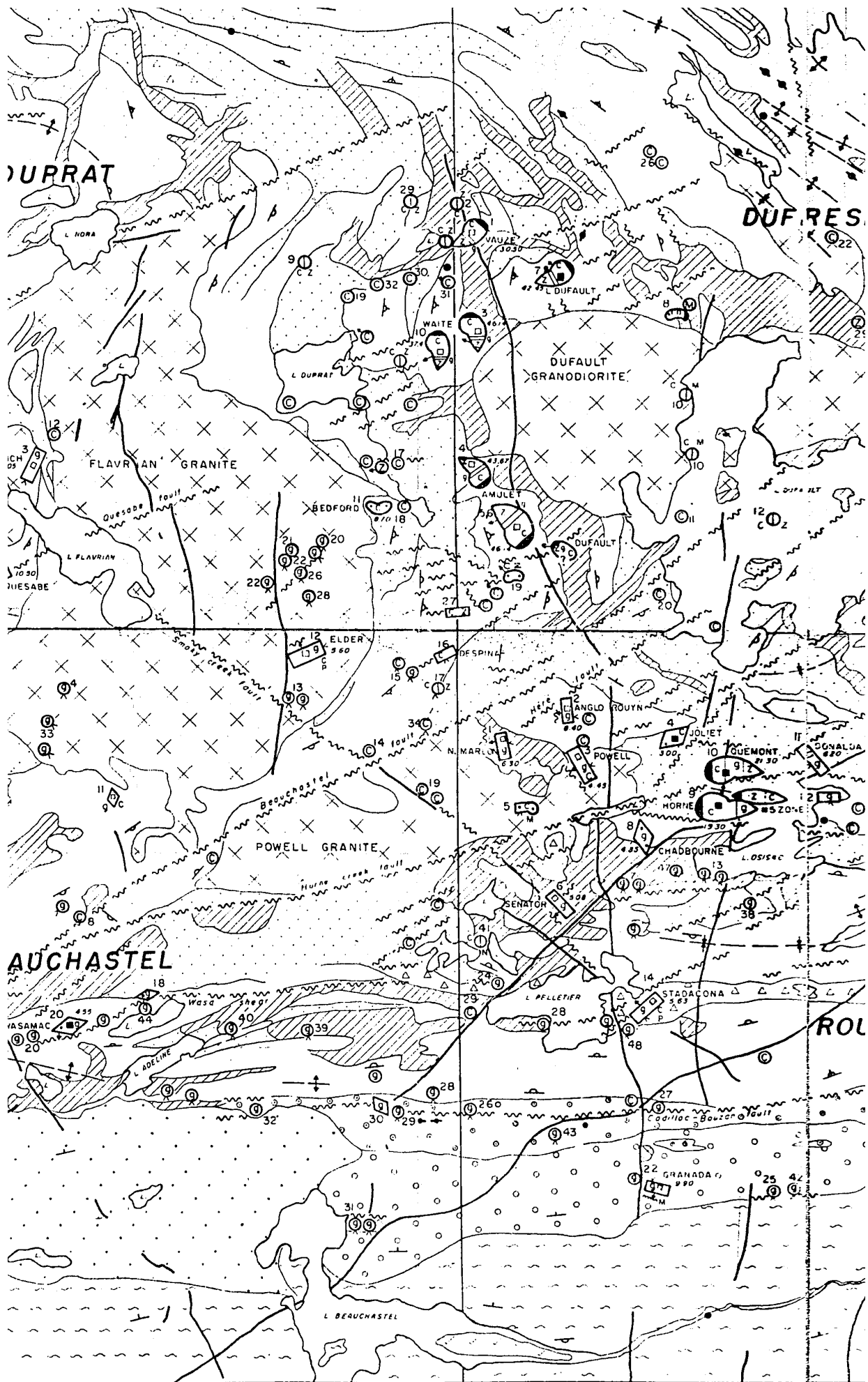
FIGURE B-1 Statistical Model For Sampling Hierarchy
(After Krumbein and Slack, 1956)

For convenience of notation and comparison with the mean squares in the analysis of variances table, all variances are shown as S^2 . More rigorously the theoretical variances should be shown as σ^2 in the lower left part of this figure (Krumbein and Slack, 1956) -









MINISTÈRE DES RICHESSES NATURELLES METALLIOGRAPHIC COM NORANDA AREA

LATE PRECAMBRIAN

Diabase, gabbro

HURONIAN (COBALT)

Graywacke, argillite
conglomerate

EARLY PRECAMBRIAN

INTRUSIVE ROCKS

Granite, granodiorite

Syenite

Porphyry, rhyolite

Diorite, gabbro

Peridotite, pyroxenite

SEDIMENTARY ROCKS

TEMISKAMING SERIES

Conglomerate, /graywacke

PONTIAC GROUP

Mica schist, amphibolite

fault

strike

anticline

syncline

1
miles

Geology modified
Q.D.N.R. by J.D.

