# SULFUR ISOTOPES AND BASE METAL ZONING IN THE HEATH STEELE B-1 OREBODY

# SULFUR ISOTOPE ABUNDANCES AND BASE METAL ZONING IN THE HEATH STEELE B-1 OREBODY,

## NEWCASTLE, NEW BRUNSWICK

By-

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SCOPE AND CONTENTS:

 $s^{32}/s^{34}$  ratios have been determined between some coexisting sulfides from the Heath Steele B-1 orebody and five other stratiform deposits in the Bathurst-Newcastle area, New Brunswick, and in crushed ore samples and pyrites from three across deposit profiles in the B-1 orebody. Zn. Cu, Pb and Ag abundances have been established across the orebody. Fractionations of S<sup>32</sup>/S<sup>34</sup> ratios between coexisting sulfides have been determined in heating experiments at temperatures of 350 to 500°C and isotope effects measured in aqueous precipitation and exchange experiments at  $s^{32}/s^{34}$  fractionations between given coexisting sulfides from all 25°C. the sulfide deposits are found to show only small variations. Isotope exchange is generally rapid in dry sulfide systems. Metal sulfides in aqueous solutions are slightly enriched in S<sup>32</sup> relative to the H<sub>a</sub>S with which they precipitate or communicate. It is concluded that the sulfide deposits have been regionally metamorphosed. The origins that have been proposed for the deposits so far are discussed and a model is suggested to explain the sulfur isotope and base metal abundances in the B-1 orebody.

ii

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iii

### TABLE OF CONTENTS

CHAPTER I. INTRODUCTI	LON
-----------------------	-----

1-1	Purpose of the present study	<b>J</b> .
1-2	Types of stratiform deposits	4
1-3	Some general features of "volcanic" type stratiform deposits	4
1-4	Geology, distribution and description of sulfide depo- sits in the Bathurst-Newcastle area, New Brunswick	9
1-4-1	Regional geology of the Bathurst-Newcastle area	9
1-4-2	Distribution of the sulfide deposits	14
1-4-3	General features of the sulfide deposits	14
1-4-4	Types of rocks associated with the stratiform deposits .	15
1-4-5	Mineralogy of the stratiform deposits	16
1-4-6	Textures in the stratiform ores of the Bathurst-Newcastle camp	19
1-5	Estimation of the temperature of formation of the strati- form deposits using the sphalerite and pyrrhotite geo- thermometers	21
1-6	Grade of metamorphism in the Tetagouche rocks	23
1-7	Relationship between the structure of the enclosing rocks and the occurrence of the deposits	27
1-8	Relationship between the distribution of sulfide mineralization and the intrusive rocks	27
1-9	Location of the Heath Steele Mine	29
1-10	Geology of the Heath Steele Mine	29
1-11	Geology of the B-1 ore zone	35
1-12	Fabric of the massive sulfides	37
1 <b>-</b> 13	Mineralogy of the B-1 orebody	39

Tage

		Page
1-14	Structure of the B-1 ore zone	40
1 <b>-</b> 15	Sulfur isotope studies on stratiform deposits	42
	Sulfur isotope studies on the sulfide deposits and country rocks of the Bathurst-Newcastle area	45
1-16	Suggested origins of the "volcanic" stratiform deposits .	51
1-17	Origin of sulfide deposits in the light of sulfur iso- tope studies	55
CHAPTER	2. MINERALOGICAL ASSOCIATIONS, BASE METAL ZONING AND METAMORPHISM IN THE B-1 OREBODY AND ASSOCIATED ROCKS	
2 <b>-1</b>	Introductory statement	64
2-2	Mineralogical associations in the B-1 orebody	64
2-3	Base metal zoning in the B-1 orebody	66
2- <sup>1</sup> +	Possible spatial relationship between the location of the axes of Zu-Pb-Ag "centers" and "porphyry" in the footwall	<b>68</b>
2-5	Relationship between across deposit base metal zoning in "volcanic" type stratiform deposits and the stratigraphy of associated rocks	69
2 <b>-</b> 6	Metamorphic silicate assemblages in the B-1 orebody and associated rocks	71
CHAPTER	3. GENERAL ANALYTICAL PROCEDURES	
3 <b>-</b> 1	Selection of samples for isotopic study	77
3-2	Brief description of the mineralogy of samples selected for isotopic study	78
3-3	Preparation of sulfide samples prior to mineral separa- tion	79
3-4	Mineral separation	80
3-5	Estimation of purity of sulfide concentrates	85
3-6	Preparation of sulfur dioxide gas for isotopic analysis .	86

## TABLE OF CONTENTS (continued)

3-7	Measurement of S <sup>32</sup> /S <sup>34</sup> raties	Page 89
3-8	Relationship between $5^{32}/5^{34}$ ratios and $55^{34}$ values .	90
3 <b>-</b> 9	Precision of mass spectrometer measurement	91
3-10	Influence of sulfide impurities in measured isotope ratios	101
3-11	Summary and conclusions regarding the precision of isotopic measurement	105
CHAPTER	4. PRESENTATION AND ANALYSIS OF SULFUR ISOTOPE DATA FOR SULFIDES FROM SOME STRATIFORM SULFIDE DEPOSITS IN THE BATHURST-NEWCASTLE AREA.	
PRESENT	ATION OF DATA	
4-1	$\delta S^{34}$ values for sulfides associated with the Heath Steele B-1 orebody	107
4-2	The distribution of sulfur isotopes in coexisting sul- fides from a sample of banded ore	109
4-3	The distribution of sulfur isotopes in pairs of co- existing sulfides associated with the B-1 orebody	115
4_4	Variations in corrected fractionation values	118 .
4-5	Relationship between fractionation values for sulfide pairs and their location in the B-1 orebody	121
4-6	Sulfur isotope variation across the B-1 orebody	121
4-7	Sulfur isotope ratios in coexisting sulfides from other stratiform deposits in the Bathurst-Newcastle area •••	129
ANALYSI	S OF THE ISOTOPE DATA	
4-8	Analysis of corrected fractionation values for some sulfide pairs from six stratiform deposits in the Bathurst-Newcastle area	134
4-9	Dependency of given fractionation values on $\delta S^{34}$ values of coexisting pyrites and on the locations of samples containing respective pairs	135
4-10	Analysis of apparent trends in $\mathcal{S}^{34}$ values for crushed ore samples and pyrites from across orebody inter-	170
		722

vi

CHAPTER	5. FRACTIONATION OF SULFUR ISOTOPES BETWEEN COEXISTING SULFIDES IN HEATING EXPERIMENTS AT TEMPERATURES	Page
	0F 350 10 500 C	
5 <b>-</b> 1	Introductory statement	142
5-2	Apparatus, reagents and experimental procedure	144
5-3	Results	148
	Discussion of results	150 152
5-4	Conclusions	156
CHAPTER	6. PRECIPITATION OF SOME BASE METAL SULFIDES FROM AQUEOUS SOLUTION AT 25°C	
6-1	Introductory statement	158
6-2	Experiment 1	159
6-3	Experiment 2	163
6-4	Experiment 3	166
6-5	Experiment 4	169
6-6	Experiment 5	172
6-7	Procedure used in filling reservoirs with $H_2S$ gas	174
6-8	Procedure used to obtain gas samples from the H <sub>2</sub> S reservoirs	175
	Possible isotope effects involved in the removal of H <sub>2</sub> S gas samples from reservoir vessels	176
6-9	Conversion of H <sub>2</sub> S gas to silver sulfide	177
6-10	Results	179
	Discussion of results	180
6-11	Conclusions	183

c

#### TABLE OF CONTENTS (continued)

#### CHAPTER 7. INTERPRETATION OF RESULTS

#### 7-1 Interpretation of the distribution of sulfur isotopes 185 7-2 Interpretation of the isotopic fractionations between coexisting sulfide pairs 186 . . . . . . . . . . . 7-3 Interpretation of the results of the heating experiments 192 7-4 Interpretation of across orebody trends in sulfur isoto-194 pic compositions . . . . . . 7-5 Interpretation of the distribution of sulfur isotopes in footwall and hanging wall rocks and in the B-l orebody 196 7-6 Significance of isotope effects accompanying precipitation of metal sulfides from aqueous solutions at 25°C . 197 CHAPTER 8. EXAMINATION OF PROPOSED THEORIES OF ORE GENESIS: A SUGGESTED MODEL 8-1 Summary of the features of stratiform deposits in the Bathurst-Newcastle area . . . . 200 8-2 Summary of features in the Heath Steele B-1 orebody . . 203 8-3 Possible relationships between across deposit base metal zoning, sulfur isotope trends and the footwall "porphyry" 205 8-4 Relationship between base metal zoning in stratiform deposits and the stratigraphy of associated rocks . . . 206 8-5 Examination of the postulated origins for stratiform deposits in the Bathurst-Newcastle area . . . . . 208 - - -8-6 Possible derivation of sulfur in the Heath Steele B-1 orebody by bacterial reduction of marine sulfate .... 220 A SUGGESTED ORIGIN FOR THE HEATH STEELE B-1 OREBODY 8-7 Introductory statement . . . 226 8-8 Chemical composition of discharge products from terrestrial fumaroles and geothermal bores . . . . . . . 227 8-9 Sulfur isotope abundances in fumarolic/geothermal 229

Page

# TABLE OF CONTENTS (continued)

8 10	A suggested model for the generation of s <sup>34</sup> enriched	Page
0-10	H <sub>2</sub> S in sub-volcanic processes	231
8-11	A suggested explanation for the isotope trends and across deposit base metal zoning in the B-1 orebody	239
8-12	Explanation of the occurrence of pyrrhotite, pyrite and magnetite in the ores in terms of a volcanic origin for the sulfur	241
8-13	A suggested relationship between the Heath Steele sulfide deposits and the "porphyry"	244
8-14	Summary and conclusions	245
BIBLIOG	RAPHY	252

## LIST OF TABLES

		Page
1-4-5	Mineralogy of stratiform deposits in the Bathurst-	17
1-13	Mineralogy of the B-1 orebody	39
2-2	Descriptions of thin sections of D.D.H. core samples .	72
3 <b>-</b> 9A	Reproducibility of isotopic measurements	93
3 <b>-</b> 9B	Extract from a mass spectrometer record book	99
3-10	Impurities in sulfide concentrates; impurity correc-	
	sulfides	102
4-3A	$\delta S^{34}$ values of coexisting sulfides from the Heath Steele B-1 orebody	110
4-3B	$6 \text{ S}^{34}$ values of coexisting sulfides from footwall and hanging wall rocks of the B-1 orebody	114
4-30	Mean fractionation values for various sulfide pairs .	117
4_4	Variations in corrected fractionation values	118
4-6A	$53^{34}$ values of total sulfur in D.D.H. pulp samples	122
<b>4-6</b> В	<pre>\$S<sup>34</sup> values of sulfides extracted from D.D.H. pulp samples</pre>	125
4-7	$5S^{34}$ values of coexisting sulfides from some other sulfide deposits	130
4-8	Significance of mean differences between fractiona- tion values for some sulfide pairs from 6 stratiform deposits in the Bathurst-Newcastle area	135
4-9	Regression curves computed for isotopic data	137
5-1	Results of heating experiments involving powdered sulfide mixtures	143

x

# LIST OF TABLES (continued)

5-2	Initial compositions of mixtures used in the heating experiments	145
5-3	Computed isotopic compositions of the sulfide mixtures before and after the experiments	151
6-1	Fractionation of sulfur isotopes in the precipitation of some metal sulfides at $25^{\circ}C$	160
8-10	Limiting fractions of the total sulfur contributed by Ordovician marine sulfate sulfur	237

Page

### LIST OF ILLUSTRATIONS

1-4-1	Geology and principal sulfide deposits of northern New Brunswick	9
1-10	Geology and ore zones, Heath Steele Mine	30
1-11	The Heath Steele B-1 orebody	35
1 <b>-1</b> 5A	Summary of the sulfur isotope variations in the Bathurst- Newcastle area	46
1 <b>-</b> 15B	Relationship between the mean isotope ratios of the deposits and their locations	49
1 <b>-17</b>	Sulfur isotope abundances in meteorites, crustal rocks, sulfide ore deposits and petroleum	55
2-3A	Frequency distributions of zinc, lead, silver and copper abundances in the Heath Steele B-1 orebody	66
2 <b>-3B</b>	Base metal zoning across the B-1 orebody	67
3-4	Mineral separation using the Frantz Isodynamic Separator	81
3-6	Schematic sketch of Apparatus used in the preparation of sulfur dioxide gas	87
4-1	Measured $SS^{34}$ values of sulfides associated with the Heath Steele B-1 orebody $\ldots$	107
4-2	The distribution of sulfur isotopes in a sample of banded sulfide ore	115
4-3	Measured $\Delta$ § S <sup>34</sup> values for coexisting sulfides associa- ted with the Heath Steele B-1 orebody	115
4-5	Relationship between corrected fractionation values for coexisting sulfide pairs from the B-1 orebody and their locations in across orebody profiles	121
4-6A	$\delta S^{34}$ values of sulfides in D.D.H. pulp samples from the B-1 orebody	126
4 <b>-</b> 6B	The atomic percentage sulfur contributions by the principal sulfides contained in B137 pulps	127

# Following Page

4-7A	Measured $\Delta_6 S^{34}$ values for coexisting sulfides in some other stratiform deposits in the Bathurst- Newcastle area	129
4-7B	Corrected fractionation data for coexisting sulfides from some stratiform deposits in the Bathurst-Newcastle area	129
5-2	Apparatus used in the heating experiments	144
5-3	Results of heating experiments	148
6-2A	Open system precipitation of base metal sulfides	159
6-2B	Apparatus used in generating H <sub>2</sub> S gas	159
6-4a	Apparatus used in Experiments 3 and 4	16 <b>6</b>
6-4B	Apparatus used in Experiment 5	166
6-7A	Apparatus used in filling reservoirs with $H_2S$	174
6-7в	Apparatus used for the removal of H <sub>2</sub> S gas samples from reservoir vessels	174
6-70	Apparatus used in conversion of H <sub>2</sub> S to cadmium sulfide	174

#### CHAPTER 1

#### INTRODUCTION

#### 1-1. Purpose of the present study

Some of the world's major zinc-lead and important copper producing deposits belong to the stratiform class (see Section 1-2) of sulfide ore deposits. Although much is already known about these deposits their origin remains a controversial issue. Some geologists believe that stratiform deposits are younger than the rocks containing them while others, particularly European geologists, have for some years favoured a sedimentary origin which requires that they formed contemporaneously with the enclosing strata. While much of the information available on these deposits appears to favour the latter origin, there appear to be no general criteria which conclusively prove this hypothesis.

A good deal of information is now available on the ranges of sulfur isotope variation in many of the stratiform deposits. Most of the deposits have relatively narrow ranges of isotopic variation and, in general, are appreciably enriched in S<sup>34</sup> relative to vein-type deposits formed in older rocks from high temperature fluids derived from intrusive igneous rocks. A major problem is to explain these features. Several different origins have been proposed so far for both the sulfur and base metals in stratiform deposits.

The aims of the present study are:

i) to examine in detail the distribution of sulfur isotopes within a typical "volcanic" type (see Section 1-2) stratiform deposit and attempt to relate these results with base metal abundance patterns and other features both within such a deposit and in the enclosing rocks.

The design of this part of the sulfur isotope study is similar to that proposed by Stanton (1960d).

- ii) to find some consistent feature which may provide a means for comparing the deposit studied in detail with similar deposits in the same camp, and perhaps also with deposits in other parts of the world.
- iii) to reproduce in experiments any isotopic fractionations which may exist between given sulfide pairs in the deposit studied.

It was anticipated that if fractionations were measurable and equilibrium could be attained in the experiments, a temperature could be obtained and compared with the very approximate temperature of regional metamorphism, ° as inferred from the metamorphic silicate assemblages. A higher temperature for the deposit would be considered to indicate a post-metamorphic origin and hence an igneous hydrothermal origin for the sulfides. On the other hand, similar temperatures might mean that the sulfides were emplaced by this mechanism before the extreme P/T conditions of regional metamorphism were attained or, alternatively, that the sulfides are of sedimentary origin. iv) to test for any possible fractionation effects in the precipitation of base metal sulfides with H<sub>2</sub>S from aqueous solutions at 25°C, since there seemed to be a fairly strong case for deposition of "volcanic" type stratiform deposits as chemical sediments.
Once this information had been obtained, it was considered that speculation on the origin of the H<sub>2</sub>S with which base metals might combine to precipitate sedimentary sulfides could be made with greater confidence.
v) to examine the features of the deposit studied in detail in terms of the general requirements of the two principal theories of ore genesis which have already been proposed.

The B-l orebody of Heath Steele Mine Ltd., Newcastle, New Brunswick, was selected for detailed study principally because of its structural simplicity, because of its considerable size and also because of the large amount of diamond drill hole information that was available. Furthermore, a considerable body of information is available for the stratiform deposits in the Bathurst-Newcastle camp since a variety of survey-type studies including two sulfur isotope investigations have already been carried out.

In conclusion, the B-1 orebody was studied in detail to obtain a better understanding of the features of a typical representative of the "volcanic" type of stratiform deposit. Acquisition of information of this kind will undoubtedly help in ultimately determining the origin or origins of this very important and controversial class of deposit.

#### 1-2. Types of stratiform deposits

Sulfide deposits bounded by either sharply defined or diffuse surfaces which are essentially concordant with the stratification in enclosing (non-intrusive) rocks have been variously described in the literature as concordant-, strata-bound-, conformable, and more recently as stratiform deposits (Stanton and Rafter, 1966). Depending on the types of stratified rocks, stratiform deposits can be divided into "normal" and "volcanic" types (Stanton, 1960d). The "normal" type deposits occur in essentially non-volcanic marine sediments and the "volcanic" type deposits are characteristically associated with various types of volcanic rocks. Examples of the first type are the Kupferscheifer deposit and some of the deposits of the Northern Rhodesian copper belt. While the sedimentary rocks associated with the "normal" type appear to have formed in relatively shallow basins on continental basements, the volcanic rocks containing the "volcanic" type were deposited in mobile geosynclinal depressions. It appears that the volcanic rocks associated with the latter type were located near the border zones of the initial geosyncline and also at the marginal areas of centrally uplifted portions.

# 1-3. Some general features of "volcanic" type stratiform deposits Stratigraphic position of the "volcanic" type deposits

In general, "volcanic" type deposits appear to occur in portions of eugeosynclinal sequences containing abundant lawas and typically acid pyroclastics or abundant chert. According to McCartney and Potter (1962), Bilibin and other Russian geologists recognized 5 major phases in

the evolution of a mobile belt and assigned rocks containing these deposits to the early phase which is initiated by localized folding and faulting, and is accompanied by intrusion of small stocks or batholiths of acid igneous porphyries of symmitic, granodioritic, dioritic or granitic composition or their plutonic equivalents. They reported that most Russian writers concerned with metallogenic concepts relate stratiform deposits to subvolcanic intrusives of this kind.

Where both basic lavas, particularly of the spilitic type, and acid volcanics are represented in a sequence, the deposits appear to be closely associated with the latter and commonly occur near the top of the acid volcanic rocks which generally overlie the basic lavas (e.g. the deposits of Spain and Portugal and the Tamagami deposits of Quebec). Closely spaced deposits are frequently contained in the one horizon or may occur at closely spaced intervals in an en eschelon arrangement or as a series of parallel lenses.

#### Types of rocks associated with the "volcanic" type deposits

While there do not appear to be any very strong consistencies in the types of rocks associated with the deposits, several common associations are evident:-

> i) the deposits are usually contained in shales or bedded tuffs or their metamorphic equivalents - which commonly have varying amounts of carbonaceous material and/or carbonate, including dolomitic types, associated with them. While many occur in contact with or slightly below a conspicuous pyroclastic unit, others occur in contact with lavas or may be enclosed by lavas.

- ii) bedded iron formation rocks are also commonly associated and may occur laterally, within the deposits, or adjacent to them. These comprise magnetic iron formation, ferruginous cherts, chloritic iron formation, sideritic rocks, etc.
- iii) deposits of some camps may occur consistently in association with clearly recognizable units of pyroclastic rocks which are not necessarily from the same stratigraphic horizon. These deposits usually occur slightly within, in immediate contact with, or slightly below a given unit.

#### Form of the "volcanic" stratiform deposits

The deposits usually occur as thin lenticular shaped bodies which are conformably enclosed by stratified rocks varying in attitude from flat lying to steeply inclined. In folded strata, the deposits may occur in either the flank or in the crest of a fold structure. Hutchinson (1965) described deposits in Cyprus that occur in essentially undeformed rocks. They are described as flat lying, characteristically irregular, lenticular, pod-like and often elongated in one dimension. They are frequently convex downward, with a synclinal form, and are thickest in the center. Irregular offshoots and protuberances are reported to be common. The "volcanic" type of deposits may range in size from a few tens of feet in major dimensions up to at least the size of the Broken Hill deposit which is approximately 20,000' x 2,000' x 500'.

#### Mineralogy of the "volcanic" type deposits

Stanton (1958) has shown that the deposits exhibit certain consistencies in their principal economic base metal abunndances. He observed that zinc may occur together with either lead or copper in varying amounts but that one of lead or copper is markedly suppressed when both These metals are contained in sphalerite, galena and chalare present. copyrite which occur in generally small amounts together with usually abundant pyrite and/or pyrrhotite. Trace quantities of arsenopyrite, tetrahedrite-tennantite, bismuthinite, etc. are usually present. Carbonate and quartz are common gangue constituents, but barite may be present and infrequently occurs in abundance (e.g. the Rammelsberg deposits). Stanton (1962-63) demonstrated that the mean proportions of carbonate, feldspar and quartz do not change with increasing sulfide content in the Mount Isa ores suggesting that this is a sedimentary rather than a replacement phenomenon. The deposits usually exhibit mineralogical banding which varies in quality within deposits and from one deposit to another. It is generally parallel with the stratification in the enclosing rocks.

Depending on the mean concentrations of the principal economic base metals present, the deposits can be considered as:-

- i) lead-zinc deposits
- ii) zinc-lead-copper (minor) deposits

iii) copper-zinc and copper deposits Usually only one of ii), iii) or gold-barite deposits occur in a given metallogenetic province (cf. McCartney and Potter, 1962). However, both zinc-lead-copper and essentially copper deposits appear to be commonly represented in the same camp.

#### Lead isotope studies

All the leads isotopically analyzed from the stratiform deposits so far have been found to approximate a single growth curve to within a few tenths of 1% (Stanton and Russell, 1959). In summarizing these relationships, Stanton and Rafter (1966) asserted that while the fit is only approximate, such leads approximate the curve by an order of magnitude better than any other group of naturally occurring leads. Stanton and Russell (1959) interpreted this to mean that leads in stratiform deposits of different ages were derived from a homogeneous U-Th-Pb system which is postulated to occur in the mantle. In order to explain the normal character of these leads, it is envisaged that they are derived from the mantle, expelled through volcanoes of mobile belts and either quickly precipitated as sulfide on the sea floor or expelled during diagenesis from associated tuff beds and localized in adjacent iron sulfide-rich sediments (i.e. a source bed mechanism).

The fact that basic volcanic rocks are characteristically abundant in eugeosynchial piles formed in the initial and early phases of the history of a mobile belt strongly supports the view that the upper mantle is tapped more or less continuously during this time. It also seems likely that the leads might have been derived from high-level acid differentiates of these mantle rocks and, since fractionation of lead isotopes in high temperature differentiation processes would be negligible, the initial ratios should be preserved.

#### Age relations with intrusive granites

Spatial relationships between intrusive granitic rocks and groups of stratiform deposits have often been invoked but never clearly demonstrated. The fact that the mineralization sometimes contained in the granites is not uncommonly of a different kind is frequently overlooked. While dating techniques hold promise of providing an objective method for resolving this problem, the relatively wide precision ranges of the methods may render the age relations ambiguous. This is not surprising because both the intrusive rocks and the deposits from the same camp are generally believed to have been emplaced during the same orogenic episode, and hence might be expected to have too small an age difference to be resolved by currently available methods.

# 1-4. <u>Geology, distribution and description of sulfide deposits in the</u> Bathurst-Newcastle area, New Brunswick

#### 1-4-1. Regional geology of the Bathurst-Newcastle area

The regional geology of a portion of northern New Brunswick in which important sulfide deposits occur is shown in Figure 1-4-1 (after Greiner and Potter, 1966). The map area includes a major portion of the 1957 G.S.C. compilation map sheet of the Bathurst-Newcastle area (Smith, 1957). The rocks in this area comprise three regional units a central Ordovician (Middle Ordovician in part) folded belt, a less intensely folded Silurian-Devonian unit in the north and a narrow unit consisting of relatively undeformed Pennsylvanian rocks in the east (Davies, 1966). The central and northern units are separated by the roughly east-west trending Rocky Brook-Millstream Fault and the Pennsylvanian rocks unconformably overlie Ordovician rocks in the east. Granitic FIGURE 1 - 4 - 1

GEOLOGY AND PRINCIPAL SULFIDE DEPOSITS OF NORTHERN NEW BRUNSWICK



stocks and batholiths intrude the Ordovician and Silurian-Devonian rock units and basic rocks of several ages intrude all three units. Serpentinites occur along parts of the Rocky Brook-Millstream Fault.

The structurally complex Ordovician Unit or Tetagouche Group has been divided into four general lithologic divisions (Skinner, 1956; Davies, 1966), namely:-

(i) the Sedimentary Division comprising:-

- a) a <u>Slate subdivision</u> consisting mainly of phyllites and fine
   to medium grained greywackes. Graphitic phyllite and schist,
   together with minor amounts of cherty, calcareous and con glomeratic rocks, are also present.
- b)a <u>Siliceous Metasedimentary rock subdivision</u> consisting of rocks of arenaceous character including feldspathic sandstones and quartz sericite schists with relatively minor slate and quartz chlorite schists. Some rocks which are similar to varieties of augen schists (see (iii) below) are also present.
- (ii) a <u>Greenstone Division</u> consisting of massive and amygdaloidal spilitic rocks, which exhibit pillow structure in places, together with massive, banded and schistose greenstones. The greenstones are intimately associated with the more abundant siliceous volcanic rocks. Slates, graphitic schists and iron formation are also associated with rocks of this Division. Together with magnetic iron formation rocks the greenstones give rise to magnetic anomalies and thus greatly facilitated the delineation of the principal feature of the regional structure (Cheriton, 1960).

- (iii) a <u>"porphyry" or Quartz-augen-schist Division</u> comprising rocks consisting of quartz and/or feldspar augen set in a microcrystalline or schistose matrix of quartz, feldspar and chlorite. Augen free quartz-sericite schist, quartz-sericitechlorite schist and sericite schist are commonly interbedded with the "porphyries". Thin units of sedimentary and basic volcanic rocks also occur in the schists in places. Intrusive, igneous flow, pyroclastic and sedimentary origins are assigned to these rocks on the basis of their variable textures. Their SiO<sub>2</sub> content is generally in the 70-75% range, and their combined  $K_2O + Na_2O$  content is from 6 to 9% with variable, though usually relatively high,  $K_2O/Na_2O$  ratios.
  - (iv) a <u>Felsic or Siliceous Volcanic Division</u> consisting mainly of massive and banded rhyolite, crystal tuff and trachyte interbedded with quartz-sericite schist, biotite-chlorite schist, phyllite, greywacke and greenstone. Breccias and agglomerates are locally abundant.

Due to the paucity of exposures, the general lack of fossils, the difficulty of determining stratigraphic facings and the structural complexity of the area,workers have been unable to determine the overall stratigraphic relationships between the principal lithologic divisions. The Divisions described above are given in order of decreasing age as suggested by Davies (1966). However, the tentative order given in the 1957 G.S.C. Map Sheet places these Divisions in the following order:- (i,b) oldest, (iv), (iii), (ii) and (i,a) - youngest.

Smith (1957) divided the Ordovician folded belt into two structural units. The boundary separating the units is represented by a strong north-northwest trending lineament that passes just west of the Heath Steele Mine. The rocks of the northeastern unit are folded into major anticlinoria and synclinoria whose axes plunge steeply northeast and southwest, and, in places, northwest. These major folds pass into smaller folds in the argillaceous metasedimentary rocks in the northeast. A strong schistosity commonly parallels the bedding in these rocks. The southwestern unit comprises rocks that are also folded about northeast trending axes, some of which plunge southwest and others northeast. Smith believed that the character of the folding in this structural unit is different from that in the northeastern unit and is characterized by recumbent folding and thrust faulting as indicated by common nearhorizontal schistosity.

Dykes and sills of olivine gabbro, gabbro, diabasic gabbro, diabase and diorite intrude rocks of all the lithologic divisions of the Tetagouche Group. Some appear to be Ordovician in age and others appear to be of Silurian and Devonian age.

Two main types of siliceous intrusive rocks have been recognized:-

i) massive granitic stocks with associated quartz and/or feldspar porphyries and aplites occurring as dykes, sills and plugs. The massive granitic rocks comprise biotite granite, granodiorite and quartz monzonite. K/Ar dating of the plutons by Tupper (1960) indicated an age of close to 390 m. years. ii) gneissic granitic rocks of uncertain origin and age. These rocks occur to the south and southwest of the Heath Steele
Mine . It has been suggested that they may be granitized sediments, recrystallized augen schists or possibly, synchronous granites intruded during Ordovician sedimentation.

The massive granite plutons are surrounded by contact metamorphic aureoles that may be detected for up to a mile or more from contacts. Biotite is the characteristic metamorphic ferro-magnesian mineral developed in the thermal aureoles. Near the granites the sedimentary rocks are altered to biotite hornfels carrying cordierite and andalusite.

Davies (1966) suggested that the metasedimentary rocks of the Tetagouche Group belong to the eugeosynclinal suite, and represent the flysch or synorogenic facies of sedimentation. The close spatial relationship between the greenstones, "porphyries" and the siliceous volcanic rocks suggests that all are genetically related and that their appearance in the eugeosynclinal sequence was initiated by at least a local dramatic change in the eugeosynclinal environment. Davies (1966) suggested that the volcanic complex appears to occupy a volcano-tectonic depression that formed in the eugeosyncline during the Ordovician as a result of downbuckling or faulting. McCartney and Potter (1962) suggested that the Bathurst-Newcastle area is located near the axis of the zone of initial deformation in the northern Appalachian mobile belt.

#### 1-4-2. Distribution of the sulfide deposits

The locations of the principal sulfide deposits are shown in Figure 1-4-1 where they are listed in order of decreasing latitude. With the exception of the Sturgeon River deposit which occurs in metasediments of the Tetagouche Group close to the Rocky Brook-Millstream Fault, the known vein-type deposits occur in Silurian rocks to the north. All the stratiform deposits occur in Tetagouche rocks to the south of this fault where most are confined within the greenstone-metasediment-"porphyry" association which forms a roughly circular, though discontinuous belt of about 30 miles in diameter. Rocks of the Siliceous Volcanic Division occur inside this belt. While the New Larder U and Kennco Murray Brook deposits are seemingly isolated from the main belt, it is noteworthy that these deposits also occur in close proximity to similarly isolated "porphyry" horizons (McAllister, 1959).

#### 1-4-3. General features of the sulfide deposits

Two distinctive classes of sulfide deposits occur in the map area shown in Figure 1-4-1. These comprise:-

- i) <u>stratiform deposits</u> generally large, massive fine grained pyrite-sphalerite-galena-chalcopyrite-pyrrhotite bodies which may be tabular, lenticular or sheet-like in shape and are concordant with the stratification in the enclosing metasediments.
- ii) <u>vein-type deposits</u> small, coarse grained pyrite-arsenopyritesphalerite-galena-pyrrhotite-chalcopyrite vein deposits which are discordant with the stratification of the enclosing rocks. These occur in faults and fracture zones.

Most of the stratiform deposits in the Bathurst-Newcastle camp are steeply dipping and have lengths ranging from 450 to 6000 feet, depths from 300 to 1500 feet and thicknesses of from 14 to 200 feet. According to Davies (1966), the estimated tonnages for 14 deposits range from 0.2 up to 28 million tons. Composites of metal assays for 7 of the deposits indicate that weight percent concentrations of zinc are greater than for lead or copper, and that in most cases copper is less abundant than lead.

#### 1-4-4. Types of rocks associated with the stratiform deposits

Holyk (1956) pointed to the close association of the sulfide mineralization with the intra-volcanic sediments and the close spatial relationship of the deposits with quartz-augen schist-sediment contacts. McAllister (1959) reported on the remarkable degree of uniformity in the types of rocks associated with the stratiform deposits. Of the 22 investigated, 18 have a chloritic host hock (i.e. chloritic metasediment) and 21 have some variety of "porphyry" forming the hanging wall, footwall or both. Insofar as most of the closely spaced deposits occur in relatively narrow belts of metasediment in contact with relatively large masses of "porphyry", such deposits can probably be considered to occur in locally equivalent stratigraphic horizons.

Most of the metasediments occurring in close association with the deposits are generally regarded to be of tuffaceous origin. A study of the schists near the Stratmat 61 deposit by Johnston (1959) showed that they contain associated agglomerate, shards, devitrified glass and also exhibited pumiceous texture. Other types of metasediments also occur.

including graphitic metasediments, cherty rocks, an assortment of ferruginous and magnetic iron formation rocks and a type of chloritic rock which is believed by McAllister (1959) and Davies and Smith (1966) to represent the silicate facies of chemically precipitated iron formation. While the graphitic metasediments do not generally appear to be more abundant in the immediate vicinity of the deposits than elsewhere, the same cannot be said for the iron formation rocks which appear to be associated in varying amounts with most of the deposits. Both the silicate (chlorite) and magnetic oxide facies run into the B.M. & S. No. 6 and No. 12 sulfide deposits.

### 1-4-5. Mineralogy of the stratiform deposits

The mineralogy of the deposits is remarkably similar and is of a relatively simple kind. With the exception of some trace constituents which have not been identified so far in all deposits, the minerals listed in Table 1-4-5, below, are common to all the deposits.

#### TABLE 1-4-5

Major constituents:

sulfides	<u>non-sulfides</u>
pyrite	quartz
pyrrhotite	chlorite
sphalerite	magnetite
galena	sericite
chalcopyrite	calcite

Trace constituents:

opaque minerals arsenopyrite marcasite (primary and secondary) bornite cubanite tennantitetetrahedrite stannite bismuthinite chalcocite covellite enargite argentite

acanthite hematite (primary and secondary) cassiterite gold silver bismuth

<u>non-opaques</u> biotite siderite barite

Certain consistencies of association are evident among the sulfides, and this has given rise to two distinctive types of mineralogical associations, namely:-

> i) massive pyrite (usually banded) containing sphalerite and galena and minor chalcopyrite and pyrrhotite. Traces of arsenopyrite and tennantite-tetrahedrite may also be present. Disseminations of this association may occur with massive sulfides. Massive sulphides generally contain 80% or more of sulphide minerals.

ii) pyrrhotite-chalcopyrite assemblages occurring as lenticular zones containing veins and pods of massive sulfides which commonly cut across the schistosity or bedding of the enclosing rocks or the mineralogical banding of the type i) association above. Mineralogical banding is a rare feature in the pyrrhotite-chalcopyrite association. The latter also occurs as disseminations either closely associated with massive pyrite or independently.

These two types of sulfide associations may occur together within a single deposit or may occur separately as individual deposits (Stanton, 1960c). Where across layering base metal zoning is evident in deposits consisting essentially of the first type of association, it is apparent that zinc and lead values are generally higher on the side nearest the "porphyry" (e.g. the Caribou deposit and some of the Heath Steele deposits) and copper is usually higher on the opposite side. In situations where the two types of association occur separately it is usually found that the pyrrhotitechalcopyrite association is generally furthest from the "porphyry" (e.g. the Heath Steele "A" deposit). In a paper dealing with the abundances of Zn, Pb and Cu in the stratiform deposits, Stanton (1958) drew attention to the consistency in the relative proportions of these metals between deposits of this class, and also between the deposits and igneous rocks. That this feature may be peculiar to this class of deposit was suggested by Richards (1963) who demonstrated that the relative abundances of the same metals from an unquestionably discordant hydrothermal deposit show considerably greater variation.

#### 1-4-6. Textures in the stratiform ores of the Bathurst-Newcastle camp

It is evident from textural studies by Lea and Rancourt (1958), Benson (1959), Stanton (1959), Roy (1961) and others that the textural relationships between the major opaque minerals are very similar in ores from the various deposits. Some of the main textural features in the massive sulfide ores which are common to the deposits include:-

- i) pyrite, arsenopyrite and hematite usually have subhedral to euhedral outlines. Magnetite grains commonly have rounded outlines but sometimes exhibit crystal faces. Intergrowths of pyrite and arsenopyrite generally exhibit mutual boundary relationships.
- ii) sphalerite, pyrrhotite, galena and chalcopyrite typically mould around the minerals mentioned above and commonly project into them, fill fractures and occur as inclusions of varying shapes (including vein-like shapes) within them.
- iii) chalcopyrite or chalcopyrite and pyrrhotite frequently occur in veins which cut across the banding of the massive sulfides.

Except for the Brunswick No. 6 ores, crystallographically controlled intergrowths do not appear to have been described in ores from any of the other deposits studied. So far two types of intergrowths have been reported to occur in the Brunswick No. 6 ores:-

iv) a) lattice intergrowths of bornite in chalcopyrite (Roy,

1961)

# iv) b) "exsolution" intergrowths of chalcopyrite in sphalerite (Stewart, 1954).

These general relationships were considered by most workers to be due to sequential deposition and replacement by igneous hydrothermal solutions. Projections of one mineral into another were interpreted as replacement embayments and "fracture fillings" were regarded as evidence of sequential deposition from high temperature mineralizing solutions. By interpreting these relations in this way, similar paragenetic sequences have been "de-In general, the sequence is believed to termined" by some workers. begin with iron oxides followed by arsenopyrite, pyrite, and then the softer common sulfides. There has been disagreement, however, as to the precise order of deposition of the "late" sulfides. At least a few of these workers (Lea and Rancourt (1958) and Dechow (1960)) have pointed to the general lack of evidence of extensive replacement and none appear to have convincingly demonstrated the occurrence of clear selectivity or "Exsolution" textures appear to provide the strongest pseudomorphism. argument for an igneous hydrothermal origin and temperatures of 300-400°C are suggested by chalcopyrite-sphalerite intergrowths.

Stanton (1959, 1960c) and Kalliokoski (1965) suggested that the observed relationships might be attributed to an entirely different process. It was suggested by Stanton (1960c) that the ores might have precipitated on the sea floor as cryptocrystalline sulfides and recrystallized with compression and heating accompanying burial and later folding. Kalliokoski cited the local occurrence of colloidal-like textures as indicating that the sulfides might have initially occurred as precipi-

tated sediments. In a paper dealing with mineral interface relations among the sulfides of stratiform deposits, Stanton (1964-65) proposed that the observed relationships between the sulfide species are due to interfacial free energy phenomena which result in simple coarsening, deformation, polygonization and recrystallization. The densities and strengths of chemical bonds affect surface energies and a general relationship between grain shape and physical properties (e.g. hardness and melting points) is suggested to follow. A parallelism of the changes in these properties with the generally observed sulfide order in "paragenetic sequences" in these ores is indicated. King (1958) drew attention to the fact that the grain size of sulfides in ores of this class increases with a progressive increase in the rank of regional metamorphism.

# 1-5. Estimation of the temperature of formation of the stratiform deposits using the sphalerite and pyrrhotite geothermometers

Benson (1960) attempted to look for temperature zoning in the Brunswick No. 12 and Heath Steele A deposits using the sphalerite geothermometer. Sphalerites were extracted from polished sections using a vibro-engraver and their iron contents determined by X-ray fluorescence analysis. As temperature differences ranging up to about 180°C were obtained from sphalerites occurring only six millimeters apart, it was concluded that the technique was generally unsatisfactory.
It was suggested that the variable iron content of the sphalerites is perhaps due to the amount of iron present in the minerals replaced by the sphalerites. An appreciable variation in the iron content of sphalerites was also reported by Colwell (1963) who found that the iron content of five sphalerites from a total of three deposits ranged from 5.8 to 10.9 weight percent and averaged 8.9 percent. However, in spite of this difficulty, Benson (1960) suggested that the temperature of formation of the Brunswick and Heath Steele deposits was 610° C at an estimated pressure of 2000 bars.

Arnold (1962) used the sphalerite and pyrrhotite geothermometers in estimating temperatures of 500 and 510° C, respectively, for single samples from the Heath Steele Mine. The estimated pyrrhotite geothermometer temperature for a single sample from the "Brunswick Mine" was  $450^{\circ}$  C and the temperature for a single sample from the Clearwater deposit was estimated to be  $470^{\circ}$  C.

It is unfortunate that the temperatures estimated above are probably erroneous since both the sphalerite and pyrrhotite geothermometers used at that time are suspect for various reasons (Toulmin and Barton, 1964; Desborough and Carpenter, 1965). It is noteworthy that an  $0^{18}/0^{16}$  analysis on a quartz-magnetite pair from the Bathurst Iron Mine situated to the southwest of the B.M. & S. No. 6 deposit indicated an equilbrium temperature of about 515° C (Kalliokoski, 1965).

## 1-6. Grade of metamorphism in the Tetagouche rocks

Some writers have attributed the local abundance of chlorite and/or sericite, the alteration of feldspars and the development of so-called bleached zones occurring in the immediate vicinity of some deposits to hydrothermal alteration of the enclosing rocks at the time of ore formation. If hydrothermal alteration has occurred, it might be expected that contact metamorphic assemblages or relics of these might be present and that possibly some unique minerals would be found in the "alteration zones" surrounding the massive sulfide deposits.

The regional metamorphic mineral suites in the metasedimentary country rocks occurring in association with stratiform deposits from three widely separated localities generally appear to belong to the quartz-albite-muscovite-chlorite subfacies of the Greenschist Facies of regional metamorphism (Turner and Verhoogen, 1960). Martin (1957) assigned rocks associated with the Anaconda Caribou deposit to the quartz-albite-muscovite-chlorite subfacies of the Greenschist Facies. Chlorite-muscovite-chlorite subfacies of the Greenschist Facies. Chlorite-muscovite-quartz assemblages were reported by Lea and Rancourt (1958) to occur in the metasediments and "porphyry" from around the B.M. & S. deposits. Dechow (1960), in describing metasediments believed to have been derived from acid volcanic rocks occurring to the southeast of the Heath Steele Mine, reported assemblages which also apparently belong to the quartz-albite-muscovite-chlorite subfacies.