VOLCANIC

Tuff, ag.

Siliceous

Intermediate

METALLIC

I/ MORPHOLOGY & HOST RELATIONS

STRUCTURE-LIMITED DEPOSITS:

a vein, dyke

b fracture zone, shear zone

STRATA-LIMITED DEPOSITS:

c lensoid masses, beds, incl.
strata-bound bodies

IRREGULAR DEPOSITS:

d irregularly-shaped masses
or zones

COMPOUND DEPOSITS:

-deposits with combined features
shown as composite of above
symbols eg: c + b

DEPOSITS

II/ ORDERS OF

NOMINAL VALUE C
PLUS PRODUCTION

1st >\$100	2nd
	(e)

Nominal value

III/ ECONOMIC METALS PRESENT IN DEPOSIT

Nominal \$ value per ton

Proportion of total nominal \$ value

127	C	9	Z
25%	25%	50%	
	C - copper (sulphide)	Z - zinc (sulphide)	
	P - lead (sulphide)	g - gold, silver	
	M - molybdenum (sulphide)	N - nickel (sulphide)	
	B - bismuth		

IV/ GANGUE or MINERALS

	m p ma pyl vei
--	----------------------------

V/ MINING STATUS

	PRODUCER
	PAST PRODUCER
	UNEXPLOITED

VI/ DISPOSITION MINERALS

VII/ MISCELLANEOUS CONVENTIONS

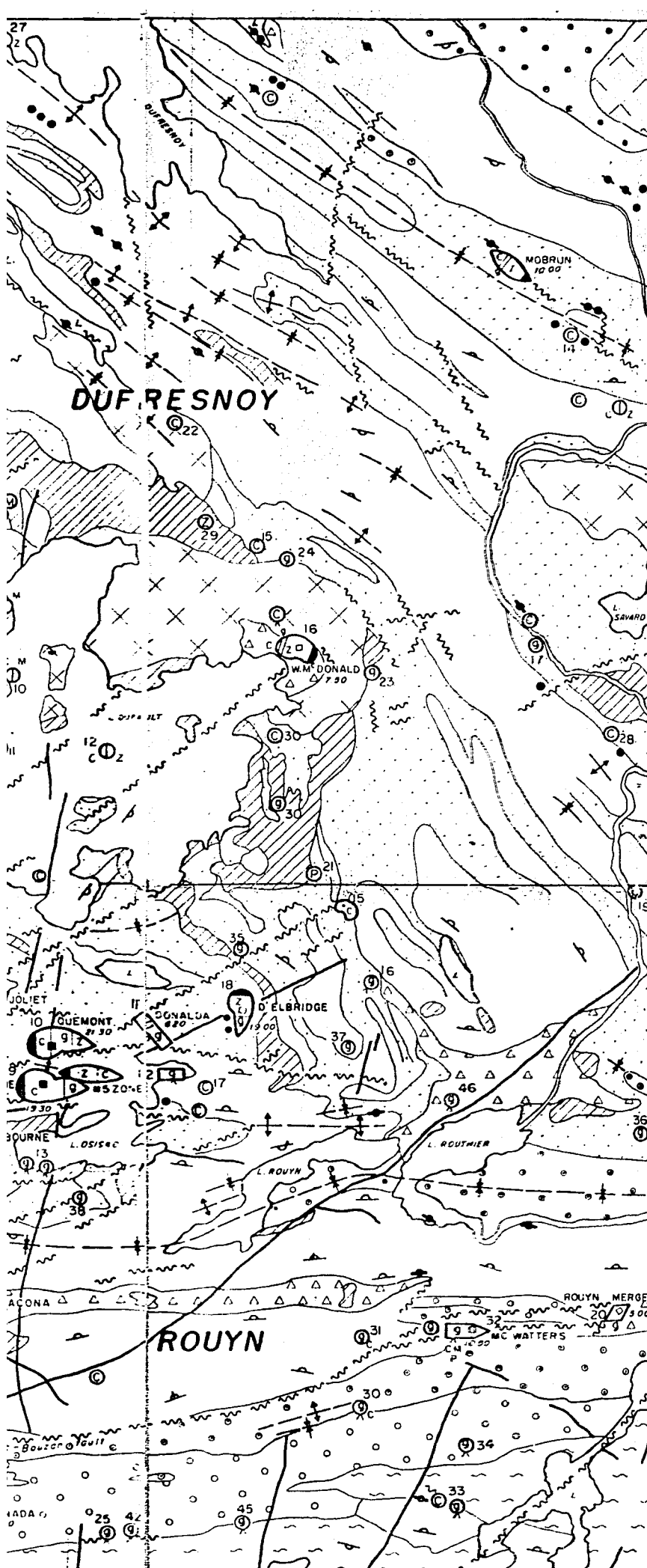
up-dip direction to surface
expression of metallized
contact or structure