Tetagouche rocks occurring in contact with the biotite granite plutons are characteristically altered to distinctive biotite hornfels and the effects may be discernible for a mile or more from the granite contacts. Near the granites the biotite hornfels may contain cordierite and andalusite. As far as the writer is aware, biotite has only been described in country rocks associated with the Kennco Clearwater and Heath Steele B-1 deposits, and in neither of these cases occurred in immediate contact with the massive sulfide deposits. The development of incipient biotite suggests that the country rocks should be assigned to the lower part of the quartz-albite-epidote-biotite subfacies of regional metamorphism provided the biotite is of regional metamorphic origin.

Petruk (1959) appears to be the only worker who has seriously looked for evidence of wall rock alteration effects in the rocks enclosing the massive sulfide deposits. He claimed to have delineated a 7' to 17' thick envelope in the enclosing rocks of the Caribou deposit where sericitization of feldspar occurred. Waves of chloritization and silicification were also reported to complement each other in a 17' zone above the deposit. Wall rock alteration at the Kennco Clearwater deposit was stated to be confined to 3' of chloritization at the base of the massive sulfides and minor biotitization in the zone of disseminated As a result of his study of the iron content of chlorites sulfides. from the Kennco deposit using an X-ray technique. Petruk made the following observations :-

- i) the iron content in a chlorite from a chlorite schist increases with an increase in the chlorite content in a rock.
- ii) intensive chloritization accompanied by an increase in the iron content in chlorite occurs near pyrrhotite mineralizations and is presumed to be due to introduction of iron into the wall rock.
- iii) the iron content of chlorite decreases near pyrite mineralization and chloritization is moderate. In this case, chloritization is believed to result from the removal of silica into the wall rock and the decrease of the iron in the chlorites is attributed to the removal of iron to form pyrite.

The so-called gangue minerals occurring in the massive sulfides comprise quartz, sericite, chlorite, magnetite, biotite, calcite, siderite and, in places, barite (Davies, 1966). Pyrometasomatic minerals such as iron garnets, iron pyroxenes, wollastonite etc. have not so far been reported in the massive sulfides or the wall rocks. A feature of the mineralogies of the country rocks, wall rocks and the gangue minerals of the massive sulfides is that quartz, chlorite and/or muscovite are generally abundant in all three. Biotite is also reported to occur in the ores, wall rocks and the country rocks. It seems that the important consideration here is the degree to which it occurs in each of these settings.

Petruk's findings on the iron contents of the chlorites from the Kennco deposit would undoubtedly be cited by some workers as definite evidence of hydrothermal alteration. However, others who consider these chloritic rocks as well as the sulfides to be facies of iron formation, might regard them as normal for iron formation rocks. Insofar as the chalcopyrite-pyrrhotite mineralization and silicate facies of iron formation would be expected to form under more oxidising conditions than the pyritic sulfides, a similar increase in the iron content of the silicate (chlorite) facies might also be expected under progressively more oxidising conditions. Plausible alternative explanations of this kind, serve to illustrate that the case for hydrothermal alteration cannot be considered proven. McAllister (1959) pointed to the fact that in an area where the degree of sericitization and chloritization depends to a marked degree on the original composition of the enclosing rocks "alteration zones" might be inferred where none exist.

On the basis of the limited data available it appears that there is no definite evidence to suggest that indisputable wall rock alteration has occurred or that contact metamorphic effects are present. The similarities of the mineralogical assemblages in the ores, the enclosing rocks and the country rocks support this view.

# 1-7. Relationship between the structure of the enclosing rocks and the occurrence of the deposits

In examining the possibility that the sulfide deposits might have been emplaced in structurally favourable sites in the metasedimentary rocks, McAllister (1959) and Davies (1966) considered that localization of deposits in fold crests is not a consistent feature since some show little apparent relationship with local folds (e.g. Orvan Brook and the Neither do the ore deposits appear to Canoe Landing Lake deposits). occur consistently in zones of unusually intensive shearing or dislocation, and where evident, large structural deformation effects have not indisputably been shown to pre-date the deposits. This is obviously not true, however, for fine structures occurring particularly near the Holyk (1956) suggested that a shear zone of margins of deposits. regional extent - in plan as well as in depth - occurring along the metasediment-volcanic contacts may have acted as channelways for mineralizing solutions. While at-depth shearing extending below deposits has on occasion been postulated (e.g. Lea and Rancourt (1958) for the B.M. & S. No. 6 deposit) to provide channelways for upward moving mineralizing solutions, this has not yet been convincingly demonstrated.

## 1-8. Relationship between the distribution of sulfide mineralization and the intrusive rocks

In the past it has been popular among some geologists of the camp to assume that a genetic relationship exists between the granitic rocks and the stratiform deposits. Roy (1961) obviously supported this idea when he claimed that the B.M. & S. No. 6, No. 12 and New Larder U deposits show a definite spatial relationship to the Bathurst granite and

that a similar spatial relationship is shown by a number of deposits located near the Nepisiguit River granite. On the other hand, Holyk (1956) claimed that there is no positive evidence for associating the deposits with the exposed granites, since any attempt to relate the known deposits with the proximity of granites in plan overlooks the possibility of proximity of granite with depth throughout the area. Sills and/or dykes of altered diabase and diabasic gabbro occur in the vicinity of some deposits; for example, in the Stratmat 61 deposit, gabbro forms part of the footwall. This association has led some writers to invoke a genetic relationship between the basic intrusive rocks and the stratiform deposits (Holyk, 1957; Benson, 1959; Johnston, 1959).

K/Ar dating of three granites by Tupper (1960) indicated an age of close to 390 million years. An average model lead age of 370 ± 20 m.y. was obtained for five galenas from four deposits, including two from the Keymet vein deposit and one from each of the B.M. & S. No. 6, No. 12 and New Larder U deposits. Tupper (1960) has interpreted the apparent overlap of these ages to indicate that the granites and the sulfides were emplaced during the same major orogenic event. The uncertainty of this model lead age appears to be considerably larger than has been indicated For example, the ages computed for these leads by Tupper, however. using the Holmes-Houtermans Model and the Russell-Stanton-Farquhar Model give mean ages of 470 and about 270 million years, respectively. With regard to the uncertainty of the model lead ages, Russell and Farguhar (1960) reported that it seemed unlikely that a precision of better than ± 100 m.y. could be obtained at the time of their writing.

#### 1-9. Location of the Heath Steele Mine

The approximate location of the Heath Steele Mine is 47°17'N and 66°05'W. It is situated in Northumberland county, about 40 miles by road to the northwest of Newcastle and roughly 50 miles by road to the southwest of Bathurst, New Brunswick. Rail access to the mine is by a Canadian National Railway spur from Bartibog on the main Newcastle-Bathurst line.

#### 1-10. Geology of the Heath Steele Mine

#### General geology

The stratiform deposits of Heath Steele Mines Limited are believed to occur in minor folds in the northern limb of a large northwest plunging anticlinal structure comprising siliceous and basic volcanic rocks and metasedimentary rocks of the Tetagouche Group (McFarlane and Gates. 1966). Acid to intermediate volcanic rocks comprising anygdaloidal flows, "flow breccias" and tuff and agglomerate are reported by Whitmore (1957) to be the most abundant rocks on the property. Α roughly east-west trending complex of metasediment and quartz-augenschists ("porphyries") swelling from about 1500 feet in width at the western end up to about 6700 feet in the central part and thinning to 3700 feet at the eastern end occurs within the acid volcanics. The acid volcanics to the south of the property wrap around a projecting nose of intermediate to basic volcanic rocks consisting principally of andesitic flows which commonly exhibit pillow structure. Whitmore reported that while the poorly shaped pillows provide uncertain structural information, it is apparent on the basis of this information that the acid volcanics lie stratigraphically above the basic volcanic rocks.

The sulfide deposits occur in the metasediment-"porphyry" complex which is shown in Figure 1-10. The orebodies of the five zones mostly occur within, or in contact with the metasedimentary rocks and more than half of the deposits have one of their surfaces in contact with "porphyry". According to Whitmore, the metasediments of the orebearing metasediment-"porphyry" complex include argillites, slates, impure arkosic and tuffaceous quartzites. It is also reported that intermediate to basic flows appear to be present in a few places. Immediately underlying the main "porphyry" horizon, particularly towards the east end of the property, there occurs a 50 to 250 foot thick unit termed the ore horizon consisting of a strikingly varied group of well bedded metasediments including magnetic, cherty or sideritic iron formation and quartz-"porphyry" beds. This zone is reported to pass downwards into thinly bedded chloritic metasediments which are commonly highly contorted and carry abundant quartz lenses and veinlets. Dechow observed that rocks similar to the overlying siliceous volcanic rocks are interbedded with the thinly bedded metasediments which are reported to be of greywacke composition. The quartz-feldspar and quartz-augen schists, or "porphyries" as they are sometimes called, outcrop as elongate bodies of varying thickness which more or less follow the regional trend. They occur in intimate association with the metasediments and each encloses the other. While quartz-feldspar "porphyry" appears to be by far the more abundant variety, fairly large bodies of quartz "porphyry" are reported to occur north of the B-1, B-3 and B-4 deposits and an abundance of thin "bands" of quartz-"porphyry" occur in the E, A-C-D, and B-2



## FIGURE 1 - 10

GEOLOGY AND ORE ZONES, HEATH STEELE MINE (after McFarlane and Gates, 1966)

## LEGEND

Acid volcanic rocks

6

- `Quartz feldspar augen schist
- Quartz augen schist ( after Dechow, 1960 )
- Metasedimentary rocks

areas. "Quartz-eye" rocks containing smaller and more angular quartz grains occur in two other locations. Dechow reported that the mineralogy of the quartz-feldspar "porphyry" consists of subhedral to euhedral quartz and feldspar grains set in a matrix of quartz, feldspar, sericite and chlorite. The feldspars are generally embayed, fractured, and aligned sub-parallel to foliation, somewhat replaced by sericite and, in places, by epidote and carbonate. Wisps, stringers, and masses of chlorite and sericite are arranged in a sub-parallel manner and give these rocks a schistose or "gneissic" appearance. In the quartz-"porphyry", subhedral to euhedral quartz phenocrysts ranging up to 3 mm. in diameter are reported to occur in a predominantly sericitic groundmass containing some penninite chlorite and muscovite.

Whitmore suggested that the "porphyry" lenses occurring interbedded with metasediments below the main "porphyry" mass are obviously sedimentary as indicated by the presence of bedded structures and abundant fragmented quartz and feldspar grains. With the exception of part of the "porphyry" in the northeast, Whitmore believed that the main mass of "porphyry" is a tuff or welded tuff as indicated by the presence of crude banding caused by crowding of phenocrysts into certain layers suggestive of sorting and stratification, the complete lack of amygdules (compared • with some of the acid volcanics) and the presence of thin sedimentary horizons within parts of the "porphyry". The "porphyry" mass in the northeast is reported to show an aphanitic contact zone commonly less than seven feet in thickness which contains fewer and smaller phenocrysts consisting chiefly of quartz. It was suggested that this zone may be the

product of hydrothermal alteration. Gourley (1957) considered that the quartz-feldspar "porphyries" are coarse arkosic sediments. Dechow, on the other hand, believed that the "porphyries" were injected as sills at the time of sedimentation but may have been extruded in places.

The siliceous volcanic rocks occurring to the southeast part of the map area are reported by Dechow to consist of schistose and banded rocks containing corroded and fractured feldspar phenocrysts occurring with and without minor amounts of quartz phenocrysts set in a quartz-sericite-chlorite matrix. The feldspars are largely of andesineoligoclase composition but some untwinned albites do occur. The feldspars are commonly replaced by chlorite, sericite, epidote and carbonate. No indisputably intrusive rocks outcrop in the map area.

Whitmore suggested that while the structure of the metasediment-"porphyry" complex is unclear, the "porphyry" masses which bound the complex overlie the sediments which form its center to produce an anticlinal structure. If correct, this interpretation means that the "porphyries" form the basal portion of a more or less continuous sequence of acid volcanic rocks which may pass downwards into basic volcanics which are reported to underlie the acid volcanics elsewhere. Dechow (1960) claimed that an unconformity exists in the southeastern part of the property where the metasediments come in contact with the acid volcanics and the "porphyry" is missing. Whitmore also noted this feature but did not comment on it. If this interpretation is correct, an unconformity of unknown extent separates the metasediment-"porphyry" complex from the acid volcanics above. Dechow suggested that the mine area is located in the

axial portion of a steeply plunging anticline as evidenced by movement of dragfolding, the dip and strike of the foliation, similarity of the volcanic rocks to the north and south, and the agreement with the regional structure. Faulting and shearing is considered by Dechow to occur in two main directions: an earlier east-west set that was closely associated with ore formation and a later north-northeast set which displaces the ore.

#### Geology and locations of the ore zones

The geology of the five principal ore zones (A,B,C,D and E) mostly occur within or in contact with the metasedimentary rocks of the metasediment-"porphyry" complex. These comprise a mixed assemblage of chloritic schists, quartz-sericite schists, iron formation and feldspathic metasedimentary rocks (McFarlane and Gates, 1966). More than half of the deposits have one of their surfaces in contact with "porphyry". Because the detailed structure of the ore-bearing complex is largely unknown, it is not possible to determine whether the orebodies occupy one or more stratigraphic horizons. However, the C deposits, the B-1, B-4, B-2 and B-3 (?) orebodies as well as the A and D deposits appear to occur in locally continuous horizons. The B-1, B-2, B-4 and B-3 ore zones are connected by an apparently continuous mineralized zone which extends beyond the B-3, covering a total distance of 5100 feet. These orebodies occur on the noses and flanks of a series of steeply plunging minor folds which follow the broadly sinuous "porphyry" contact zone. However in detail, this contact is complicated by minor folding, offsetting shear zones and faults of some displacement. The B-l orebody

dips steeply to the north and the other B zone deposits dip steeply to the south. The four western zones (A, C-1, C-4 and D) are grouped around a local trough-shaped structure in the southern part of the metasedimentary-"porphyry" complex (McFarlane and Gates, 1966). The C orebodies lie along the northern edge of the structure and A and D zones occur to the south. The C zones are localized in folds which are roughly parallel with the metasediment-"porphyry" contact and the D zone occurs in an east striking shear zone which dips at  $50-70^{\circ}$  to the north. Shearing and faulting are reported to be common in the A and D zones. The E zone occurring to the north consists of three east-west striking tabular bodies dipping  $50-60^{\circ}$  to the south.

The B-l orebody is enclosed by a hanging wall of quartz-"porphyry" which exhibits a north striking schistosity and fracture cleavage (Dechow, 1960) and a footwall of highly sheared and crenulated chlorite schist. The B-l, which is of the pyrite-sphalerite-galena-chalcopyrite type, grades eastward into a minor development of iron formation that is rich in magnetite. Copper is more abundant near the footwall and zinc and lead become more abundant toward the hanging wall. Whitmore (1957) noted the presence of copper mineralization occurring locally in abundance in the footwall metasediments down to depths of 50-100 feet. The B-l was capped by a 45 foot thick gossan and supergene enrichment penetrated into the massive sulfides down to depths of about 80 feet below the surface. Immediately lying below the gossan was a 2-6 foot thick zone containing a 2-6 inch thick layer of mud which was rich in silver minerals including acanthite and argentite. The other B zones

are reported to be similar to the B-1. The A zone occurs in chloritic schist in contact with a "porphyry" hanging wall. Both ore types are represented, with the more abundant zinc-lead ore of the pyrite-sphaleritegalena-chalcopyrite type occurring closest to the "porphyry". Copper ores, consisting at least in part of well banded chalcopyrite-pyrrhotite ore lenses appear to be more abundant below the zinc-lead mineralization, but are reported by McFarlane and Gates (1966) to also partly enclose the The north dipping D orebody appears to be essentially of the zone. pyrite-sphalerite-galena-chalcopyrite type with an irregular development of chalcopyrite-pyrrhotite ore occurring along its hanging wall. The closest development of "porphyry" which strikes essentially parallel with the length of the deposit is a tongue-like projection to the south. The C and E zones appear to comprise both ore types with the copper-rich ores being more abundant. The C deposits occur in chloritic "tuff" and the E deposits occur in metasediments and "tuffaceous" rocks.

#### 1-11. Geology of the B-1 ore zone

The B-l ore zone essentially consists of a single large massive sulfide body - the B-l orebody proper - and a minor lens of massive sulfide which occurs in the footwall metasediments close to the B-l. Other much smaller lenses and pods of massive sulfides together with horizons of disseminated sulfides occur in both the footwall and hanging wall rocks. The B-l orebody and associated massive sulfide bodies have more or less tabular to lenticular shapes and, in general, occur conformably within the steeply dipping enclosing rocks as shown in Figure 1-ll. The B-l

FIGURE 1 - 11



orebody occurs in immediate contact with quartz-"porphyry" which forms the hanging wall and is contained in generally deformed chlorite-rich metasediments which in places show thinly bedded structure. The footwall contact is relatively sharp in places, but in others it is gradational with thin lenses of massive sulfides or bands of disseminated sulfides contained in the metasediments. Lenticular masses of both chloritic metasediment and of quartz-"porphyry" are intercalated with the massive sulfides in parts of the B-1 and are themselves generally mineralized to A limited amount of "porphyry" also occurs in the varying degrees. footwall metasediments and, locally, in direct contact with the massive sulfides as shown in Figure 1-10. In a few of the vertical sections through the B-l established from D.D.H. information, the "porphyry" is observed to project into the chloritic metasediments and massive sulfides of the footwall as blunt "plug-like" masses. Beds of magnetic iron formation are present in the massive sulfides extending eastward from the B-1 but are relatively rare in the B-1. On the other hand, magnetite is a common gangue mineral in the massive sulfides.

The B-1 orebody is tabular to lenticular in shape in sectional view. However, while it is generally bounded by sub-parallel surfaces in its central and eastern parts, its surfaces curve and swell locally to varying degrees. The deposit is thickest towards its eastern end above the 8600 level where it swells locally to about 230 feet in thickness. The deposit becomes thinner beyond this local thickening; the horizontal inter-

section in the B-l pit above is reported by Dechow (1959) to have a maximum thickness of 150 feet and a length of about 500 feet. The 8600 level intersection averages about 150 feet in thickness in the eastern and central parts and the western part tapers irregularly and sinuously out to a thickness of about 10 to 40 feet where the deposit forms part of a zone of less important mineralization. The eastern end constricts abruptly in the 8600 level intersection for which the overall length is about 1000 feet. Below the 8600 level the deposit appears to show a slight, though variable overall decrease in thickness with depth at the western end where some drill hole information is available. An isopach map of the deposit constructed using "true" thicknesses determined from D.D.H. information is also shown in Figure 1-11.

#### 1-12. Fabric of the massive sulfides

Mineralogical layering or banding is a prominent feature of the B-l orebody. This is evident in hand specimens of massive sulfides as a series of commonly flat layers of fairly uniform thickness, which individually consist of mineralogical assemblages made up of mixtures of sulfides or of sulfides and gangue constituents that occur in essentially constant proportions within given layers. Marked changes in the proportions of constituents between adjacent layers gives rise to conspicuous banding. In the case of disseminated sulfides occurring in metasediments, the banding coincides with the stratification, and in the case of massive sulfides the mineralogical banding is observed to be generally parallel with the stratification in adjacent metasediments or with massive sulfide

country rock contacts. In parts of the B-1 where the hanging wall contact is offset by small faults, or deformed by small drag-folds, the mineralogical banding in the high-grade lead-zinc ore appears to be more or less sympathetically deformed but locally the banding may be diffuse In these settings, cross-cutting "veins" together with . or even absent. isolated "clots" or "pods" of coarse grained sulfides occurring in finer grained sulfides are common features. Although similar features are present in places throughout the deposit, the overall attitude of the mineralogical banding, where evident, is generally parallel with the bounding surfaces of the deposit. An additional feature which is evident in both deformed and relatively undeformed banded ore in parts of the B-l is the occurrence of "clots" of coarse grained quartz-feldspar intergrowths which commonly have minor amounts of coarse grained sulfides associated with them. They are generally elongated in the plane of the banding and appear to locally transgress the banded massive sulfides along sharp irregular contacts. These "clots" range in size in exposed surfaces from about 0.5" up to about 5 feet in length and may attain widths of about 1.5 feet.

Mineralogical banding is most evident in the high-grade leadzinc ore but can also frequently be observed in essentially barren pyrite where the proportions of pyrite to non-sulfides vary vertically. While the sulfides of sphalerite-pyrite-galena ore bands usually appear to be fairly uniformly distributed throughout the bands, some of the thicker bands exhibit across band variations in the proportions of these minerals. The thicknesses of individual sphalerite-pyrite-galena bands range from less than 0.05" up to about 1" but are usually not

more than 0.2 inches in thickness. While some bands have relatively uniform thicknesses over 4 or 5 inches, most pinch and swell to some extent and usually cannot be traced for more than several feet.

#### 1-13. Mineralogy of the B-1 orebody

No detailed account of the mineralogy of the B-1 mineralization has been published so far. Dechow (1960) and Roy (1961) microscopically examined sulfides from the B-1 as parts of larger survey studies of the mineralogies of the Heath Steele deposits. The minerals identified in the deposit so far are given in Table 1-13, below.

#### TABLE 1-13

Major constituents:

sulfides

other minerals

magnetite

chlorite muscovite

(calcite)

quartz

pyrite sphalerite pyrrhotite chalcopyrite galena

Minor to trace constituents:

tetrahedritetennantite (calcite) feldspar

#### secondary minerals

covellite chalcocite acanthite argentite

Other constituents that are reported to occur in the Heath Steele deposits as a whole are arsenopyrite, primary and secondary marcasite, bismuthinite, native bismuth, freibergite, hematite, graphite and anglesite. Roy and Dechow postulated similar paragenetic sequences for the mineral suites from the deposits. Pyrite and arsenopyrite (and magnetite), together with some of the quartz, carbonate and calcite are considered to be the earliest formed. While sphalerite, pyrrhotite, galena, tetrahedrite, chalcopyrite and marcasite are considered to be later, Dechow and Roy do not agree on the paragenetic order. The sequence given here is the one proposed by Roy. Dechow considered that pyrrhotite, sphalerite, chalcopyrite and galena formed in this order with a considerable degree of overlap. Dechow also proposed that some of the marcasite is primary and constitutes the last formed primary sulfide. The textures in the primary ores were termed "porphyritic" by Dechow who noted a general lack of evidence of extensive replacement relations between the sulfides.

#### 1-14. Structure of the B-1 ore zone

The B-1 ore zone apparently occurs on the flank of some relatively large folded structure. However, the effects of deformation are evident in both the B-1 orebody and the enclosing rocks. Some of the structures which have been observed in the metasediments below the footwall include:-

- i) crenulation of the banding in thinly bedded rocks.
- ii) the development of elliptical pods of quartz (Flaser structure) from initially cherty bands in the siliceous schists.
- iii) fragmentation of some feldspars and the subsequent separation of the fragments in the plane of the schistosity.
  - iv) occurrence of early stage development of kink structure in muscovite schists.

The hanging wall contact of the B-1 is locally deformed by small faults and small drag-folds. Kalliokoski (1965), in describing a dislocation feature on the B-1 hanging wall, reported that the sphalerite-pyrite banding of the ore cuts across the folation in the quartz-"porphyry" indicating that the ore has moved relative to the "porphyry". The development of quartz "veins" in the porphyry opposite this zone of dislocation was also noted. It was further suggested that the features observed in the ores are the end product of shearing, folding and recrystallization by an unknown but substantial amount, tending to destroy textural evidence pertaining to conditions of genesis. The development of slickenslides in the massive sulfides provides indisputable evidence of at least limited post-mineralization deformation effects. It is considered probable that the overall shape of the B-1 orebody has been affected by deformation as suggested by the similarity in the shapes of its hanging wall and footwall contacts as seen in sectional views. In places these are sinuously curving. McFarlane and Gates (1966) suggested that the economic concentrations of galena-sphalerite and chalcopyrite within the B-l are controlled by minor folds and undulations.

#### 1-15. Sulfur isotope studies on stratiform deposits

A considerable amount of sulfur isotope research has been carried out fairly recently on sulfides from stratiform deposits of the "volcanic" type. The Buchan's deposits were studied by Jensen (1959), the New Brunswick deposits by Dechow (1960) and Tupper (1960), Meggen by Buschendorf et al. (1962), some layered Spanish deposits by Freidrich et al. (1963), Rammelsberg by Anger et al. (1966), Mount Isa by Solomon (1965) and a total of five eastern Australian deposits, including some measurements on sulfides from Mount Isa, by Stanton and Rafter (1966). In comparing the sulfur isotopic data available at that time for Broken Hill, Mount Isa, Captain's Flat, the Heath Steele and B.M. & S. No. 6 and No. 12 deposits, Cartagena and Meggen deposits, Stanton and Rafter (1966) observed the following general features:-

- i) the mean  $\delta S^{34}$  values for all deposits are generally greater than the meteoritic value, and it is extremely rare for an individual analysis to show a negative value.
- ii) the range of variation within individual orebodies is consistently close to 7%.
- iii) there is no characteristic mean value for the deposits as a group, and the means range from close to meteoritic (+1 for Broken Hill) to approximately that of the present sea water value (+18.2 for Meggen) and 98 per cent of the values are evenly distributed between these two extremes.

iv) measured samples from Broken Hill and Mount Isa can be grouped on a stratigraphic basis, and any small differences are related to stratigraphy rather than locality.

v) no apparent age effect was observed.

Compilation of 90 isotopic measurements on sedimentary sulfides by Stanton and Rafter (1966) show a total spread of more than 85%, and the histogram pattern of the values does not exhibit any distinctive trend.

In a recent study designed to establish the spread in isotopic values for Mount Isa sulfides, Solomon (1965) obtained a spread of 26.8% for 41 sulfide determinations. The lightest and heaviest values were respectively +4 and +30.8%, and the overall mean is about +16%. It is apparent from the data that the mean of the galenas is lighter than the means of either the sphalerites or the pyrites. More recently the results of an excellent study of the distributions of sulfur isotopes in the Rammelsberg deposit were presented in a paper by Anger et al. (1966). The Rammelsberg deposit consists of five steeply inclined essentially parallel lenses occurring in shales. Two of the lenses are notably larger and exhibit well developed across deposit mineralogical zoning which grades stratigraphically upward from pyritic ore partly rich in chalcopyrite through sphalerite-pyrite ore, barite-poor zinc-lead ore and finally into barite-rich zinc-lead ore. Isotopic analyses were made on the barite gangue, pure sulfides and mixed sulfides from complete sample profiles through the orebodies. The overall ranges of isotopic variations of the pure sulfides were found to be as follows:-

pyrite: -12 to +25

chalcopyrite, galena and sphalerite: +5 to +22

barite: +12.5 to +35.6%.

Mixed sulfides from the Altes Lager were found to be as light as -20%. The mean of the barites is about +23%, a value which is very close to the value determined for M. Devonian evaporites of Europe and North. America. Analyses of concretionary pyrite, which is fairly abundant in the surroundings of the orebodies and especially in the shales underlying the ore lenses, gave values ranging from about -35 to +55%, but the bulk of the analyses are reported to cover the same range as the ore pyrites The mean value for ore sulfides other than (i.e. about 0 to +28%). pyrite is about +15%. Where across orebody trends in  $\delta S^{34}$  values for sulfides are evident, the sphalerites, galenas and chalcopyrites show similar progressive enrichments in  $\delta S^{34}$  from about +10 near the base up to around +20%, near the top of the Neues Lager. The trend patterns are essentially identical in the two profiles which are about 140 meters apart. While barite values generally show fluctuations of about 5%, in given horizons, there only appears to be a marked overall trend across the Grauerzkörper where the lower barites have values of. about +15 and the upper barites have values of approximately +25‰.

While the means of the Mount Isa and Rammelsberg deposits fall within the range of variation for the stratiform deposits considered by Stanton and Rafter (1966), the overall ranges of isotopic variation for their sulfides are roughly as extensive as the entire range of variation

for the deposits considered by these writers. The absence of pyrite values which are appreciably lighter than associated sulfide values appears to constitute a difference between the isotope data for the Mt. Isa sulfides and the Rammelsberg sulfides.

In an abstract presented at the 1967 Geological Association of Canada meeting in Kingston, Sangster (1967) showed that the  $\delta S^{34}$ values of "normal" and "volcanic" types of stratiform deposits of different ages are lighter than sea water sulfate sulfur (Thode and Monster, 1963) of corresponding seas by about 10 to 16%, respectively. The average enrichment of  $S^{34}$  in coexisting sulfate minerals is reported to be 1.4 and 3.7%, respectively.

## Sulfur isotope studies on the sulfide deposits and country rocks of the Bathurst-Newcastle area

Two sulfur isotope studies have so far been carried out on sulfide deposits of the Bathurst-Newcastle area. Tupper (1960) undertook a survey of sulfur isotope abundances in individual sulfides and sulfide mixtures from 26 sulfide deposits. For six of the deposits only one to

two samples were analyzed. In addition, some pyrites were analyzed from metasediments and intrusive igneous rocks. At about the same time Dechow (1960) investigated sulfur isotope abundances in individual and mixed sulfides from 5 Heath Steele deposits and also analyzed pyrites from a variety of country rocks. A complementary study was made by Dechow on supergene products from the B-1 pit but no significant fractionation effects were detected.

The summary figures from Tupper (1960) and Dechow (1960) showing sulfur isotope variation in sulfides of the Bathurst-Newcastle area are combined below in Figure 1-15A. The determined ranges and mean isotopic values for each of the deposits and the country rock groupings are indicated. The number of samples used in determining the ranges and means are given in brackets following the identification of each grouping. The following observations can be made from the results of these studies:-

> With two exceptions, the stratiform i) sulfide deposits. deposits are considerably enriched in S<sup>34</sup> relative to the vein-type deposits. In the case of the exceptions, some. values from the Nigadoo vein deposit overlap the overall range of variation of the stratiform deposits and the reverse situation is shown by the stratiform Armstrong Brook The overall means of the two classes of deposits deposit. differ by roughly 10 per mil.. While most of the stratiform deposits have minimum ranges of variation of about 6 to  $8\%_{\circ}$ , those for which the ranges are shown as broken lines (e.g. B zone C.M. & S. and the New Larder U deposit) have overall spreads of up to about 15%. It is evident

## FIGURE 1 - 15A

#### Summary of the Sulfur Isotope Variations in the Bathurst - Newcastle Area

## Stratiform Sulfide Deposits



that the Nigadoo deposit has a comparable spread.

- ii) <u>intrusive rocks</u>. The mean values for two pyrite samples from each of the intrusive granites and gabbros can be considered normal for these types of rock. On the other hand, analyses on two pyrites from what Dechow described as the South Little River pink gneissic granite gave values that are within the range of variation of the Heath Steele sulfide deposits.
- Tupper obtained a spread of approximately iii) country rocks. 40%, and a mean of about -5%, for 24 pyrites occurring mostly in metasediments of the Tetagouche Group. Most of these samples were collected from widely separated localities which, in general, are not in the immediate vicinity of The majority of the pyrites analyzed by sulfide deposits. Dechow were taken from metasediments, "porphyries" and siliceous "volcanic" rocks occurring generally in close proximity to the Heath Steele deposits. With few exceptions, the isotopic values fall within the range of variation of the deposits. However, disseminated sulfides in porphyry close to the B-2 deposit were found to have a value of about +21%. Disseminated pyrites from two additional siliceous "volcanic" samples, at least one of which occurred in the southeast part of Dechow's map area (Dechow, 1960) gave "anomalously light" isotopic values of about +1 and -3%.. The former was described as an acid tuff and the latter as a peculiar soda rich flow(?) rock containing

abundant disseminated sulfides. The disseminated sulfides in both these rocks were considered to be syngenetic (i.e. Analyses were also made on unspecified sulsedimentary). fides from three basic volcanic rocks containing pyrite and Values close to the meteoritic mean value were pyrrhotite. obtained for two of these and a value of about +20%, was obtained for sulfides from the third which is reported to outcrop to the south of the D zone where considerable deformation is present. Dechow suggested that the first two samples are syngenetic and that the sulfides from the last mentioned sample may in some way be associated with ore formation.

Both writers attempted to test for isotopic fractionation between sulfide species and/or pairs of sulfides by comparing means of given groups. While some of Dechow's within deposit groupings appear to show an enrichment of  $S^{34}$  in pyrite relative to the associated sulfides, others do not and it was concluded that no positive fractionation was detected. It was suggested, however, that pyrrhotite appeared to be generally enriched in  $S^{34}$  relative to chalcopyrite. By comparing mean values for groups computed using data from all of the stratiform deposits, Tupper reported that the sphalerite-galena group appeared to be about 1%, heavier than the pyrite and the chalcopyrite-pyrrhotite groups. The trend was not considered meaningful because pyrite samples were heavily weighted from deposits with relatively high  $S^{32}/S^{34}$  ratios. Tupper (1960) stated that a systematic decrease in the mean  $S^{32}/S^{34}$  ratios of deposits located progressively farther outward from the C.M. & S. "A" and "B" zone deposits appeared to be evident in the early part his study. He asserted that whether this trend exists or not, the similarity in the mean values of closely spaced deposits from different parts of the area favours several localized sources, closely related in space, but each having individual characteristics slightly different from the others. Small stocks or cupolas occurring at depth are postulated as possible sources.

Since it is evident that the mean isotopic compositions of deposits occurring in apparently continuous stratigraphic horizons are very similar, it is considered worthwhile to examine the possibility that the mean \$534 values of such groups of deposits might show strong correlation with their presumed stratigraphic position. If the locations of the deposits showing the most similar  $s^{32}/s^{34}$  ratios are joined, lineaments are obtained which approximately parallel the local stratigraphy as shown in Figure 1-15B. If there were any overall relationship between the stratigraphic positions of these groups of deposits and their mean isotopic compositions, it might be expected that the maximum variation between groups would occur across rather than along the regional strike. A line of some chosen intermediate  $s^{32}/s^{34}$  ratio value drawn between these lineaments might then be expected to approximate the trend of the It can be seen in Figure 1-15B that the 22.00 s<sup>32</sup>/s<sup>34</sup> regional strike. value line roughly outlines the central siliceous core of the central volcanic complex, tending to enclose deposits with lighter means and

## <u>FIGURE 1 - 15</u>B

## RELATIONSHIP BETWEEN THE MEAN ISOTOPE RATIOS

## OF THE DEPOSITS AND THEIR LOCATIONS



 $\star$  after Tupper ( 1960 ) and Dechow ( 1960 )

exclude those with heavier means. The Kennco Clearwater deposit which occurs about 10 miles south of the map area is an exception. This apparent relationship does not apply in detail, however, especially if possible complications resulting from folding are not considered. Obviously the possibility that this apparent pattern might also result from systematic variations in the isotopic composition of sulfur derived from a hypothetical granitic source cannot be ruled out. However, it is considered that there may be a more satisfactory explanation.

The distribution pattern for the disseminated sulfides in metasediments does not appear to be in any way similar to the pattern above. In fact, three of the five heaviest values (22.00 - 22.04) form a lineament which almost coincides with the lightest lineament (22.08 - 22.07) for the stratiform deposits. The two heaviest values occur near the B.M. & S. No. 6 deposit and in the vicinity of the Caribou and Murray deposits. Other sedimentary sulfides occurring less than 2 miles from the B.M. & S. and Caribou deposits have isotopic ratios of 22.2 and 22.53, respectively.

The similarity of the means and the relatively narrow ranges of sulfur isotope variation in the stratiform deposits are considered by both Tupper and Dechow to indicate that the deposits were derived from homogeneous sources. Tupper suggested that the source sulfur might have become enriched in  $S^{34}$  as a result of assimilation of heavy sulfur, or by the loss of isotopically lighter volatiles, or possibly due to fractionation effects that might have occurred during transportation from the source to the site of deposition. Tupper appealed to limited mixing

of two separate sources of sulfur which were closely related in space and time to account for both the vein-type and the stratiform deposits. Dechow postulated that variation in sulfate/sulfide ratios or variation in the isotopic composition of sulfate sulfur in granitized source rocks might account for the differences between the two types of deposits.

#### 1-16. Suggested origins of the "volcanic" stratiform deposits

It has been customary in the past for different investigators to appeal to one of three early postulated origins for the "volcanic" stratiform deposits, namely:-

i) an igneous hydrothermal replacement origin

ii) a lateral secretion or source bed origin

iii) a so-called "syngenetic" or sedimentary origin

According to Cook (1933), these three theories of ore genesis were more or less established on a firm basis by European geologists in the first half of the 19th Century.

A magmatic hydrothermal origin for sulfide ore deposits proposes that sulfide ore constituents are derived directly from intrusive igneous rocks during their emplacement and that these constituents are transported in fluids to their present sites of deposition. Many veintype deposits within intrusive rocks or in adjacent older rocks are clearly of this origin. An igneous hydrothermal replacement origin, on the other hand, often requires that these fluids replace host rocks at some favourable structural site, often preserving their fine structures, rather than squeezing into or filling fractures. Attendant with this concept is the "room" problem which is almost always overlooked by proponents of this origin even for some of the very large stratiform In its most general form the Source Bed Concept postulates deposits. that disseminated heavy metals generally occurring as sulfides in some sedimentary source rock are remobilized by some means and are later concentrated to form sulfide deposits in favourable sedimentary horizons. that are commonly capped by impermeable rocks (e.g. shales). Α "syngenetic" or sedimentary origin postulates that metals are precipitated as sulfides from aqueous solution. Stanton (1960b, 1960c) suggested that the stratiform deposits were characteristically deposited in eugeosynclinal areas, within nearshore sediments laid down in off-reef lagoons or related sedimentary environments in the region of volcanic island arcs, the metals being supplied to the basins of deposition by seaboard and/or submarine fumaroles. It is believed that crustal warping, regional thrust faulting along oceanic margins, volcanism, island arc formation, metal-bearing fumarolic discharges, and shoreline sedimentation accompanied by intensive bacterial activity, are all related and are

sequential phenomena conducive to the concentration of sulfides in a marine setting.

Numerous variations of these general concepts have been appealled to in the past to explain the origin of the stratiform deposits. The Bathurst-Newcastle deposits are examples for which all of these origins have been postulated. The general geological requirements necessitated by these three origins are:-

i) igneous hydrothermal replacement origin

- a) favourable structures (e.g. fold crests, fracture zones) in replaceable host rocks (e.g. limestones).
- b) favourable connecting structures (e.g. faults, shear zones) to provide channelways for the transport of mineralizing fluids.

c)intrusive igneous source rocks of the same age as the ores.

ii) lateral secretion or Source Bed origin

- a)replaceable host rocks, generally adjacent to impermeable strata.
- b)permeable, or suitably fractured strata which, if not of a replaceable nature themselves, occur between the potential source rocks and replaceable host rocks.
- c)source rocks containing appreciable concentrations of base metals are present in the sequence in direct contact with permeable strata.
- d)evidence of movement of meteoric or hydrothermal solutions within strata or granitization of the sequence at depth.
- iii) syngenetic or sedimentary origin
  - a) occurrence of the "volcanic" type deposits in eugeosynclinal successions containing lavas, and/or pyroclastics and associated sediments (Oftedahl (1958); Stanton (1958)).
  - b) precipitation of base metal sulfides on a flat or gently sloping sea floor through which issue hydrothermal fluids
     by means of fractures or some kind of feeder conduits.
  - c) intrusive igneous source rocks occur in the sedimentaryvolcanic pile at unknown depths below the deposits.

The two main theories which most frequently have been applied to these deposits are the igneous hydrothermal replacement theory and the sedimentary-volcanic exhalative theory.

#### 1-17. Origin of sulfide deposits in the light of sulfur isotope studies

Meteoritic sulfur has been shown by various writers to have a very narrow range of variation (Thode et al., 1961). For this reason it has been chosen as the reference value and corresponds to a  $S^{32}/S^{34}$ ratio of approximately 22.2. Shima et al. (1963) and Smitheringale and Jensen (1963) demonstrated that sulfur from basic igneous rocks have ranges of variation of up to about 8%, and have means which clearly correspond to the meteoritic value (see Figure 1-17). These writers suggested that mantle sulfur can therefore be considered to have essentially the same value as meteoritic sulfur. A general trend favouring an enrichment in  $S^{34}$  of about 5% in the sulfides of acid differentiates and in sulfide deposits associated with the basic intrusives of the Newark Group was observed by Smitheringale and Jensen. On the other hand, the basic lavas associated with these intrusive rocks contain sulfides which have a mean value of about -5%. Sulfides from sulfide deposits at the base of the Insizwa Sill of South Africa were also found to have lighter values than disseminated sulfides from the overlying intrusive rocks (Shima et al., 1963). If it can be assumed that there has been no contamination of the Newark Group intrusive suite from external sources of sulfur, it appears that fractionations of about 15%, favouring both enrichment and impoverishment of S<sup>34</sup> relative to the meteoritic

. 55



mean can be expected in igneous processes. However, for those ore deposits that are intimately associated with intrusive igneous rocks from which it is almost certain that their solutions were derived, the ranges of variation in isotopic values are generally less than 10%, and the means are generally within a few per mil of the meteoritic value. Examples of such deposits are those of the Cordilleran region of the western United States. The sulfur in these deposits is generally considered to be derived from the mantle (Jensen and Dechow, 1962).

While the isotopic values of sulfides from most mafic and acid igneous rocks fall within the range -2 to  $+10\%_{0}$ , the overall range of variation for igneous rocks is considerably greater than this (about 45%). This naturally raises the question as to whether the sulfur in some igneous rocks which exhibit relatively heavy isotopic means might be due to contamination of magmas from crustal materials having unusual isotopic compositions. Ault and Kulp (1959) suggested that if sufficiently large bodies of crustal rocks were involved, isotopic values of sulfides in siliceous batholiths might be expected to be close to the meteoritic mean, provided isotopic homogenization were complete. It has since been shown by Gross and Thode (1965) that sulfide sulfur in some Canadian granites is unusually heavy, ranging up to about +30%. No notably light sulfur was found, however.

Apart from meteoritic sulfur and presumably also mantle sulfur, present-day sea water sulfate sulfur appears to show the smallest variation of any of the sulfur reservoirs and has an essentially constant value of +20%. It is clear, however, that it has not always had this value. Thode and Monster (1963) and Holser and Kaplan (1966) demonstrated that

the isotopic composition of sea water sulfate sulfur, as indicated by studies on evaporites, has varied by about 20%, since the Cambrian. Since the fractionation accompanying precipitation of  $CaSO_{\rm L}$  from sea water has been found to be not greater than 2%, (Holser and Kaplan, 1966), the lighter evaporite values are fairly reliable indicators of the isotopic compositions of sea water sulfate sulfur. Insofar as the oceans represent a vary large reservoir of sulfate sulfur which has varied in isotopic composition with time, sea water sulfate sulfur has to be considered as a potentially important influencing factor on both the sedimentary sulfide sulfur reservoirs and on certain ore forming processes. A parallelism in the pattern of variation of petroleums from Silurian, Devonian, Mississippian and Pennsylvanian rocks with part of the sea water sulfate sulfur trend has been demonstrated by Thode and Monster (1965). A similar trend is suggested by Sangster (1967) to occur for stratiform deposits throughout geologic time. These workers observed a fairly constant fractionation of about 15%, between the sulfur in evaporites of a given age and the sulfur in petroleums and stratiform ores of similar age. If a similar trend exists for sedimentary sulfides, it might be expected that the fractionation would be approximately 30 to 35%..

Crude oil sulfur, apparently occurring as organically bound sulfur, shows very narrow ranges of variation from 2%, up to 9%, in a single oil field and over the above-mentioned periods shows an overall range of variation of 17%, (from -4 to +13%,). The overall range of variation for sedimentary sulfides of all ages is about 85%, with a mean

of about -15%. Large variations in isotopic composition are characteristic of sedimentary sulfides, and are often found in closely spaced samples. This is well illustrated by results obtained by Jensen (1965) for sulfides from a concretion of hand specimen size taken from below a coal seam in Wyoming. An overall range of approximately 40%, was determined for the concretion. Sulfides from sandstone-type uranium deposits and red-bed copper deposits characteristically show wide ranges of isotopic variation from about 20%, up to more than 50%, and usually have large negative means (about -30%).

Studies have been carried out on recent marine sediments to determine the isotopic abundance of sulfur in the various sulfur compounds found in the sediments. Kaplan et al. (1963) studied the isotopic abundances of sulfur in elemental sulfur, free sulfide (S<sup>-</sup>), FeS, organic sulfur, sulfate and pyrite contained in the top 4 meters of sediments off southern California. They found that the quantities of these constituents vary with environment and depth in the sediments and that pyrite is by far the most abundant form. Pyrites from both oxidising and reducing sediments show an overall enrichment in S<sup>32</sup> relative to sea water sulfate sulfur of from 9 to 62%, with a mean enrichment of about -20%. Values for interstitial  $SO_4^{-1}$  range from about +12 to about +30 (+18, mean), free sulfide ranges from -28 to +18 (mean, +2.7) and free and organic sulfur range from about -20 to +10 and average A material balance calculation indicated that the total about -5%. sulfur content (up to about 1% of the dry sediment weight) is far in excess of the sulfate sulfur trapped in the interstitial water, suggesting that additional sulfate was extracted from the overlying sea water at

the sediment-water interface. A similar study by Thode et al. (1960) on sulfur compounds from greater depths (20, 80 and 160 feet) in recent marine sediments off northeast Venezuela showed that all the sulfur compounds are depleted in S<sup>34</sup> by 10 to 20% in relation to sea water sulfate sulfur. The maximum sulfur content was found to be approximately 0.2% of the dry weight of the sediments and pyrite sulfur together with sulfate sulfur were found to constitute about 70 weight percent of Sulfide sulfur (S<sup>-</sup> ion) was found to be the heaviest the total sulfur. form (+12 to +14%) followed by sulfate sulfur (+3 to +11%) and organic sulfur (+5 to +9%) and pyrite sulfur (+1 to +5%) found to be the light-The isotopic composition of sulfate sulfur shows an enrichment est. in  $S^{32}$  with increasing depth from +11 at the 20 foot level to +3%, at the Its concentration at the 80 and 160 foot levels is 160 foot level. approximately four times as great as its concentration at the 20 foot level. This led Thode et al. to conclude that little, if any, of the sulfate at depth is residual sea water sulfate, but that after burial sulfate has been produced by oxidation of pyrite in situ.

These results serve to illustrate that large isotope effects can be attributed to anaerobic bacterial reduction of sea water sulfate. Nakai and Jensen (1964) succeeded in producing fractionations of up to 62‰ in laboratory experiments conducted at 32°C using sea water in contact with marine mud containing bacteria and organic materials. It was predicted that in the case of an infinite sulfate supply, the fractionation factor between sulfate and sulfide (S<sup>=</sup>) should remain constant at 20‰. Nakai and Jensen found that aerobic oxidation of pyrite and sulfur was very slow and produced insignificant enrichment in S<sup>32</sup> in the sulfate formed. Kaplan and Rittenberg (1964) found that enrichment in  $S^{32}$  in the S<sup>=</sup> is inversely proportional to the rate of reduction when organic hydrogen donors are used. Kaplan et al. (1963) suggested that anaerobic bacterial reduction of  $SO_4^{-}$  releases S<sup>=</sup> which reacts with iron to form FeS and this in turn reacts with bacterially derived elemental sulfur to yield pyrite, i.e. FeS + S<sup>o</sup> = FeS<sub>2</sub>. Jensen (1965) suggested that pyrite is formed by the reaction  $Fe_2O_3 + 4H_2S = 2FeS_2 + H_2 + 3H_2O_{\bullet}$ 

In accordance with these findings, biogenic origins have been postulated for petroleums, native sulfur deposits of salt dome cap rocks (Thode et al., 1954) and sedimentary sulfides. The sulfur in sandstone-type uranium deposits and red-bed copper deposits is generally also believed to be of biogenic origin (Jensen and Dechow, 1962).

Sulfide deposits having spreads of about 6 to 15%, and means which are usually displaced by more than 5%, to the positive side of the meteoritic value appear to stand apart from deposits of probable biogenic origin and also those of indisputable igneous hydrothermal origin. This group includes nearly all the stratiform deposits, the Broken Hill deposit being a notable exception. Tupper (1960) suggested that the base metals and sulfur of the Bathurst-Newcastle deposits were derived from small stocks and cupolas associated with the main batholith and that the heavy sulfur in the stratiform deposits was produced as a result of a distillation mechanism or magmatic assimilation of heavy sulfur. Von Gehlen (1965) expressed essentially the same ideas when he suggested that the isotopic data for the minerals of the Meggen and Rammelsberg deposits are consistent with a mantle derivation only if it is assumed

that strong assimilation of unusual crustal material or extreme fractionation in a secondary magma chamber has occurred. Dechow (1960) proposed an igneous hydrothermal replacement origin for the Heath Steele deposits but suggested a deep seated source bed origin for both the base metals and the sulfur. It was proposed that granitization of Ordovician eugeosynclinal marine sediments containing graphite, sulfates and sulfides might have caused disequilibrium reduction of the sulfates at temperatures of 700 to 800 degrees C. A fractionation factor was obtained by assuming that the lowest measured ratio in the ores (equivalent to +18.5‰) was formed from original sulfate and the highest ratio (equivalent to +8‰) formed from original sulfide, thus:-

$$\frac{s^{34}/s^{32} \text{ in sulfate}}{s^{34}/s^{32} \text{ in sulfide}} = \frac{1/+18.5}{1/+10} = 1.009$$

The temperature interval was thus obtained by comparing this fractionation factor with the equilibrium values determined by Sakai (1957) for the exchange reaction:-

$$s^{34}o_4^{=} + s^{32=} = s^{32}o_4^{=} + s^{34=}$$

It was further suggested that the differences between the massive sulfide deposits in Ordovician rocks and the fissure deposits in the Silurian rocks can be accounted for by variations in the amounts of sulfate to sulfide in the source rocks, or possibly a change in the isotopic ratio of sea water sulfate in the ocean from which the sulfate was derived. Solomon (1965) speculated that the broad spread (27%) and general heaviness of the Mount Isa sulfides are indicative of a biogenic origin. Sangster

(1967) appealed to a similar origin for all the sulfur in the "normal" type stratiform deposits and most of the sulfur in the "volcanic" type deposits. He envisaged that the mean isotopic compositions of the "volcanic" type deposits are lighter than the "normal" type deposits because there has been minor dilution with isotopically light volcanic  $H_{S}$  (0 to +10%). A relatively uniform fractionation of roughly 15%. in environments of more or less unrestricted ocean circulation is appealled to in order to explain the relatively narrow spreads of most of the deposits. Anger et al. (1966) interpreted their results as indicative of a sedimentary-hydrothermal origin for the Rammelsberg deposits. They suggested that the sulfides of copper, lead and zinc and only about 50% of the pyrite were derived from "submarine springs", while the very light pyrites formed by bacterial reduction of marine sulfate. The barite is thought to have been derived from magmatic Ba<sup>2+</sup> ions and sulfate ions derived mainly from sea water sulfate and to a small extent from hydrothermal sulfate. It was suggested that periodic isolation of the basin from the open sea may account for the S<sup>34</sup> enrichment in some of the barite.

It is evident from previous studies on stratiform deposits that the principal difficulty is to account for the general enrichment of the ore sulfides in  $S^{34}$ . However, while various mechanisms have been proposed to account for the enrichment in  $S^{34}$ , no serious attempt has been made so far to relate detailed isotope findings with metal abundances or features in the associated rocks. Neither has it been demonstrated that the distribution of sulfur isotopes in these deposits has been influenced by regional metamorphism. This is obviously an important

requirement if a sedimentary origin is appealed to. The present study is designed, therefore, to determine whether the distribution of sulfur isotopes within the Heath Steele B-1 orebody and a number of other deposits in the same camp can be explained in terms of regional metamorphism and whether any possible pre-metamorphic features are evident in the B-1 orebody. It can also be expected that the silicate assemblages in the massive sulfides, the wall rocks and the country rocks should be similar if the deposits formed by precipitation on the sea floor and have been subsequently metamorphosed. The base metal distributions have been studied to determine whether any relationship exists between them and possible pre-metamorphic features of sulfur isotope distributions. If a relationship were found to exist this would support the view that both the metals and sulfur were derived from a common source.

The results of a study of silicate assemblages from within and around the B-l orebody and the distribution of some base metals within the B-l are presented in CHAPTER 2. The results of the sulfur isotope studies are presented in subsequent chapters.

#### CHAPTER 2

# MINERALOGICAL ASSOCIATIONS, BASE METAL ZONING AND METAMORPHISM IN THE B-1 OREBODY AND ASSOCIATED ROCKS

#### 2-1. Introductory statement

This part of the present study was carried out to determine the pattern of base metal zoning, particularly across the layering in the B-1 orebody, to determine whether any spatial relationship exists between the zoning and "porphyry" occurring in the footwall rocks, and to ascertain whether the metamorphic grade of the silicate assemblages in the orebody and adjacent wall rocks is higher than that of regional metamorphism in the country rocks. Patterns of base metal zoning in other "volcanic" type stratiform deposits are related to the stratigraphy of associated rocks to determine whether a consistent relationship exists between these features.

#### 2-2. Mineralogical associations in the B-1 orebody

Although the mineralogical composition of the massive sulfides is variable, several consistencies in sulfide mineralogical association are evident in the B-1 orebody:-

i) sphalerite and galena characteristically occur together, usually in association with pyrite but pyrrhotite<sup>1</sup> may also be present in minor amounts.

<sup>&</sup>lt;sup>+</sup> Pyrrhotite assumes the proportions of a major mineral to the exclusion of pyrite in some sphalerite-galena rich ores in the "A" deposit.

- ii) sphalerite and galena are commonly absent in chalcopyrite rich assemblages and rarely attain minor proportions in this association.
- iii) pyrrhotite is generally present in chalcopyrite-rich assemblages, and either pyrite or pyrrhotite may occur to the virtual exclusion of the other.
  - iv) pyrite and pyrrhotite appear to be ubiquitous, but commonly show preferences of association with other sulfides. Assemblages containing only these two sulfides occur in places.
    - v) pyrite is the only sulfide which commonly occurs without associated sulfides.

It is generally observed from assay information that pyrite-rich assemblages associated with high-grade lead-zinc ores contain very little copper. Magnetite is a common mineral in the orebody and occurs in any of the above associations, usually as a minor constituent. It frequently assumes major proportions as intergrowths with "barren" (i.e. lacking in ore minerals) pyrite but rarely occurs in sufficient abundance to justify its being termed banded magnetic iron formation, however. Quartz and chlorite also appear to be generally non-selective in their associations.

Interlayering of layers consisting of the above-mentioned mineralogical associations has produced the mineralogical banding in the deposit. The overall variation in the frequency of occurrence of these mineralogical associations moving across the B-1 orebody is such that remarkably consistent changes in the mean concentrations of the economically important base metals are found across the orebody.

#### 2-3. Base metal zoning in the B-1 orebody

This part of the present study has been carried out to determine the pattern of overall across orebody variations in the concentrations of zinc, copper, lead and silver. The base metal concentrations have been taken from zinc, lead, copper and silver assay information for 33 diamond drill holes which intersect the entire orebody. The drill core from each intersection was generally broken into 5 foot lengths, the core split and crushed and each sample analyzed for zinc. lead, copper and silver. For the purpose of this study the B-1 orebody has been arbitrarily divided into five layers of proportionately constant thicknesses. Since the orebody is essentially lenticular in shape and generally of non-uniform thickness, each layer varies in thickness also, and its thickness at any given place is one fifth of the true orebody thickness at the same location. These are referred to as the A-, B-, C-, D-, and E-layers moving across the orebody from footwall to the hanging wall. Since it is believed that the steeply dipping enclosing rocks have probably not been overturned, the footwall of the orebody is considered to be in contact with the older metasediments. A split core sample length was considered to occur in the layer containing its center. In this way sample lengths from all of the intersecting drill holes have been assigned to their respective layers.

Figure 2-3A shows percentage frequency distribution patterns of the concentrations for each of the base metals (in vertical columns) for the respective layers. The concentration intervals for zinc, lead and copper increase by equal weight percent increments and the intervals for silver represent 1/320 fractions of these. The single vertical



lines represent arbitrarily chosen equal molar abundance values (x 320 for silver). While the number of samples in each of the zinc, lead and copper populations in the respective layer groupings are similar, the number of samples in the silver populations of respective layers are appreciably smaller. This is because silver assays were not always carried out in addition to the routine zinc, lead and copper assays, particularly on obviously low grade lead-zinc cores. The geometric means of the concentrations for each of these essentially log normal type distributions were calculated on a computer and the mean values are shown plotted against the respective layers in Figure 2-38. The means were also computed for larger groups of zinc, lead and copper assay values which included values from an additional 10 diamond drill hole intersections and the patterns for these larger populations were found to be very similar. The means of these populations are presented in Figure 2-3B for comparison. The mean molar abundances of the larger zinc, lead and copper populations together with the means for Zn, Pb and silver from the smaller populations of the respective layers have been recalculated to 100 per cent and the values are shown plotted on the triangular diagrams at the bottom of Figure 2-3B.

The results clearly indicate that the concentrations of zinc and lead consistently increase moving across the orebody towards the hanging wall while copper shows a consistent decrease in the same direction. Silver is the only metal which shows an inconsistent trend favouring an overall increase towards the hanging wall. The mean concentrations of copper and lead for the entire orebody indicate that copper is the





more abundant of the two. Whitmore (1957) reported that copper mineralization is present down to 100 feet below the B-1 orebody.

# Variations in Zn, Cu, Pb and Ag concentrations in the plane of the mineralogical layering

Higher grades of zinc-lead-silver ore within any given layer (i.e. A to E) occur in parts of layers which generally overlie each other, such that "zones" of highest concentrations of these metals have conical to cylindrical forms whose axes project through the orebody essentially normal to the mineralogical layering. The base metal zoning in the plane of the layering within any of the layers is characterized by a decrease in the concentrations of zinc, lead and silver and an increase in the concentration of copper moving radially away from the axes of the zinc-lead-silver "centers".

The greatest variation in base metal concentrations is across the layering rather than within it, especially when intersections are closely spaced.

#### 2-4. Possible spatial relationship between the location of the axes of Zn-Pb-Ag "centers" and "porphyry" in the footwall

The footwall rocks consist of fine grained metasediments and "porphyry". The latter occurs as lenses and, in places, as "plug-like" bodies which appear to intrude both the fine grained metasediments and the massive sulfides. The "porphyry" occurs in direct contact with the massive sulfides in the vicinity of the Zn-Pb-Ag "centers" and also as a large mass which becomes rapidly thicker (in excess of 150 feet) away from the "porphyry" underlying the "centers" (see Figure 1-11). The "plug-like" character of the "porphyry" in the vicinity of "center" C<sub>1</sub> is evident in the vertical sections (S12 and S14) shown in Figure 1-11.

Since the axes of the "centers" are underlain by local developments of "porphyry" it appears that a spatial relationship exists between these features. It is apparent, however, that a spatial relationship does not exist in general between "porphyry" and massive sulfides. The large mass and smaller bodies of "porphyry" occurring in direct contact with massive sulfides at the footwall probably formed around a principal submarine volcanic vent and associated satellite vents, respectively. The "plug-like" bodies are possibly true igneous porphyries.

### 2-5. Relationship between across deposit base metal zoning in "volcanic" type stratiform deposits and the stratigraphy of associated rocks

In camps where conspicuous acid pyroclastic units or acid lavas are present, there appears to be a general consistency in the direction of base metal zoning in single zinc-lead-copper and copper-rich deposits and also a similar consistency in the stratigraphic order in which closely spaced zinc-lead-copper and copper-rich deposits occur. In copperrich deposits such as the Matagami deposits of Quebec, the Kuroko-type deposits of Japan and apparently also in the Bayerland deposits on the German-Czechoslovakian border, minor to insignificant amounts of sphalerite are concentrated towards the surfaces of the deposits that are in contact with stratigraphically younger rocks. Across orebody zoning favouring an increase in lead-zinc values with a complimentary decrease in copper values towards the stratigraphic tops of zinc-lead-copper type deposits is observed in the Rammelsberg deposits, the San Dionisio and

North lodes of the Rio Tinto Mine, the Keating's and Elliot's deposits at Captains Flat, and apparently also in the Heath Steele B-1 deposit.

Copper- and zinc-lead-rich ores may also occur in separate bodies. The copper-rich bodies of the Heath Steele A deposit and Horne deposits of the Noranda area appear to stratigraphically underlie closely associated zinc-lead-rich bodies. This relationship does not apply to the Mount Isa deposit of Australia, however. In this case, copper-rich ores occur separately in different though probably equivalent facies (Stanton, 1962-63). This copper mineralization occurs in abundant "silica-dolomite" facies of probable sedimentary origin. Neither abundant acid lavas nor abundant acid pyroclastics similar to those associated with other deposits considered here are associated with the Mt. Isa deposit.

Where brittle rhyolites or porphyries underlie the deposits (e.g. the Rio Tinto deposits) these are generally ramified by pyrite veinlets and impregnations of sulfides that may locally contain significant copper values. Hutchinson (1965) reported that while rocks underlying the Matagami deposits are in places intensively altered, there is an apparent lack of clear structural features providing channelways for upward moving solutions. Roscoe (1965) noted that the volcanic rocks overlying many of these deposits are massive, unaltered and unmineralized. The "axes" of these below-deposit mineralized zones appear to be essentially normal to the stratification. In reporting on the consistency in the pattern of stratigraphic base metal zoning in the Noranda deposits, some of which are overturned, Roscoe (1965) concluded that the deposits were formed when the strata were in a sub-horizontal position.

It is concluded that the base metal zoning in "volcanic" type deposits similar to those in the Bathurst-Newcastle camp appears to show a consistent relationship with the stratigraphy of associated rocks. This relationship can only reasonably be interpreted as indicating that these deposits were formed when the underlying strata were in a subhorizontal position.

# 2-6. <u>Metamorphic silicate assemblages in the B-1 orebody and associated</u> rocks

A number of D.D.H. core samples of representative lithologies from within and around the B-l orebody have been examined in thin section. Brief descriptions of these sections are given in Table 2-6 where the rocks are listed in order of their occurrence moving from east to west. The S numbers (e.g. Sl2) refer to vertical sections locations used in this thesis (see Figure 1-11) and the symbols HW, E and A and FW respectively denote the location in the hanging wall rocks, the top (E) and bottom (A) layers in the B-l and the footwall rocks.

## TABLE 2-6

## DESCRIPTIONS OF THIN SECTIONS OF D.D.H. CORE SAMPLES

Sample(D.D.H.) No.	mple(D.D.H.) Location D.D.H. footage		Description
B119 <b>-</b> 4	415	S1,HW	" <u>porphyry</u> "-quartz-feldspar augen in a quartz-muscovite-chlorite matrix: possible altered lithic fragments
B120-8	220	Sl,HW	hydrothermal vein in a chloritic rock- crystallized quartz-feldspar (adularia ?) intergrowths; minor biotite partly altered to chlorite, minor sericite and a trace of calcite
B118-2	45	S1,FW	altered cherty argillite-finely inter- banded chert and chlorite-muscovite- quartz schist. Disseminated sulfides are abundant in the latter
B121-12	119	S2,HW	altered detrital sediment-50% of the rock consists of fragments and subhedral quartz grains of similar size (about l mm.) fairly evenly dispersed in a dark green translucent variety of chlorite. Disseminated sulfides and a trace of calcite also occur
B114-9	240	S3,HW	altered detrital sediment-fine grained banded rock consisting of quartz and relic feldspar fragments contained in a matrix dominantly of quartz and chlorite. A small number of partially replaced biotite grains occur in decussate inter- growths of dark chlorite; some dissemina- ted sulfide
B114-2	138	83,A	<u>altered cherty argillite</u> -similar to Bll8-2, above. Muscovite is dominant in the muscovite-chlorite schist layers; traces of epidote and disseminated sul- fides
B97-4	108	s4,HW	<u>chert interlayered with detrital sedi-</u> <u>ment-the latter consists of dispersed</u> quartz augen in a strongly pleochroic dark green schistose chlorite matrix

B112-8	149	S5,HW	chert interlayered with detrital sedi- ment-similar to B97-4, above. Traces of muscovite and sulfide are present
B100-1	36	s7,Fw	thinly banded cherty argillite-chert bands with minor chlorite and traces of muscovite interlayered with muscovite- chlorite-quartz schist bands. Dis- seminated sulfides are more abundant in the latter
B102 <b>-1</b>	10	S9,FW	thinly banded siliceous argillite- consists dominantly of quartz-chlorite- sericite schistose material enclosing some elliptical bodies of fine to medium grained quartz aggregates. Very fine grained disseminated sulfide occurs throughout the section
B101-10	243	Sll,HW	chert with interbanded detrital sediment- chert (with minor chlorite) shows regular grainsize variation; contains discontinu- ous strings of sulfides. A 1 cm. thick band similar to Bl21-l2 occurs in the chert
B75-13	246	S12,HW	" <u>porphyry</u> "-subhedral and anhedral quartz augen in a quartz-muscovite-chlorite schist matrix. Disseminated sulfides are present
B88 <b>-7</b>	241	S12,E	thinly banded magnetic iron formation- with thin bands of interlayered pyrite. Non-opaques are dominantly muscovite and chlorite with some calcite
B75-4	23	512,FW	thinly banded argillaceous chert-the chert contains about 40% chlorite with coarser grained bands containing almost all of the disseminated pyrite. Traces of calcite are present
B125 <b>-</b> 4	44	513,FW	altered detrital sediment-consists of dispersed unidentifiable angular lithic fragments (up to 6 mm.) contained in a schistose muscovite-chlorite matrix. Traces of epidote are present

B71-1	4	S14,FW	thinly banded disseminated sulfides-fine grained sulfides occurring in bands with different sulfide/non-sulfide ratios and variable sulfide grainsizes between bands. The non-opaques are dominantly chlorite and calcite. Traces of muscovite are present
B78-2	17	S15,A	siliceous metasediment-quartz-muscovite- chlorite schist. Traces of sulfide are present

All of the assemblages contain chlorite which is usually of a dark green variety and at times shows strong pleochroism. Most sections contain guartz, muscovite and disseminated sulfides and a small number contain traces of epidote and calcite. A brown variety of biotite was observed in two sections where it occurred as a minor constituent. In thin section B120-8 biotite is associated with a 1 inch "thick" irregular feldspar-quartz vein contained in a chloritic rock. The pale pinkish feldspar (adularia ?) occurs in association with quartz as intergrowths of well developed crystals showing rhomb-shaped cross sections. The crystal intergrowths project inwards from the vein walls and the biotite is associated with what appear to be inclusions of host rock which have been caught up in the vein. The biotite is replaced to varying degrees by a medium green chlorite. Thin section B114-9 is different from the other sections of metasediment insofar as the rock is generally coarser grained than the other sections and the feldspar augen have been more intensively altered. With the exception of these two sections, the suite of metamorphic minerals identified in metasediments from the footwall rocks, from within the lower part of the B-1 orebody, and from hanging wall rocks is essentially the same as the one described by Dechow (1960) for the acid volcanic rocks in the south of the map area. If these suites are of regional metamorphic origin, they can be assigned to the quartz-albite-muscovite-chlorite subfacies of the Greenschist Facies of regional metamorphism (Turner and Verhoogen, 1960). Clearly if sections B120-8 and B114-9 were included, the quartz-albite-epidotebiotite subfacies of the Greenschist Facies has to be invoked and the

apparent lack of relic biotite in the other sections attributed to its complete destruction by retrograde metamorphism. While this does not seem reasonable, it is not possible to resolve the problem at this time. It is also possible that further work may demonstrate that similar intergrowths of quartz and pink or cream coloured feldspars, which also occur as "clots" of varying size within the massive sulfides of the B-1, may be of igneous hydrothermal origin and that these induced local contact metamorphic effects in the containing rocks. Perhaps the biotite in Bll4-9 has been produced in this way. Aggregates of coarse grained sulfides, usually chalcopyrite and sphalerite, are commonly associated in minor amounts with some of these "clots".

It is concluded that hydrothermal wall rock alteration effects are not evident in the rocks enclosing the B-1 orebody. The similarity of the silicate assemblages from within the orebody and its enclosing rocks with those in Tetagouche country rocks described by previous workers, favours a regional metamorphic origin for the silicates in each of these settings.

#### CHAPTER 3

#### GENERAL ANALYTICAL PROCEDURES

#### 3-1. Selection of samples for isotopic study

Drill core and hand specimen samples of zinc-lead ore, copperrich ore and essentially barren pyrite with and without pyrrhotite, showing the best developed mineralogical banding were initially selected for study. Samples were chosen from this material for isotopic study only if the following requirements were satisfied:-

- i) the sample was free of any kind of veining (e.g. by sulfides, silicates or calcite)
- ii) isolated aggregates of relatively coarse grained sulfide and/ or feldspar were absent
- iii) the banding was relatively flat in well banded samples
  - iv) the final massive sulfide sample slices visually appeared tobe as mineralogically homogeneous as possible.

Most of the selected samples consisted of well banded massive sulfide but a few samples of disseminated sulfide were also chosen. The majority of the massive sulfide samples were taken from sphalerite-pyrite-galena ore bands whose thicknesses exceeded several millimeters. The remaining massive sulfide samples consisted mainly of copper-rich ore samples and some samples of essentially barren pyrite.

# 3-2. Brief description of the mineralogy of samples selected for isotopic study

The mineralogical associations comprising the massive sulfides from which the final samples were sliced were of four principal types. However, massive sulfides having mineralogical compositions intermediate between types 1 and 2 and types 2 and 3 were also found to be common. These are briefly as follows:-

- i) sphalerite-pyrite-galena ore bands (#) consisting essentially of these minerals (generally totalling more than 80 modal %) usually occurring together with variable, though generally. minor amounts of any one, or a combination of chlorite, quartz, magnetite and pyrrhotite. Among the samples studied, pyrrhotite was only found to occur in major amounts in association with sphalerite and galena in samples of high grade zinc-lead ore from the A deposit. Calcite was found to attain the proportions of a minor phase in only a few of the samples.
- ii) massive sulfide consisting of essentially barren pyrite ((bp) i.e. lacking, or containing only very small concentrations of the ore minerals), or rarely of barren pyrite-pyrrhotite assemblages (ms) which may contain any one or all of the non-sulfides mentioned above.
- iii) massive sulfide (ms) consisting essentially of pyrite accompanied minor to major proportions of chalcopyrite (copperrich ore). Pyrrhotite is usually always present in this association and frequently occurs as a major phase. Occasionally sphalerite and galena are present in small concentrations

and the associated non-sulfide minerals are usually the same as in i) above.

iv) massive sulfide (ms) consisting essentially of chalcopyrite and pyrrhotite accompanied by minor to trace amounts of any one, or a combination of, magnetite, chlorite and quartz. In some ores of this type, chalcopyrite and pyrrhotite may occur as alternating mono-mineralic bands.

It is emphasized that samples of this type were collected in situ from banded copper-rich ore lenses and not from crosscutting vein material which is generally of similar mineralogical composition.

Disseminated sulfides (ds) occur in varying amounts in the footwall and hanging wall rocks and the sulfide associations of these are similar to those outlined above. When the proportion of total sulfide exceeds about 80 modal percent in a given sample the sample is termed massive sulfide. However, the proportions of total sulfide present in the disseminated sulfide samples from which sulfides were extracted for analysis did not exceed about 20 modal percent.

#### 3-3. Preparation of sulfide samples prior to mineral separation

The procedure used in preparing samples for mineral separation comprised the following operations:-

i) the portions of samples selected for study were sliced from
 D.D.H. core samples (hand specimens were cored) in the plane
 of the mineralogical banding (where evident) and adjacent un wanted sulfide was cut or ground away using a diamond saw

and emery wheel. Sample slices rarely exceeded 6 millimeters in thickness and had masses of less than 30 grams.

ii) hand crushing of samples.

- iii) sieving, using nylon bolting cloth supported in leucite frames, and retaining the 200- to 325+ fractions for separation.
  - iv) repeated decanting of the 200- to 325+ fractions with distilled water using 500 ml. beakers, until 6 to 8 cm. water columns became relatively clear after 25-30 second duration standing periods.
    - v) several washings with acetone to remove excess water, and
      a short drying period under a heat lamp.

#### 3-4. Mineral separation

With the exception of magnetite and pyrrhotite, all other minerals were separated from prepared samples using the Frantz Isodynamic Separator. The heavy liquid separation technique (using tetrabromoethane) was only employed in several cases where the concentration of quartz in pyrite and galena concentrates exceeded about 15 modal percent. Pyrite concentrates were obtained from synthetic sulfide mixtures by leeching with 2:1 HCl. Pyrite concentrates from pulp samples and pyrites from sample No. 29 were improved by leaching out traces of galena and sphalerite.

#### Separation of magnetite and pyrrhotite

Separation of magnetite and pyrrhotite from samples was achieved using a small hand magnet wrapped in plastic sheeting. When of sufficient size for isotopic determination, the pyrrhotite rich fraction was further

purified by repeatedly passing the magnet over a sample a few millimeters above it, so as to make the pyrrhotite jump onto the magnet. After no additional pyrrhotite-rich fraction could be induced to adhere to the magnet, the magnet was carefully removed from the plastic wrapping above a sheet of sulfide-free paper causing the pyrrhotite fraction to drop onto the paper. This operation was repeated until the proportion of essentially non-magnetic grains became very small.

#### Separation of ore minerals using the Frantz Isodynamic Separator

Gaudin and Spedden (1943) demonstrated the feasibility of obtaining relatively pure sulfide mineral concentrates for some sulfides from sulfide ores using the Frantz Isodynamic Separator. They showed that most sulfides exhibit some measure of magnetic susceptibility with some displaying relatively consistent susceptibilities while other, even within the same ore, have variable susceptibilities, possibly arising from compositional variations. Separations were even achieved in the 200 to 400 mesh range. Their findings are summarized in Figure 3-4.

It was found that while the order of magnetic response of the common sulfides in the Heath Steele ores is in general agreement with the findings of these workers, the ranges of magnetic response differed slightly for chalcopyrite and appreciably for pyrite. In only a few samples, particularly of massive or disseminated barren pyrite, was it found that small proportions of the pyrite concentrates showed no magnetic response, thus deviating from the conclusion of Gaudin and Spedden that pyrite is wholly non-susceptible.

FIGURE 3 - 4

MINERAL SEPARATION USING THE FRANTZ

#### ISODYNAMIC SEPARATOR

(after Gaudin and Spedden, 1943)



The remaining common minerals comprising the ores are listed in order of decreasing magnetic response:-

chlorite (and calcite) sphalerite chalcopyrite pyrite galena, quartz

Mainly because of variations in the proportions of composite minerals grains from sample to sample, and partly because of the slight differences in magnetic response exhibited by some of the minerals present (e.g. sphalerite, chalcopyrite and pyrite), it was found necessary to slightly modify the general procedure outlined below. However, for most samples, the following procedure was found to give satisfactory results:-

#### Separation of chlorite and calcite

Passage through the separator set with 15 degrees cross slope, 25 to 35 degrees longitudinal slope and a current of 0.5 to 0.6 amps separated chlorite, calcite and usually some composite grains consisting of pyrrhotite and/or magnetite with other sulfides. In sphalerite-rich samples the first pass was made with a cross slope of 8 degrees and a current of 0.5 amps.

#### Separation of sphalerite

After removal of chlorite and composite grains consisting sphalerite and more magnetic minerals, the bulk of the sphalerite was separated from samples on the magnetic side using a setting of 15 degrees cross slope, 25 to 35 degrees longitudinal slope and a current of 0.7 to 0.8 amps. A final pass of this concentrate through the separator with a 35 degree cross slope, 35 degree longitudinal slope and 1.5 amps current removed all sphaleritepyrite composite grains.

<u>Notes</u>: 1. One iron-poor sphalerite from the Wedge deposit required a setting of 15 degrees cross slope and a current of 1.5 amps for its separation.

2. The synthetic sphalerite from the A mix of the 450°C experimental run was separated using settings of 25 degrees and 30 degrees cross slopes and a current of 1.5 amps. The sphalerite from the 500°C run was separated using settings of 8 degrees cross slope and 0.5 amps and 25 degrees and 1.5 amps.

#### Separation of chalcopyrite

Chalcopyrite was separated on the magnetic side of the separator with the cross slope set at 15 degrees and a current of between 0.85 and 1.05 amps. Since the sphalerite content of type 3 massive sulfide assemblages was always very low, the practical difficulty of separating these two minerals into concentrates did not present a problem. Because of small magnetic differences contaminating sphalerite could be entirely removed from chalcopyrite concentrated with an accompanying loss of some chalcopyrite. Removal of composite chalcopyrite-pyrite grains from chalcopyrite concentrates, on the other hand, could not be achieved with any degree of confidence due to the difficulty of distinguishing between yellow pyrite and chalcopyrite under the binocular microscope. Polished section mounts were made of these concentrates in order to determine their purity.

### Separation of pyrite

The magnetic susceptibility of pyrite was found to be quite variable, ranging from pyrites showing no magnetic response at 1 degree side slope and a current of 1.5 amps up to pyrites which could be separated on the magnetic side for side slopes up to 6 or 8 degrees and a current of 1.5 amps. It was observed that pyrites occurring in chalcopyrite-rich assemblages were generally the most magnetic and appeared to be more yellow in colour than pyrites from essentially chalcopyrite-free assemblages, possibly due to the presence of copper as an impurity in the Separations of pyrite concentrates were usually obformer. tained by passing a sample through the separator set at 4 to 6 degrees cross slope and a current of 1.5 amps to remove composite grains of pyrite and chalcopyrite or of pyrite and sphalerite and again through at 4 degrees cross slope and 1.5 amps to remove composite grains of pyrite and galena.

#### Separation of galena and quartz

Galena and quartz showed negligible magnetic response. Pyrite was commonly separated from galena and quartz by passing the sample through the separator at about 0.3 degrees cross slope (according to the machine orientation at the time) and a current of 1.5 amps. Although this produced a very pure galena concentrate, it was generally accompanied by the loss of a sizeable portion of the galena fraction.

In order to remove quartz from both pyrite and galena concentrates in which the content of quartz exceeded about 15 to 20 modal percent, the concentrates were treated with tetrabromoethane (sp. gr. 2.94). The ranges of magnetic response of the common minerals in the Heath Steele ores is also schematically shown in Figure 3-4.

#### 3-5. Estimation of purity of sulfide concentrates

The purity of sulfide concentrates was visually estimated in the following manner:-

- i) the total number of sulfide grains occurring in the 100 x field of view of a binocular microscope was counted
- ii) for concentrates containing more than about 5 modal percent of quartz, the total number of quartz grains was also counted
- iii) the average number of mineral grains counted in several visual traverses from the center to the periphery of the field of view was determined
- iv) the modal percentage sulfide purity was estimated from

$$100 - \left(\frac{a}{3.14 (c)^2 - a} \times 100\right),$$

and for concentrates containing more than about 5 modal percent of quartz

$$100 - \left(\frac{a - b}{3.14 (c)^2 - b} \times 100\right)$$
where	a = total number of foreign sulfide grains
	b = total number of quartz grains
	c = average number of mineral grains occurring
	along the radius of the field of view
3 <b>.</b> 14(c	) <sup>2</sup> = estimated total number of mineral grains in the field of view

100 = total number of grains reduced to <math>100

The purities of sphalerite concentrates were consistently excellent, generally higher than 95% and frequently approaching 100%. Pyrite constituted the main impurity. The purity of galena and pyrite concentrates were usually good to excellent, and generally in the 90 to 98% range. Pyrite was the only important sulfide impurity in galena concentrates and galena was the principal contaminant in pyrite concentrates. Some of the poorer pyrite concentrates were further purified by leeching galena and sphalerite contaminants with 2:1 HCl. It is important to note here that no significant differences in isotope ratios were found for relatively pure natural pyrites burned before and after the leeching treatment. Chalcopyrite and pyrrhotite concentrates were frequently poor to fair (75-90%), the main impurities being pyrite in chalcopyritepyrite assemblages and chalcopyrite in pyrrhotite concentrates from chalcopyrite-pyrrhotite assemblages. Very pure chalcopyrite concentrates were obtained from chalcopyrite-pyrrhotite assemblages.

#### 3-6. Preparation of sulfur dioxide gas for isotopic analysis

A method of preparation of sulfur dioxide gas for isotopic analysis has been developed by Thode and others at McMaster University. It involves burning a sulfide sample in a purified stream of oxygen at  $1350^{\circ}$ C to produce SO<sub>2</sub> which is sealed in a pyrex breakseal after removal of excess oxygen, water and carbon dioxide (Thode et al., 1961). Com-

bustion at this high temperature is found to yield only a small proportion of  $SO_3$  (preferentially enriched in  $S^{34}$ ) and the fractionation effects produced in burning are reported by Thode et al. (1961) to be negligible. This method of preparation was used in the present study and is briefly described below.

The apparatus used in preparing SO<sub>2</sub> gas comprises an oxygen purification line, a high temperature combustion furnace, and a vacuum line for the purification of SO, as shown in Figure 3-6. The oxygen purification line consists of a source oxygen cylinder (1), a simple mercury safety valve (2), an activated charcoal trap (3), and electric furnace (4) maintained at about 720°C, a concentrated sulfuric. acid trap (5), .an Ascarite/ $P_2O_5$  trap (6), a ball-type flow meter (7) and a coil immersed in liquid oxygen (8). This in-line arrangement of apparatus ensures that a source of pure dry oxygen is available throughout the burning period. Purified oxygen enters the combustion tube at location (9). The combustion tube is mounted in a Sentry electric furnace (model 5, size 2) whose temperature is controlled by a time percentage input switch. Sulfur dioxide is produced in the combustion tube by roasting natural or synthetic sulfides in a pure oxygen stream at temperatures around 1350°C. The exhaust gases emerging from the combustion tube are led directly into the vacuum line which consists of low ( $\leq 3 \times 10^{-4}$  mm. of mercury) and high  $(\leq 1 \times 10^{-5}$  mm. of mercury) vacuum parts. Two coils and an adjustable mercury manometer form a part of the low vacuum line which has stopcock inlets for gases entering from the furnace (10) and the atmosphere (11) and stopcock outlets to the mechanical pump (12) and high vacuum portion of the line (13). The high vacuum part of the line comprises a yield measuring

# FIGURE 3-6

SCHEMATIC SKETCH OF APPARATUS USED IN THE PREPARATION OF SULFUR DIOXIDE GAS



manometer incorporating a bulb (14), a breakseal manifold carrying 6 breakseals (15), 4 U-tubes ((16)-(19)), a thermocouple-type vacuum measuring gauge (20), a dry ice trap for collection of mercury and water vapours (21), and a mercury vapour pump (22). The high vacuum part of the line has a stopcock inlet-outlet (13) from the low vacuum part and a stopcock outlet (23) to the mechanical pump (24). The low vacuum part of the line is open to the atmosphere while burning, its function during this time being to trap the products of furnace combustion. Its other functions are the partial removal of both excess source oxygen and of water. The function of the high vacuum part of the line is the removal of trace amounts of source oxygen and water, and of carbon dioxide.

The sequence of operations involved in obtaining a pure SO<sub>2</sub> gas sample from an aliquot (containing about 10 milligrams of sulfur) of metal sulfide sample is as follows:-

> i) The sulfide sample is burned in steadily flowing oxygen at a temperature of approximately 1350°C for a period of 5 minutes. During this period, SO<sub>2</sub> together with small amounts of water and CO<sub>2</sub> are frozen down in the coils by the liquid oxygen traps. Unburned oxygen passes through and escapes into the atmosphere.

ii) Most of the excess oxygen is pumped away by the mechanical pump while the oxygen traps remain in place. The gases are warmed to room temperature, a rough measurement of the yield is made, and the gases refrozen again using liquid oxygen. Remaining traces of oxygen are pumped away by the mercury pump.

iii) Water is removed from the warmed gases as they pass through

traps on the high vacuum line (U - tubes (19), (18) and (17)). The freezing mixture used in the traps consists of powdered dry ice in an equal volume mixture of chloroform and carbon tetrachloride.  $SO_2$  and  $CO_2^{\cdot}$  are frozen in U - tube (16) using liquid nitrogen and are then isolated. The water is warmed and removed by pumping under low and high vacuum.

- iv) CO<sub>2</sub> is removed from SO<sub>2</sub> using freezing ethyl chloride (melting point -138.7°C). The gases are warmed, frozen (in U -tube (17)) with ethyl chloride over a period of 2 minutes, the vacuum gauge opened, and then pumped on with high vacuum for 15 seconds. This procedure is repeated except for extending the second pumping period to 25 seconds.
  - v) The SO<sub>2</sub> sample is warmed, its volume accurately measured if the yield is required, and finally frozen in a breakseal. The gas sample is removed from the line.