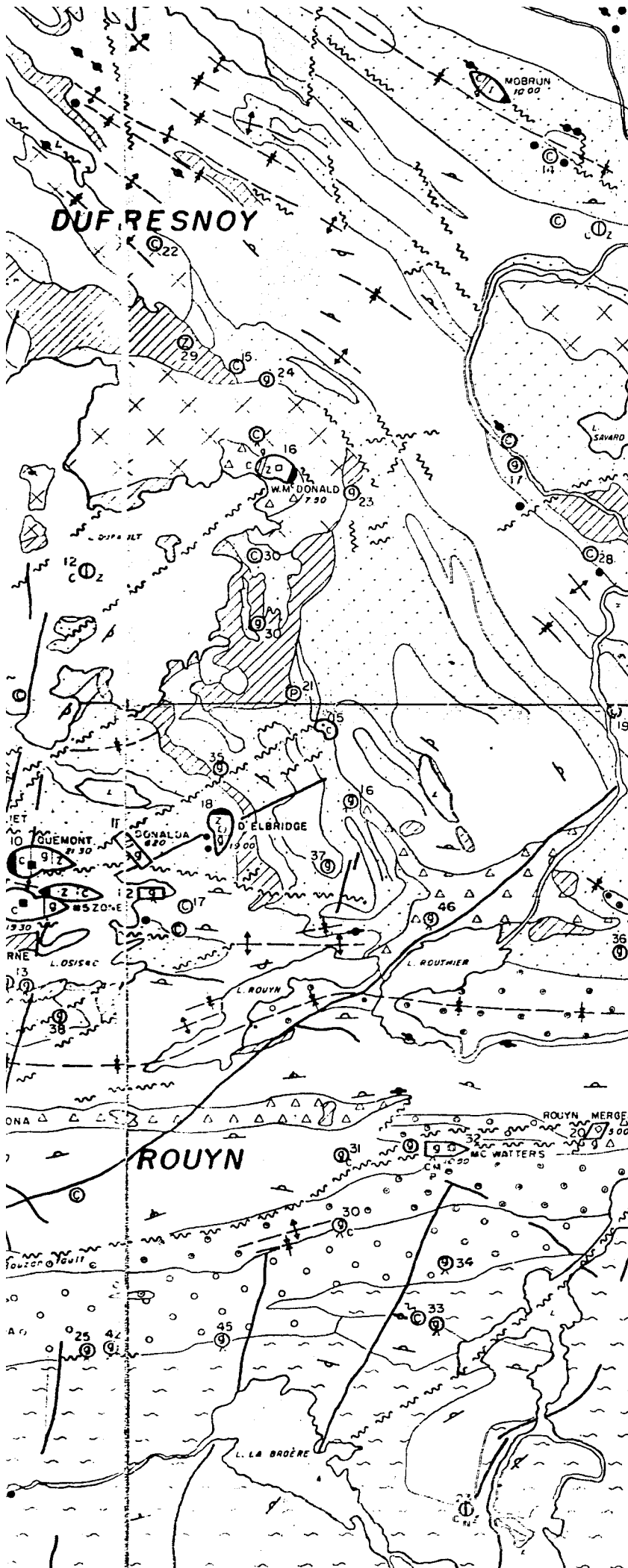
orientation

• barren sulphide occurrence

• barren sulphide occurrence

3 Number of deposit per
Metallic Mineralisation
Map No. B 835, Q.D.N.R.





PROTEROZOIC (CUBAL)
 Graywacke, argillite
 conglomerate

EARLY PRECAMBRIAN

INTRUSIVE ROCKS
 Granite, granodiorite
 Syenite
 Porphyry, rhyolite
 Diorite, gabbro
 Peridotite, pyroxenite