# 3-7. Measurement of S<sup>32</sup>/S<sup>34</sup> ratios

Sulfur dioxide gas samples were analyzed on the 6 inch, 90 degree sector type mass spectrometer described by Wanless and Thode (1953). The design of this machine permits simultaneous collection of the two ion beams,  $S^{32}O^{16}O^{16}$  and  $S^{32}O^{16}O^{17}$  (masses 64 and 65) and  $S^{34}O^{16}O^{16}$  (mass 66), and the measurement of their ion currents using a null method. A magnetic valve system allows rapid comparison of the sample gas with a standard SO<sub>2</sub> sample.

# 3-8. Relationship between $S^{32}/S^{34}$ ratios and $\delta S^{34}$ values

MacNamara and Thode (1950) showed that whereas the  $S^{32}/S^{34}$  ratio for terrestrial samples varied by as much as 10%, the ratio for meteoritic sulfur was remarkably constant. Furthermore, this value was found to coincide approximately with the median ratio found for terrestrial sulfur and to fall within the range of ratios for igneous rocks. It was therefore suggested that the  $S^{32}/S^{34}$  ratio for meteoritic sulfur is the primordial value, and that fractionation processes in the earth's crust have given rise to the observed 10% spread.

The  $S^{32}/S^{34}$  ratio for any given sample is more conveniently expressed relative to the sulfur isotope ratio for meteorites as a  $\delta S^{34}$  value, defined as:-

$$\delta S^{34}(\%_{o}) = \frac{(S^{34}/S^{32})_{sample S} - (S^{34}/S^{32})_{meteoritic S} \times 1000}{(S^{34}/S^{32})_{meteoritic S}}$$

Unfortunately there has been a general lack of agreement between sulfur isotope researchers as to what value should be assigned to meteoritic sulfur in computing  $\delta S^{34}$  values. The  $S^{32}/S^{34}$  ratios which have already been assigned range from 22.20 to 22.225. It is evident that this unhappy situation is largely unjustified, when it is remembered that it is not possible to determine absolute  $S^{32}/S^{34}$  ratios to better than  $\pm 0.05$  per cent or about  $\pm 0.1$  in ratio units.

In the present investigation the writer has followed Thode et al. (1961) in assigning meteoritic sulfur a ratio of 22.225. All measurements are expressed in  $\delta S^{34}$  units.

#### 3-9. Precision of mass spectrometer measurement

Monster (1963) reported on the accuracy of mass spectrometer measurements for the period March, 1960 to December, 1962. For the socalled identical sample test in which line standard  $SO_2$  is admitted to both reservoirs, and the two samples run against each other, it was found that the two samples rarely differed by more than 0.2%. During this period, an  $S^{34}$  enriched reservoir standard ( $\delta S^{34} = + 29.3\%_0$ ) was also run against the line standard a total of 64 times and the standard deviation found to be 0.35%. From this it was concluded that accuracy decreases with increasing isotopic difference between line standard  $SO_2$  and an unknown sample. Mixing or memory effects are believed to be responsible for this.

Some idea of the expected magnitude of total errors including those due to burning and sample preparation can be obtained from the standard deviations computed for 3 groups of different meteoritic troilites with  $\delta S^{34}$  values very close to the line standard value. These were all burned and analyzed by Monster. The standard deviations were found to range from 0.12 for 4 samples run on the same day to 0.5 for 18 samples run over a period of 11 days.

Note: Since possible isotopic variations in troilite from a given meteorite cannot be ruled out, it seems reasonable that, for the purpose of attempting to estimate the error inherent in sample preparation, one should look to the group showing the smallest standard deviation, i.e. 0.12%. This precision value can conservatively be accepted as representing a minimum precision for

sample preparation (at least for samples whose  $S^{32}/S^{34}$  ratios are close to the average meteoritic value) when all other contributing errors are ignored. It is probably better than this, however.

The total precision for differences between replicates in a group of 44 chemically prepared replicates with  $\delta S^{34}$  values varying from -5 to +11 was found to be ±0.33%.

Monster concluded that with the existing methods of analysis no overall precision of better than 0.3 to 0.4% can be claimed.

#### Precision determinations made in this study

Sulfide standards including Park City pyrite (averaging +3.29‰) and Canyon Diablo troilite ( $\delta S^{34} = 0$ ) were usually burned along with batches of every 6 to 12 samples and were analyzed in essentially the same order. The samples were analyzed in 6 groups over a period of approximately 15 months. The results of isotopic measurements made on standards and of differences between values (i.e.  $\Delta \delta S^{34}$ ) for replicate samples are given in Table 3-9A.

The overall precision for each of the first 5 groups of standards ranged from  $\pm 0.19\%$ , to  $\pm 0.57\%$ , and the average of these 5 precision values is  $\pm 0.33\%$ . When 3 of the 59 analyses which deviate by more than 2 standard deviations from the overall mean of the respective group are rejected, the average of the five precision values is  $\pm 0.26\%$ . The smallest standard deviation determined for standards run with a group of samples (group 4) is  $\pm 0.19\%$ . Explanation of abbreviations used in TABLE 3-9A

M.S.Std.:	mass spectrometer gas standard
P.C.P. :	Park City pyrite standard
C.D.T. :	Canyon Diablo Troilite
n;∆ <sub>29</sub> :	number of samples; subscript indicates number of samples
R :	Range of variation in $\delta S^{34}$ or $\Delta \delta S^{34}$ values
M,mean :	arithmetic mean
s :	standard deviation (S = $\left(\frac{\Sigma(x-M)^2}{n-1}\right)^2$ ; M = $\frac{\Sigma x}{n}$ )
•	values deviating by more than 25 from the mean of the larger population
** :	values suspect - sample homogeneity is questionable.

93 ·

TABLE 3-9A

Group	1 (G-1)	Group	2 (G-2)	Group	3 (G-3)	
(13/4/66	to 9/5/66)	(13/5/66	to 11/6/66)	(29/6/66	to 16/8/66)	)
M.S.Std.	Value,+1.53	M.S.Std.	Value,+1.34	M.S.Std.	Value,+1.50	
P.C.P.	<u>Replicates</u>	<u>C.D.T.</u>	<u>Replicates</u>	<u>P.C.P.</u>	Replicates	3
δs <sup>34</sup> %。	∆§s <sup>34</sup>	6s <sup>34</sup> %。	۵85 <sup>34</sup>	۶s <sup>34</sup> %。	Δ <b>δ</b> s <sup>34</sup>	۵8s <sup>34</sup>
+3.11	$(\delta \text{ value})$	-0.48	(6 range	+3.50	(Srange	0.16
+2.92	+ 4)	-0.73	0 to -3)	+3.34	+11 to +1	15) 0.46
+2.93	0.16	+0.32	0.25	+3.15	0.38	0.36
+2.44*	0.13	+0.82	0.16	+3.31	0.06	0.21
+3.09	ж. А.	-0.43	0.05	+3.07	0.01	0.22
+3.30	n=2	-0.42	(Srange	+3.78	0.50	0.02
+3.37	R=0.03	+0.52	+14 to +18	)+4.24*	0.21	0.16
+3.36	M=0.15	-0.25	0.04	+3.26	0.09	0.05
+3.37	S=0.02	-0.47	0.69	+3.08	0.07	0.15
+3.10		-0.01	0.04	+3.35	0.21	0.16
		-0.07	0.07	+3.03	0.15	0.38
n=10		+1.51*	0.41	+3.12	0.05	
M=+3.1		-0.05	1.52*		0.12	n=34
s=0.28		+0.31	,	n=12	0.11	R=0.60
omit *		-0.15	n=9	M=+3.35	0.27	M=0.20
n=9		+0.20	M=0.36	S=0.35	0.08	<u>S=0.17</u>
R=0.45			s=0.49	omit *	0.60	
M=+3.17		n=16	omit *	n=11	0.01	
<u>s=0.18</u>		M=0.00	n=8	R=0.75	0.01	
		S=0.57	R=0.65	M=+3.27	0.00	
		omit *	M=0.21	S=0.22	0.44	
		n=15	<u>S=0.23</u>		0.40	
		R=1.55			0.17	
		M=-0.06	•		0.04	
		<u>s=0.43</u>	•		0.47	

Group	4 (G-4)	Group 5 (G-5)					
(20/2/67 to 3/3/67)		(29/4/67 to 23/5/67)					
M.S.Std.	Value,+1.81		M.S.Sta	.Value,+1.85	•		
P.C.P. §s <sup>34</sup> %。	۵§5 <sup>34</sup>	P.C.P. 85 <sup>34</sup> %.	۵ <b>8</b> s <sup>34</sup>	•	۵8s <sup>34</sup>		
+3.73	0.55	+3.77	0.13	n=29	0.22		
+3.04	1.79*	+3.19	0.03	R=0.41	0.22		
+3.31	0.25	+3.28	0.06	M=0.15	0.03		
+3.26	0.13	+3.05	0.23	<u>S=0.11</u>	0.14		
+3.23	0.24	+2.90	0.41		0.13		
+3.40	0.04	+3.61	0.06	Δδs <sup>34</sup>	0.04		
+3.33	0.34	+3.47	0.40	(Srange	0.18		
+3.40	0.28	+3.17	0.00	-5 to +5)			
+3.10	0.03	+3.24	0.02		n=24		
+3.24	0.08		0.09	0.12	R=0.44		
+3.09	0.15	n=9	0.02	0.00	M=0.13		
+3.41	0.33	R=0.87	0.23	0.20	<u>S=0.1</u>		
	0.31	M=+3.3	0.24	0.00			
n=12	0.12	<u>s=0.27</u>	0.28	0.16			
R=0.69	0.92		0.12	0.07			
M=+3.3	0.59	Replicates	0.24	0.44			
S=0.19	0.38	$\Delta \delta s^{34}$	0.01	0.06	: :		
		(Srange	0.12	0.06			
Replicate	es n=19	+7 to +18)	0.25	0.11			
Δδs <sup>34</sup>	M=0.39		0.08	0.11			
(Srange	s=0.4	0.06	0.05	0.28			
+13 to +1	L5) omit*	0.18	0.30	0.06			
	n=18	0.07	0.17	0.28			
0.46	R=0.89	0.22	0.13	0.09			
0.32	M=0.31	0.06		0.03			
	<u>S=0.22</u>		A A A A A A A A A A A A A A A A A A A	0.15			

Gro	oup 6 (G-6)		Grouped data summary			
(29/6/67 to 9/7/67)			(P.(	C.P.)		
M.S.Std.Value,+1.85			n=43, R=1.80,	mean $\delta s^{34} = +3.27$		
Replicates	s		<u>S=0.29;</u> omitting *	values,		
۵٤s <sup>34</sup> %。	Δδs <sup>34</sup>	Δδs <sup>34</sup>	n=41, R=0.88,	M=+3.27, <u>S=0.18</u>		
(§range	· ( & range		Replica	te data		
+12 to +1	5)-3 to +6)		Heavy Samples	Light Samples		
			( $\delta$ range +7 to +18)	(8 range -5 to +6)		
0.32	0.28	0.30		<u>G-1</u>		
0.47	0.10	0.03		mean $\delta \Delta_{p} = 0.15$		
0.09	0.06	0.48		s = 0.02		
0.30	0.32	0.11	<u>G-2</u>	<u>G-2</u>		
0.26	0.22	0.10	$mean \delta \Delta_5 = 0.25$	$\mathrm{mean}\delta\Delta_3 = 0.15$		
0.07	0.24	0.11	s = 0.29	S = 0.10		
0.13	0.09	0.09	<u>G-3</u>			
0.52	0.02	<u>0.18</u>	mean 6∆ <sub>34</sub> = 0.20			
0.24	0.06		, S = 0.17			
1.22**	0.44	n=27	<u>G-4</u>			
2.09**	0.17	R=0.46	$\mathrm{mean}\delta\Delta_{18} = 0.31$			
0.33	0.26	M=0.19	S = 0.22			
0.00	0.22	S=0.12	<u>G-5</u>	<u>G-5</u>		
	0.36		$mean \delta \Delta_{29} = 0.15$	$\operatorname{mean}^{\delta\Delta}_{24} = 0.13$		
omit **	0.22		S = 0.11	S = 0.10		
n=11 ·	0.21		<u>G-6</u>	<u>G-6</u>		
R=0.52	0.17		$\mathrm{mean}\delta\Delta_{11} = 0.25$	$\mathrm{mean} \mathrm{sam}_{27} = 0.19$		
M=0.25	0.08		S = 0.16	S = 0.12		
<u>s=0.16</u>	0.17		Replicate (	Composites		
			Heavy Samples	Light Samples		
			* and ** values	* values omitted		
	ta de la composición		omitted R=0.92	R=0.48		
			$\operatorname{mean} \delta \Delta_{97} = 0.21$	$mean \delta _{56} = 0.16$		
			S = 0.18	S = 0.11		

Experience has shown that differences in isotope ratios for replicate samples tend to be smaller when the replicates are analyzed con-This implies that the precision of measurement on the mass secutively. spectrometer fluctuates with time, and that the precision is most likely to remain relatively constant over short periods. All replicate samples have been analyzed in this way. Mean differences in isotope ratios for replicate analyses have also been determined for the respective groups, and are found to range (excluding group 1) from 0.15%, to 0.39%, for samples relatively enriched in  $S^{34}$ , while the mean differences for 2 groups of samples with values grouped about the meteoritic mean are 0.13 and 0.19%. The mean differences between replicates for 97 relatively "heavy" sample replicates is 0.21%, while the mean for 56 "light" sample Standard deviations computed for the replicate replicates is 0.16%. differences for these two sample assemblages are 0.18%, and 0.11%, res-From the grouped data summary in Table 3-9A it can be seen pectively. that the means and standard deviations of replicate differences for groups 2, 5 and 6 are larger for the "heavy" samples. This decrease in precision for "heavy" samples is in agreement with the findings of Monster.

Reasonable estimates of the overall precisions of measurement for replicates can be obtained from the computed standard deviations for replicate differences. Since the standard deviations for replicates are linearly related to the differences between the replicate values it is possible to obtain estimates of overall replicate precisions directly. In this way, an overall precision of ±0.25%, is obtained for the 97 "heavy" sample replicates, and ±0.16% for the 56 "light" sample replicates. On

this basis, the best overall precision for a single group of "heavy" replicates is  $\pm 0.16\%_{\circ}$ .

In order to illustrate within-day fluctuations in mass spectrometer measurement, the following data are presented:-

Δ δ S <sup>34</sup> ( δ S <sup>3</sup>	4 range +13 to +18)	
0.28		
0.49		
0.25	Note:	•
0.02	each of the acco	ompanying values represents
0.56	an apparent isot	topic difference between 2
0.30	measurements on	the same gas sample. Both
0.56	measurements we	re made on the same day. The
0.74	samples are draw	wn from groups 2, 3 and 4.
0.25		
0.03		·
0.04		
- 0 72		

m = 0.32; s = 0.24

It is important to note that, while the data above indicates that fluctuations in machine measurement can be relatively large, the group as a whole is probably biassed in favour of large deviations because the initially measured values were often suspected.

A detailed record of the performance of the mass spectrometer over a two day period is presented in Table 3-9B. While all of the samples were prepared by the writer, about one third were analyzed by E.L. Speelman. Sample replicates and sample re-runs are clearly indicated in the Table. A sample re-run involved a second measurement of the isotopic composition of a different gas aliquot from the same gas sample. Sample re-runs are bracketed with the initially analyzed samples. The apparent discontinuities in machine performance are also indicated. While it is not known whether this 2 day record of machine performance is representa-

TABLE 3-9B	6
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Sample	Date of Analysis	<b>د</b> s <sup>34</sup> (%)	
(W-3,po)	10/6/66	(+14.45)	+14.40
(W-3,s)	х 1	(+14.60)	+14.69
C.D.T.		-0.15	
A-1,po		+14.61	Relatively
A-l,cp		+1.4.57	heavy values
B101-3B,p		+14.60	
B101-3,cp		+15.40*	
B101-3,t		+13.02*	? operator:
(B101-3B,p)	·	(+14.29)	writer
B-2,po		+14.33	
B-2,cp		+14.01	
B104-7,s		+14.85	
B104-7,g		+12.56	
A-3, po		+14.52	
A-3,cp		+14.98	
C.D.T.		+ 0.20	
A-2, po		+14.17	
A-2,cp#	10/6/66	+14.00	E.L.Speelman
A-2,cp#	11/6/66	+13.96	writer
A-2,cp <sup>#</sup>		+14.65	Relatively
A-2,cp <sup>#</sup>		+14.61	heavy values
B-1,po		+13.68	1?
B-1,cp		+13.42	
B-2,cp)		(+13.89)	
B101-3B,p)		L(+14.18)	
(A-3,po)		(+14.44)	
(A-3,cp)		(+15.10)	
(A-2,po)		$L_{(+14,43)}$	
A-2,cp)		(+14.16)-	
(A-1,po)		(+13.88)	
(A-1,cp)	•	(+14.13)	-
(B-2.00)	11/6/66	(+14,20)	

Extract from a mass spectrometer record book

# : replicate samples

discontinuity

( ): sample reruns

\* : value suspect (very small sample)

tive of day-to-day performance, it is considered to be worthy of examination, as such records are rare. The following observations can be made from it:-

- i) operator errors appear to be negligible, or at least essentially the same, thus cancelling out.
- ii) the durations of the two periods which favour a relative heavying of isotope ratios (prominent machine fluctuations) appear to be shorter than periods for which machine performance might be described as "normal".

Note: This feature of performance does not appear to be atypical, since different operators have observed (personal communication) that a triplicate analysis usually shows closest agreement with the lighter of the two replicates, for which there was initially no reason for anticipating poor replication. Thus it is inferred that these poor replicates "straddle" a "boundary" of a discontinuity in machine performance.

iii) precision for replicates and re-runs within these periods is reasonably good, with  $\Delta \delta S^{34}$  values usually smaller than 0.2%, while across "discontinuities" these values can vary by at least as much as 0.6%. Thus it appears that short-term precision for replicates is generally better than the estimated overall precision value of  $\pm 0.25\%$  for "heavy" replicates and is closer to  $\pm 0.15\%$ , when the machine performance is "normal".

In view of the recurrence of situations which are suggestive of the occurrence of "discontinuities" in machine performance, the writer has followed previous workers and adopted an arbitrary classification of replicate agreement: a difference in  $\Delta \delta S^{34}$  values of up to 0.1%, was considered excellent, a difference of up to 0.2%, was usually considered satisfactory, while the occurrence of larger differences has

MILLS MEMORIAL LIBRARY, MCMASTER UNIVERSITY generally been used as a basis for analyzing a sample in triplicate. The arbitrary rules which have been used in selecting analyses are as follows:-

- i) <u>replicate analyses</u>: both values are averaged and s computed directly.
- ii) <u>triplicate analyses</u>: a) if all of the values are more or less
  evenly separated, all are averaged and s computed accordingly.
  - b) if two are grouped such that the difference in values between them is not greater than 0.2%, and the third deviates from the nearest value by more than 0.4%, the latter is rejected and the mean and s computed from the first two analyses.
- iii) more than three analyses: (c) the equivalents of (a) and (b) above also apply. (d) if samples are grouped in 2 groups, all are averaged and s determined using all of the analyses.

#### 3-10. Influence of sulfide impurities in measured isotope ratios

Inherent in the measured isotope ratios for the natural and synthetic sulfides are errors arising from sample impurity, sample burning and mass spectrometer measurement. While it is clearly impossible to correct for the last two potential errors, it is possible and sometimes necessary to correct for sample impurity. Where this error has not been corrected for in some of the Figures the isotope data are reported as measured values.

At the top of Table 3-10 are listed the various sulfide concentrates together with their purity ranges, mean (weighted) modal percent impurities and the principal sulfide contaminants that give rise to these

TABLE 3-10

Concentrate	Estimated j (mean impuri	ourity ranges ty (weighted))	Principal Contaminants (% of total S contributed	
	B-1	Other deps.	by 10% of contaminant)	
p, #	90-99 (4)	90-98 (6)	g (4), s (6) - rare	
p, other ms.	85-95 (9)	-	cp (6), po (7)	
s, #	85-99 (3)	90-99 (3)	p (18)	
g, #	93-99 (4)	94-99 (3)	p (23)	
cp, other ms.	70-95 (13)	85-90 (11)	p (17)	
po, other ms.	75-95 (11)	85-90 (13)	p (15), cp (9)	

Mean fractionations between coexisting sulfides from the B-1 orebody Results for 12 # samples from which coexisting s, p and g, have been separated

Weighted means of fractionations

 $\Delta \delta s_{p-g}^{34} = 2.48^{*}, 2.7^{**} \qquad \text{Weighted mean of } \delta s_{p-g}^{34} \text{ of } pyrite = +14.9^{*}$   $\Delta \delta s_{s-g}^{34} = 1.65^{*}, 1.86^{**} \qquad (= 0.85^{*} \text{ for } 22^{*} \text{ B-l } p\text{-s pairs and } 0.82^{**} \text{ for } 24^{**} \text{ B-l } p\text{-s pairs})$   $\frac{\text{Results for 7 ms. samples containing } p\text{-cp pairs}}{p\text{-cp}} = 0.69^{*}, 0.97^{**?} \qquad \text{W. mean of } \delta s_{p-g}^{34} \text{ of pyrite } = +14.2^{*}$ 

Results for 5 ms. samples containing p-po pairs  $\Delta \delta s_{p-po}^{34} = 0.52^*, 0.68^{**?}$  W. mean of  $\delta s^{34}$  of pyrite = +14.3\*

\* w. means computed for uncorrected data.

\*\* w. means computed for corrected data.

impurities in the respective sulfide concentrates. The bracketed values following the contaminants indicate the approximate weight percent of sulfur contributed by 10 modal percent of the contaminant in otherwise pure sulfide concentrates. The lower half of the table shows fractionation values for pyrite-sphalerite (p-s), sphalerite-galena(s-g), pyrite-galena (p-g), pyrite-chalcopyrite (p-cp) and pyrite-pyrrhotite (p-po) pairs from the B-l orebody. The p-s, s-g and p-g pairs were taken from the same 12 pyrite-sphalerite-galena ore bands (#). Mean uncorrected fractionation values for the various groups of sulfide pairs are listed first (\*) and are immediately followed by corrected mean fractionation values (\*\*).

It is evident from the Table that the only fractionation values that have not been altered by correction are those for p-s pairs. Mean corrected fractionation values for p-g, s-g, p-cp and p-po pairs are larger than corresponding uncorrected values by 0.22, 0.21, 0.28(?) and 0.16(?)‰, respectively.

The 12 pyrite, sphalerite and galena concentrates have mean uncorrected values of +14.9, +14.07 and +12.42%, respectively. If these are corrected for the average levels of impurities, that is, 4 modal % of galena in pyrite, 3 modal % of pyrite in sphalerite and 4 modal % of pyrite in galena, mean values of +14.95, +14.02 and +12.17%, are obtained for "pure" pyrite, sphalerite and galena, respectively.

i.e.	pyrite conc.	0.985 (P) + 0.016 (G) = +14.9%	(1)
	sphalerite conc.	0.943 (S) + 0.057 (P) = +14.07%.	(2)
	galena conc.	0.902 (G) + $0.098$ (P) = +12.42	(3)

solution of the equations yields

P	(pure	pyrite)	=	+14.95%。
S	(pure	sphalerite)	=	+14.02%。
G	(pure	galena)		+12.17%。

where: the values 0.985 and 0.016 in equ. (1) are the fractions of the total sulfur contributed by 96 modal % of pyrite and 4 modal % of galena, respectively.

Increases of 0.1, 0.2 and 0.3%, would thus be observed for p-s, s-g and p-g fractionations, respectively. To obtain some idea of the maximum errors that can be expected for concentrates prepared in this way and where fractionations are of similar magnitude, it may be assumed that a pyrite concentrate contains 10 modal % of galena, and sphalerite and galena each contain 10 modal % of pyrite. If pure pyrite, sphalerite and galena are assigned values +14, +13 and +11.5%, respectively, the true and apparent (bracketed) fractionations are as follows:-

 $\Delta S S^{34} p-s = 1.0, (0.74):$  a decrease of 0.26%.  $\Delta S S^{34} s-g = 1.5, (1.07):$  a decrease of 0.43  $\Delta S S^{34} p-g = 2.5, (1.81):$  a decrease of 0.69

It can similarly be shown using the mean impurity values given in Table 3-10 that more reasonable estimates of pyrite-chalcopyrite, pyrite-pyrrhotite and pyrrhotite-chalcopyrite (by difference) fractionations are:-

 $\Delta \delta S^{34}$  p-cp = 0.9(7), an increase of 0.2(8)%  $\Delta \delta S^{34}$  p-po = 0.6(8), an increase of 0.1(6)%  $\Delta \delta S^{34}$  po-cp = 0.2(9), by difference

A corrected mean fractionation of 0.2(1)% is obtained for 5 po-cp pairs from the A deposit if it is assumed that the chalcopyrites (mean, +14.5) are pure and that the pyrrhotites contain 13 modal percent of chalcopyrite. This agrees reasonably well with the po-cp fractionation value obtained above.

It can be concluded that the uncorrected fractionation values for various sulfide pairs are minimum values and that, in general, the mean corrections which need to be added in order to give more realistic estimates are 0.3%, 0.2%, and 0.1%, for p-g, s-g and p-s pairs, respectively. While the level of uncertainty of fractionations between p-cp, p-po and po-cp pairs is considerably larger, it appears that respective corrections of about 0.3%, and 0.2%, for the first two pairs would make their fractionations more realistic. It is therefore evident from the variability in purities of the analyzed concentrates that some of the scatter in the plotted fractionation data can be attributed to this cause.

# 3-11. Summary and conclusions regarding the precision of isotopic measurement

- i) Within a 15 month period the reproducibility of the mass spectrometer measurements was found to range from ±0.1%, to ±0.57%, for five groups of standards analyzed in this time. The average reproducibility for the five groups of standards was ±0.33%,.
- ii) Precision was found to be better for groups of replicates
  whose isotopic values deviated by the smallest amount from
  the isotopic composition of the line-standard SO<sub>2</sub>.

- iii) "Short-term" precision for consecutively analyzed replicates appears to be better than the overall precision for a group of replicates. For "heavy" sample replicates the overall precision is estimated to be about ±0.25%, but is considered to be approximately ±0.15%, and sometimes better when the mass spectrometer is performing well. It is suggested that the poorer overall precision for replicates is due to periodic fluctuations in machine performance, probably resulting from electronic instability.
  - iv) While it has not been possible to determine the relative importance of each of the various potential sources of error, sample re-runs using the same sample gases suggest that most of the total error is inherent in the mass spectrometer measurement. The error arising from sample preparation may be appreciably less than ±0.1%.
    - v) Impurities in sulfide concentrates can give rise to relatively large errors, especially in the case of pyrite impurities in galena where 10 modal % of pyrite can give rise to an apparent heavying of 0.7%. This cause of error must be considered in determining fractionation values.

#### CHAPTER 4

PRESENTATION AND ANALYSIS OF SULFUR ISOTOPE DATA FOR SULFIDES FROM SOME STRATIFORM SULFIDE DEPOSITS IN THE BATHURST-NEWCASTLE AREA

#### PRESENTATION OF DATA

4-1.  $\delta S^{34}$  values of sulfides associated with the Heath Steele B-1 orebody

 $\delta S^{34}$  values of coexisting sulfides and of some individual sulfides from the B-l orebody are presented in Table 4-3A and isotope values of sulfides from footwall and hanging wall rocks of the B-l orebody are given in Table 4-3B.  $\delta S^{34}$  values of sulfides in consecutive crushed ore samples and of some separated pyrites from three D.D.H. intersections of the B-l orebody are given in Tables 4-6A and 4-6B, respectively. The uncorrected values of all of these sulfides are plotted in Figure 4-1.

The following observations can be made from Figure 4-1:

- i) The range, mean and standard deviation of  $\delta S^{34}$  values for a total of 71 crushed ore samples or pulps from the B-1 orebody are 3.6, +13.8 and ±0.6%, respectively. The range, mean and standard deviation for 10 pulps from the footwall meta-sediments are respectively 0.9, +14.6 and ±0.3%.
- ii) The total variation in 6S<sup>34</sup> values for all sulfides from the B-1 orebody is 6.2%, and the means for 61 pyrites, 28 sphalerites and 13 galenas are respectively +14.1, +13.4, and + 12.1%. Twenty two of the 71 pyrites and two of the 28 sphalerites were separated from 22 pulp samples. The means



of 9 chalcopyrites and 4 pyrrhotites are +14 and +13.6%, respectively.

iii) Two pyrites from the footwall metasediments were found to have values of +14.9 and +16.3%, and a single pyrrhotite from the same rocks has a value of +14.7%. The pyrrhotite value and the mean of the two pyrites are respectively 1.1 and 1.5%, heavier than the means of the B-1 pyrrhotites and the B-1 pyrites. The range, mean and standard deviation of  $\delta S^{34}$ values for all sulfides from the hanging wall rocks are 8.6, +16 and  $\pm$  2.55%, respectively. The means for 6 pyrites, 4 sphalerites and 2 galenas from these rocks are respectively +16.7, +15.5 and +15.3%. The heaviest value was found to be +21.5%, and is therefore one of the heaviest values determined for sulfides from the Bathurst-Newcastle area.

It is inferred from Figure 4-1 that pyrites appear to be enriched in  $S^{34}$  relative to sphalerites, which in turn, appear to be heavier than galenas. The means of chalcopyrite and pyrrhotite values appear to be generally similar to the means of both pyrites and sphalerites. Comparison of the means of the footwall pulps, of the B-1 pupls, and of the hanging wall sulfides suggests that the  $\delta S^{34}$  value of sulfur in the orebody is slightly lighter than the sulfur in the footwall rocks, and perhaps appreciably lighter than the sulfur in the hanging wall rocks. Analysis reveals that the mean of the footwall pulps is 0.8 ± 0.67%, heavier than the mean of the B-1 pulps at the 68% confidence level and that the mean of the hanging wall sulfides is 2.2 ± 1.8%, heavier than the mean of the B-1 pulps at the 50% confidence level (see Section 4-8).

The mean and range of variation for 21 B-1 zone pyrites determined by Dechow (1960) are shown in Figure 4-1. Identical values obtained for 2 chalcopyrite samples from the B-1 orebody are also shown. Unfortunately Dechow analyzed sphalerites and galenas together, thus rendering comparison with the data obtained here on relatively pure mineral concentrates impossible. While a close correspondence between both the mean values and the ranges of variation for Dechow's B-1 Zone pyrites and the B-1 orebody pyrites is apparent, a truer comparison necessitates a consideration of footwall and hanging wall pyrites as well, thus moving the mean closer to +15 and increasing the range of pyrite values by slightly more than 4% This corresponds to an increase of about 70% of the range determined to Dechow. The 2 chalcopyrite samples analyzed by Dechow occurred in quartz veinlets, thereby differing from the chalcopyrites re-It is noteworthy, however, that these values correspond ported here. with the lightest value determined in the present study.

# 4-2. The distribution of sulfur isotopes in coexisting sulfides from a sample of banded ore

A large banded sample of massive sulfide consisting chiefly of faintly banded pyrite in which are contained three clearly defined pyritesphalerite-galena (p-s-g) ore bands was selected for study of the distribution of sulfur isotopes among given sulfides. A 1.5 inch slab (sample 29: see Table 4-3A) was sliced from this sample normal to the plane of the relatively flat mineralogical banding and the individual sample slices were cut from diamond drill hole cores drilled through the slab in the plane of the banding. Insofar as selection of samples for the study of coexisting sulfides was restricted to relatively undeformed massive sul-

# Explanation of Terms and abbreviations used in the TABLES following.

Sulfi	lde	5		Locat	ion	
p	:	pyrite		loc.	:	location
S	:	sphale	rite	lat.	:	latitude (in feet)
g	:	galena		dep.	:	departure (in feet);"A" deposit
cp	:	chalco	pyrite	el.	:	elevation (in feet)
po	:	pyrrho	tite	x.c.	:	mine cross-cut
t(?)	:	tennan	tite-tetrahedrite(?)	FW	:	footwall
pulp	:	crushe	d ore sample	FWL	:	footwall lens
H.Sp.	.:	hand s	pecimen	HW	1	hanging wall
				D.D.H	•:	diamond drill hole
Desci	rip	tion		<u>Purit</u>	χ:	estimated modal % of total sulfide present
Ър	:	"barren tially sulfide	n" p <b>yrite, essen-</b> free of other es		*:	purity estimated in polished section
dp	:	dissem	inated pyrite	Measu	red	mean SS <sup>34</sup> values
ds	:	dissem	inated sulfides		*:	value suspect due to small sample size
ms	:	sulfide	e assemblages with $(\leq 20\%)$ amounts of	*	*:	isotopic reversal
		silicat	tes	±	5:	t standard deviation
#`	:	sphale (s-p-g)	rite-pyrite-galena ) ore band	<u>No. o</u> for was	f <u>s</u> exa rej	amples considered: 2/3, ample, indicates that 1 value jected and the mean and s
suffi	xea	3 -,b:	sample slice showed banding	wer	e co	omputed from the remaining 2.
	• •	,c:	appreciable chlorite content	•		
		cht.:	cherty matrix			
		,m:	appreciable magne- tite content			
		<b>,</b> p:	sulfides occurred in porphyry matrix.			
						х.

 $\delta\,\mathrm{s}^{34}$  values of coexisting sulfides from the heath steele B-1 orebody

	Sample			Location					c 34.					
				a b		e Ge	e Figures				05 (%)		۲ ور	គ្គ
Thesis Ref. No.	D.D.H. No.	Sample No.	Sulfide	D.D.H. footag (from collar)	Layer	Vertical Section No.	Description	Purity	Mean <b>S</b> S <sup>34</sup>	++ גט	No. of analy- ses considere	Corrected mea $\delta s^{34}$		
1	в	78-1,	p	2	A	S15	ms	98	+14.2		l			
2	В	78-2,	p	17	A		bp	95	<b>. +1</b> 5		1			
3	в	78-3,	р	37	в		bp,m	98	+15		1			
4	B7 B7 B7	8-4-1, 8-4-1, 8-4-2,	p s p	67 67 67	с с с		# bp <sub>s</sub> m	98 98 98	+14.5 +13.6 +13.3	0.2 0.4	2 1 2	+14.5 +13.5 +13.3		
5	B B B	78-5, 78-5, 78-5,	p s g	77 77 77	C C C		#	95 96 94	+14.6 +13.6 +12.9	•	1 1 1	+14.7 +13.5 +12.6		
6	B B	78-6, 78-6,	p po	114 114	E E		ms,b	98 75 ?	+14.1 +13.2	0.2	2 1			
7	B B	78-7, 78-7,	p s	121 121	E E		ms,b	98 98	+14.5 +13.9		1 1	+14.5 +13.9		
8	B7 B7 B7 B7 B7	8-8A-1 8-8A-1 8-8A-2 8-8A-3 8-8A-3	p s p s	125 125 125 125 125 125	E E E E		# #,b #	99 99 98 98 98	+13.4 +13.0 +13 +14.2 +13.1	0.1 0.3 0.1	1 2 1 2 1	+13.4 +13.0 +14.2 +13.1		
9	В7 В <b>7</b>	8-8B-1, 8-8 <b>B-1</b> ,	,p ,s	125 125	E E		#	98 99	+15.4 +15.1		1 1	+15.4 +15.1		
10	B B B	89-2, 89-2, 89-2,	p s g	86 86 86	B B B	<b>S</b> 6	#	95 98 99	+13.4 +12.6 +10.5	0.1 0.2 0.1	2 3 2	+13.5 +12.6 +10.4		

11	B 89-3, s B 89-3, g		C C		#	99 98	+14.0 +12.3	0.2 0.1	4/5 2/3	P
12	в 89 <b>-4, р</b> в 89-4, s	123 123	с с		#	98 98	+12.2 +11.1	0.1 0.0	2 2	+12.2 +11.1
13	B 89-5, p B 89-5, s B 89-5, g	200 200 200	e e e		#	98 98 98	+16.3 +15.3 +13	0.0 0.2	2 3 1	+16.3 +15.3 +12.8
14	B 89-6, p B 89-6, s B 89-6, g	204 204 204	E E E		#	98 99 98	+16.2 +15.7 +13.6	0.1 0.1	2 3 1	+16.2 +15.7 +13.4
15	B100-3-1,p B100-3-1,cp B100-3-2,p B100-3-2,cp	76 76 76 76	A A A A	S7	ms Ms	90-95 85-90* 95 80-85*	+14.1 +13.1 +14.3 +13.3		1 1 1 1	
16	B 100-6, p B 100-6, po B 100-6, cp	177 177 177	C C C		ms	95 90-95* 85*	+14 +13.4 +13.1	0.2	2 1 1	
17	B101-2-1,p B101-2-1,s B101-2-2,p B101-2-2,cp	46 46 46 46	A A A A	S7	ms,b ms	98 98 90 <b>-</b> 95 80 <b>-</b> 90 <b>?</b>	+13.5 +12.9 +12.7 +12.1		1 1 1 1	+13.5 +12.9
18	B101-3-1,cp B101-3-1,t(?) B101-3-2,p	61 61 61	B B B		ms ms	85 90 85 <b>?</b>	+15.4* +13* +14.4		1 1 1	
19	B 101-4, p	109	В		ms	90	+12.6		l	
20	B 101-5, p B 101-5, s	144 144	C C		ms,m	95 98	+13.6 +13		1 1	+13.6 +12.9
21	B 101-6, p	180	D;		ms,m	98	+12.8		1	
22	B 101-7, p B 101-7, s B 101-7, g	191 191 191	D D D		#	95 98 96	+14.1 +12.9 +12.0*	0.1 0.2	2 3 1	+14.1 +12.9 +11.8*
23	B 101-9, p B 101-9, s B 101-9, g	240 240 240	e E E		#	95 98 95	+12.8 +12.3 +10.1		1 1 1	+12.8 +12.3 + 9.7

24	B101-10-1,p	243	E	1	#	95	+12.4	1	1	12.4
	B101-10-1,s	243	E			98	+11.5		1	+11.5
	B101-10-1,g	243	Е	1		95	+10.2		1	+ 9.9
	B101-10-2,p	243	Е		#	95	+12.5		. 1	+12.5
`	B101-10-2,5	243	Е			98	+11.6	-	1	+11.6
25	B104-5-1, p	349	A	S15	ms	90-95	+14.7		1	
	B104-5-1,po	349	A		· ·	98*?	+14.1		1	
	B104-5-1,cp	349	A			90-95*	+14.5		1	
	B104-5-2, p	349	Α		#	90-95	+15.5		1.	+15.5
	B104-5-2, s	349	A	1		98	+14.6		1	+14.6
	B104-5-2, g	349	A			98	+13.3		1	+13.2
26	B 104-7, s	-398	A		#	90-95	+15	0.1	2	
	B 104-7, g	398	A			96	+13.1	0.6	2	
27	B109-3-1,p	492	в	S12	ms	95	+15.9		1.	
	B109-3-1,cp	492	B			>95*	+15.4		1	
	B109-3-2,p	492	В		ms	95	+13.8		1	· ·
	B109-3-2, po	492	В			90-95*	+13.5	1	1	
	B109-3-2,cp	492	В		ĺ	90?	+13.2		1	
	B109-3-3, po	492	В		ms,m	95*	+15.4		1	
	B109-3-3,cp	492	в			70-75*	+15.7		1	
28	B127-10-1,p	166	E	S12	#	95	+14.5		1	+14.5
	B127-10-1,s	166	Е			98	+14.1		1	+14.1
	B127-10-1 g	166	F	1		95	+12.7	1 · · ·	2	+12.5

#### hand specimen samples (H.Sp.)

<u>H.Sp.-1</u>(loc: lat. 23,145 N., dep. 40,363 E., el. 8600 1; x.c. 89)

3/4 S12 |ds,c +14.8 10.2 H.Sp.1-1, p A 99 29 4 99 +14.8 0.2 H.Sp.1-2A,p approx. 50E bp 4 +14.7 # 99 +14.7 0.1 H.Sp.1-2B,p 98 2 +13.6 +13.6 0.0 H.Sp.1-2B,6 1 +11.7\* 99 +11.7\* H.Sp.1-2B,g +14.8 4 99 H.Sp.1-2C,p bp 0.2 4 +14.5 # 99 +14.5 0.2 H.Sp.1-4A,p 2 98 +13.4 +13.4 0.1 H.Sp.1-4A,s 4 99 +14.3 0.1 H.Sp.1-4B,p bp 3 2 99 +14.2 0.2 H.Sp.1-5, p ms H.Sp.1-6A,p +14.4 dp,c 99 0.2 -5 4 99 +14.5 H.Sp.1-6B,p # 0.3 +14.5 98 +13.4 0.1 H.Sp.1-6B,s +13.4 1 H.Sp.1-6B,g 94 +11.7 +11.2 99 +14.5 0.1 2 H.Sp.1-6C,p bp +14.2 # 99· H.Sp.1-8A,p +14.2 1 l H.Sp.1-8A,s >90 +13.5 +13.4 2 H.Sp.1-8B,p 99 +14.8 bp,c 0.1 H.Sp.1-9, p 99 4/5 +14.7 0.2 ms 23,344 N., 40,496 E., el. 8600 1; x.c. 93) H.Sp.-2(loc: 30 **S9** H.Sp.2, D # 90-95 +13.3 р +13.3 1 H.Sp.2, +12.4 1 8 95 +12.3

# TABLE 4-3B

# $\delta\,{\rm s}^{34}$ values of coexisting sulfides from footwall and hanging wall rocks of the B-1 orebody

### Sulfides in the B-l footwall rocks

31	B 101-1, p B 101-1, p	30 30		S7	ds,c	99 95*	+14.9 +14.8		1 1	+14.9 +14.8	
32	365 <b>-</b> 15, p	516			ds,cht	98	+16.3		1		
Sulfides in the B-1 hanging wall rocks											
33	в 78-9, р	154		S15	dp,cht	99	+14		1	[	
34	в 78-10,р	222			dp,cht	99	+14		1		
35	В 101-11, в	252		S7	ds,p	98	+12.9		1		
36	B 101-12,p B 101-12,s	273 273			ds,p	98 98	+21.5 +18	0.0	2 1	+21.5 +18	
37	B 101-13,5	287			ds,p	98	+13.1		1		
38	365 <b>-</b> 1, p	114		S12	ds,cht	99	+15.4	0.1	2		
39	365-5, p 365-5, s 365-5, g	210 210 210			#, c	99 98 99	+18.2 +17.8 +15.8	0.2 0.3 0.2	3 5 2	+18.2 +17.8 +15.8	
40	365 <b>-</b> 8, p	283			ds,	90-95	+17.2	0.6	2	+17.3	
•	365 <b>-</b> 8, g	283			CNT-C	93	+14.7	0.3	2	+14.1?	

fide assemblages that visually appeared to be mineralogically homogeneous, sample slices were taken from within the p-s-g ore bands. The locations and cross sectional areas of the sample slices are shown in Figure 4-2. Measured  $\delta S^{34}$  values of the sulfide concentrates are plotted in the lower half of the Figure 4-2 where they are accompanied by tabulated fractionation values for coexisting p-s and p-g pairs from the respective p-s-g ore bands.

Unfortunately the precision of measurement could not be determined for the pyrite and sphalerite from sample 8A and for the galenas from samples 2B and 6B since there was only sufficient sulfide present in each of these concentrates for single analyses. The precision of measurement for all other sulfides was excellent. Corrections for pyrite impurities in the sphalerite and galena concentrates of samples 8A and 6B yield corrected p-s and p-g fractionations of 0.8 and  $3.3\%_{\circ}$ , respectively. It is evident from Figure 4-2 that  $6S^{34}$  values of pyrites show very little variation. The same is true for both the sphalerites and the galenas. With the possible exception of the pyrite in sample 8A, there is no significant variation in  $\delta S^{34}$  values of pyrites within or across the ore bands studied. The p-s fractionations in samples 2B, 4A and 6B are constant.

## 4-3. The distribution of sulfur isotopes in pairs of coexisting sulfides associated with the B-1 orebody

Measured  $\delta S^{34}$  values for coexisting sulfides associated with the B-1 orebody are given in Tables 4-3A and 4-3B. These are plotted in Figure 4-3 as  $\Delta \delta S^{34}$  sulfide, - sulfide, against  $\delta S^{34}$  pyrite or  $\delta S^{34}$  cp or s



FIGURE 4-3



for respective sulfide pairs. The measured values for coexisting sulfides from p-s-g or p-s assemblages have been corrected for sulfide impurities present in the concentrates and these values are tabulated in the extreme right hand columns of Tables 4-3A and 4-3B. The corrected fractionation values for p-s, s-g and p-g pairs are similarly plotted in Figure 4-7B. Corrected values for chalcopyrites and pyrrhotites are not presented because of the generally unreliable nature of the purity estimations. Mean fractionation values and regression curves computed for each of the scatter plots are shown in each of the Figures.

It is evident from the \$534 values of coexisting sulfides given in the Tables that pyrites are consistently enriched in S<sup>34</sup> relative to all other sulfides and that sphalerites are consistently heavier than Fractionations between pyrrhotites and chalcopyrites appear to galenas. be relatively small. Although some variation is present in the fractionation values for each of p-s, s-g and p-g pairs, it is evident that, with the exception of the p-s fractionation in sample 36, the magnitudes of these fractionations are fairly consistent within certain limits. Insofar as the sulfides in sample 36 were disseminated, they are not considered to be strictly coexisting. The weighted means and ranges of variation of uncorrected and corrected fractionations between sulfide pairs in massive sulfide assemblages from the B-1 orebody are given in Table 4-3C below. Standard deviations are given for the corrected fractionation values.

TABLE 4-3C

(No.)	pair	M.U.F.	R 	(No.)	pair	M.C.F.	R 	S.D. S.D.(±)		
(13) (12)* (12)* (12)*	р-g р-g s-g р-s	+2.5 +2.5 +1.7 +0.8	1.6 1.6 1.6 0.9	(13) (12)* (12)* (12)* (24)	р-8 р-8 5-8 р-5 р-5	+2•7 +2•7 +1•9 +0•8 +0•8	1.5 1.5 1.7 0.8 0.9	0.49 0.49 0.54 0.31 0.26		
(5) (7)	p-po p-cp	+0.5 +0.7	0.8 0.8	(5) (7)	p-po p-cp	+0.7 +1.0	n.d. n.d.	n.d. n.d.		
where	(13) (12)* M.U.F. M.C.F. p s g po cp R S.D. n.d.	:::::::::::::::::::::::::::::::::::::::	13 pairs pairs from same 12 samples weighted mean of uncorrected fractionations (% <sub>o</sub> ) weighted mean of corrected fractionations (% <sub>o</sub> ) pyrite sphalerite galena pyrrhotite chalcopyrite range of variation standard deviation							

Corrected means for p-po and p-cp fractionations were determined by correcting the means of the measured fractionations for maximum levels of impurities estimated to be present in respective sulfide concentrates. Unfortunately these values are not considered to be very reliable because the sulfide impurities in the concentrates were estimated in polished section mounts where often fewer than 100 mineral grains were visible in a single field of view at a magnification that permitted mineral identification. Purities of other sulfide concentrates were estimated in fields of view containing from 800 to 1200 grains.
#### 4-4. Variations in corrected fractionation values

It was shown in Section 4-2 that the magnitudes of fractionations between given sulfide pairs are very similar in closely spaced samples from the same large banded ore specimen. The fact that fractionations between the same pairs in samples from different parts of the B-1 orebody show appreciably larger variations, raises the question as to whether fractionations definitely vary between given pairs or that the variation might be due largely to experimental error. In order to answer this question one must look more closely at fractionations in samples where good precision of measurement was obtained for high purity concentrates. The samples which meet these requirements are listed in Table 4-4 below, together with their locations and the corrected fractionation values and precisions for respective sulfide pairs.

#### TABLE 4-4

#### Samples from D.D.H. B89

14) S6,E (204'), p-s\* = +0.5 ± 0.14 13) S6,E (200'), p-s = +1.0 ± 0.2 12) S6,C (123'), p-s = +1.1 ± 0.1 11) S6,C (111'), s-g = +1.8 ± 0.22 10) S6,B ( 86'), p-s = +0.9 ± 0.22 10) S6,B ( 86'), s-g = +2.2 ± 0.22 10) S6,B ( 86'), p-g = +3.1 ± 0.14

Sample from D.D.H. BlOl

22) S7, D (191'), p-s = +1.2 ± 0.22

Hand Specimen No. 29

29-2B) S11/12.A, p-s = +1.1 ± 0.1 29-4A) S11/12.A, p-s = +1.1 ± 0.22

Sample from D.D.H. 365 39) S12,HW (210'), p-g = +3.4 ± 0.28

p-s\* - sphalerite is unusually light in colour

The distances separating Sections 6, 7, 11 and 12 are respectively 100 feet, 200 feet and 100 feet. The precision of each fractionation value was obtained by taking the square root of the sum of the squares of the precisions of measurement for respective sulfides.

It is evident from the data that the only fractionation value which is significantly different from others of the same kind is the value for sample 14). It may be significant however, that the sphalerite of this pair was noted to be considerably lighter in colour than most other sphalerites from the B-1, suggesting a lower iron content. The variation between the p-s fractionation of sample 14) and the largest p-s fractionation in Table 4-4 above is  $0.7 \pm 0.3\%_{0}$ . On the basis of this established variation it must therefore be concluded that some variation is present, at least among p-s fractionations.

Among corrected fractionation values for given sulfide pairs where precisions are low or unknown, "true" variations in fractionation values can only be estimated with a relatively high level of uncertainty. It is possible to obtain some idea of the magnitudes of variations by subtracting the estimated range of variation due to errors of measurement from the observed ranges of variation. If there were no variation in fractionation values for given pairs it might be expected that the observed ranges would be very similar to the estimated precision range, provided this estimate was accurate. A precision range of 1.6%, which is only slightly smaller than the maximum observed range of 1.7%, (see Table 4-3C), is obtained when a very low machine precision value of ±0.6%, is assumed for both sulfides of given pairs. While this probably

represents a maximum, it is considered that a precision of ±0.24%. computed from the standard deviation of the differences between heavy replicate values represents a probable minimum. This corresponds to a precision range of  $2 \times \pm ((0.24)^2 + (0.24)^2)^{\frac{1}{2}}$  or about 0.7%, which is 0.2%, smaller than the range of variation observed for 97 heavy replicate differences. Hence if it is assumed that at least 0.7%, of the observed ranges of variation in fractionation values can be attributed to errors of measurement it has to be inferred that maximum values of 0.2, 0.8 and 1.0%, for p-s, p-g and s-g fractionations, respectively, cannot be accounted for and thus are possibly due to true variations. It is not implied, however, that 0.2%, represents the true maximum range of variation of p-s fractionations around a mean of about 0.8%.

On the basis of the limited data available for fractionations between high purity sulfide pairs where good precision of measurement was obtained it is concluded that fractionations for given sulfide pairs show excellent agreement except for one p-s pair in which the sphalerite appears to contain less iron than other sphalerites. For fractionations between sulfide pairs where the precision of measurement is either low or unknown it is estimated that generally less than 0.2, 0.8 and 1.0%, of the observed ranges of variation for p-s, p-g and s-g pairs, respectively, probably cannot be attributed to errors of measurement. However, it is emphasized that these estimates are not considered to be very reliable in view of the assumptions involved. A maximum variation of 0.7  $\pm$  0.3%, is indicated for p-s pairs.

# 4-5. Relationship between fractionation values for sulfide pairs and their location in the B-1 orebody

In order to test for possible local systematic variations in fractionations across the B-1 orebody, sulfide pairs were analyzed in samples from the B89 intersection (section 6). A single sample was also chosen from D.D.H. Blol (Section 7), located 100' to the west of D.D.H. B89. The p-s fractionations for these samples are plotted against the respective layers containing them as shown at the top of Figure 4-5. The remaining part of the Figure shows p-g, s-g and p-s fractionations plotted against respective containing layers, but some of these samples are widely separated within given layers. The first part of each sample number is the thesis reference number (see Tables 4-3A and 4-3B), and the S number following is the section number as indicated in Figure 1-11. Numbered linear regression lines are also shown.

It is apparent that fractionation values for given pairs are generally independent of the layer containing them. Unfortunately it was impractical to test for within layer variations due to limited data. However, in view of the relative constancy of fractionations between some widely separated pairs given in Table 4-4, it is anticipated that significant variations would not be found.

#### 4-6. Sulfur isotope variation across the B-1 orebody

The distribution of sulfur isotopes in total sulfur of crushed ore samples and in sulfur of pyrites extracted from some of these has been studied in three across orebody diamond drill hole intersections, including B137, B138 and B125-B126. The data is given in Tables 4-6A and 4-6B

<u>FIGURE 4 - 5</u>

RELATIONSHIP BETWEEN CORRECTED FRACTIONATION VALUES FOR COEXISTING SULFIDE PAIRS FROM THE B-1 OREBODY AND THEIR LOCATIONS IN ACROSS OREBODY PROFILES



location (layer)

# TABLE 4-6A

# $\delta$ s<sup>34</sup> values of total sulfur in d.d.h. pulp samples d.d.h. B137 pulps

## Massive Sulfides

Pulp No.	Location			$\delta_{\rm S}^{3^{\rm J}}$	+	
	D.D.H. Footage	Thesia	Ref.			
<b>A404</b> 4 45	36-41 41-46	E	<b>s</b> 8	+12.9 +13.6	0.2 0.1	3 2
46 47 48	46-51 51-56 61-66			+13.4 +13.6 +13.1	0.0 0.2 0.1	2 4 2
49 50 51	66-71 71-76 76-81	D	S8	+13.2 +14.2 +14.3	0.1 0.0 0.1	322
52 53 54	76-81 81-86 86-91			+14.2 +14.2 +14.2	0.1 0.2 0.1	3 3 2
22 56 57 58	91-96 96-101 101-106	ō	<b>s</b> 8	+13.6 +13.6 +14	0.1	2 2 2
59 60 61	111-116 116-121 121-126			+13.5 +13.4 +13.2	0.1	22
62 63 64	126-131 131-136 136-141	B	<b>S</b> 8	+12.5 +11.3 +13.3	0.5 0.3 0.1	3 3 2
65 66 67	141-146 146-151 151-156			+13.1 +13.9 +14	0.0	2 3 2
68 69 70	156-161 161-166 166-171	Ā	s8	+13.8 +14.2 +14	0.3 0.1 0.1	423
71 72 73	171-176 176-181 181-186			+13.7 +14.4 +14.5	0.1 0.1 0.1	222
74 75	186-191 191-196			+13.9	0.0	2

76 A4077	196-201 201-206	S8	+14.5   +14.7	0.1 0.2	23
	D.	D.H. B138 PULPS			
	Disseminated Sulfi	des in Footwall	Sediment	8	
A4078 79 80 81 82 83 83 84 A4085	300-305 305-310 310-315 315-320 320-325 325-330 330-335 335-340	S14	+14 +15.4 +14.8 +14.8 +14.5 +13.9 +14.6 +14.6	0.0	2/3 2 1 1 1 1 1 1
	Massi	ve Sulfides			
A4086 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 A4107	340-345 345-350 350-355 355-360 360-365 365-370 370-375 375-380 380-385 385-390 390-395 395-400 400-405 405-410 410-415 415-420 425-430 425-430 430-435 435-440 445-450 450-455	S14	+14.9 +13.9 +14.5 +14.5 +14.8 +14.4 +14.6 +14.8 +14.8 +14.8 +13.8 +13.8 +13.6 +13.6 +13.6 +13.6 +13.6	0.0 0.2 0.1 0.1 0.2 0.3 0.1	2 1 1 1 1 2 1 1 1 2 1 1 2 1 1 2 1 2 1 2

Disseminated Sulfides in Footwall Sediments

(B138 completed in massive sulfides)

## D.D.H. B125 PULPS

# Massive Sulfides

A16741	0-6	B	S13	+14	1
42	6-11			+13.9	1
43	11-16			+14	1
44	16-21	_		+13.9	1
45	21-26	Ā	S13	+13.6	1
46	26-30			+13.9	1
47	30-36	<u>.</u>		+14.2	11
A16748	36-42			+13.8	11

(B125 completed in footwall sediments)

## D.D.H. B126 PULPS

## Massive Sulfides

A16749	0-6	D	S13	+13.5	1	1
50	6-12			+13.6		1
51	12-17			+14		1
52	17-22			+14.2		1
53	22-26			+14.3		1
54	26-29	Ē	S13	+14.4	0.2	2
55	Missing					
56	37-42			+13.1	0.0	2
A16757	42-45	ļ		+13.3		1
	(B126 completed	in hong	ing woll	nooka)		
	(Pres combresed	Terre	me war	r rooro)		

# TABLE 4-6B

# $\delta s^{34}$ values of sulfides extracted from D.D.H. pulp samples

Location			Purity	<b>8</b> s <sup>34</sup>		
38.5 38.5 43.5 43.5 68.5 73.5 88.5 93.5 103.5 123.5 133.5 143.5 143.5 163.5 173.5 183.5 183.5 183.5	E D C B A	<b>S</b> 8	* 98 * 98 * * * * * * * * * * *	+13.4 +12.8 +12.9 +12.9 +13.7 +13.7 +13.7 +13.7 +13.7 +13.7 +13.7 +13.3 +13.3 +13.4 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +13.7 +14.3 +14.	0.1 0.2	2/3 2 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
D.	D.H. B	138 PYR	ITES			
347.5 362.5 402.5 417.5 447.5 452.5		<b>S14</b>	* * * *	+14.5 +15 +14 +14.8* +13.9 +14.1	0.5 0.2 0.1	1 1 2 2 2
	Location 38.5 38.5 43.5 43.5 68.5 73.5 88.5 93.5 103.5 123.5 133.5 143.5 143.5 143.5 148.5 163.5 173.5 183.5 188.5 193.5 D. 347.5 362.5 402.5 417.5 447.5 452.5	Location 38.5 E 38.5 43.5 43.5 68.5 73.5 D 88.5 93.5 C 123.5 E 133.5 E 143.5 143.5 143.5 148.5 163.5 A 183.5 188.5 193.5 D.D.H. E 347.5 362.5 402.5 417.5 447.5 452.5	Location 38.5 E S8 38.5 43.5 43.5 68.5 D 88.5 93.5 C 123.5 E 133.5 E 143.5 143.5 143.5 148.5 163.5 T 173.5 A 183.5 188.5 193.5 S 193.5 S 188.5 193.5 S 193.5 S 188.5 193.5 S 193.5 S 193.5 S 144 362.5 402.5 417.5 452.5 S	Location       Purity         38.5       E       S8       *         38.5       F       S8       *         38.5       98       *       *         38.5       98       *       *         38.5       98       *       *         43.5       98       *       *         43.5       98       *       *         43.5       98       *       *         93.5       C       *       *         93.5       C       *       *         103.5       C       *       *         123.5       B       *       *         133.5       B       *       *         148.5       *       *       *         163.5       T       *       *         183.5       *       *       *         193.5       *       *       *         347.5       \$       \$       *         402.5       *       *       *         402.5       *       *       *         447.5       *       *       *         447.5       *       * </td <td>LocationPurity<math>\delta s^{34}</math>38.5ES8*38.5F9843.5*43.59843.5*43.59843.59843.59843.5*68.5*73.5D*+13.7103.5C**103.5C**123.5B**143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*144.5143.5143.5**144.5144.5145.5**144.5*144.5***&lt;</td> <td>LocationPurity<math>\delta S^{34}</math>38.5ES8*+13.40.138.598+12.80.243.5*+13.7+14.243.598+12.968.5*+13.773.5D*93.5*+13.7103.5C*103.5C*103.5T*103.5*+13.3143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*144.5163.5*173.5A**193.5***144.2145.5145.5****144.2*145.5***************************************<!--</td--></td>	LocationPurity $\delta s^{34}$ 38.5ES8*38.5F9843.5*43.59843.5*43.59843.59843.59843.5*68.5*73.5D*+13.7103.5C**103.5C**123.5B**143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*144.5143.5143.5**144.5144.5145.5**144.5*144.5***<	LocationPurity $\delta S^{34}$ 38.5ES8*+13.40.138.598+12.80.243.5*+13.7+14.243.598+12.968.5*+13.773.5D*93.5*+13.7103.5C*103.5C*103.5T*103.5*+13.3143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*143.5*144.5163.5*173.5A**193.5***144.2145.5145.5****144.2*145.5*************************************** </td

# D.D.H. B137 SULFIDES

\* purity estimated to be better than 95%.

and is plotted in Figure 4-6A. The locations of these diamond drill hole intersections are shown in Figure 1-11. D.D.H. B137 intersects the entire orebody at section 8 and B125 and B126 respectively intersect the footwall and hanging wall at section 13, located about 300 feet to the west of section 8. The B125-B126 intersection is complete except for a 12-foot thick section of massive sulfide near the middle of the orebody. B138 is located 80 to 100 feet to the west of the B125-B126 intersection where it is collared in chloritic metasediments containing disseminated sulfides and terminates in high grade lead-zinc ore after intersecting an estimated 2/3 to 4/5 of the true orebody thickness.

Pulp samples were prepared from D.D.H. B137 and D.D.H. B138 by Heath Steele Mines Ltd. by crushing consecutive 5 foot lengths of split 1 1/4" diameter drill core. Some of the pulp samples for B125 and B126 were prepared from cores which were shorter and longer than 5 feet. The pulp samples were further mixed prior to burning. All of the B137 pulps were initially analyzed in replicate and pulps A4047, -56, -62, -63, -66 and -68 were reburned and analyzed at a later date. As acceptable agreement with the initial replicate results was obtained, it was concluded that the overall pattern of variation for the pulp values is not significantly influenced by machine drift. Pulps from the other drill holes were therefore analyzed singly, as were most of the pyrites extracted from some of the B137 and B138 pulp samples. After the patterns of variation for total sulfur in the pulps were obtained, pyrites were generally extracted from B137 and B138 pulps showing more or less extreme isotopic values in the pulp patterns.



The across orebody variations in  $5S^{34}$  values in each of the three profiles are generally characterized by a saw-tooth type of variation consisting of essentially small fluctuations of variable amplitude. However, it is evident that portions of the patterns for the B137 and B126 intersections are smoothly continuous. It appears that the patterns of variation for disseminated sulfides in the footwall metasediments of the B138 intersection and possibly also for the B137 intersection are continuations of the patterns in the massive sulfides above, even though total sulfur may be only one tenth as abundant as in the massive sulfides. For this reason the patterns of variation of total sulfur in both the massive sulfides and the disseminated sulfides are considered together in the analysis of the B137 and B138 profile data. An overall trend favouring an enrichment in S<sup>32</sup> towards the hanging wall is apparent in the B137 and B138 profiles.

The similarity in the patterns of  $8S^{34}$  variation of total sulfur in pulps and of sulfur in pyrites, particularly in the case of the B137 intersection where more pyrites have been analyzed, suggests that most of the sulfur in the pulps accurs in pyrite. The atomic percentage sulfur contributions by the principal sulfides contained in the B137 pulps are shown in Figure 4-6B. These have been calculated from assay values for lead, ainc, copper and total sulfur by assuming that sphalerites contain a mean iron content of 9.5 weight percent and that the stoichiometries of galena and chalcopyrite are respectively PbS and CuFeS<sub>2</sub>. The assumed iron content of the sphalerites was obtained by averaging the three values for Heath Steele sphalerites reported by Colwell (1963). The

FIGURE 4-6B



atomic percentages of sulfur occurring in sphalerites, galenas and chalcopyrites were computed accordingly and the percentage of sulfur occurring in iron sulfides, known to be present largely in the form of pyrite, was obtained by subtracting the sum of the percentage contributions of sulfur present in sphalerites, galenas and chalcopyrites from the total sulfur. The proportions of sulfur contributed by iron sulfides, chalcopyrite and by sphalerite and galena in each of the massive sulfide pulps from the B137 and B138 intersections are schematically shown in Figure 4-6A. The total sulfur in each of the pulps has been normalized to one mole. It is evident from the Figures that the iron sulfides usually account for more than 90% of the total sulfur and that other sulfides are relatively minor contributors.

It is concluded that across orebody variation in  $\delta S^{34}$  values of total sulfur are largely due to similar variations in pyrite sulfur. The small differences between 6S<sup>34</sup> values of pulps and corresponding pyrites, especially among those containing relatively high concentrations of lead and zinc. suggest that  $6S^{34}$  values of associated sulfides are probably not greatly different from the pyrite values; that is, not appreciably greater than 1 and 3%, for sphalerite and galena, respectively. This view is supported by the fact that sphalerites separated from pulps A4044 and A4045 were found to be less than 1%, lighter than associated pyrites. However, it is apparent from the larger gradients of the regression curves for the pulps that the overall patterns of variation for the latter have at least been affected to a small degree by the sulfur contributions from sphalerites and possibly galenas, particularly in the pulps near the hanging wall.

#### 4-7. <u>Sulfur isotope ratios in coexisting sulfides from some other</u> stratiform deposits in the Bathurst-Newcastle area

Both measured and corrected  $6S^{34}$  values for coexisting sulfides from five other deposits are presented in Table 4-7. Uncorrected fractionation values for p-g, s-g, p-s, po-cp and po-s pairs from these deposits are plotted in Figure 4-7A. Corrected fractionations for p-g, s-g and p-s pairs from a total of 8 p-s-g assemblages from 5 deposits together with similar pairs from 12 p-s-g assemblages from the B-l orebody are plotted in Figure 4-7B. Also shown in Figure 4-7B are corrected fractionations for an additional 12 p-s pairs from the B-l orebody. FIGURE 4 - 7A

MEASURED  $\Delta s s^{34}$  values for coexisting sulfides in some other stratiform deposits in the bathurst-newcastle

AREA



FIGURE 4 - 7B

CORRECTED FRACTIONATION DATA FOR COEXISTING SULFIDES

FROM SOME STRATIFORM DEPOSITS IN THE BATHURST-NEWCASTLE AREA



LEGEND

Coexisting sulfides from other deposits

Coexisting sulfides associated with the B-1 orebody O pairs from one of the same 12 p-s-g assemblages pairs from other p-s-g and p-s assemblages omitted from regression analysis	(41,42) (46) (47,48) (49) (50,51)	Heath Steele B-2 deposit Heath Steele A deposit C.M.& S. Wedge deposit B.M. & S. No. 6# deposit B.M. & S. No. 12# deposit pairs from one of the same 8 p-s-g assemblages p-s pair from other p-s-g assemblage : omitted regression curve identification
	20	regression curve identification number

# TABLE 4-7

# $\delta s^{34}$ values of coexisting sulfides from some other sulfide deposits

## Heath Steele B-2 orebody

41	B131-5-1,p   50	#	98	1.	+13.5	:	1  +13.5
	B131-5-1,s 50		99	· ·	+12.8		1 +12.8
	B131-5-1.g 50		99	· · ·	+10.9		1 +10.9
	B131-5-2.p 50	ds	<b>q</b> 98	· · ·	+13.2 0	).1   2	2 +13.2
	B131-5-2,8 50		99	.	+12.7 0	0.0 I 2,	/3 +12.7
	<u>H.Sp3(loc: 12</u>	4' S. of mine Re:	f. Line, 4	E.	of 996+2	25 W., 80	630 L)
42	H.Sp.3. p	1#	190-95	. 1 .	+15.3		1  +15.4
	Н. Sp. 3. в		98		+14.6		1 +14.6
	H.Sp.3. g	· •	94	<b>I</b> . •	+12.8		1 +12.4

#### Heath Steele "A" deposit

1. Samples from a copper ore lens (approx. loc: 20,070 N., 29,890 E., 8965 el.)

43	H.Sp.1-1,po	FWL,	ms	90-95*	+14.5	0.3	3
		A dep.					1
	H.Sp.1-1,cp	_		85 <b>-9</b> 0*	+14.2	0.2	4
	H.Sp.1-2,po		ms	85-90*	+14.3		1
	H.Sp.1-2.cp			90*	+14.4	0.4	3
	H.Sp.1-3.po		ms	90*	+14.4	0.1	2
	H.Sp.1-3.cp			90*	+14.6	0.4	3
	H.Sp.1, pulp	(composite chir	sample	e).	+1.4	I	1 1
44	H.Sp.2-1,po	FWL,	ms,m	80-85*	+13.7		11
	H.Sp. 2-1.cp			90*	+13.4		1
•	H.Sp. 2-2.po		ms.m	80-85*	+14.3		1
	H.Sn. 2-2. cn			90-95*	+14		1

	2. Sample (appro	es o: ox. 1	f lead-z	inc re 0,0 N.	from a 1 , 20,890	LO <sup>®</sup> (hic) D <sup>®</sup> , el	c ore hor 8965)	izon		
45	H.Sp.3-1 H.Sp.3-1 H.Sp.3-2 H.Sp.3-2 H.Sp.3-3	,5 ,5 ,90 ,8	, ,	Aldep. Aldep.	ms ms	98 98 98	+13.6 +12.3 +14.2 +14.4 +14.7		1 1 1 1	:
	H.Sp. 3-3	, pu , g				98	+13.4		1	
46	H.Sp.4, H.Sp.4, H.Sp.4,	p s g		A dep.	#	90-95 98 95	+14.7 +14.6 +12.8	0.2 0.2 0.1	2 2 2	+14.7 +14.6 +12.6
	Co	onsol	Lidated	Mining a	nd Smelt	ting Wedg	ge Deposi	t		
47	H.Sp.2, H.Sp.2, H.Sp.2,	p s g	весt. 820 I	E	<b>#,</b> Ъ	85 95 95	+ 9.9* +10.2 + 8.1		1 1 1	+10** +10.2 + 8.0
48	H.SpU, H.SpU, H.SpU,	p s g	un- known		#,b	90 98 95	+ 8.7 + 7.3 + 5.9	0.1 0.1	2 2 1	+ 8.8 + 7.3 + 5.5
	,	Bru	nswick M	ining an	d Smelti	ng No.6	Deposit			
	H.Sp1	(100	cation u	nknown -	ore du	np, No. 6	Pit).			
49	H.Sp.1, H.Sp.1, H.Sp.1,	p s g			#	95 98 95	+15.4 +15.2 +13.1	0.6 0.1	2 2 1	+15.5 +15.2 +12.8
	<u>1</u>	Brune	swick Min	ning and	Smeltin	ng No.12	Deposit			
•	H.Sp1() co	Locat	tion: u	ncertain , 950 le	; dep. 4 vel.)	ю,423 E.	, 5'W of	footwa	11	
	H.Sp4(] co	Locat	tion: w t, x.c.	ncertain , 950 le <sup>.</sup>	; dep. 4 vel.)	ю,366 е.	, 60'W o:	f footw	all	
50	H.Sp.1, H.Sp.1, H.Sp.1,	p s g			#	98 99 98	+15.8 +15.5 +13.8	0.1 0.0	2 2 1	+15.8 +15.5 +13.7
51	H.Sp.4, H.Sp.4, H.Sp.4,	р 8 8			#	98 98 96	+16.0 +15.1 +13.1	0.0 0.3	3/4 2 1	+16.0 +15.1 +13.0

With the single exception of sample 47, in which pyrite was found to be slightly lighter than the coexisting sphalerite, all pyrites were found to be heavier than coexisting sphalerites and sphalerites heavier than coexisting galenas. Samples 47 and 48 were unique insofar as they were very finely banded thus making it impossible to obtain sample slices from single sphalerite-galena rich p-s-g bands. With the exception of sample 47, it is evident from Figure 4-7A that the respective ranges of variation and means of p-g, s-g and p-s fractionations for other deposits are very similar to the B-1 data. The fractionations for given pairs also appear to be generally independent of  $\delta S^{34}$  values of the coexisting pyrites. The means, ranges of variation and standard deviations for the corrected fractionations between all p-g, s-g and p-s pairs from the other deposits are as follows:-

No. of samples	pair	M.C.F.	<u>R</u>	<u>S.D.(±)</u>
(8)	p-g	+2.6	1.3	0.49
(8)	s-g	+2.1	0.6	0.2
(8)	р-в	+0.7	1.7	0.56

Note: the symbols used here are the same as those in Table 4-3C.

The measured fractionations between five relatively high purity po-cp pairs from two copper ore lenses of the A deposit were found to have a mean of approximately +0.1%, and a range of 0.5%. Pyrrhotites were slightly heavier than chalcopyrites in 3 out of the 5 pairs. Analyses of two po-s pairs from the same deposit indicate that fractionations between these sulfides are very small.

Dechow (1960) analyzed 8 po-cp pairs from the Heath Steele A, B-2, D and E Zones. The mean and range of variation of fractionations between these pairs are +0.5 and 1.8%, respectively. Five out of the 8 pairs appear to have occurred in coarse grained aggregates in veins.

#### ANALYSIS OF THE ISOTOPE DATA

Several consistencies are apparent in the isotope data presented in the previous Sections of this Chapter. These include:-

- i) fractionations between given pairs of coexisting sulfides from the six deposits are fairly similar, with fractionations between p-g pairs appearing to be larger than for s-g pairs, which in turn, appear to be larger than for p-s pairs.
- ii) fractionation values for given pairs appear to be generally independent of  $\delta S^{34}$  values of coexisting pyrites and, in the case of B-1 pairs, also appear to be independent of the locations of samples containing respective pairs.
- iii) patterns of variation in  $SS^{34}$  values for total sulfur in crushed ore samples and for sulfur in pyrites are very similar in across orebody profiles and these appear to favour an overall enrichment in  $S^{32}$  towards the hanging wall of the B-l deposit.

The purpose of the following Sections is to analyze these apparent consistencies and make some decision as to their significance.

#### 4-8. Analysis of corrected fractionation values for some sulfide pairs from six stratiform deposits in the Bathurst-Newcastle area

It was shown in Section 4-3 that mean corrected fractionations and standard deviations for p-g, s-g and p-s pairs in the same 12 p-s-g assemblages from the B-l orebody are respectively  $+2.5 \pm 0.49$ ,  $+1.9 \pm 0.54$ and  $+0.8 \pm 0.31\%$ . Mean corrected fractionations and standard deviations for p-g, s-g and p-s pairs in the same 8 p-s-g assemblages from five other deposits were shown in Section 4-7 to be  $+2.6 \pm 0.49$ ,  $+2.1 \pm 0.2$  and  $+0.7 \pm 0.56\%$ , respectively. If it is assumed that fractionation values for given pairs approximate a continuous probability distribution of the Gaussian type, it is possible to determine the confidence intervals for which they are significantly different. For given confidence levels, the confidence limits for the difference between the mean fractionation values for different sulfide pairs is obtained from

$$z_{c} ((S_{D_{1}})^{2} + (S_{D_{2}})^{2})^{\frac{1}{2}}$$

where  $z_c$  and the S.D.'s respectively represent the confidence coefficient and the standard deviations for each group of pairs (cf. Spiegel, 1961). The confidence coefficients corresponding to various confidence levels are obtained from normal curve area tables. The maximum confidence levels for which the differences between mean fractionation values for various pairs are significantly different are given in Table 4-8.

TABLE	48
-------	----

	<u>B-1 orebody</u>								
		mean	difference	confidence limits	% confidence				
M P-g	- M <sub>s-g</sub>		+0.6	± 0.49	50				
M P-g	- Мр-в	=	+1.7	± 1.5	99				
M 8-g	- M <sub>p-8</sub>	8	+1.1	± 1.03 ± 0.8	90 80				
	<u>Other</u> de	posits							
M P-g	- M <sub>s-g</sub>	-	+0.5	± 0.36	50				
M P-g	- M p-8		+1.9	±1.7	98				
M <sub>8-g</sub>	- M p-s	2	+1.4	±1.38	98				

where: M = the mean fractionation value (%) for the pair indicated

If differences that are not significant below the 68% confidence level are considered unacceptable, it follows from Table 4-8 above that significant differences do not exist between mean fractionation values for p-g and s-g pairs from both the B-l orebody and the other deposits. It is evident, however, that differences between mean fractionations for other pairs are significant at higher confidence levels.

# 4-9. Dependency of given fractionation values on $\delta S^{34}$ values of coexisting pyrites and on the locations of samples containing respective pairs

Insofar as fractionation values for given high purity pairs for which good precision of measurement was obtained generally approach constant values regardless of the  $\delta S^{34}$  values of coexisting pyrites, it is considered that a linear regression model is suitable for the analysis of fractionation values as a function of  $\delta S^{34}$  values of coexisting pyrites. Since fractionation values for given pairs from the B-l orebody also appear to be generally independent of the locations of samples containing respective pairs, this model is also considered satisfactory for the analysis of fractionation values as a function of location.

The apparent lack of dependency of fractionation values on these variables is tested by determining whether or not the slope values (beta's) of linear regression lines computed for the 95% confidence level include zero. Where the beta values include zero, the hypothesis that beta = 0 is accepted and the fractionations are considered to be independent of the respective variables at the 95% confidence level. In these analyses, Y and X in the general linear equation  $Y = \alpha + \beta X$  are respectively equated with the fractionation values and the  $6 \text{ s}^{34}$  values of coexisting pyrites or the respective layers in the B-l orebody. The curve equations, 95% confidence limit values for  $\alpha$  and  $\beta$  and the correlation coefficients were calculated on a computer for all groups of fractionation data. Most of this statistical data is presented in Table 4-9. The identification numbers used in the Table correspond with the curve numbers in the various Figures.

It can be seen from the statistical data presented in Table 4-9 that zero is included by the limiting values of the beta's computed at the 95% confidence level for all uncorrected and corrected fractionation values between given pairs plotted against 65<sup>34</sup> values of coexisting

# TABLE 4-9

REGRESSION CURVES COMPUTED FOR ISOTOPIC DATA

•	•	ц		ts ·	· E	<b>0</b>	· 89 H	tt v
e N		pti	•	oin	issi ion +βx	den val	μ t t t t t t t	ati cie
urv		្រារ		lf p	igre luat = α	nfi ter	Lim	rel
0		Des			Be de	ပိုင်	А	COE
	a	vs.	b	Ň	α + β	(%)	< β <	(9)
Coexi	isting su	ulfic	les asso	ciat	ed with the He	eath	Steele B-1 orebo	dy
1	∆p-g	<b>v</b> s.	p	13	13.16-0.032	95	-0.22 to 0.15	-0.115
2	∆s-g	<b>v</b> s.	P	14	11.07-0.083	95	-0.32 to 0.15	-0.217
3	∆p-s	¥8.	р	24	2.58+0.048	95	-0.04 to 0.14	+0.239
4	∆p-s	<b>V</b> 8.	v.pos.	10	4.09+0.002	95	-0.07 to 0.07	+0.018
5	∆p-g	¥8.	v.pos.	12	14.37-0.024	95	-0.12 to 0.07	-0.185
6	∆s-g	¥8.	v.pos.	12	8.33+0.027	95	-0.07 to 0.13	+0.186
7	∆p-s	V8.	v.pos.	24	5.44-0.038	95	-0.07 to-0.01*	-0.462
D.D.F	D.D.H. samples from the B-1 orebody							
8	pulp	¥8.	v.pos.	34	16.57+0.056	90	+0.01 to 0.1	+0.332
8	pulp	¥8.	v. pos.	34	16.57+0.056	80	+0.02 to 0.09	+0.332
9	р	<b>V</b> 8.	v. pos.	16	17.16+0.045	60	+0.002 to 0.09	+0.235
10	pulp	<b>vs.</b>	v. pos.	16	7.48+0.048	60	0.01 to 0.09	+0.284
11	pulp	¥8.	v. pos.	30	7.01+0.112	95	0.07 to 0.15	+0.712
12	p	V8.	v. pos.	6	9.84+0.084	80	0.0003to 0.17	+0.610
Coexisting sulfides from other deposits								
13	Δ	¥8.	P	7	10.54+0.057	95	-0.09 to 0.21	+0.396
14	Δ	vs.	р	9	10.49-0.068	95	-0.17 to 0.04	-0.508
15	Δ 105	₹8.	р	8	-0.48+0.119	95	-0.01 to 0.25	+0.686
Corrected sulfur isotope data from all deposits								
Note: curves computed for equivalent uncorrected data are presented for comparison and are denoted by (UC)								

16	∆p-g	vs.	p	jı	.2 j	13.04+0.019	95	-0.2	to 0.24	+0.061
(UC)	∆p–g	vs.	р	1	2	13.27-0.036	95	-0.25	to 0.18	-0.117
17	Δ	<b>v</b> s.	P	נן	2	10.20-0.035	95	-0.27	to 0.20	-0.105
(UC)	Δ	<b>vs.</b>	p	1	.2	10.4 -0.075	95	-0.29	to 0.14	-0.236
18	Δ	vs.	p	1	2	2.838+0.053	95	-0.08	to 0.18	+0.273
19		vs.	p	2	24	2.657+0.051	95	-0.04	to 0.14	+0.241
(UC)	Δ p-s	¥8.	p	2	24	2.58+0.048	95	-0.04	to 0.14	+0.239
<u>Other</u>	deposi	ts								
20	∆p-g	¥8.	р	1	8	12.43+0.018	95	-0.16	to 0.19	+0.104
(UC)	Δp-g	vs.	p		8	11.93-0.004	95	-0.15	to 0.14	-0.026
21	∆5-g	<b>V8.</b>	р		8	10.89-0.020	95	-0.09	to 0.05	-0.266
(UC)	Δ_8-9	<b>V</b> 8.	p		8	10.15-0.029	95	-0.11	to 0.05	-0.347
22	Δ	¥8.	p		8	1.54+0.039	95	-0.15	to 0.23	+0.201
(UC)	Δ	¥8.	p		8	1.78+0.025	95	-0.16	to 0.21	+0.133
(UC)	Δp-s	¥8.	P		9	1.77+0.025	95	-0.14	to 0.19	0.132
All de	posits									
23	∆p-g	¥8.	p	12	20	13.00+0.011	95	-0.1	to 0.12	+0.050
24	∆s-g	<b>V8</b> .	p	2	x o	10.03-0.013	95	-0.11	to 0.09	-0.063
25	∆p-s	¥8.	p	2	0	2.96+0.024	95	-0.07	to 0.12	+0.120
26	∆р-в	₹8.	P	3	52	2.79+0.033	95	-0.04	to 0.11	+0.160
Curves computed for data from heating experiments										
27	g	¥5.	т		4	14.11+0.212	95	-0.02	to 0.44	+0.942
28	8	¥8.	т		4	18.17+0.204	95	-0.1	to 0.51	+0.900
29	8	¥8.	T		3	19.59+0.180	95	-0.23	to 0.59	+0.984
30	۵ 8-2	¥8.	T		4	13.07-0.016	95	-0.34	to 0.31	-0.144
31	۵-g	¥8.	T		3	14.47-0.039	95	-0.8	to 0.72	-0.549

pyrites. It is apparent from the similarity in the values of correlation coefficients computed for uncorrected and corrected data from the same groups that there is no consistent improvement for the corrected data; that is, the combined effect of the degree of scatter and of the degree of deviation of the best fit line from zero slope is not generally minimized for the corrected data. Where fractionation values for sulfide pairs from the B-1 orebody are plotted against the respective layers containing them, it is evident that the beta's computed at the 95% confidence level include zero in 3 out of 4 cases.

It is therefore concluded from this analysis that fractionations between p-g, s-g and p-s pairs from the B-l orebody and also from the five other deposits are essentially independent of  $\delta S^{34}$  values of coexisting pyrites. The fractionation values for given pairs from the B-l orebody are also independent of the locations of samples containing respective pairs.

# 4-10. <u>Analysis of apparent trends in 65<sup>34</sup> values for crushed ore samples</u> and pyrites from across orebody intersections

Since the larger deviations in the isotope patterns of variation for the pulps and pyrites from the B137 intersection are known to be real, it is apparent that any kind of so-called "best-fitting" curve cannot be claimed to be better than an approximation. For this reason, the simplest model might be used as a first approximation to objectively test the profile data for the existence of any significant across orebody trends in  $\delta S^{34}$  values. The principal differences between the pulp data and the fractionation data analyzed in the previous Section are that the observed variations among the B137 pulp values are known to be real within

fairly narrow precision limits and that the pulp data is complete. In view of these important differences, together with the fact that overall trends in  $\$S^{34}$  values are apparent in the Bl37 and Bl38 intersections, it is considered valid to use the linear regression model to test the hypothesis that beta  $\neq 0$  for acceptable confidence levels. Where the limiting values for beta do not include zero at acceptable confidence levels, a trend is considered to exist.

It can be seen from Table 4-9 that the limiting values for beta do not include zero at the corresponding confidence intervals. Thus the B138 and B137 pulp trends are significant at the 95 and 90% confidence levels, respectively, and the trends for the pyrites from these profiles are respectively significant at the 80% and 60% levels. One of the principal reasons that lower confidence levels are required in order to establish significant trends for the pyrites is that pyrites were often extracted from pulps which exhibited more or less extreme values. Presumably if pyrites had been analyzed from all of the pulps, the confidence limits required to establish overall trends in their variation patterns would not have differed appreciably from the confidence limits for the pulp trends. The weakness of the trend in the data for the B125-B126 profile is evident from the low (60%) confidence interval required to establish its significance. A trend cannot be considered to be established for this profile even this low confidence level, mainly because an equivalent of 3 values are missing.