SEDIMENTARY ROCKS
TEMISKAMING SERIES
 Conglomerate, /graywacke
PONTIAC GROUP
 Mica schist, amphibolite

VOLCANIC
 Tuff, c
 Silice
 Interm

1
 miles

Geology mod.
 Q.D.N.R. by

METALLIC

I/ MORPHOLOGY & HOST RELATIONS
STRUCTURE-LIMITED DEPOSITS:
 a vein, dyke
 b fracture zone, shear zone
STRATA-LIMITED DEPOSITS:
 c lensoid masses, beds, incl. strata-bound bodies
IRREGULAR DEPOSITS:
 d irregularly-shaped masses or zones
COMPOUND DEPOSITS:
 -deposits with combined features shown as composite of above symbols eg: c + b

II/ ORDERS OF DEPOSIT
 NOMINAL VALUE PLUS PRODUCT
 1st > \$100 2nd
 Nominal val

III/ ECONOMIC METALS PRESENT IN DEPOSIT
 Nominal \$ value per ton
 Proportion of total nominal \$ value
 127 25 25 50
 C - copper (sulphide)
 Z - zinc (sulphide)
 P - lead (sulphide)
 g - gold, silver
 M - molybdenum (sulphide)
 N - nickel (sulphide)
 B - bismuth

IV/ GANGUE MINERALS

V/ MINING STATUS
 PRODUCER
 PAST PRODUCER
 UNEXPLOITED

VI/ DISPOSITIVE MINERALS

VII/ MISCELLANEOUS CONVENTIONS
 up-dip direction to surface
 expression of metallized contact or structure
 barren sulphide occurrence
 barren occurrence

Example of COMBINED NOTATIONS

3 Number of deposit per Metallic Mineralisation Map No. B 835, Q.D.N.R.

1 partly strata-bound
 II nominal metal value
 III main metals are #21
 IV nominal concentration
 V associated magnet.
 VI past-producer
 VII deposit is sulphide
 VIII host rock or struct

MINISTÈRE DES RICHESSES NATURELLES METALLIOGRAPHIC COMPILATION NORANDA AREA

LATE PRECAMBRIAN

Diabase, gabbro

HURONIAN (COBALT)

Graywacke, argillite conglomerate

EARLY PRECAMBRIAN

INTRUSIVE ROCKS

Granite, granodiorite

Syenite

Porphyry, rhyolite

Diorite, gabbro

Peridotite, pyroxenite

SEDIMENTARY ROCKS TEMISKAMING SERIES

Conglomerate, /graywacke

PONTIAC GROUP

Mica schist, amphibolite

fault, schist zone

strike & top of beds

anticlinal axis

synclinal axis

miles 1 0 1

Geology modified from map No. M 265,
O.D.N.R. by J Dugas & W A Hogg, 1962.

VOLCANIC ROCKS

Tuff, agglomeratic rocks

Siliceous lava & breccia

Intermediate & mafic lavas

METALLIC

I/MORPHOLOGY & HOST RELATIONS

STRUCTURE - LIMITED DEPOSITS:

- a vein, dyke
b fracture zone, shear zone

STRATA - LIMITED DEPOSITS:

- c lensoid masses, beds, incl. strata-bound bodies

IRREGULAR DEPOSITS:

- d irregularly-shaped masses or zones

COMPOUND DEPOSITS:

- deposits with combined features shown as composite of above symbols eg: c + b

DEPOSITS

II/ORDERS OF METAL CONTENT

NOMINAL VALUE OF METALS: RESERVES PLUS PRODUCTION (in millions of \$)

1st > \$100	2nd 100 - 2.5	3rd < 2.5	minor
	(etc.)		

Nominal values: Cu - 30⁰/lb.
Zn - 12.5⁰/lb.
Pb - 12.5⁰/lb.
Au - \$35/oz.
Ag - \$1/oz.

III/ECONOMIC METALS PRESENT IN DEPOSIT

Nominal \$ value per ton

Proportion of total nominal \$ value

127 C - copper (sulphide)
Z - zinc (sulphide)
P - lead (sulphide)
g - gold, silver
M - molybdenum (sulphide)
N - nickel (sulphide)
B - bismuth

IV/GANGUE or ASSOCIATED MINERALS

m magnetite
p pyrite / pyrrhotite
A vein quartz

V/MINING STATUS

PRODUCER
 PAST PRODUCER
 UNEXPLOITED

VI/DISPOSITION OF METALLIC MINERALS

concentrated or massive
 dispersed or disseminated

VII/MISCELLANEOUS CONVENTIONS

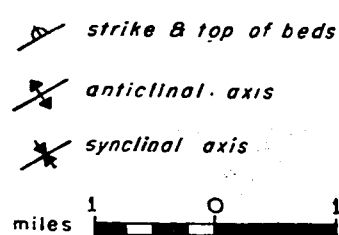
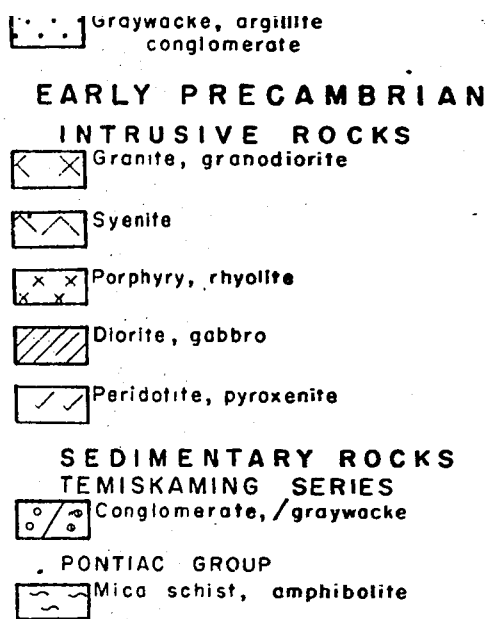
up-dip direction to surface expression of metallized contact or structure

orientation of symbol gives strike

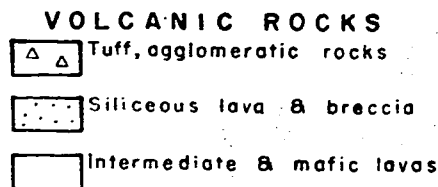
• barren sulphide occurrence

• barren sulphide-graphitic argillite occurrence

³ Number of deposit per
Metallic Mineralisation
Map No. B 835, O.D.N.R.



Geology modified from map No. M 265, O.D.N.R. by J Dugas & W.A. Hogg, 1962.



METALLIC

I/MORPHOLOGY & HOST RELATIONS

STRUCTURE-LIMITED DEPOSITS:

- a vein, dyke
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DEPOSITS

II/ORDERS OF METAL CONTENT

NOMINAL VALUE OF METALS: RESERVES PLUS PRODUCTION (in millions of \$)

1st >\$100	2nd 100-2.5	3rd <2.5	minor
	(etc.)		

Nominal values: Cu - 30¢/lb.
Zn - 12.5¢/lb.
Pb - 12.5¢/lb.
Au - \$35/oz.
Ag - \$1/oz.

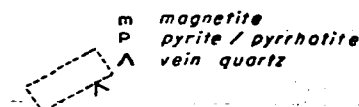
III/ECONOMIC METALS PRESENT IN DEPOSIT

Nominal \$ value per ton

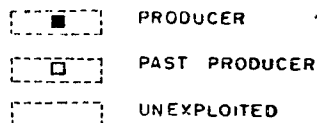
Proportion of total nominal \$ value

127	C	g	Z
25%	25%	50%	
	C - copper (sulphide)	Z - zinc (sulphide)	
	P - lead (sulphide)	g - gold, silver	
	M - molybdenum (sulphide)	N - nickel (sulphide)	
	B - bismuth		

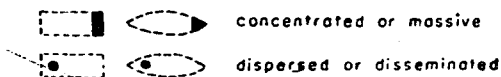
IV/GANGUE or ASSOCIATED MINERALS



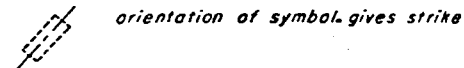
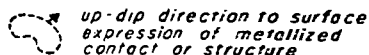
V/MINING STATUS



VI/DISPOSITION OF METALLIC MINERALS



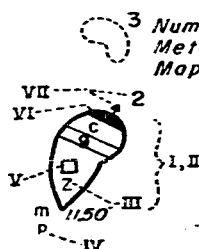
VII/MISCELLANEOUS CONVENTIONS



barren sulphide occurrence

barren sulphide-graphitic argillite occurrence

Example of COMBINED NOTATIONS



- I partly strata-bound irregular deposit.
- II nominal metal values greater than \$100,000,000.
- III main metals are \$Zn 60%, \$Au, Ag 10%, \$Cu 30% nominal concentration equals \$11.50 per ton.
- IV associated magnetite and pyrite
- V past-producer
- VI deposit is sulphide body
- VII host rock or structure projects surface up-dip to NE.