It is concluded from this analysis that trends exist in the patterns of isotope variation for pulp samples from two of the three across orebody intersections. A suggestion of a similar trend is also evident in the incomplete pattern for the Bl25-Bl26 intersection. The trend for the Bl37 pyrites is similar, though weaker than the trend for the Bl37 pulps. The Bl37 and Bl38 pulp trends favour an overall enrichment in S<sup>32</sup> of approximately 0.8 and 1.2%, respectively, moving from the footwall towards the hanging wall.

#### CHAPTER 5

FRACTIONATION OF SULFUR ISOTOPES BETWEEN COEXISTING SULFIDES IN HEATING EXPERIMENTS AT TEMPERATURES OF 350 TO 500°C

#### 5-1. Introductory Statement

This series of experiments was designed to test for sulfur isotope fractionations between coexisting pyrite, sphalerite and galena over a temperature range of 250 to 550°C. The principal objective of these experiments, assuming that isotopic equilibrium could be achieved, was to determine isotopic fractionation as a function of temperature and from this to estimate temperatures at which the observed isotopic fractionations in the B-1 ores were generated.

Charges of up to 30 grams consisting of various proportions of natural and synthetic sulfides together with elemental iron and sulfur were sealed under vacuum in quartz and vycor capsules and held at temperature for periods of 2 to 12 weeks. The isotopic composition of individual sulfur bearing components was measured prior to heating. At the end of an experiment mineral separations were performed and the isotopic compositions of coexisting sulfides determined.

Unfortunately all of the vycor capsules from the 250°C experiment and 3 out of the 4 from the 450°C experiment burst during heating. Quartz, however, proved to be a satisfactory capsule material and successful runs were carried out at 350°C, 400°C and 500°C. The experimental results are presented in Table 5-1.

## TABLE 5-1

#### RESULTS OF HEATING EXPERIMENTS INVOLVING POWDERED SULFIDE MIXTURES

 $\delta s^{34}$  values of sulfur in mixture ingredients

ingredients	5s <sup>34</sup> %。		
Heath Steele, p reagent ZnS precipitated PbS(1) precipitated PbS(2)	+13.4 + 5.4 + 1.9 +11.8	0.1 0.0 0.1 0.1	(2) (2) (2) (2) (3)
mixture A, total S	+ 7.8	0.1	$\frac{1}{2}$

6S<sup>34</sup> values of coexisting sulfides extracted after heating

mixture, sulfide*	mean heating temp. °C	mean furnace temp.°C	employment of Al foil	duration of heating	<b>δ</b> s <sup>34</sup> (	%。)	
A,p A,s A,g B,p B,s B,g C,p	365 <b>±7</b>	464	affirmative	50 days	+13 + 4.7 + 3.8 + 1.7 + 1.8 + 1.2 + 3.8	0.3 0.1 0.1 0.1 0.1 0.1 0.1	(2) (2) (2/4) (2/3) (2/3) (3)
C,g D,p D,g A,p A,s A,g B?,p B?,g	408±7	454	negative	30 days	+ 1.9 0.0 - 1.5 +12.3 + 4.6 + 4.0 + 1.2 + 0.3	0.0 0.1 0.1 0.1 0.2 0.0	(2) (2) (2) (3) (3) (2) (3)
A,p A,s A,g	442 <b>±7</b>	537	affirmative	30 days	+12.8 + 5.4 + 4.7	0.2 0.1 0.0	(2/3) (2) (2)
A,p A,s A,g B,p B,s	505±7	590	negative	28 days	+12.3 + 5.7 + 4.9 + 1.8 + 1.9	0.1 0.1 0.2 0.1 0.4	(2) (2) (3) (2) (2)
B,g					+ 0.5	0.1	(2)

\* purity estimated to be better than 90%

#### 5-2. Apparatus, reagents and experimental procedure

#### i) Apparatus

The two types of capsules used in the heating experiments are shown in Figure 5-2A. The larger diameter capsules were made from 7 cm. lengths of 22 x 18 mm. quartz and 22 x 19 mm. vycor tubing and were used in the 350 and 450°C experiments. The smaller diameter capsules were made from 12 cm. lengths of 7 x 4.5 mm. quartz tubing and were successfully used in the 400 and 500°C experiments. As noted above, vycor capsules burst during the experiments.

Figure 5-2B shows the apparatus which was used as a precaution against capsule explosion during sealing under vacuum.

The apparatus used in the heating experiments comprises a 6" x 2" diameter mild steel capsule container with asbestos covered screw-on caps, an enclosing 8" x 3" diameter copper tube with detachable sheet copper ends, accommodation for three thermocouples for measuring temperatures within the capsule container as shown in Figure 5-2C, a muffle furnace and a potentiometer for measuring the E.M.F.'s of the thermocouples. With the exception of the potentiometer the apparatus used in the heating experiments is shown in Figure 5-2C. In each of the 350 and 450°C experiments, four sealed capsules containing different mixtures were supported by a framework of copper wire inside the aluminum foil lined steel container and the outer copper jacket was also covered with aluminum foil. In each of the 400 and 500°C experiments, two capsules containing different mixtures were individually supported on perforated asbestos cloth pads inside an unlined container. The capsules were separated by a perforated mild



steel partition which was firmly secured inside the container and ran parallel with its length. Only a single thermocouple, entering the steel container at its center, was used in each of the 400 and 500°C experiments, since good temperature agreement was obtained between the three thermocouples used in each of the 350 and 450°C experiments. The copper jackets enclosing the steel containers of the former experiments were not covered with aluminum foil.

ii) Reagents

The initial compositions of the mixtures used in the heating experiments are given in Table 5-2 below. The  $\delta S^{34}$  values of the sulfur in the various components are presented in Table 5-1.

#### TABLE 5-2

<u>Mixture</u>	Component	Mass (gm.)
A-	H.Steele pyrite	64.0
	reag. ZnS	53.0
	ppt. PbS1	63.3
B	reag. Fe°	30
	subl. S°	34.4
	reag. ZnS	53
	ppt. PbS1	63.3
С	reag. Fe°	29.9
	subl. S°	34.4
	ppt. PbS <sub>2</sub>	66
D	reag. Fe°	29.9
	subl. S°	34.1
	ppt. PbS	63.3

The pyrite used in the A mixture was extracted from Heath Steele pyritic ore, purified and pulverized to a fine powder in a Spex Industries ball mill. In the B, C and D mixtures reagent grade metallic iron powder and sublimed sulfur were mixed in the proportions necessary to form pyrite, with the iron slightly in excess. To each of mixtures A and B were added 3.3 grams of a mixture consisting of equal molar proportions of iron and sulfur to provide up to 4% of iron in the sphalerite formed. Lead sulfide precipitates of different isotopic composition and zinc sulfide reagent powder were added to the respective mixtures in the amounts indicated. The lead sulfide precipitates were prepared by a method similar to that described in Section 6-2 of Chapter 6.

The components of the mixtures were mixed by hand grinding in an agate mortar.

#### iii) Procedure

- a) Capsules were filled to about 1 to 2 cm. below the constrictions using a small glass funnel and a length of wire to prevent clogging of the funnel's delivery tube as shown in Figure 5-2A.
- b) Each capsule was slowly evacuated for about one hour, and tapped gently from time to time to prevent "explosive discharge" of air pockets and an accompanying loss of some of the mixture.
- c) At the end of this time an aluminum collar was moved over the constriction and the capsule partially immersed in a dewar containing liquid nitrogen. The collar was bolted into position on the safety box (see Figure 5-2B), a piece of soft asbestos sheeting was placed over it and the capsule extension

tube glassblown free under vacuum at the constriction.

- d) Capsules containing different mixtures were carefully loaded into the furnace as shown in Figure 5-2C, brought to temperature over one to two-day periods and kept at temperature for the times indicated in Table 5-1.
- e) The E.M.F. for each of the thermocouples<sup>1</sup> was measured daily using a potentiometer that was initially calibrated at room temperature for a chromel alumel thermocouple using a platinum versus platinum-10-percent rhodium thermocouple.
- f) After completion of the experiments, the charges were cooled down to room temperature over periods of 4 to 6 hours. Each of the capsules was carefully broken open and the contents transferred to a vial.
- g) A thin outer crust of whitish crystallized ZnS was formed in all of the capsules containing ZnS<sup>2</sup>. Care was taken to remove this material from the mixtures prior to further treatment. The sulfide mixtures were then crushed, sieved, washed and dried

<sup>1</sup> The thermocouple temperatures in the 350°C experiment did not usually vary by more than a few degrees with the thermocouple closest to the back of the furnace generally recording the highest temperature. The standard deviation for the overall temperature variation was found to be ±5°C. The standard deviations of the temperature variations in the 400°, 500° and the early part of the 450°C experiments are very similar to this value. When all errors involved in the measurements are considered, a maximum total extimated error of ±7°C is obtained.

<sup>&</sup>lt;sup>2</sup> The sphalerite formed within the sulfide mixtures ranged in colour from a pale brown to a dark reddish brown.

and the sulfides separated magnetically to form mineral concentrates of sphalerite and/or galena. Each of these concentrates contained small amounts of pyrite.

h) The sphalerite and galena of respective concentrates were leeched with 2:1 HCl to form H<sub>2</sub>S which was quantitatively converted to Ag<sub>2</sub>S as described in Section 6-9 of Chapter 6. Pyrite concentrates were prepared by leeching portions of unseparated sulfide mixtures. These sulfides were stored prior to burning.

#### 5-3. Results

The final sulfide mixtures were friable, though completely crystallized, fine-grained aggregates consisting essentially of pyrite and galena and of pyrite, sphalerite and galena. Small amounts of pyrrhotite were also found to be present in these mixtures. A trace of elemental sulfur was found condensed on the wall of the  $350^{\circ}$  D mixture capsule and the odour of H<sub>2</sub>S was detected in several other capsules.

The results of the heating experiments are presented in Table 5-1 and the data is shown plotted in Figure 5-3. The upper half of the Figure shows the final measured  $6S^{34}$  values of A mixture sulfides plotted against corresponding mean temperatures of the experiments. The compositions of the initial components are also indicated. The lower half of Figure 5-3 shows the measured fractionations between sulfide pairs from the various mixtures plotted against temperature. The statistical data for the regression lines are given in Table 4-9.


It is apparent from the data given in the upper half of Figure 5-3 that the isotopic compositions of all of the sulfides in the A mixture runs have changed with heating, such that the fractionations between given pairs appear to show an overall decrease with increasing temperature. While linear regression lines computed for s-g fractionations (see the lower half of Figure 5-3) appear to indicate a slight overall decrease in fractionation values with increasing temperature, this trend is not significant. The s-g fractionations vary from 0.6 to  $0.9\%_{\circ}$ . The maximum variation between initial and final  $\delta S^{34}$  values for a given component is 3% for the galena from the 500° A mixture experiment.

The initial overall range in  $\delta S^{34}$  values for B mixture components has been reduced from 5.4 to 0.6 and 1.4%, respectively, in the 350 and 500°C experiments. The p-s fractionations for the B mixture experiments are equal and slightly negative (-0.1%) and the  $\delta S^{34}$  values of the pyrites and sphalerites from the 500°C experiment are only 0.1%, heavier than their 350°C counterparts. Galena from the 500°C run, on the other hand, is 0.7%, lighter than the galena from the 350°C experiment. The differences between the initial and final sphalerite values in both mixtures are approximately 3.5%.

The largest fractionations were obtained for p-g pairs from the  $350^{\circ}$ C and  $350^{\circ}$  C mixtures. The initial differences between the components in each of the C and D mixtures were 12 and 2‰, respectively, with the lead sulfides being relatively enriched in  $S^{34}$ . The final pyrites from the C and D mixtures were found to be 1.9 and 1.5‰, heavier than the respective coexisting galenas.

The following consistencies are observed in the experimental results:-

- i) galenas are isotopically lighter than any of the coexisting sulfides, even in cases where the sulfur in the PbS precipitates was not the lightest among the initial components of a given mixture.
- ii) the s-g fractionations for the A mixture experiments are similar and there is an apparent slight overall decrease in their magnitudes with increasing temperature.
- iii) the p-s fractionations from the 350° and 500° B mixture experiments appear to be the same.

#### Discussion of results

If it is assumed that the proportions of galena, sphalerite and pyrite, as represented by elemental iron and sulfur, are approximately constant in the initial reactants and final products it is possible to test whether significant contamination has occurred among sulfides from a given mixture by comparing the calculated bulk isotopic composition of the initial mixture with the composition computed using the measured values of the final sulfides. The computed compositions are given in Table 5-3 below.

#### TABLE 5-3

Mixture	Computed initial composition	Compositions computed after heating experiments			
	· · · · · · · · · · · · · · · · · · ·	350°	400°	450°	500°C
A mixture*	+9.4 ± 0.1	+9.3	(+9.0)	+9•5	+9.4
B mixture	+1.6 ± 0.2	+1.7	-	-	+1.6
C mixture	+3.5 ± 0.2	+3•5	-	-	-
D mixture	+0.2 ± 0.2	(-0,3)		-	-

( ) one or more of the final sulfides in the mixture is contaminated

measured composition is +7.8 ± 0.1

It is apparent from these calculations that there has been serious contamination in one or more of the final sulfide concentrates in each of the 350° D mixture and the 400° A mixture. It is evident that the p-g fractionation value in the 350° D mixture is a minimum value. It is believed that the 400° A mixture pyrite has been contaminated by the lighter sphalerite and/or galena, thus accounting for the relatively light 65<sup>34</sup> value of the 400° A mixture after heating. It is considered that contamination of galena by sphalerite or vice versa is highly unlikely because the relatively large difference in the magnetic susceptibilities of these minerals ordinarily makes complete separation possible. Appreciable contamination of galena concentrates by pyrite, on the other hand, was often encountered. Fortunately acid leeching with 2:1 HCl quantitatively liberates PbS (or ZnS) sulfur but does not dissolve pyrite. It is concluded that the purities of the final sulfides from mixtures other than the 350° D and 400° A mixtures were excellent. The reason for the 1.6%, difference in the measured and calculated isotopic compositions for the A mixture is not known, but it is inferred that it is probably due to a weighing error. Since this constant error would be carried through all of the calculations for the A mixtures, it can be shown that it would not affect the relative differences between the computed compositions.

#### Significance of the experimental results

The following observations and inferences can be made from the experimental results:-

- a) appreciable exchange of sulfur isotopes has occurred between coexisting sulfides at moderate temperatures over relatively short periods of time. While it has not been the purpose of this study to investigate the nature or determine the relative importance of the exchange processes involved, it is presumed that these processes include crystallization, solid state diffusion and gaseous phase transport.
- b) the total range of isotopic variation for all of the initial components in any given mixture is consistently larger than the total range for the final sulfides of the same mixture.
- c) the results for the A and B mixtures have been strongly influenced by the differences between the nature pyrite of the A mixtures and the pyrite-forming components of the B mixtures.
- d) the results for the A and B mixture experiments strongly suggest that the bulk isotopic compositions of given sulfides

change progressively with increasing temperature and presumably also when mixtures are heated for extended periods at constant temperatures provided isotopic equilibrium has not been achieved. Comparison of the 500° and 350° B mixture results suggests that the bulk compositions of given sulfides have not only continued to change with increasing temperature but that the p-g and s-g fractionations have become larger at the higher temperature. Since this is contrary to what might be expected, it appears that at least the 350° B mixture results are probably disequilibrium results.

e) if the iron and sulfur of the C and D mixtures reacted to form pyrite before the experimental temperature had been attained, it seems likely that the bulk isotopic composition of first formed pyrite would not have been very different from the composition of the elemental sulfur. If this were so, it might be presumed that the differences between the bulk isotopic compositions of the pyrites and galenas became progressively smaller until they were equal and then continued to change with further heating until the present compositions were attained.

It is apparent that isotopic equilibrium has not been achieved in at least some of the experiments mainly because fractionations between given sulfide pairs from different mixtures held at similar temperatures do not agree within their precision limits. It is evident, however, that while equilibrium has probably not been achieved, the experiments clearly demonstrate that galena shows a consistent preference for the light iso-

tope, regardless of the composition of the initial PbS precipitates. This indicates that galena exchanges readily in sulfide systems. In view of e) above, it is suggested that if the  $350^{\circ}$  C mixture p-g fractionation is not an equilibrium value, both  $350^{\circ}$  p-g fractionations are smaller than the true equilibrium value at this temperature. While the s-g fractionations for the A mixture experiments are fairly similar and appear to show a slight overall decrease in magnitude with increasing temperature, it is possible that this apparent consistency may be fortuitous since there appears to be some evidence that the bulk isotopic compositions of the individual sulfides were continuously changing. It is conceivable that the galena might have exchanged more readily with the pyrite than did the sphalerite, thus making the s-g fractionations smaller than the corresponding equilibrium values.

It seems that the B mixture results are similar insofar as the B mixture p-s fractionations appear to be constant while the fractionation values for given associated pairs are appreciably different at the two temperatures. This appears to suggest that the rate of sulfur isotope exchange between galena and each of the associated sulfides is greater than the rate of exchange between pyrite and sphalerite. If these speculations for the A and B mixtures are correct, it appears that sulfur isotope exchange has occurred most readily between pyrite and galena. It is not implied, however, that equilibrium should be most easily attainable between pyrites and galenas. It is concluded that isotopic equilibrium has not generally been achieved in the experiments. Possible exceptions, however, are the s-g fractionations for the A mixture experiments and the p-g fractionation for the 350° C mixture.

In order to obtain some idea of the closeness of approach of the experimental systems to equilibrium systems one can compare the former with the small amount of data available for coexisting sulfides from hydrothermal sulfide ore deposits. If such deposits were not formed under equilibrium conditions, they at least represent the closest approach to equilibrium systems in nature insofar as their sulfides were probably held at temperature for very long periods of time. Tatsumi (1965) measured sulfur isotope fractionations between coexisting sulfides from ore deposits of Japan which are believed to have formed at rather low to intermediate temperatures. It was found in any given suite of coexisting sulfides that pyrite was the heaviest sulfide and galena was generally the lightest with chalcopyrite, sphalerite, bornite and tetrahedrite showing intermediate values. Fractionations between three s-g pairs from two low temperature deposits were close to +3%, while a single p-g pair from one of these deposits gave a value of +3.2%. The fractionation for a single p-s pair from an additional low temperature deposit was found to be 1.9%. Fractionations for two s-g and two p-s pairs in ores from higher temperature deposits associated with quartz porphyries and quartz diorites were found to be 1.2 and 1.7%, and 0.4 and 0.4%, It was concluded from this study that the degree of fracrespectively. tionation is higher in ore deposits formed at lower temperatures.

It seems reasonable to assume that these deposits formed over a temperature range which at least included the range over which the experiments were conducted, namely, 350 to 500°C. It then becomes apparent that the experimentally determined s-g fractionations in the A mixtures

are appreciably smaller than the collest equilibre (i.e. (i.

Comparison of the mean fractionations were found.

# 5-4. Conclusions

The following conclusions can be made from the experimental results:-

a) appreciable sulfur isotope exchange occurred between some sulfides (including pyrite formed from iron and sulfur during the experiments) of dry sulfide mixtures heated in evacuated quartz capsules for periods of 2 to 6 weeks.

- b) natural pyrite was found to exchange with the associated sulfides to only a very limited extent in all of the experiments but tended to exchange more readily at higher temperatures.
  On the other hand, synthetic pyrite formed from iron and sulfur during the experiments exchanged readily with galena but its exchange with sphalerite appears to be more difficult.
- c) the largest fractionations obtained were 1.9 and 1.5% for p-g pairs from the 350°C heating experiments.
- d) comparison of the experimental results with presumed equilibrium fractionation data for some Japanese ore deposits formed at low to moderate temperatures strongly suggests that equilibrium was not achieved in any of the experiments.
- e) comparison of the mean fractionation values for the B-1 orebody with the very limited data available for the same Japanese deposits suggests that the B-1 orebody was formed at a temperature intermediate between the temperature extremes for the Japanese deposits.

#### CHAPTER 6

# PRECIPITATION OF SOME BASE METAL SULFIDES FROM AQUEOUS

### SOLUTION AT 25°C

### 6-1. Introductory statement

The principal aim of these experiments was to test for isotopic fractionation in the precipitation of base metal sulfides from aqueous solutions at 25°C, and to determine the directions and magnitudes of any observed fractionations. A further aim of this study was to determine if sulfur isotope exchange would occur between sulfides and  $H_2S$  gas over periods of from one to twelve days.

The following experiments were undertaken:-

- i) <u>open system experiments</u> in which H<sub>2</sub>S gas of known isotopic composition was bubbled through metal salt solutions to rapidly precipitate base metal sulfides.
- ii) <u>closed system experiments</u> in which base metal sulfides were precipitated in closed vessels containing  $H_2S$  gas of known isotopic composition and were allowed to communicate with the  $H_2S$  for periods of from 25 hours to 12 days.
- iii) <u>a closed system experiment</u> in which metal sulfides of known isotopic composition were allowed to communicate with H<sub>2</sub>S gas of different isotopic composition. Each of the sulfides was contained in a small volume of distilled water.

With one exception, sulfide precipitates, reagent and Heath Steele sphalerite were burned directly to  $SO_2$ . In one case a precipitated sulfide was first converted to silver sulfide. The H<sub>2</sub>S gas samples were converted to silver sulfide and then burned. The experimental results are presented in Table 6-1.

#### OPEN SYSTEM EXPERIMENTS

#### 6-2. Experiment 1

The purpose of this experiment was to test for isotopic fractionation in the precipitation of base metal sulfides from solution with isotopically light  $H_2S_*$ 

#### i) Apparatus

The apparatus used in this experiment is shown in It comprises a pure nitrogen source (1), a lecture Figure 6-2A. bottle of high purity  $H_2S$  (2) fitted with a needle valve (3), a slightly constricted glass manifold (4) with tygon connections (5) to two  $H_{2}S$ bypass/sample tubes (6), an in-line stopcock (7), a four-way glass manifold (8) with tygon connections to four stoppered 500 ml. conical flasks (9), four stoppered 50 ml. test tubes (10), and a four-way glass exhaust manifold (11). The H<sub>2</sub>S source is connected to the glass sample manifold by rubber vacuum tubing. The remaining parts of the apparatus are connected by tightly fitting tygon tubing. Each conical flask contains a different metal salt solution and the test tubes contain distilled The flasks are supported in a metal frame and together with the water. test tubes are partially immersed in a constant temperature bath maintained at 25°C.



# TABLE 6-1

# FRACTIONATION OF SULFUR ISOTOPES IN THE PRECIPITATION OF SOME METAL SULFIDES AT 25°C

# experiment 1 (4 minutes duration)

Sample	<b>δ</b> s <sup>34</sup> % <u>, +</u> S	No.	
initial H <sub>2</sub> S prec. ZnS prec. PbS prec. CuS prec. FeS final H <sub>2</sub> S	$ \begin{array}{c cccc} -1.7 & 0.1 \\ -2.2 & 0.2 \\ -2.9 & 0.1 \\ -2.3 & 0.1 \\ -2.1 & 0.0 \\ -1.7 & 0.0 \\ \end{array} $	(2) (4) (2) (3) (2) (2)	

#### experiment 2(12 minutes duration)

initia	l sulfide	+13.8	0.1	(2)
initial	LHS	+13.6	0.0	(2)
prec.	ZhS	+13.1	0.1	(2/3)
prec.	PbS	+12.9	0.0	(2)
prec.	CuS	+13.3	0.1	(2)
prec.	FeS	+12.8	0.1	(2)
final a	sulfide	+14.3	0.1	(2)

experiment	4	(12)	davs	duration	)

initial reag. B89-3 initial reag. initial prec. prec. prec. final final reag. final	Zns , s PbS H_S ZnS PbS CuS FeS H_S ZnS , s	+5.5 +14 +27.5 -1.8 -2.5 -2.7 -2.3 -2.4 -1.3 +5 +13.4	0.2 0.1 0.1 0.0 0.1 0.2 0.1 0.1 0.1 0.2	(2) (4/5) (2) (3) (2) (2/3) (3) (1) (2) (3) (3) (1) (2) (3) (4)
final final reag.	, s PbS	+13.4 +25.9*	0.2	(4) (4)
•				•

experiment 5(10 days duration - vessel agitated daily)

initial	H_S	- 1.8**	1	,
prec.	Pfs	- 5.4*	0.1	(2)
final	H <sub>2</sub> S	- 1.5	0.1	(2)
	<i>C_</i>			

# experiment 3(25 hours duration)

initial	HS	- 1.8	0.1	(2)
prec.	Zńs	- 1.9	0.1	(3)
prec.	PbS	- 1.9	0.3	(3)
prec.	CuS	- 1.9	0.2	(2)
final	H <sub>2</sub> S	- 1.5	0.2	(3)

#### Abbreviations

prec.:	precipitate		
reag.:	reagent	grade	
	cher	nical	

\* value is suspect \*\* inferred value

#### ii) Reagents

The salt solutions were prepared shortly before the experiment. Each was made up as follows:-

- a) 61 gm. of lead acetate were dissolved in about 250 ml. of distilled water at room temperature. The solution was buffered to pH 3 to 3.5 by adding about 100 ml. of 17 N acetic acid.
- b) 41 gm. of zinc acetate were dissolved in approximately 250 ml. of distilled water and buffered with about 100 ml. of acetic acid.
- c) 28.6 gm. of cupric acetate were similarly treated.
- d) 41.5 gm. of ferrous chloride crystals (FeCl<sub>2</sub>.4H<sub>2</sub>O) were taken from a freshly opened bottle, dissolved in about 100 ml. of distilled water and rapidly filtered to remove reddish-brown oxide residues. Sodium acetate solution and 17 N acetic acid were added until a pH of 4.5 to 5.0 was obtained.

#### iii) Procedure

a) The pressure heads of the metal salt solutions above the bases of the pyrex-tygon tubes leading into individual precipitation flasks were equalized by adjusting the lengths of the short tygon tubes attached to the ends of the pyrex tubes. The pressure heads in the distilled water tubes were also adjusted so as to be less than in the precipitation flasks. Nitrogen could finally be made to bubble simultaneously through all of the firmly stoppered vessels under a pressure of not more than 12 cm. of water.

- b) The vessels were transferred in their metal container to the constant temperature bath and allowed to come to thermal equilibrium over a period of approximately one hour. Nitrogen was continuously flushed through the entire apparatus during this period.
- c) The nitrogen source was isolated and the needle value slowly opened until the  $H_2S$  began to bubble through all of the metal salt solutions. After 15 seconds had elapsed the stopcocks of one sample tube (6) were closed to isolate a sample of the initial  $H_2S$ . During the next  $3\frac{1}{2}$  minutes several adjustments of the needle value screw were made in order to ensure a relatively steady flow of  $H_2S$  in all four vessels.
- d) At the end of this time the second bypass/sample tube (6) was isolated in order to obtain a sample representative of the final H<sub>2</sub>S. The needle valve of the H<sub>2</sub>S cylinder was closed 15 seconds after this.
- e) The manifolds were quickly disconnected from the supply and exhaust tubing and moved with the reaction vessels in their container to the fume hood.
- f) Small volumes of the mother liquors were quickly removed and set aside to later test for unprecipitated lead, zinc, iron and copper.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> Excesses of all ions were indicated, showing that precipitation was continuous throughout the experiment.

- g) The flasks were then immediately filled with distilled water as a precaution against post-precipitation exchange with  $H_2S_{aq}$ . The precipitates of lead, copper and iron allowed to settle and were then decanted. These precipitates were filtered using fast 20 cm. filter papers, and washed several times with distilled water and finally with acetone. The zinc sulfide was transferred into tubes and centrifuged. The supernatant liquid was decanted and the precipitate washed several times with distilled water and finally with acetone. The dry precipitates were stored in a vacuum dessicator.
- h) The H<sub>2</sub>S gas samples were frozen down in the projecting fingers of the sample tubes (6) using liquid nitrogen. After about 5 minutes the sample tubes were glassblown free at the constrictions and then stored.

# 6-3. Experiment 2

The purpose of this experiment was to confirm the results of the previous experiment using  $H_2S$  that is relatively enriched in the heavy isotope.

#### i) Apparatus

Relatively heavy  $H_2S$  was generated in the apparatus shown in Figure 6-2B. The apparatus consists of a pure nitrogen source (1), a round bottomed reaction flask (2), a water cooled condenser (4), a stoppered 250 ml. conical flask (5), and a U-tube (6) contained in a dry ice trap (7). The components of this part of the apparatus are connected by tight fitting tygon tubing and the stopcocks and ground glass seals are greased with high temperature stopcock grease. The tubing from the U-tube (6) is connected to a bypass/sample manifold similar to that shown in Figure 6-2A. The remaining part of the apparatus is the same as that shown in Figure 6-2A.

#### ii) Reagents

Metal salt solutions were prepared as described in Section 6-2. Approximately 12 gm. of Heath Steele pyrrhotite-chalcopyrite ore of known isotopic composition was pulverized to a fine powder in a Spex Industries ball mill and this was mixed with an equal mass of granular tin metal. 350 ml. of 2:1 HCl was prepared.  $H_2S$  was generated by reacting the ore sulfides with 2:1 HCl in the presence of metallic tin<sup>1</sup> which acts as a reducing agent and prevents oxidation of the  $H_2S$ .

#### iii) Procedure

a) The powdered ore-metallic tin mixture was carefully loaded into the reaction flask (2), the ground glass joints were greased and the detachable pieces of glassware then secured in place. Approximately 200 ml. of distilled water were added to the conical flask (5) and the rubber stopper firmly fitted in position.

b) The pressure heads of the salt solutions above the bases of the tubes leading into the precipitation flasks were equalized as described in Section 6-2.

 $FeS_2 + 4H^+ + Sn^{2+} \Rightarrow 2H_2S + Fe^{2+} + Sn^{4+}$ 

<sup>&</sup>lt;sup>1</sup> Anger et al. (1966) quantitatively decomposed pyrite as well as other sulfide minerals by treatment with HCl and metallic tin. The reaction for pyrite is given as

c) The reaction vessels were partially immersed in the constant temperature bath and the manifolds connected with the  $H_2^S$  delivery and exhaust tubes.

d) Stopcocks S1 and S3 were then closed and nitrogen was flushed through the apparatus for a period of about one hour. During this time the U-tube was packed in a dry ice trap and approximately 50 ml. of 2:1 HC1 were added to the acid reservoir of the reaction flask and the rubber stopper firmly secured in place.

e) At the end of this period S2 was closed, S1 and S3 quickly opened and the acid forced into the reaction flask. After the reservoir was almost empty S3 and S1 were quickly closed and S2 reopened. More acid was added to the reservoir and the procedure repeated until approximately 350 ml. of acid had been transferred into the reaction flask. The heating collar (3) was not used.

f) Approximately one minute after the generation of  $H_2S$  had commenced the first sample tube was isolated as described in Experiment 1. The second sample tube<sup>1</sup> was isolated 10 minutes later. After one additional minute had elapsed stopcocks (7) (see top half of Figure 6-2A),S4 and S2 were quickly closed and the nitrogen flow stopped.

g) The reaction flask and precipitation vessels were disconnected and removed to different fume hoods.

h) Stopcocks S4, S2 and S3 of the reaction flask were opened and the flask set aside to cool.

<sup>1</sup> Conversion of this H<sub>2</sub>S to silver sulfide yielded insufficient of the latter for isotopic analysis.

i) Small volumes of the mother liquors were set aside to later test for unprecipitated metal ions.<sup>1</sup>

j) The sulfide precipitates and H<sub>2</sub>S gas samples were treated as described in experiment 1.

k) After about half-an-hour of cooling, excess acid was poured from the reaction flask and the residue of sulfides and metallic tin was filtered and washed several times with distilled water. The residue was subsequently dried and stored.

#### PRECIPITATION AND EXCHANGE IN CLOSED VESSELS

# 6-4. Experiment 3

The purpose of this experiment was to test for sulfur isotope exchange between final  $H_2S$  reservoir gas and base metal sulfides which were initially precipitated from solutions in contact with the same reservoir gas 25 hours earlier.

#### i) Apparatus

The apparatus is shown in Figure 6-4A. It is important to note that the component shown enclosed by the frame was not a part of the apparatus used in this experiment. The apparatus comprises a 1000 ml.  $H_2S$  reservoir (1) connected by 8 mm. pyrex tubing to a four "fingered" manifold (2) from which extend four detachable precipitation/exchange tubes (3). Each is joined to the manifold by a ground glass joint and firmly held in position by a spring. All of the stopcocks and ground glass joints were greased with low temperature Apiezon grease.

<sup>&</sup>lt;sup>1</sup> Excess of all ions were indicated.



#### ii) Reagents

Metal salt solutions were prepared prior to experiment 3 as follows: 19 gm., 11 gm. and 6 gm. of each of lead-, zinc- and cupric acetate reagents, respectively, were dissolved in separate 100 ml. volumes of distilled water and stored in stoppered pyrex bottles. Ferrous chloride solution was prepared immediately prior to the start of the experiment by reacting about 15 grams of reagent grade iron metal powder with 60 ml. of 1:1 HCl in a 100 ml. beaker which was partially immersed in cold water. After all effervescence had ceased the solution was filtered (using fast filter paper) into 20 ml. of solution containing several grams of hydroxy ammonium chloride (NH2.OH.HC1) in order to reduce oxidation of ferrous iron. NaOH solution was slowly added until the pH increased to 3 - 3.5. The solution was filtered again to remove the blue-green precipitate of ferrous hydroxide. 15 ml. of the filtrate were transferred to a precipitation/exchange tube. About 3 additional grams of hydroxy ammonium chloride reagent were dissolved in the remaining ferrous chloride solution prior to storage.

#### iii) Procedure

a) 6 to 7 ml. aliquots of the copper, lead and zinc acetate solutions were pipetted into the precipitation tubes and the pH of the solutions adjusted to about 3.5 by carefully adding small volumes of 17 N acetic acid and dilute NaOH solution.

b) The ground glass surfaces of the precipitation tubes were greased and the tubes then firmly secured in place on the manifold (2) with springs. c) The manifold was then partially evacuated using a mechanical vacuum pump and stopcock S4 closed under vacuum.

d) The  $H_2S$  gas reservoir and the precipitation/exchange vessel were clamped in position in the constant temperature bath as shown in Figure 6-4A.

e) Stopcocks Sl and S3 of the  $H_2$ S reservoir were opened and the  $H_2$ S in this section of the glassware removed using a low pressure air jet. The apparatus was then glassblown together using connecting 8 mm. pyrex tubing and the glassware was tested for leaks using a Tessler coil.

f) After waiting for about one hour, the connecting tubing was re-evacuated, stopcock Sl closed, and stopcocks S2 and S4 quickly opened in this order.

g) The precipitation/exchange vessel was gently aggitated from time to time.

h) The experiment was stopped after 25 hours by closing all stopcocks and the connecting tubing was cut.

i) The H<sub>2</sub>S reservoir and the precipitation/exchange vessel were moved to separate fumehoods where they were dismantled.

j) The sulfide precipitates were transferred to filter funnels and the precipitates of zinc, lead and copper repeatedly washed with distilled water and finally with acetone. The ferrous sulfide precipitate<sup>1</sup> was first washed with about 100 ml. of a solution containing about 5 gm. of each of hydroxy ammonium chloride and ammonium chloride.

<sup>&</sup>lt;sup>1</sup> The amount of ferrous sulfide obtained was insufficient for isotopic analysis.

k) When dry, the sulfides were transferred to vials and stored in a vacuum dessicator.

# 6-5. Experiment 4

The purpose of this experiment was twofold :-

- a) to test for sulfur isotope exchange between final H<sub>2</sub>S reservoir gas and base metal sulfides which were initially precipitated from solutions in contact with the same reservoir gas 12 days earlier.
- b) to test for sulfur isotope exchange between final H<sub>2</sub>S gas and sulfides in solutions in contact with appreciably lighter H<sub>2</sub>S reservoir gas over the same period. This is the same reservoir gas as in a) above.

#### i) Apparatus

The apparatus used in this experiment is shown in Figure 6-4A. It is the same as that used in experiment 3 except for the addition of an exchange vessel which is blown onto the tube connecting the  $H_2S$ reservoir and the precipitation/exchange vessel. The exchange vessel consists of two parts separated by a ground glass joint. The lower part of the vessel was designed to accommodate three truncated test tubes in which are contained metal sulfides in small volumes of solution. The upper part of the vessel is joined to a stopcock.

#### ii) Reagents

The base metal salt solutions prepared in experiment 3 were also used in this experiment. 134 mg., 120 mg. and 130 mg. aliquots of PbS reagent powder, zinc sulfide reagent powder and Heath Steele B89-3 sphalerite grains (200-), respectively, were loaded into small truncated test tubes.

#### iii) Procedure

a) The small truncated test tubes containing the weighed aliquots of metal sulfides were partly filled with about 2 ml. of distilled water for which the pH was about 4.5 to 5.0. These were carefully loaded into the lower half of the exchange vessel, the ground glass surfaces greased and the two halves joined and firmly secured with springs.

b) This vessel was partially evacuated, special care being taken to prevent contamination<sup>1</sup> from the floating sulfide films in the sample tubes. Stopcock S5 was closed under vacuum and the vessel set aside.

c) Approximately 12 ml. aliquots of each of the stored lead-, zinc- and cupric acetate solutions were transferred to precipitation tubes and the pH adjusted to 4 to 4.5. To a portion of the stored ferrous chloride solution (now a pale grass green colour with a small amount of pale yellow brown precipitate at the bottom) was added a small volume of NaOH solution until a pH of 4.5 was obtained. This solution was filtered and 20 ml. of the filtrate transferred to a precipitation tube.

<sup>1</sup> A small amount of spilling from the ZnS reagent tube was observed.

d) The ground glass surfaces of the precipitation tubes were greased and the tubes firmly secured in place on the manifold. The vessel was then partially evacuated and stopcock S4 closed under vacuum.

e) The apparatus was clamped in position in the constant temperature bath and the various parts joined together with 8 mm. pyrex tubing. The glassware was tested for leaks.

f) After waiting about an hour, the connecting tubing was reevacuated, stopcock Sl closed and stopcocks S5, S4 and S2 opened in this order.

g) The exchange vessels were gently aggitated for about one minute each day.

h) The experiment was stopped by closing all the stopcocks. The apparatus was dismantled and the parts transferred to fumehoods.

i) The precipitated sulfides were treated as described in experiment 3. The reagent sulfides and sphalerite were also filtered and thoroughly washed with distilled water.

j) When dry, the reagent lead sulfide and sphalerite were examined under a binocular microscope at 100 x magnification to check for possible visible contamination by the reagent Zns but no visible contamination was observed.

k) All the sulfides were stored in a vacuum dessicator.

#### 6-6. Experiment 5

The purpose of this experiment was also to test for sulfur isotope exchange between final H<sub>2</sub>S reservoir gas and lead sulfide which was initially precipitated from solution in contact with the same reservoir gas 10 days earlier. However, this experiment was different from experiments 3 and 4 in that the exchange vessel was removed from the constant temperature bath each day and its contents shaken vigorously for a few minutes. i) <u>Apparatus</u>

The apparatus used in this experiment is shown in Figure 6-4B. It consists of a sealed 500 ml.  $H_2S$  reservoir (1) connected by a pyrex crosspiece ((2), (4) and (5)) to an 8 mm. stopcock (6) which, in turn, is joined to a 12 ml. capacity solution reservoir (7). The breakseal breaker (3) consists of a 1 inch length of steel nail and a lead pellet (melted in one end of the tube) sealed in a short length of 4mm. pyrex tubing. This was carefully inserted to rest against the  $H_2S$  reservoir breakseal.

#### ii) <u>Reagents</u>

Lead acetate solution was prepared by dissolving 510 mg. of lead acetate in 10 ml. of distilled water.

#### iii) Procedure

a) The lead acetate solution was carefully pipetted into the into the solution reservoir (7). Approximately 1 ml. of 17 N acetic acid was added and the reservoir filled to the base of the ground glass surface of the stopcock by adding a small volume of distilled water. The pH of the solution was 3 to 3.5.

b) The stopcock was greased, carefully inserted and then closed.

c) A "four-membered" 8 mm. pyrex crosspiece, whose horizontal arms consisted of a constricted tube joined to a stopcock (8) and a break-seal (5), was joined to the stopcock extension of the solution reservoir. This piece was then joined to the 8 mm. tubing extending beyond the  $H_2S$  reservoir breakseal breaker.

d) The crosspiece was evacuated, tested for leaks and the stopcock extension (8) finally removed at the constriction (4) while under vacuum.

e) The apparatus was immersed in the constant temperature bath for a period of about one hour, then quickly removed, the breakseal broken and the stopcock (6) opened. It was returned to the bath as soon as possible.

f) The exchange vessel<sup>1</sup> was removed from the bath each day and its contents vigorously shaken for a few minutes.

g) After 10 days the apparatus was removed from the bath and as much of the solution and lead sulfide as possible was transferred to the solution reservoir and the stopcock closed. The apparatus was firmly clamped in a vertical position and a magnetic breaker carefully moved up against the horizontally positioned breakseal (5).

h) The  $H_2S$  sample tube was joined to the tubing extending beyond the breaker, tested for leaks, and finally isolated from the vacuum pump. The breakseal was broken and the  $H_2S$  allowed to exchange for  $l_2^4$  hours before the sample tube was closed and finally removed.

<sup>&</sup>lt;sup>1</sup> On the seventh day a hairline crack was observed at the end of the sealed constriction (4). The experiment was continued as there was no detectable odour of H<sub>2</sub>S. However, subsequent testing under vacuum revealed the existence of a small leak.

i) The solution reservoir was removed from the apparatus and its contents transferred to a filter funnel. The PbS was repeatedly washed with distilled water, and set aside to dry.

j) The PbS was later converted to cadmium sulfide and finally silver sulfide using the method described in Section 6-9. Unfortunately an increase in the nitrogen flow rate caused some HCl acid washings (see Figure 6-7C)to move over into the cadmium acetate solution and also caused a small loss of cadmium sulfide precipitate due to spilling. The cadmium sulfide precipitate was washed into a 1000 ml. beaker and converted to silver sulfide by the addition of 50 ml. of 0.5 N AgNO<sub>3</sub> solution. A copious amount of silver chloride was also precipitated with the silver sulfide. An additional 50 ml. of AgNO<sub>3</sub> was added and then concentrated ammonia until the silver chloride dissolved.

k) The silver sulfide precipitate was filtered and washed several times with concentrated ammonia and finally with distilled water. It was then dried in an oven and stored.

# 6-7. Procedure used in filling reservoirs with $H_2S$ gas

The apparatus used in filling the reservoir vessels is shown in Figure 6-7A. The leak-free reservoir vessels used in experiments 3 and 4 were blown on to an 8 mm. pyrex connecting tube from which projected 3 stopcock outlets. To each of these was attached a rubber vacuum tube leading from the  $H_2S$  lecture bottle, a similar tube leading to the mechanical vacuum pump, and a specially mounted rubber balloon, respectively. The detail of the balloon mounting is shown in the inset of Figure 6-7A.



The balloon was sealed in place by a short length of tightly fitting vacuum tubing and on outer circle of tightened wire. The  $H_2S$  reservoir used in experiment 5 was joined to the apparatus above by a ground glass joint.

The glassware comprising the apparatus was tested for leaks, and the balloon and tube leading from the  $H_2S$  source were tested for their ability to hold vacuum and retain air at a pressure of slightly more than one atmosphere. The entire apparatus was finally evacuated, the vacuum pump isolated and pure anhydrous  $H_2S$  slowly released into the apparatus until the balloon was filled to about one half capacity. The  $H_2S$  source valve,  $H_2S$  inlet stopcock and the stopcock on the extension leading to the balloon were closed and the  $H_2S$  allowed to equilibrate between the remaining part of the filling apparatus and the reservoir used in experiment 5 and the reservoirs used in experiments 3 and 4 for 1.5 and 10 hours, respectively.

The reservoir vessel used in experiment 5 was weighed before and after filling. It was sealed under vacuum by freezing down the  $H_2S$  with liquid nitrogen and the stopcock extension blown free at the constriction:(X) - see Figure 6-4B.

6-8. Procedure used to obtain gas samples from the  $H_2S$  reservoirs

The apparatus used to obtain representative gas samples from the  $H_2S$  reservoirs before and after experiments is shown in Figure 6-7B. In each case the  $H_2S$  reservoir vessel and the  $H_2S$  sample tube were clamped (only the reservoir vessel was firmly clamped) in the position shown.

When a breakseal had to be broken, as in experiment 4, a magnetic breaker was carefully inserted. The sample tube was then blown onto the tubing extending from the reservoir vessel, the sample tube clamp tightened and the weld annealed. The sample tube was evacuated, tested for leaks and finally isolated while under vacuum. In the case of reservoir vessels possessing stopcocks, the latter were opened quickly. The  $H_2S$  in the reservoir and sample tube was allowed about  $1\frac{1}{2}$  hours to equilibrate before closing all stopcocks and removing the sample tube.

Possible isotope effects involved in the removal of H<sub>2</sub>S gas samples from reservoir vessels

The technique described above is routinely used in mass spectrometry to obtain representative samples of gas from a gas reservoir. In this situation, a very small sample of gas is allowed to enter an evacuated sample space (2 to 3 cc.) from a 2 to 4 liter reservoir of gas under a pressure of usually less than 2 atmospheres. Appreciable fractionation effects can be absent for a year or more even when one sample per day is extracted. Fractionation effects do become apparent, however, as the gas pressure decreases. This effect is apparent in the following series of measurements made on consecutive  $SO_2$  gas samples extracted from a 350 ml. reservoir containing  $SO_2$  under an estimated pressure of less than 5 cm. of mercury:

Date	Measured	<b>s</b> s <sup>34</sup>	value
30/6	+12.9	(0)	
8/8	+13.1	(0)	
10/8	+13.1	(9)	
11/8	+13.1	(0)	
12/8	+13.2	(7)	

After measurement, each SO<sub>2</sub> sample was pumped away. The ratio of sample volume to reservoir volume was approximately 0.02.

No significant fractionation effect was observed in removing  $H_2S$  samples from the reservoir vessels of experiments 3 and 4 before the experiments. This is evident from a comparison of the mean of their isotopic values (averaging -1.7(6)%, for 5 analyses) with the mean value (averaging -1.6(7)%, for 4 analyses) obtained for 2 samples isolated from a continuously flowing stream of  $H_2S$  from the same source cylinder. The procedure described above was not involved in collecting the latter samples. The initial pressure of the  $H_2S$  in the reservoir vessels was slightly in excess of 1 atmosphere and the ratio of sample tube volume to reservoir volume was 0.043.

While it has not been possible to determine whether or not any significant fractionations occurred in the removal of samples from the reservoirs after the experiments (the  $H_2S$  pressures were less than one atmosphere), it can probably be safely assumed that if fractionation did occur it would favour lightening of the  $H_2S$  sulfur in the sample tube and this is not likely to have been greater than 0.1%. If measurable fractionation had occurred, however, one would have to regard observed fractionations between the final  $H_2S$  and the sulfides as minimum values.

6-9. Conversion of H<sub>2</sub>S gas to silver sulfide

Each of the  $H_2S$  filled sample tubes was connected to form part of the apparatus shown in Figure 6-7C. To stopcock outlets S4 and S5, S2, S7, and S9 were connected tightly fitting tygon tubes. The tubes leading to stopcock outlets S1-S2 and S7 were connected to the same

nitrogen source. The middle section of glassware was blown onto the pyrex tube leading into the first precipitation vessel. The latter was firmly stoppered and had an outlet leading to the second vessel. Each of these was partially filled with approximately 350 ml. of cadmium acetate solution of the following composition:-

62.6 gm. cadmium acetate

500 ml. of 17 N acetic acid

2000 ml. of distilled water.

Nitrogen was initially flushed through the Cd-acetate solutions, entering the apparatus through stopcock S7. After several minutes stopcocks S6, S5 and S4 were opened. About 15 minutes later S2 was opened periodically for 10 second intervals and finally left open after approximately one half hour. S7 was closed soon after. The  $H_2S$  was thus flushed into the first Cd-acetate precipitation tube where it was entirely absorbed. The nitrogen flow was stopped after approximately 3 hours and the GdS removed for further treatment.

The apparatus used in the conversion of the sulfur in PbS and ZnS to  $H_2S$  is also shown in Figure 6-7C. The procedure used in generating  $H_2S$  is the same as that described in Section 6-3 except that the reactants in the reaction flask were heated to about 80°C. The  $H_2S$  was flushed out with nitrogen as it formed, washed with distilled water to remove any hydrochloric acid and absorbed in the Cd-acetate solution. The nitrogen flow was stopped after 8 to 10 hours. The yellow CdS precipitate was transferred to a 1000 ml. beaker and converted to silver sulfide by adding 0.5 N silver nitrate solution in excess (usually about 50 ml.). The silver sulfide was coagulated by boiling for approximately 30 seconds, filtered using a glass wool filter, washed several times with concentrated ammonia (to remove any silver chloride present) and finally with distilled water. The silver sulfide was oven dried at 100 to 120°C.

#### 6-10. Results

The experimental results are presented in Table 6-1. The results for experiments 1 and 2 indicate that metal sulfides precipitated from solution are enriched in  $S^{32}$  relative to the reactant  $H_2S$  and that the fractionation is independent of the isotopic composition of the  $H_2S$  under these experimental conditions. In experiment 1 the sulfur isotope fractionation between the  $H_2S$  gas and the sulfides range from 0.4 for FeS up to 1.2 for PbS and average 0.7%, for the 4 sulfides. The isotopic composition of the "heavy"  $H_2S$  used in experiment 2 did not remain constant during the experiment but increased from +13.6 up to some value less than +14.3%. If the smaller value of +13.6 is used, minimum fractionations between the source  $H_2S$  and the precipitated sulfides range from 0.3 for CuS to 0.8 for FeS and average 0.6%, for all of the sulfides.

Metal sulfides were precipitated in the presence of excess  $H_2S$ in closed vessels in experiments 3, 4 and 5. In experiment 3 (25 hours duration) the fractionations between the final  $H_2S$  and each of ZnS, PbS and CuS precipitates were found to be the same, namely 0.4‰. The

fractionations in experiment 4 (12 day duration) range from 1.1 in the case of CuS up to 1.5 for PbS and average 1.2% for the 4 sulfides. It is therefore evident that there is an increase in the magnitudes of the fractionations between the final  $H_2S$  and precipitated sulfides with an increase in the duration of the exchange period. The questionable 4%. fractionation obtained in experiment 5 suggests that larger fractionations are obtainable in exchange systems that have been aggitated. No systematic variations are apparent between the isotopic values of precipitated sulfides from experiments 1, 2, 3 and 4.

As a part of experiment 4, three sulfides contained in solution were allowed to communicate with the same  $H_2S$  that was used for simultaneous precipitation of metal sulfides. The results indicate that each of the sulfides exchanged with the  $H_2S$  in slightly acid solutions and became slightly enriched in the light isotope over the duration of the experiment. The final value for the reagent PbS (after exchange) is suspect because very poor agreement was obtained between 4 separate analyses ranging from +24.7 to +26.8. Since excellent agreement was obtained between the initial duplicate values for the unreacted PbS, and the differences above are larger than the uncertainty of measurement it is concluded that the final PbS must have been isotopically inhomogeneous.

#### Discussion of results

The reactions involved in the aqueous precipitation of metal sulfides (neglecting polysulfides) with H<sub>2</sub>S gas are as follows:-
$$H_{2}S_{gas} = H_{2}S_{aq}$$
(1)

$$H_{2^{\circ}aq} = H^{+} + HS^{-} (K^{*}_{1} = 8.4 \times 10^{-8})$$
 (2)

$$HS_{aq}^{-} = H^{+} + S^{-} (K_{2}^{*} = 1.2 \times 10^{-13})$$
 (3)

$$S^{=} + M^{2+} (metal) = MS$$
 (4)

\* dissociation constants at 25°C, after Kolthoff and Sandell (1952).

The exchange reaction for which fractionations have been measured incorporates all of these reactions. The generalized reaction is:-

$$H_2 S_{gas}^{32} + M S_{2}^{34} = H_2 S_{gas}^{34} + M S_{2}^{32}$$
 (5)

The isotope exchange between  $H_2S_{gas}$  and  $HS_{aq}$  in solution has been investigated by Szabo (1950). According to his results the equilibrium constant for the reaction

$$H_2S_{gas}^{32} + HS_{aq}^{34} = H_2S_{gas}^{34} + HS_{aq}^{32}$$

is 1.006 at 25°C. Unfortunately partition function ratios are unavailable for HS<sup>-</sup> and the equilibrium constant cannot be calculated. However, the equilibrium constant for the reaction

$$H_2S_{gas}^{32} + S_{aq}^{34=} = H_2S_{gas}^{34} + S_{aq}^{32=}$$
 (7)

was calculated by Tudge and Thode (1950) and found to be 1.015 and 1.013 at 0° and 25°C, respectively. These writers believed that it is reasonable to assume that the (K-1) for reaction (6) will be about one half of (K-1) for reaction (7), thus indicating a fairly good agreement between theory and experiment. Tudge and Thode (1950) calculated a 25°C

equilibrium value of 1.009 for the reaction

$$Pbs^{32} + s^{34=} = Pbs^{34} + s^{32=}$$
 (8)

and a value of 1.004 (or 4%) for the overall 25°C reaction

$$H_2 S_{gas}^{32} + PbS^{34} = H_2 S_{gas}^{34} + PbS^{32}$$
 (9)

While it is evident that the overall direction of the isotope effects observed in the precipitation experiments is compatible with that indicated by Tudge and Thode (1950) for reaction (9) above, it appears that, with the possible exception of the results from experiment 5, isotopic equilibrium was not achieved in the experiments. It is also apparent that this overall effect could only be produced in disequilibrium reactions provided the combined effect of reactions (1), (2) and (3) has been more important than the opposite effect indicated for reaction (8). It is interesting to note that the questionable 4%, fractionation obtained in experiment 5 shows good agreement with the equilibrium value computed by Tudge and Thode. A mass balance calculation, using the measured isotope values, the weighed mass of initial reservoir  $H_2S$ (0.0254 moles of S) and the computed mass of sulfur (0.0014 mole) combined with lead as precipitated PbS, gives a satisfactory  $\delta S^{34}$  value (-1.66%) for the inferred value of the initial reservoir H<sub>o</sub>S (mean of 9 analyses is -1.71%), i.e.

$$\frac{0.024}{0.0254} \times (-1.44, av.) + \frac{0.0014}{0.0254} \times (-5.35) = -1.66\%$$

This suggests that the 4% fractionation observed between the H<sub>2</sub>S and precipitated PbS of experiment 5 is probably fairly reliable.

The results of these experiments demonstrate that if the base metal sulfides of the Heath Steele ores were initially precipitated at low temperatures from sea water it is necessary to appeal to source  $H_2S$ which was heavier than the sulfides. If most of the free  $H_2S$  escaped from the depositional environment over a period of several days it seems unlikely that  $H_2S$ -metal sulfide fractionations would be much greater than about 1%. However, if the  $H_2S$  remained in the depositional environment for long periods of time and was appreciably more abundant than the sulfide sulfur, it seems likely that the sulfide sulfur might be lighter than the source  $H_2S$  by up to about 4%. The experiments clearly indicate that the overall heaviness of the sulfide sulfur cannot be attributed to fractionation effects accompanying initial precipitation or subsequent exchange with isotopically light source  $H_2S$ .

## 6-11. Conclusions

The following conclusions can be made from the results of the 25°C precipitation and exchange experiments:-

i) base metal sulfides precipitated from solution with  $H_2S$  gas in open systems are enriched in  $S^{32}$  relative to the  $H_2S$  gas by up to about 1%. The fractionations appear to be independent of the initial composition of the  $H_2S$ .

- ii) closed system sulfur isotope exchange between H<sub>2</sub>S gas and precipitated sulfides in slightly acid solution yields larger fractionations with increasing time and might achieve equilibrium values of about 4%, over much longer periods or perhaps over periods of about 10 days if the systems are aggitated.
- iii) reagent ZnS, reagent PbS and fine grained Heath Steele sphalerite were separately contained in slightly acid solution and allowed to communicate with appreciably lighter  $H_2S$  gas in a closed system over a period of 12 days. A slight lightening of their  $6S^{34}$  values was also observed thus indicating that some exchange had occurred.
  - iv) the overall heaviness of the Heath Steele sulfide sulfur cannot be attributed to fractionation effects accompanying marine precipitation of base metal sulfides or of their subsequent exchange with isotopically lighter  $H_2S$ . If the ore sulfides were initially formed in this way it is therefore necessary to appeal to source  $H_2S$  which was at least as heavy as the ore sulfide sulfur.

### CHAPTER 7

#### INTERPRETATION OF RESULTS

## 7-1. Interpretation of the distribution of sulfur isotopes in a sample of banded ore

The isotopic values of coexisting sulfides from within two sphalerite-pyrite-galena ore bands and of pyrites immediately adjacent to these bands were determined in a large specimen of banded ore (Sample No. 29). It was found that fractionations for p-s pairs were constant and p-g fractionations showed fairly good agreement in two samples separated by about 5 inches from within the same band. The same fractionation value was found for one of the p-s pairs from the second band, while the other p-s pair showed poor agreement, perhaps due to experimental error. The isotopic compositions of the pyrites from essentially barren pyrite adjacent to the ore bands were found to be essentially the same as for the pyrites from within the bands. The overall range of variation in isotopic values for all of the 13 pyrites measured was about  $0.8\%_{o}$ .

The essentially constant fractionation values for the three p-s pairs for which good precision was obtained together with the similarity of the two s-g and p-g fractionations suggests that isotopic equilibrium has probably been attained. The similarity of  $\delta S^{34}$  values for given sulfides from within and adjacent to ore bands indicates that local isotopic homogenization has occurred with respect to given sulfides.

## 7-2. Interpretation of the isotopic fractionations between coexisting sulfide pairs

It was shown in Chapter 4 that  $\delta S^{34}$  values of pyrites from the B-1 orebody were consistently enriched in S<sup>34</sup> relative to all the other coexisting sulfides analyzed and that sphalerites were consistently enriched in S<sup>34</sup> relative to galenas. It was found that the magnitudes of fractionations for p-s, s-g and p-g pairs are fairly consistent within certain limits both within the B-l orebody and also between 5 other deposits. The mean corrected fractionations and standard deviations for p-s, s-g and p-g pairs from the same 12 p-s-g assemblages of the B-l orebody are  $0.8 \pm 0.3$ ,  $1.9 \pm 0.5$  and  $2.5 \pm 0.5\%$ , respectively. The differences between the means of the p-s and s-g fractionations and between the means of s-g and p-g fractionations were found to be significant at the 95% and 50% confidence levels, respectively. The difference between the means of p-s and p-g fractionations was significant at the 99.7% confidence level. Where good precision of measurement was obtained, it was found that the fractionations for 5 high purity p-s pairs from generally widely separated parts of the B-1 orebody were constant within the limits of precision of measurement. However, one p-s pair for which the sphalerite apparently had a relatively low iron content demonstrated that not all p-s fractionations are constant and it was suggested that a relationship might exist between fractionation values and the chemical compositions of the sulfides. With the exception of one p-s pair from the Wedge Mine where the sphalerite was found to be heavier than the pyrite, all other fractionations for p-s, s-g and p-g pairs from 5 additional deposits were found to be essentially the same as those in the B-1 orebody.

Analysis of the various fractionations as a function of the locations of given pairs within the B-1 and also as a function of the  $\delta S^{34}$ values of respective pyrites showed that the fractionations are generally independent of these parameters at the 95% confidence level. Since the precisions of the fractionation values for most of the given sulfide pairs from the B-1 orebody are unknown, an attempt was made to estimate the "true" ranges of variation. This was attempted by subtracting an assumed range of variation, which could be entirely attributed to errors of measurement assuming that fractionations for given pairs were constant, from the observed ranges. On the basis of the conservatively assumed range of 0.7%, attributed to errors of measurement, it was suggested that generally less than 1.0%, 0.8%, and 0.2%, of the observed ranges for s-g, p-g and p-s pairs, respectively, could not be attributed to errors of measurement. It was pointed out, however, that if the poorest machine precision of ±0.6% is assumed, the observed ranges can generally be accounted for. Since it was considered that this precision is probably too low it was tentatively concluded that there is probably some variation in the fractionation values for given pairs. The maximum established difference between p-s pairs was found to be  $0.7 \pm 0.3\%$ .

It was suggested by Clayton and Epstein (1958) and Epstein (1959) that consistency in the magnitudes of fractionations for 3 or more given mineral pairs is a good indication that isotopic equilibrium has been attained between coexisting minerals. Epstein (1959) suggested that if pairs of quartz and calcite formed at the same temperature in isotopic equilibrium but in the presence of water of different isotopic composition, the bulk isotopic compositions would vary accordingly but the frac-

tionations would remain constant. If this is true, the same situation should also apply to sulfide pairs formed in the presence of a fluid containing sulfur compounds of varying bulk isotopic compositions, or in the situation where pre-existing sulfides of different bulk isotopic compositions attained equilibrium at a constant temperature accompanying prolonged heating. If, on the other hand, isotopic equilibrium had either not been attained or had been attained over a fairly wide range of temperatures within a single deposit, it would be expected that the mean and range of variation in fractionation values for any given group of sulfide pairs would be generally indistinguishable from those in other groups. This situation obviously does not apply for the B-l orebody nor for the other deposits as a whole.

If it is assumed that the general consistencies in the fractionation data indicate that isotopic equilibrium was either attained or closely approached at a fairly uniform temperature in the B-1 orebody and apparently also in each of the other five deposits, some of which are widely separated from the B-1 orebody, it must also be assumed that the temperature which gave rise to these fractionations was essentially the same both within the deposits and in the immediately adjacent country rocks. A study of the silicate mineral suites in the massive sulfides and in the immediately adjacent wall rocks of the B-1 orebody supports the view that P/T conditions were fairly uniform in these rocks. Even more significant is the fact that the silicate mineral suites in the country rocks are similar, thus indicating that wall rock alteration is not evident. Hence the maximum P/T conditions attained in these settings appear to have been essentially the same and correspond to those of

regional metamorphism.

In view of the many assumptions that would have to be made in order to satisfactorily explain the observed consistencies, it is considered highly improbable that an igneous hydrothermal replacement process or any other process could have emplaced the deposits after regionaal metamorphism. However, it is possible that the deposits could have been emplaced by an igneous hydrothermal replacement process prior to or perhaps during the early phase of regional metamorphism. It is therefore concluded that regional metamorphism is the only process which satisfactorily accounts for the observed consistencies.

Unfortunately the P/T conditions of regional metamorphic facies are poorly known. Turner and Verhoogen (1960) estimated that the Greenschist Facies forms under temperatures and pressures of  $300-500^{\circ}$ C and  $P_{H_2O} = 3000-8000$  bars, respectively. Insofar as the regional metamorphic mineral suites of the Bathurst-Newcastle area suggest that the highest grade attained in the Greenschist Facies was in the lower part of the quartz-albite-epidote-biotite subfacies (Turner and Verhoogen, 1960), it might accordingly be expected that temperatures were less than 500°C and were possibly in the 350-450°C range. A single  $0^{18}/0^{16}$ analysis on a quartz-magnetite pair from the Drummond Iron Mine reported by Kalliokoski (1965) suggested a temperature of 515°C, which is in excess of the expected maximum based on Turner and Verhoogen's estimate.

The biotite in the rocks enclosing the sulfide deposits shows evidence of retrograding to chlorite. This naturally raises the question as to whether retrograde metamorphism would cause re-equilibration of sulfur isotopes at progressively lower temperatures. The fact that relatively small fractionations are observed between sulfides from deposits formed at intermediate temperatures suggests that isotopic fractionations are frozen-in at these temperatures. This is observed, for example, in some Japanese deposits (Tatsumi, 1965) and also in the New Calumet deposit of Quebec.

It might thus be expected that heating at lower temperatures alone would not produce significant re-equilibration between massive coexisting sulfides. Insofar as re-equilibration of sulfur isotopes between sulfide species presumably necessitates the breaking of metal-sulfur bonds. it is anticipated that recrystallization accompanying dynamic alteration of sulfide ores might greatly facilitate this process at lower temperatures, if it is at all possible. Since some of the textural features in the stratiform deposits in question are believed by Kalliokoski (1965) to have resulted from dynamic effects accompanying regional metamorphism. it might be expected that fractionations between coexisting sulfides from such deposits would show some variation and that the smallest fractionations are probably most representative of the highest regional meta-While the samples selected for isotopic study did morphic temperature. not include ores showing marked deformation features, all consisted of crystallized sulfides in which the mineralogical banding showed at least It was mentioned earlier that some slight evidence of deformation.

variation of fractionations is evident at least among p-s pairs. The established constancy of fractionations among 5 widely separated p-s pairs while another for which the sphalerite appeared to be relatively deficient in iron was different from the others by 0.7 ± 0.3% suggests that compositional variations should not be overlocked. If, however, the 5 larger p-s fractionations were largely due to retrograde effects, it is difficult to explain the excellent agreement between these values since one might expect an approach to constancy of isotopic fractionations only among pairs showing the smallest fractionations. Perhaps this situation is more easily explained on the basis of a model in which it is assumed that essentially uncrystallized mixtures of sulfides of essentially the same isotopic composition were subjected to regional metamorphism. Heating and recrystallization accompanying metamorphism might then be expected to generate fractionations that would approach larger equilibrium values. This implies of course that the smaller fractionations for given sulfide pairs are disequilibrium fractionations which have not attained equilibrium values perhaps due to factors such as variations in grainsize, sulfide-gangue relationships, etc. Unfortunately it is not possible to resolve this problem at this time. However, if retrograde effects were responsible for the apparent variations. estimated minimum fractionations would be approximately 0.6 -0.7% for p-s pairs, 1.4% for s-g pairs and 2.1% for p-g pairs.

It is concluded that the general consistencies in the isotopic fractionation values between given coexisting sulfide pairs from the least deformed ores, from different parts of the B-1 orebody and between all 6 of the deposits investigated strongly supports the view

that the fractionation values closely approach equilibrium values that were produced at a fairly uniform temperature. The similarity in the metamorphic mineral suites in the country rocks and the enclosing rocks of the deposits together with those of the ores attests to the fact that all the suites apparently belong to the lowest part of the quartz-albiteepidote-biotite subfacies of the Greenschist Facies of regional metamorphism. The within deposit and between deposit uniformity in temperature suggested by the fractionation data is thus supported by independent geological evidence, and these facts together are considered to indicate that the massive sulfide deposits have been subjected to regional metamorphism. The possibility that variations in isotopic fractionations between p-s pairs from within the B-l orebody might be due to retrograde effects cannot be assessed at this time. It is suggested that compositional variations among sulfide species might be an important factor in determining equilibrium fractionations at given temperatures.

## 7-3. Interpretation of the results of the heating experiments

The results of the heating experiments demonstrate that appreciable sulfur isotope exchange occurs between sulfides of dry sulfide mixtures over the temperature range 350 to 500°C in relatively short periods of time. Galenas were found to be consistently enriched in S<sup>32</sup> relative to coexisting pyrites and sphalerites and synthetic pyrite was found to exchange more readily with associated sulfides than natural pyrite. Pyrite-galena fractionations of 1.9 and 1.5%, were the largest obtained and it was suggested that these are probably smaller than the 350°C equilibrium value. A comparison of the experimental results with

presumed equilibrium fractionation data for some Japanese deposits which are considered to have formed at least over the same temperature range suggested that isotopic equilibrium was not achieved in any of the experiments.

While it has not been possible to estimate the temperature or narrow range of temperatures at which the Heath Steele sulfides equilibrated, the experiments serve to illustrate that sulfur isotope exchange is rapid in sulfide systems at intermediate temperatures. In view of this, it seems highly probable that isotopic equilibrium would at least be closely approached if not achieved during long heating periods at the higher temperatures of Greenschist Facies regional metamorphism in either massive sulfide deposits consisting of crystallized sulfides formed at lower temperatures and therefore having larger fractionations, or in essentially of uncrystallized sulfide mixtures in deposits consisting which isotopic differences between given sulfides might have been variable or non-existent. It is uncertain, however, whether or not regional metamorphism would cause extensive re-equilibration between already crystallized sulfide ores which equilibrated at a temperature higher than the regional metamorphic temperature. It seems reasonable to expect that temperatures within given massive sulfide deposits should at least closely approach constant values during regional metamorphism. especially in view of the excellent heat conductive properties of massive sulfide ores.

It is concluded that the results of the heating experiments cannot be used to determine the equilibrium temperature of regional metamorphism, since it is not known how closely the observed fractionations approach equilibrium values.

## 7-4. Interpretation of across orebody trends in sulfur isotopic compositions

It was shown in Chapter 4 that slight overall trends in isotopic composition of total sulfur favouring an enrichment in S<sup>32</sup> towards the hanging wall were evident in two diamond drill hole profiles and was also The sulfur in pyrites extracted from some weakly developed in a third. of the crushed ore samples showed very similar patterns of variation and reflected all the major variations in the total sulfur trends. It was also demonstrated from the assay values that the total sulfur trends are largely due to the contribution of sulfur from pyrite. The total sulfur trends appear to continue into the disseminated sulfides of the footwall metasediments, particularly in the case of the B138 intersection and apparently also in the case of the B137 intersection. The patterns of sulfur variation are characterized by a "saw-tooth" type of variation which covers a total range of variation of about 3.5%, in the B137 intersection. Some parts of the trend patterns appear to be more or less smoothly continuous and usually terminate in abrupt discontinuities.

While it is evident that the isotope trends are not dependent on the abundances of lead, zinc, silver or copper in the profiles, it is known that consistent across orebody trends also exist for these metals. The latter are characterized by an overall increase in the abundances of lead, zinc and silver and a corresponding decrease in copper moving across the deposit from the footwall towards the hanging wall. A feature which is shared by the sulfur isotope and base metal trends is their marked variability moving across the deposit but no in-detail relationship appears to exist between the trends. For example, the  $SS^{34}$  values of pulp pyrites do not appear to correlate with the abundances of any one of lead, zinc, silver or copper. It seems reasonable to assume, however, that a process which is capable of fractionating base metals should also be capable of fractionating sulfur isotopes. It is therefore considered possible that the isotope and base metal trends may be genetically related.

The question as to whether these trends might be primary features or secondary features resulting from regional metamorphism must be considered. While it has been shown that isotopic homogenization among given sulfides may occur locally on the scale of the mineralogical layering, it is evident both from the isotopic ranges of given sulfides as well as from the variation in total sulfur values that isotopic homogenization can be no more than a local phenomenon within the B-1. Inasmuch as regional metamorphism would be expected to homogenize rather than generate isotopic differences among given sulfide species throughout the deposit, it is considered that the existing variation must be of premetamorphic origin. However, the fact that localized homogenization is evident, suggests that regional metamorphism probably reduced the premetamorphic range of isotopic variation.

## 7-5. Interpretation of the distribution of sulfur isotopes in footwall and hanging wall rocks and in the B-1 orebody

The mean, range of variation and standard deviation for the disseminated sulfides in the footwall rocks is +14.6, 0.9 and ±0.3%, respectively. The mean and range of variation for 69 out of 71 pulps from the B-1 orebody are respectively about +13.9 and 2%. The mean, range and standard deviation for all 71 pulps which include two appreciably lighter values are +13.8, 5 and ±0.5%, respectively. The mean, range of variation and standard deviation for 12 separate sulfides including 4 sphalerites and 2 galenas from the hanging wall rocks are respectively By way of comparison, the overall range of varia-+16. 8.6 and ±2.6%. tion of all the individual sulfides from the B-1 orebody is 6.2%. The difference between the means of the footwall and B-l orebody pulp values is  $0.8 \pm 0.7\%$  at the 68% confidence level. The mean of the  $\delta S^{34}$  values for the 12 hanging wall sulfides differs from the mean of the B-1 pulp values by 2.2  $\pm$  1.8%, at the 50% level.

Insofar as the heavier sulfur values of the disseminated sulfides of the footwall pulps from the B137 and B138 intersections appear to be continuous with the values in the lower parts of the B-1, it is considered probable that these values are representative of the sulfur values in the footwall metasediments immediately adjacent to the deposit. Even if this generalization is not true, it is apparent that at least the sulfur values of the disseminated sulfides immediately below the B138 and probably also for those below the B137 intersections are related in a systematic way to the sulfur values in the B-1 orebody. Since 5 of the 12 values from the hanging wall rocks are heavier than the heaviest sulfide value from the B-1, it is considered that a "discontinuity" in  $6S^{34}$  values probably exists above the B-1 orebody. Presumably the mean  $\delta S^{34}$  values for hanging wall pulp samples would differ significantly from the B-1 pulp values at least at the 68% confidence level, especially since total sulfur values can be expected to have smaller ranges than the sulfur in individual sulfides.

The apparent overall continuity between the isotopic values moving from the disseminated sulfides in the immediately adjacent footwall metasediments up through the B-l orebody to the hanging wall contact is interpreted as probably indicating that this sulfur was derived from the same source and that the observed variations reflect isotopic changes in the source sulfur. Apparently either the same source, or a similarly behaving source has given rise to the base metal zoning in the B-l which also appears to continue into the footwall rocks, as evidenced by their generally high Cu/Zn + Pb ratios. The apparent relative enrichment in S<sup>34</sup> in the hanging wall rocks is interpreted to indicate that the isotopic composition of the source sulfur changed for some reason, or perhaps that this sulfur has been derived from a related or modified source.

# 7-6. Significance of isotope effects accompanying precipitation of metal sulfides from aqueous solutions at 25°C

The results of the precipitation experiments conclusively demonstrate that precipitated sulfides of iron, copper, lead and zinc are enriched in  $S^{32}$  by up to about 1%, relative to the isotopic composition of source  $H_2S$  when precipitation takes place in aqueous solution at 25°C. Larger fractionations ranging up to about 4%, appear to be attainable

where precipitated sulfides are allowed to remain in solution in contact with the source H<sub>o</sub>S for extended periods of time. Lead and zinc sulfide powders together with 200-325 mesh sphalerite grains were found towerchange slightly with isotopically lighter H<sub>2</sub>S in aqueous solutions having pH's of approximately 4. Tudge and Thode (1950) estimated the 25°C equilibrium fractionation between H<sub>2</sub>S and PbS to be 4% favouring an enrichment of  $S^{32}$  in the PbS. Hence the direction of the fractionation between PbS and H<sub>2</sub>S determined in the experiments is in agreement with. the direction of theoretically predicted equilibrium fractionation. It is interesting to note that studies of the sulfur isotopic composition of  $SO_4^{-}$ , free S<sup>-</sup>, elemental sulfur and pyrites from recent marine sediments by Thode et al. (1960) and Kaplan et al. (1963) demonstrated that S<sup>-</sup> was generally isotopically heavier than any of the other reduced forms of sulfur. Kaplan et al. (1963) reported that the average pyrite was found to be 23% lighter than the average S<sup>-</sup> and FeS was found to be about 14% lighter. By way of comparison Thode et al. (1960) estimated the 25°C equilibrium fractionation between S<sup>-</sup> and PbS to be about 9%.

It is concluded from the results of the experiments that disequilibrium fractionations between sulfur in  $H_2S$  and sulfide sulfur of up to about 1%, are obtained in the rapid precipitation of metal sulfides of iron, zinc, copper and lead from aqueous solution at 25°C. While it is probable that precipitation of sulfides from aqueous solutions at higher temperatures would yield slightly different fractionations with the source  $H_2S$ , it is expected that the overall direction of the fractionation will be the same since the two step dissociation of  $H_2S_{aq}$  to S<sup>-</sup> should remain the rate controlling step in this disequilibrium process. Equilibrium fractionations of up to about 4% favouring an enrichment of  $s^{32}$  in the sulfide at 25°C might be attainable for metal sulfides other than lead provided the sulfides remain in intimate contact with the source H<sub>2</sub>S for extended periods of time. Obviously appreciable lightening of the sulfide sulfur would only be observed with time where the dissolved  $\mathrm{H}_{2}\mathrm{S}$  reservoir is much larger than the sulfide sulfur reservoir, even in a situation where isotopic equilibrium were attained. It is considered unlikely, however, that any appreciable exchange might be expected to occur between either the dissolved  $H_{p}S$  or the sulfide sulfur and sea water sulfate sulfur at relatively low temperatures due to the considerable strength of sulfur-oxygen bonding in sulfate. Thus it seems reasonable to expect that if the stratiform sulfides were precipitated on the sea floor from available H<sub>2</sub>S it can safely be assumed that the isotopic composition of the latter was enriched in  $S^{34}$  relative to the metal sulfides.

#### CHAPTER 8

EXAMINATION OF PROPOSED THEORIES OF ORE GENESIS: A SUGGESTED MODEL

## 8-1. <u>Summary of the features of stratiform deposits in the Bathurst-</u> Newcastle area

#### Distribution

The stratiform deposits occur in folded Ordovician Tetagouche rocks. They are largely confined to the quartz-feldspar augen schistgreenstone belt surrounding an acid volcanic core which may stratigraphically overlie the former association (Davies, 1966). According to McAllister (1959), the Murray Brook and New Larder U deposits which are isolated from this belt also occur in metasediments in close association with similar acid pyroclastic units. With the exception of one deposit occurring in Ordovician rocks close to the Rocky Brook-Millstream Fault, all the vein-type deposits occur in less intensively deformed Silurian rocks to the north.

The occurrence of the "porphyry"-greenstone association in the eugeosynclinal sequence is interpreted to coincide with an early period of deformation in the eugeosyncline which was accompanied by outpouring of basalts and contributions by explosive acidic vulcanism.

#### Geological setting

The stratiform deposits in the "porphyry"-greenstone belt occur in metasediments either in contact or in close association with conspicuous "porphyry" units which are generally believed to consist largely

of acidic pyroclastic material. The metasediments belong to the intermediate Greenschist Facies of regional metamorphism and appear to have been derived from argillites, cherty argillites with thinly interbedded siltstones, graphitic sediments and some iron formation rocks. The detrital metasediments appear to be largely composed of volcanic detritus. The stratiform deposits generally have lenticular outlines and are conformably enclosed by metasediments/"porphyry" which may either occur in crests or troughs of folded structures or in the limbs of larger folded structures. Shearing is often intense in the enclosing rocks. In contrast, the vein-type deposits have sheet-like forms and are characteristically discordant with the enclosing rocks.

#### Mineralogy

The larger stratiform deposits consist essentially of massive pyrite and in places contain economic concentrations of sphalerite, galena and usually less abundant chalcopyrite. Chalcopyrite-pyrrhotite ores may occur in immediate association with the former type or as separate bodies, often in close proximity to the zinc-lead bodies. Where these two types of mineralization occur together within a single deposit or separately, the chalcopyrite-pyrrhotite type appears to be furthest removed from locally abundant "porphyry". The zinc-lead bodies frequently exhibit well developed mineralogical banding which roughly parallels the stratification in the enclosing rocks. The chalcopyrite-pyrrhotite bodies generally do not exhibit banding but commonly show transgressive relationships with the zinc-lead type ores and/or the enclosing metasediments. The non-opaque mineralogy in the massive sulfides is similar

to that in the wall rocks and the country rocks. Definite wallrock alteration has not been identified in the case of the stratiform deposits but is recognized in the case of the vein type deposits which have similar mineralogies except for the relative abundance of arsenopyrite.

## Previous sulfur isotope studies

Most of the stratiform deposits have narrow spreads of about 6%, but several have ranges of variation of up to about 15%, and the means range from about +7 up to about +15%. Sedimentary sulfides show a total spread of approximately 40%, and a mean close to -5%. The sulfide values in the "porphyry" are similar to stratiform sulfide values. The appreciably lighter sulfur in the intrusive granites and gabbros appear to be similar to the sulfides in most of the vein-type deposits. The mean values of stratiform deposits occurring along strike are very similar and the means for those situated stratigraphically closer to the acid volcanic core rocks appear to be generally lighter. The relatively narrow range of sulfur isotope variation for given deposits has been suggested to indicate a relatively homogenized source for the sulfur. Lead isotopes

The lead isotope abundances in the stratiform and vein-type deposits are similar and fit a single U-Th-Pb growth curve. This is interpreted as suggesting that the leads of the ores have been derived from the mantle and deposited without significant contamination with highly radiogenic lead. They are therefore believed to be representative of the source lead at the time of separation from the mantle. Model lead ages of 270 to 470 million years have been determined for these leads. Geothermometer studies

Although temperatures generally in the 450 to 500°C range have been determined using the sphalerite and pyrrhotite geothermometers these cannot be considered reliable.

### 8-2. Summary of features in the Heath Steele B-1 orebody

- i) The B-1 orebody occurs between footwall schists composed mainly of quartz, chlorite and muscovite and a thick cover of quartz-augen schist (quartz "porphyry"). The ore zone and its enclosing rocks occur on the flank of some folded structure and dip to the north at about 70°. Whitmore (1957) suggested that the "porphyry" stratigraphically overlies the metasediments.
- ii) The B-l orebody is a thick lenticular body of massive sulfide which exhibits mineralogical banding but this has been destroyed in places as a result of deformational effects. Bands of metasediment and "porphyry" type rocks are interlayered with the massive sulfides in parts of the deposit and minor developments of "porphyry" also occur in the footwall.

The "porphyry" has "plug-like" outlines in section in some of these locations and is possibly of intrusive origin. Irregular "pod-like" bodies consisting of coarse grained quartz-feldspar intergrowths occur with and without minor amounts of coarse grained sulfides in some parts of the deposit. It is believed that these may be genetically related to the "porphyry".

- iii) The deposit is composed essentially of pyrite and contains lesser amounts of sphalerite, chalcopyrite and galena. Pyrite together with pyrrhotite, magnetite, chlorite and quartz constitute the principal gangue minerals. Mineralogical zoning favouring an overall progressive enrichment of zinc, lead and silver and a progressive decrease in copper moving from the footwall towards the hanging wall "porphyry" is evident.
- iv) The non-opaque mineralogy of the ores, wall rocks and country rocks is characterized by the development of abundant quartz, chlorite and muscovite, but traces of biotite have been found in some of the more distant wall rocks. This assemblage belongs to the quartz-albiteepidote-biotite subfacies of the Greenschist Facies of regional metamorphism, provided the biotite is of regional metamorphic origin. It is possible, however, that the biotite might have been produced by local contact metamorphic effects associated with minor hydrothermal activity related to the formation of the "porphyry". v) A sulfur isotope study of the isotope abundances in coexisting sulfides from the B-1 orebody indicated that fractionations between given mineral pairs are fairly consistent and are not related to locality or the  $\delta S^{34}$  values of respective coexisting pyrites. The fractionations for similar pairs from 5 other stratiform deposits are very similar and it was concluded that isotopic equilibrium was either attained or at least closely approached in the B-1 and between the other deposits in response to regional metamorphism.

While local homogenization with respect to given sulfides is clearly indicated, complete within deposit homogenization has definitely not been attained as evidenced by the spread in  $\delta S^{34}$  values for given sulfides. Across deposit trends favouring an overall enrichment in  $S^{32}$  towards the hanging wall are evident for both pulps and pyrites from two profiles and a similar though much weaker trend is apparent in a third profile. The  $\delta S^{34}$  values of sulfides in the footwall metasediments appear to be related to the values of sulfides in the orebody but the sulfides in the "porphyry" appear to be appreciably heavier than the latter. The trends are believed to be pre-metamorphic features.

# 8-3. Possible relationships between across deposit base metal zoning, sulfur isotope trends and the footwall "porphyry"

The locations of higher grades of zinc-lead-silver ore in any given layer (i.e. A to E) occur in parts of layers which generally overlie each other, such that the "zones" of highest Zn, Pb and Ag concentration have cone shaped forms whose axes project through the orebody essentially normal to the mineralogical layering. Zoning is also evident in the plane of the layering moving radially away from the axes of these "zones" or "centers". The greatest variation is across the layering rather than within it, especially when intersections are closely spaced. "Porphyry" occurs in contact with the footwall massive sulfides in the vicinity of the lead-zinc-silver "centers" and in places it occurs as "plug-like" bodies which project into both the metasediments and the massive sulfides. A spatial relationship appears to exist between these features. It is

also apparent that across deposit base metal trends, the sulfur isotope trends and the "centers" may all be genetically related since the directions of these trends and the "axes" of the "centers" are all essentially normal to the stratification in the enclosing rocks.

## 8-4. <u>Relationship between base metal zoning in stratiform deposits and</u> the stratigraphy of associated rocks

It was shown in Chapter 2 that there is a remarkable consistency between the pattern of base metal zoning in "volcanic" type stratiform deposits similar to those in the Bathurst-Newcastle camp and the stratigraphy of associated rocks. This feature is evident in deposits where the stratigraphic relationships are known and has been found to occur in deposits in Europe, Japan, Australia and in other deposits in Canada. The Mount Isa deposit of Australia is the only deposit known where this consistency does not apply. In this deposit copper-rich ores occur separately from lead-zinc ore lenses in different though probably equivalent facies (Stanton, 1962-63). With the exception of this deposit, the base metal zoning is characterized by relatively greater abundances of zinc and lead towards the stratigraphic tops while copper tends to be more abundant towards the bottoms of single Zn-Pb-Cu or essentially copper-rich deposits. If, on the other hand, chalcopyrite-pyrrhotite ore is abundant, it may either occur in intimate association with Zn-Pb-Cu ore towards the bottoms of single deposits or occur as separate deposits stratigraphically below Zn-Pb-Cu type deposits.

This relationship has also been observed in deposits occurring in overturned strata. So far there do not appear to be any deposits which show reverse relationships. According to Whitmore (1957), the "porphyries" in the Heath Steele Mine area stratigraphically overlie the metasediments and therefore the stratiform deposits. Hence, on the basis of this suggested relationship, the zoning relations in the Heath Steele B-1 and A deposits are in agreement with the above-mentioned consistency. The base metal zoning in the Anaconda Caribou and the Heath Steele D deposits appear to be related to nearby "porphyry" in the same manner as the B-1 orebody.

The only reasonable interpretation for this remarkable consistency, as Roscoe (1965) pointed out for the Matagami deposits, is that the deposits were emplaced while the enclosing strata were in essentially horizontal positions. The character of the zoning indicates that hydrothermal solutions were initially enriched in copper and later became more enriched in zinc and lead. A similar relationship is observed in zoned deposits closely associated with igneous intrusive source rocks (e.g. the Butte, Montana deposit) and such relationships are generally believed to result from changing P/T conditions, with the zinc and lead rich ores probably forming at lower temperatures (Bateman, 1958, p. 314-315). However, the fact that rocks overlying some of the Matagami deposits are unmineralized and unaltered while those below the deposits are both mineralized and altered (Roscoe, 1965) is difficult to explain unless it is accepted that ore formation ceased prior to the deposition of the overlying strata.

## 8-5. Examination of the postulated origins for stratiform deposits in the Bathurst-Newcastle area

For a given theory to be considered reasonable it should satisfactorily account for the features observed in a deposit, and if some of these are secondary the ore forming process must be convincingly shown to pre-date such features. In addition, it is generally required that the presumed processes involved in a given mode of origin can also reasonably relate the deposits in space and time with a potential source or sources for both the base metals and the sulfur and, if these are not evident, to provide some reasonable explanation for their absence.

Stanton (1960d) suggested that the chief sources of sulfur for ore sulfides are:

- i) sulfur-bearing exhalations from mafic and primary granite or granodiorite intrusives.
- ii) sulfur compounds expelled during granitization, and hence derived from a wide variety of sediments and pyroclastic rocks.
- iii) sulfur compounds exhaled during vulcanism, and particularly those derived from beneath the continental crust.
- iv) older evaporite beds.
  - v) older sedimentary sulfides.
- vi) ocean water sulfate.

Sources i), ii) and iii) are also likely sources for base metals but v) and vi) are possible sources. One limitation which must be considered in examining the various theories of genesis with relation to the stratiform deposits is that the lead isotope data suggests that significant contamination with crustal leads or radiogenic materials has not occurred. With respect to the sulfur isotope data, any theory which is considered reasonable should account for

- i) the general heaviness of the sulfur and the similarity in the isotopic means for deposits occurring along strike, but not necessarily occurring in close geographic proximity.
- ii) the narrow range in isotopic variation for given deposits.
- iii) the across deposit sulfur isotope and base metal trends in the
  - Heath Steele B-1 deposit.

These features together with some of the more general features are examined below in terms of the presumed requirements of the modes of origin which have been proposed so far.

## An igneous hydrothermal replacement origin

An igneous hydrothermal replacement origin proposes that moderate to high temperature hydrothermal fluids containing base metals and sulfur are derived from primary intrusive igneous rocks and that these fluids are transported to favourable structural sites where host rocks are selectively replaced. Hydrothermal fluids are probably also produced by granitization of volcanic/sedimentary rocks at the bottoms of geosynclinal sequences but the mechanisms of transport and ore emplacement at higher levels in the crust would be essentially the same. Shear and fault zones are appealled to as feeder channelways and fold crests/troughs are considered particularly favourable for ore emplacement provided the rocks are suitable for replacement. Mineralogical zoning is usually attributed to deposition from hydrothermal solutions over a range of P/T conditions and mineralogical banding is generally presumed to result from selective replacement of sedimentary bands caused by initial compositional variations in the host.

Although Roy (1961) claimed that the Brunswick No. 6, No. 12 and New Larder U deposits show a definite spatial relationship to the Bathurst granite and that similar spatial relationships are shown by a number of deposits around the Nepisiguit River granite, spatial relationships have not been consistently demonstrated between stratiform deposits and exposed granite or other intrusive rocks. It does not necesarily follow, however, that possible source rocks do not occur at depth. Age relations between exposed granites and model lead ages are ambiguous and probably misleading because of a possible ±100 m.y. uncertainty attributed to the lead ages (Russell and Farguhar, 1960, p. 58). The similarity in the lead isotope abundances and the overlap in sulfur isotope ratios from a few of the deposits has been cited as evidence that both vein-type and stratiform deposits are genetically related. It does not necessarily follow, however, that both types of deposit were emplaced at the same time and there are differences which suggest that the deposits may have different geological histories. The chief differences are the occurrence, with one exception, of the vein-type deposits in Silurian rocks, the presence of wall rock alteration effects adjacent to the ore veins, the relative abundance of arsenopyrite in the veintype deposits and a marked difference in the sulfur isotope abundances between most of the representatives from both classes.

Although it seems reasonable to invoke a possible relationship with structure in the case of the B.M. & S. No. 6 and No. 12 deposits, the structural settings of the stratiform deposits, in general, are not of a consistent character and there does not appear to be any convincing evidence that mineralizing solutions were introduced along fault or shear zones associated with folding. These features together with the absence of convincing wall rock alteration effects are fairly serious criticisms.

While the textural relations between the sulfides were at one time considered good evidence that the ores are of igneous replacement origin, it has been suggested that similar relationships might also be produced by recrystallization accompanying regional metamorphism. Even "lattice-type" intergrowths consisting of bornite and chalcopyrite, which were once believed to form by "chilling" of hydrothermal solutions, have been produced by slow cooling of sulfurrich natural bornites (Brett, 1964). Since Brett and Yund (1964) suggested that the maximum temperature of formation of sulfur-rich bornites is less than 75°C and demonstrated that it is possible to exsolve chalcopyrite from natural representatives on heating at 75 to 400°C it does not seem unreasonable to expect that these textures, if not of supergene origin, may also form in response to heating accompanying regional metamorphism.

It does not seem reasonable to appeal to fractionation of sulfur isotopes during separation of metals and sulfur from a parent magma in the crust in order to account for the general heaviness of sulfur in the stratiform deposits since sulfur isotope ratios measured in unequivocal

hydrothermal deposits so far are not appreciably different from the sulfur in parent igneous rocks. It seems reasonable to expect that if serious contamination with heavy sulfur occurred, it took place either at the source or during transportation to the site of deposition. If it is assumed that the sulfides in the "porphyries" are genetically related to the ore sulfides, which seems reasonable in view of their close spatial relationship, it does not appear that there is any likely source of heavy sulfur in Ordovician rocks in the camp since evaporites appear to be absent. It seems that the only source of sulfur in these rocks is present in sedimentary pyrites which have a mean value of approximately -5% (Tupper, 1960). It is unlikely, therefore, that contamination with this pyrite sulfur during transport would produce the observed enrichment in S<sup>34</sup>. While it is uncertain whether fractionation processes accompanying transportation through unique channelways over varying distances might produce isotopic heavying if sulfides were deposited along the way, it seems unlikely that such fractionation effects would give rise to such similar mean ratios. Hence, in view of the apparent difficulty of producing such similar mean values either by contamination or fractionation effects accompanying transportation, it seems that contamination by heavy sulfur at the source is the most likely of the various possibilities and that assimilation or exchange with a large reservoir of heavy sulfur by the source magma must be invoked in order to account for the general heaviness of the sulfur. Such a source is not evident nor does it seem reasonable to expect one in consolidated Ordovician eugeosynclinal rocks. In view of this, Dechow's (1960) model (see Section 1-17) for initially obtaining heavy sulfide sulfur

for the Heath Steele Deposits is perhaps feasible only if it is assumed that his Ordovician "source rocks" contained trapped connate water and that the mean  $6S^{34}$  value for total sulfur in these rocks was greater than about  $\pm 10\%$ . The heaviest  $SS^{34}$  value for total sulfur determined in recent marine sediments so far is  $\pm 7\%$  (Thode et al., 1960). By analogy, a mean value of up to  $\pm 10\%$ , is feasible for wet Ordovician sediments near the sediment-water interface since Ordovician marine sulfate-was about 3%, heavier than the present value (Thode and Monster, 1963). It seems reasonable to assume, however, that sediments from immediately below the sediment-water interface will be different from those occurring in the basal parts of a eugeosynclinal pile. The latter would probably be more compacted, contain less connate fluid and perhaps have mean sulfur isotopic compositions that more closely resemble sulfide values in the indurated Ordovician metasediments.

The generally narrow range in isotopic variation for given deposits is comparable with the ranges observed in hydrothermal veintype deposits. Dechow's explanation for the range of isotopic variation in the Heath Steele deposits is contradictory because he first assumed sulfur isotopic equilibrium between original sulfate and sulfide having isotopic compositions equivalent to the heaviest (+18.5%<sub>o</sub>) and lightest (+10%<sub>o</sub>) values in the ores, respectively, and later admitted that attainment of isotopic equilibrium was very unlikely. While it is uncertain what the isotopic composition of sulfate sulfur may have been if it were present in dissolved sulfate in trapped connate water, it is evident that the lightest value (+10%<sub>o</sub>) in the ores is unrealistic for original sulfide sulfur in Ordovician sediments (-5%<sub>o</sub>). If, on the other hand, the sulfate sulfur had been present as evaporite sulfate for which the  $SS^{34}$  value was approximately +23%. (Thode and Monster, 1963), neither the heavy nor the light sulfide sulfur in the ores can be equated with the probable isotopic compositions of the original sulfate and sulfide in Ordovician source rocks.

If an igneous hydrothermal replacement origin is postulated, it must be assumed that the sulfur isotopic and bulk chemical composition of the fluid or fluids changed in a fairly systematic manner. While it is perhaps possible that such a mechanism might give rise to similar across deposit sulfur isotope and base metal trends, the base metal distribution patterns in the plane of the mineralogical layering cannot be satisfactorily explained in terms of either a post- or pre-regional metamorphic igneous hydrothermal replacement origin. The pattern of base metal zoning moving radially away from the axes of Zn-Pb-Ag "centers" is contradictory to the proposition that the axes of the "centers" mark the location of possible "ore-pipes" from which high temperature hydrothermal solutions migrated outwards and selectively replaced sedimentary layers. In order for the zoning to be consistent with relationships observed in zoned deposits of certain hydrothermal origin (e.g. Butte, Montana and the Cornwall deposits of England) the reverse pattern should be present, that is, copper-rich ores grading outwards into zinc- and lead-rich ores since P/T conditions should decrease away from "ore-pipes" (Bateman, 1958, p. 314-315). Alternatively, one would have to propose that cooling ore solutions migrated inwards towards the axes of the "centers", but this does not seem reasonable. It also overlooks the apparent spatial relationship between the "centers" and the underlying "porphyry" bodies.

It is concluded that there does not appear to be any evidence which unambiguously supports an igneous hydrothermal replacement origin for the Heath Steele B-1 deposit. The enrichment of S34 in the deposits cannot be satisfactorily accounted for in terms of this mode of origin. While the "source bed" model proposed by Dechow would probably give rise to enrichment in S<sup>34</sup>, it does not seem likely that a source of heavy sulfate sulfur would have existed in Ordovician rocks near the bottom of the eugeosynclinal pile. The most serious difficulties confronting these models are presented by the base metal zoning. The base metal zoning in the plane of the mineralogical layering in the B-l cannot be satisfactorily explained either in terms of a pre- or post-regional metamorphic replacement origin. The consistent relationship between across deposit zoning and stratigraphy in deposits of similar kind, cannot be reasonably explained in terms of such an origin unless the containing strata were in a sub-horizontal position at the time of emplacement. Furthermore, the absence of alteration and mineralization in rocks immediately overlying some of the deposits strongly suggests that an igneous hydrothermal replacement origin is untennable in any event.

## A volcanic-exhalative origin

This origin presumes that hydrothermal fluids generated by sub-volcanic processes occurring at the time of eugeosynclinal deposition moved upward through progressively younger essentially unconsolidated rocks and were finally expelled at the sediment-water interface. The base metals in these fluids which form insoluble sulfides are precipitated with available H<sub>2</sub>S as sulfides close to exhalative "vents". There

is uncertainty as to the origin of the sulfur, promoted mainly by the fact that the isotopic composition of  $H_2S$  derived from terrestrial sulcanism is appreciably lighter than the sulfide sulfur in the stratiform ores. The general requirements of this mode of origin are:-

 i) the deposits should have lenticular, tabular or sheet-like forms and be conformably enclosed by stratified rocks, usually by sediments consisting of volcanic detritus and/or pyroclastic rocks.

Apart from these, there should be no general requirement as to the type of sediments occurring in close association with the deposits, provided the sulfur has not been derived from marine sulfate by bacterial reduction, e.g. carbonaceous sediments.

 ii) if the massive sulfides are banded or bedded the attitude of this layering should be consistent with the stratification in the enclosing rocks.

This implies that the sulfides occurring towards the stratigraphic tops of deposits were last deposited.

iii) there should be evidence of possible channelways for the supply of base metals from below the bottom of a given deposit and, if more or less centrally situated, some evidence that these persisted through the massive sulfides as they continued to form.

The attitude of such "feeder conduits" should ideally project through and below the base of a given deposit in a direction which is essentially normal to the stratification of the sulfides and enclosing rocks.
iv) if the proportions of metals and isotopic composition of the hydrothermal fluids changed with time this should be preserved as across deposit zoning but only for those metals having insoluble sulfides.

Within layer zoning might also occur in response to the variable behaviour of the different metals during precipitation as they move upwards and outwards from "vents".

- v) while evidence of source rocks should ideally be present, the absence of such rocks cannot be considered a serious criticism since these cannot usually be found for lavas in eugeosynclinal sequences.
- vi) the effects of regional metamorphism and deformation should be evident in the ores, but it might also be expected that relic features indicative of the initial very fine grained or gel-like character of sulfide precipitates may be present in ores contained in low grade rocks.

The highly variable iron content of sphalerites in ores in low grade rocks may thus reflect the variability in the composition of the initial precipitates but homogenization should be approached at higher grades of regional metamorphism. Deformational features in massive sulfides should be compatible with the behaviour of sulfides under conditions similar to those experienced by metasediments but it is not necessary that they should have responded in the same way.

The first part of requirement i) is satisfied and, apart from magnetic and chloritic iron formation which are usually present and possibly formed during ore deposition, the association of carbonaceous sediments does not appear to be a consistent feature. The occurrence of carbonaceous sediments presumably indicates that there was an abundant supply of organic material in these locations. Requirement ii) is generally satisfied and requirement iii) appears to be satisfied, at least in the case of the Heath Steele B-1 orebody even though similar features have apparently not been recognized in other stratiform deposits in the Bathurst-Newcastle area. Evidence for this is afforded by the presence of "plug-like" masses of "porphyry" occurring in immediate contact with massive sulfides of high grade zinc-lead "centers" whose axes project through the deposit essentially normal to the layering and the fact that copper mineralization is present for some distance below the deposit (Whitmore, 1957). The "plug-like" masses of "porphyry" are believed to mark the approximate location of "vents". Probable channelways extending below stratiform deposits have been recognized in the Kuroko-type deposits of Japan and in some deposits in Spain and Quebec. Rocks overlying some of the Matagami deposits of Quebec are notably different from the underlying rocks in that they are unaltered and unmineralized, suggesting that mineralization ceased prior to deposition of these rocks.

Across deposit zoning and within layer zoning is evident in the B-1 orebody and the former pattern is apparently consistent with the pattern of zoning observed in similar deposits where the stratigraphic relations are known. As mentioned earlier, this can only reasonably be

interpreted as indicating that deposition occurred while the enclosing rocks were in a sub-horizontal position and the lack of mineralization and alteration in rocks overlying some deposits strongly favours a sedimentary origin for the deposits. While exposed source rocks do not appear to be evident in the Bathurst-Newcastle area, it is considered significant, however, that all the deposits occur in intimate association with "porphyry" and most of these occur in a roughly circular belt consisting of metasediments intercalated with abundant "porphyry" and greenstone. Insofar as this lithological association is unique in the exposed sequence of Ordovician rocks, it can safely be inferred that there must have been widespread changes in the depositional environment to account for the abundance of basic lavas and acid pyroclastics. Since structural information appears to favour the view that "porphyry" occurs stratigraphically above the massive sulfides (Whitmore, 1957), it seems reasonable to interpret this relationship as suggesting that ore formation was associated with initial magmatic de-gassing and that this was a necessary prerequisite to the explosive ejection of some of the probable source magma as pyroclastic materials which are similar in composition to rhyolite (Davies, 1966).

Requirement vi) is generally satisfied. Stanton (1960c; 1964-65) and Kalliokoski (1965) interpreted the existing textural features to be due to recrystallization accompanying diagenesis and later regional metamorphism and it was suggested by King (1958) that the grainsize of the ores is a function of the rank of metamorphism. Kalliokoski (1965) pointed to the presence of extremely fine grained sulfide intergrowth textures which are suggested to have formed from sulfide gels. The

70

same writer suggested that the minerallgical banding has been deformed and even destroyed in places in response to dynamic metamorphism. Cross-cutting relationships by the softer sulfides, particularly by chalcopyrite-pyrrhotite veins are presumably due to solid state mobilization and injection into the less competent wall rocks and pyritic ore. Although there is evidence of faulting and the development of minor cleavage in copper-rich ores, the structural features of the massive sulfides seem to be generally unlike those in the wall rocks, suggesting that the sulfides have tended to flow and recrystallize rather than yield by shearing. While the present contribution indicates that local homogenization with respect to sulfur isotope ratios in given minerals is fairly complete, the findings of Benson (1960) indicate that the iron content of sphalerites can vary appreciably over very small distances. The appreciably smaller range of variation and the generally higher iron content of sphalerites in Norwegian stratiform deposits occurring in Lower Amphibolite Facies rocks, reported by Vokes (1962), suggests that at least further chemical homogenization occurs in response to higher grades of regional metamorphism.

It is concluded that with the possible exception of source rocks, the general requirements of a volcanic-exhalative origin appear to be satisfied.

### 8-6. Possible derivation of sulfur in the Heath Steele B-1 orebody by bacterial reduction of marine sulfate

Stanton (1960d) suggested that the sulfur in these deposits is probably of volcanic derivation, since sea water sulfate, though present, would be exceeded in abundance many times by volcanic sulfur. In a

later paper, Stanton and Rafter (1966) reserved judgement on the possible origin of the sulfur presumably because of the appreciably lighter isotopic composition of terrestrial volcanic H<sub>2</sub>S and the apparent lack of correlation with the present day sea water sulfate sulfur value. In comparing the mean ratios of the "normal" and "volcanic" type deposits with the values for sulfur in evaporites of similar age, Sangster (1967) found a parallelism between the deposits and evaporites. The Mt. Isa and Rammelsberg deposits were given as examples of the "normal" type and the Bathurst and Buchans deposits were cited as examples of the "volcanic" type. The "normal" and "volcanic" type sulfides were found to be 10.4 and 16.5%, lighter and coexisting sulfates (e.g. barite) were found to be about 1.4 and 3.7%, heavier, respectively, than the corresponding sea water sulfate values as determined from evaporites. Sangster postulated that all the sulfur in the "normal" type deposits and a significant proportion of the sulfur in the "volcanic" type deposits, was formed by bacterial reduction of contemporaneous sea water sulfate in unrestricted basins or environments. He suggested that the means of the "volcanic" type are lighter because some isotopically light volcanic H2S has been incorporated in these deposits.

Harrison and Thode (1957) calculated the kinetic isotope effect in the chemical reduction of sulfate to sulfide at temperatures of 18 to  $50^{\circ}$ C and found that  $S^{32}O_{4}^{=}$  should react 2.2% (fractionation factor is approximately 1.02) faster than  $S^{34}O_{4}^{=}$  at these temperatures. Nakai and Jensen (1964) reported that bacterial reduction of sulfate produces a fractionation factor of 1.020 which remained constant in their reduction experiments. In the case of an infinite supply of sulfate it was proposed that the fractionation factor between sulfate and sulfide would remain constant at about 1.020 which corresponds to a fractionation of approximately 20%. Laboratory experiments by Kaplan and Rittenberg (1964) demonstrated that the degree of isotopic enrichment could be controlled by regulating the rate of reduction and the enrichment was found to be inversely proportional to reduction rate when hydrogen donors were used. Smaller mean fractionations can therefore be expected when reduction rates are rapid and this in turn is dependent partly on the food source available. In any event, Sangster's model requires that the conditions under which bacterial reduction might have occurred must have been very different from those which gave rise to a total spread of about 40%, and a mean of -5%, in the Ordovician sediments. It must also be assumed that conditions were very uniform in the depositional environment in which deposits formed at essentially the same time.

A very necessary requirement for this model is that there must be an abundant source of organic compounds serving as a food source for the bacteria. There appear to be only two possible sources, and the first seems more likely

i) organic material deposited in the sediments

ii) possible volcanic constituents such as CO,  $CO_2$  and  $CH_4$ . It is evident that while the mean isotopic values for sulfides in the footwall metasediments of the B-1 orebody have values which are systematically related to those in the massive sulfide ores above, there must have been little or no organic matter in these sediments. Nor does organic material appear to be present in significant amounts in the

gangue of the massive sulfides. It must therefore be presumed that if organic material was present initially, it must have been consumed either by oxidation or bacterial action. Fortunately it is possible to obtain some idea of the amount of organic material that would be needed in the ore sediments initially to account for the sulfide sulfur in the B-1 orebody. Kaplan et al. (1963) used the following generalized equation to account for the oxidation of organic carbon compounds

$$2CH_20 + SO_4 = 2H_20 + 2CO_2 + S^2$$

and computed that 0.63 mg of  $S^{-}$  are produced for every 0.5 mg of organic carbon used in bacterial sulfate reduction. 0.5 mg of C and 0.63 mg of  $S^{=}$  are equivalent to 0.24 cm<sup>3</sup> of graphite, 0.24 cm<sup>3</sup> of pyrite and 0.39 cm<sup>3</sup> of pyrrhotite. Hence, if it is assumed that organic carbon was the principal food source and was initially contained in the ore sediments as there do not appear to be any important graphitic horizons along strike in the vicinity of the deposit, it is apparent that the volume of organic material was probably at least as abundant as the pyrite in pyritic ore and about 60% as abundant as other sulfides in non-pyritic ore. Insofar as pyrite usually accounts for more than 90% of the sulfide sulfur in the ores to a first approximation and sulfides constitute about 80% by volume of the ore, it seems that the initial ore-bearing sediment should have contained a minimum of 80 to 90% of organic matter, provided none of the H<sub>2</sub>S generated was lost. It is therefore concluded that while an organic food source seems feasible provided there was no appreciable loss of H<sub>o</sub>S, there appears to be no evidence to indicate that it may have existed. While volcanic organic compounds cannot be ruled out,

it is uncertain whether they would be suitable as a food source.

The across orebody trends are probably explainable on the basis of this model if it is assumed that

- i) a progressively larger proportion of isotopically light volcanic H<sub>2</sub>S was contributed over the period of ore formation.
- ii) the  $\delta S^{34}$  value of available  $SO_4^{\pm}$  remained relatively constant and that the rate of sulfate reduction decreased slightly producing an overall enrichment in  $S^{32}$ . The rate of reduction increased abruptly during deposition of the hanging wall sulfides.
- iii) the  $\delta S^{34}$  value of available  $SO_4^{\pm}$  was becoming depleted in  $S^{34}$  due to increasing contributions of lighter volcanic or terrestrial sulfate and the rate of reduction remained fairly constant.

Unfortunately it is not possible to determine whether these assumptions are reasonable. It is interesting to note, however, that opposite and appreciably larger trends have been observed in the Rammelsberg deposit (Anger et al., 1966). In this case, the sulfur of the barite is believed to have become heavier due to periodic isolation of the depositional basin from the ocean.

In order to account for the abundance of pyrrhotite, often to the exclusion of pyrite, in copper-rich ores and the association of pyrite and magnetite throughout the deposit, one must appeal to Eh-pH equilibrium conditions at the time of deposition which were different

from those found so far in recent marine sediments. While there may be a reasonable explanation for this, it seems difficult to explain the occurrence of magnetite rich bands or of magnetic iron formation in massive pyrite if the availability of H<sub>2</sub>S was principally dependent on bacterial reduction of sulfate, especially insofar as  $pS^{=}(-\log a_{B^{=}a_{0}})$  in recent marine sediments appears to have been too low to permit formation of iron oxides (Fe<sub>2</sub>0<sub>3</sub> in this case). Hence, in order to explain this feature it must be assumed that  $Fe^{2+}/Fe^{3+}$  hydroxides were precipitated from solution above the sediment-water interface when the concentration of S<sup>=</sup> in the water above the sediments was low possibly due in part to there having been insufficient time for its build-up prior to further outpouring of hydrothermal solutions, or perhaps because current action may have flushed it out of the depositional environment. While this seems feasible, it is difficult to explain why the ferrous/ferric hydroxy compounds would not have been subsequently converted to sulfides as the concentration of S<sup>-</sup> increased and ultimately diffused upward through the hydroxide bands into the water above the sediment-water interface so as to provide sulfide sulfur for precipitation of further sulfides as required by the model.

While it is possible that a very special type of bacterial sulfate reduction process might generate sulfides with mean  $\delta S^{34}$  values similar to those observed in the stratiform deposits, there are a number of the features observed in the Heath Steele B-1 orebody that do not appear to be satisfactorily explained by this model. The principal difficulties appear to be that of providing an abundant food source in the absence of evidence that one might have existed and to explain the ubiquitous association of magnetite and pyrite together with other sulfides in ores where the activity of  $S^{\pm}$  in the ore sediment pore fluids should have been sufficiently great to convert iron hydroxides to sulfides. Nor is it possible to account for the across deposit trends unless various assumptions are made. It is possible that the observed features might be more satisfactorily explained by an alternative model, and this will be developed in the following section.

#### A SUGGESTED ORIGIN FOR THE HEATH STEELE B-1 OREBODY

#### 8-7. Introductory Statement

The purpose of this section is to examine the possibility that the features observed in the Heath Steele B-1 orebody might be more satisfactorily explained in terms of a volcanic origin for the sulfide sulfur. While a volcanic source for the sulfur seems reasonable insofar as various sulfur species, including H<sub>2</sub>S and SO<sub>2</sub>, are known to be important constituents in gaseous discharge products in geothermal regions and from fumaroles associated with terrestrial vulcanism, there appears to be one important difference: all 65<sup>34</sup> determinations for such H<sub>2</sub>S have shown that it is appreciably lighter (in the +10 to -20% range) than the mean sulfide value in stratiform deposits and this fact has apparently prompted Sangster (1967) to appeal to a biogenic origin for most of the sulfur. It is believed, however, that a comparison with the isotopic compositions of H<sub>2</sub>S from terrestrial vulcanism is possibly misleading because this H<sub>2</sub>S may not be representative of the H2S generated in sub-volcanic processes occurring in eugeosynclines.

# 8-8. Chemical composition of discharge products from terrestrial fumaroles and geothermal bores

Ellis (1957) and Matsuo (1961) have summarized much of the available analysis data for volcanic discharge products. Unfortunately some of the sulfur constituents have been analyzed as a group and some of the less abundant gases have not been determined. The results of Matsuo (1961) for fumarolic products from the Japanese volcano Showashinzan are particularly useful due to their completeness. Some general features of fumarolic/geothermal discharge products include

- i) temperatures are usually in the 100 to 750°C range, and these may vary widely between fumaroles in the same area.
- ii) H<sub>2</sub>O accounts for 99% or more by volume of the products and is accompanied by approximately 0.5% of CO<sub>2</sub>. Other gases occurring in trace amounts include H<sub>2</sub>S, SO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, Ar, O<sub>2</sub>, HCl, HF, B, Br, I and CO (Matsuo, 1961).
- iii)  $SO_2$  is found to be about an order of magnitude more abundant than  $H_2S$  at the highest temperatures but the reverse situation is found at the lowest temperatures.
- iv) sulfate sulfur appears to be appreciably less abundant than  $SO_2$  or  $H_2S$  in most high temperature fumarolic products and may even be absent, but has been found to occur together with polythionate  $(S_xO_6^{-})$  in concentrations comparable with  $H_2S$  in geothermal discharges of the Wairakei area of New Zealand (Rafter and Wilson, 1963). Sulfate may be very abundant in crater lakes, however (Sakai, 1957).

Mizutani (1962b) analyzed volcanic incrustations from the volcano Showashinzan for major elements and found them to be very low in Al<sub>2</sub>O<sub>3</sub> and CaO compared with average igneous rocks, including granites. It was reported that the proportions of silica and total iron decrease while Na<sub>2</sub>O, K<sub>2</sub>O, CaO, MgO and total sulfur increase with temperature lowering. The approximate temperature of formation of the incrustations was based on the observed correlation between their colour and the temperature of the wall rocks on which they occur. Mizutani also analyzed these incrustations for their base metal content and found them to contain appreciable amounts of various heavy metals such as Ba, Zn, Te, As, Pb, Cu, Sr, Cd, Th, Cr and Sb. The concentrations of copper and lead in the low temperature sublimates were found to be several hundred times greater than in a lava sample from the area and zinc was found to be about 50 times more abundant. When the concentrations of zinc and lead in the sublimates were plotted against the approximate temperature of formation (200 to 700°C) it was found that there is a pronounced tendency for their concentration to increase with temperature lowering, and Pb/Zn ratios to increase in the same direction. The relationship was found to be much less distinct for copper. These results led Mizutani (1962) to conclude that lead and zinc are more volatile than copper under fumarolic conditions.

Matsuo (1961) believed that chemical equilibrium is not generally attained in fumarolic gases. Although attempts have been made to account for the compositional changes with decreasing temperature, the suggested mechanisms do not satisfactorily explain all the observed features. Mizutani (1962a) suggested that mixing high temperature gases

with ground water has probably given rise to most of the observed relations in the lower temperature gases. Ellis (1957) asserted that the total sulfur contents of gases liberated from volcanic craters are much higher than their estimated content in magmatic gases and he attributed this to recycling of sulfur in craters.

#### 8-9. Sulfur isotope abundances in fumarolic/geothermal sulfur compounds

It is found that where  $SO_{2}^{4=}$ ,  $SO_{2}$ ,  $H_{2}S$  and  $S^{=}$  coexist under fumarolic or geothermal conditions, there is a progressive depletion in the heavy isotope from  $SO_{4}^{=}$  to  $S^{=}$ . The same general order is predicted from theoretical equilibrium calculations (Sakai, 1957), thus suggesting that natural systems may approximate and even attain isotopic equilibrium. Sakai and Nagasawa (1958) measured isotopic compositions of fumarolic  $H_{2}S$  and  $SO_{2}$  in the temperature range 100 to 600°C and obtained fractionations that agreed fairly well with the equilibrium values corresponding to the vent temperatures. The isotopic ratios of both compounds were explained in terms of a simplified system containing only  $H_{2}S$ ,  $H_{2}O$ ,  $SO_{2}$  and  $H_{2}$  and interacting as follows

$$H_2S + 2H_2O \neq SO_2 + H_2$$

The isotopic composition of Showashinzan  $H_2S$  was found to vary from about -2 to -8%, and composition of the source sulfur was estimated to be about -3%, for the volcano Showashinzan. The source sulfur in volcano Shirane is reported to have a similar composition.

Rafter and Wilson (1963) found that fractionations between sulfate and  $H_2S$  from geothermal fluid having temperatures of up to 270°C did not agree well with the theoretical value at this temperature, but corresponded to a theoretical temperature of 360 to 370°C. There is some uncertainty, however, as to the actual temperature of the fluid underground. The isotopic compositions of the sulfate and H<sub>2</sub>S were found to average about +22 and +3.5%, respectively, and the mean composition of total sulfur was found to remain fairly constant at approximately +12%, over a six year period. HoS appears to have reacted completely with SO, to produce sulfur in the fumaroles of White Island which is probably related to the geothermal activity of the Wairakei geothermal area of New Zealand. The isotopic composition of the total sulfur discharged by these fumaroles ranged from -1 up to about +10%.. It is perhaps significant that the isotopic composition of the sulfate sulfur from the Wairakei geothermal bore fluid and the White Island fumaroles shows only a very small variation and is slightly heavier than the mean value for ocean sulfate.

While these results serve to illustrate that isotopic equilibrium appears to be attained between  $H_2S$  and  $SO_2$  in volcanic gases at moderate to high temperatures, it does not appear that equilibrium has been attained between sulfate and  $H_2S$  at temperatures below 300°C, but this is uncertain. These writers favoured an igneous origin for the source sulfur based on determined or estimated compositions of the total sulfur. It does not appear that the isotopic composition of total sulfur in geothermal/fumarole discharge products from the Wairakei/White Island area can be considered truly representative of the source sulfur because of the

variability reported for the White Island sulfur and perhaps also because of the relative heaviness of the sulfur in the Wairakei geothermal fluid. Such variability might even be expected since there is always the possibility of periodic mixing with oxygenated groundwater, side reactions which Oana and Ishikawa (1966) have shown capable of producing  $H_2S$  and  $H_2SO_4$  by heating water containing either elemental sulfur or  $SO_2$  at relatively low temperatures and the differential loss of some sulfur species, particularly sulfate. Oana and Ishikawa (1966) attributed the variability in isotopic composition of sulfates associated with hot springs to such reactions and their results suggest that the sulfates produced will not readily re-equilibrate with coexisting species, at least at temperatures below about 300°C. The fact that the isotopic composition of sulfate sulfur from New Zealand geothermal/volcanic areas and in Mt. Shirane crater lake of Japan are only slightly heavier than sea water sulfate sulfur raises the question as to whether sea water might be contaminating some terrestrial volcanic systems. This possibility does not seem unreasonable either from the geographical or geological point of view.

# 8-10. A suggested model for the generation of S<sup>34</sup> enriched H<sub>2</sub>S in subvolcanic processes

If the stratiform ores precipitated on the sea floor in the vicinity of submarine volcanic vents, it is evident that the hydrothermal fluids which contributed the base metals must have been transported from parent magmas to the sediment-water interface by means of volcanic vent systems. Even if parent magmas were intruded into more or less indura-

ted sedimentary-volcanic sequences at great depths below the sedimentwater interface, it is clear that part of such a vent system would pass through unconsolidated detrital sediments containing connate water. Communication between connate water and hydrothermal fluids within vent systems must, therefore, have occurred. Such a situation is potentially very different from one in which true igneous hydrothermal deposits form in crustal rocks where reservoirs of heavy sulfur are generally not available. Volcanoes which are surrounded by ocean, such as the White Island volcano of New Zealand, probably represent an intermediate situation since the vulcanism is separated from an enormous reservoir of heavy sulfur by considerable thicknesses of volcanic rocks.

It seems reasonable to expect that  $S^{34}$  enriched  $H_2S$  could be generated in submarine volcanic vent systems if the isotopic composition of sulfate sulfur in connate water was similar to that of sea water and if this sulfate could enter vent systems and exchange with sulfur compounds in hydrothermal fluids.

Unfortunately it is not possible to predict with any degree of certainty what the isotopic composition of sulfate sulfur contained in connate water in Ordovician sediments may have been since sulfur isotope studies on recent marine sediments off Southern California and sulfate in connate waters associated with U. Devonian petroleums have shown that  $SO_4^{-1}$  in connate waters can be either enriched or depleted in  $S^{34}$  relative to sea water sulfate (cf. Thode et al., 1958; Kaplan et al., 1963). However, it appears that sulfate in connate water is generally enriched in  $S^{32}$  relative to sea water sulfate and it was suggested

by Thode et al. (1960) that this is probably due to oxidation of pyrite in situ. Thode et al. (1958) found that the mean enrichment in  $S^{32}$ for sulfate in connate waters associated with U. Devonian petroleums is approximately 5%, relative to evaporites of similar age. Studies by Thode et al. (1960) and Kaplan et al. (1963) revealed that interstitial sulfates ( $SO_{4}^{\pm}$ ) contained in recent marine sediments down to depths of 160 and 13 feet below the sediment-water interface show mean  $S^{32}$  enrichments of 13%, and 2%, respectively. It appears that both the content of connate water and the abundance of  $SO_{4}^{\pm}$  generally decrease with increasing depth of burial (cf. Kaplan et al., 1963).

It seems inevitable that high temperature hydrothermal fluids within submarine volcanic vent systems would communicate with connate water contained in vent walls, especially where these consist of coarser detrital sediments which have relatively high permabilities. However, in order to ensure that the isotopic composition of the sulfate sulfur communicating with such fluids was never appreciably different from the connate sulfur reservoir value, it is necessary to appeal to a steady supply of fresh connate sulfate to the vent walls. This could only be accomplished over short periods of time by admitting connate water into the vent system. A study of D/H and  $0^{18}/0^{16}$  ratios in thermal and surface waters in geothermal areas by Craig (1963) strongly suggests that in a number of cases the water discharged by hot springs is largely recrycled surface water. Insofar as the model proposed here is similar in principle to the geothermal situation, it seems that connate water may enter submarine volcanic vent systems.

It is necessary to consider to what extent sulfate contained in connate waters might be expected to exchange with sulfur compounds in high temperature fluids. Dunford et al. (1957) measured sulfur fractionations between SO2 and 100% H2SO4 held at temperatures of 200, 300 and 400°C over periods of 16, 7 and 3 days, respectively. The initial SO<sub>2</sub> was enriched in S<sup>34</sup> relative to the sulfuric acid. The fractionations were found to agree reasonably well with calculated equilibrium values for the exchange reaction between  $SO_4^{=}$  and  $SO_2^{-}$ . Oana and Ishikawa (1966) succeeded in obtaining a fractionation factor of 1.023 between sulfate and sulfur at a temperature of 300°C over a period of 3.5 hours. Since the equilibrium fractionation factor obtained from Sakai's (1957) curves is approximately 1.028 at this temperature, it is evident that the experimentally determined value of +24.3%, is only about 20% smaller than the equilibrium value. In view of these findings, it seems reasonable to expect that sulfate derived from connate water would exchange readily with hydrothermal sulfur compounds at expected temperatures of 500 to 700°C. Isotopic equilibrium may even be achieved in less than a few hours. Although it is possible to obtain some idea of the probable minimum duration of a single "exchange-precipitation-quiescence" event corresponding to a single sulfide ore band in the B-1 orebody, it is clearly impossible to estimate how much time might have been available for a single exchange event within a hypothetical, vent system. This would be dependent on a number of variables including the geometry and length of the vent system. By assuming that most of the silicate gangue (approximately 20% by volume) in the B-1 orebody (150 feet in thickness) represents contemporaneously

deposited sedimentary material and that this accumulated at one of the highest sedimentation rates  $(24 \text{ cm}/20^2 \text{ years}: \text{Hardin, 1962})$  reported so far, it is found that a 1 mm. thick ore band took at least 1.8 days to form. The time available for exchange corresponding to a 1 mm. thick ore band would accordingly have been less than this. The entire deposit is estimated to have taken at least 3750 years to form.

If connate water sulfate and magmatic sulfur compounds were mixed the isotopic composition of the final  $H_2S$  would depend on

- i) the initial isotopic composition of the total sulfur in the two reservoirs
- ii) the relative proportions of connate water sulfate to magmatic sulfur

iii) the temperature of the hydrothermal fluids.

It seems likely that the temperature of fluids in contact with a granitic parent magma would show little variation during ore formation and may easily have been as high as 700°C (Turner and Verhoogen, 1960, p. 55). It is evident that the temperatures of these fluids should decrease in the vent system chiefly due to adiabatic cooling (Ellis, 1957), heat loss at the vent walls and mixing with connate water. It is possible, however, that these effects may produce a fairly uniform temperature lowering provided the vent geometry is not appreciably altered during ore formation.

The isotopic composition of magmatic sulfur was probably similar to meteoritic sulfur but may have been as heavy as +5%. Assuming that the isotopic composition of sulfate sulfur in connate water was not ap-

preciably different from that of Ordovician marine sulfate (+23%: Thode and Monster, 1963) and that sulfur of similar composition entered the vent system during ore formation, it is possible to roughly estimate the proportions in which sulfur from the two reservoirs were mixed to produce  $H_{2}S$  having an isotopic composition of  $+14\%_{o}$ , the mean value for the B-1 orebody and chalcopyrite-pyrrhotite ores from the A deposit. Since the fractionation involved in precipitating FeS and CuS in the marine environment can probably be considered negligible in view of the present findings, it is reasonable to assume that a mean value of +14%. is representative of the H<sub>2</sub>S contributed by the early hydrothermal solu-The limiting proportions of Ordovician sulfate sulfur (+23%) tions. that are required to exchange with igneous sulfur having a value of zero % can be obtained if it is assumed that isotopic equilibrium was attained and that the total sulfur had limiting values corresponding to the values for  $SO_h$  and S. Sakai's (1957) curves were used to obtain equilibrium fractionation factors corresponding to various temperatures for the exchange reactions

$$s^{32}o_4^{=} + H_2s^{34} = s^{34}o_4^{=} + H_2s^{32}$$
 i)

$$H_2 s^{32} + s^{34=} = H_2 s^{34} + s^{32=}$$
 ii)

 $\delta S^{34}$  values were then calculated for  $SO_4^{-}$  and  $S^{-}$  in equilibrium with +14%, H<sub>2</sub>S at the various temperatures (see Table 8-10).

TABLE 8-10

T°C	δS <sup>34</sup> (%) approx.			
	so <sub>4</sub> =	H <sub>2</sub> S	S	F ·
1000	+10.5	+14	+13	0.56 < F < 0.85
800*	+20	+14	+12.5	0.54 < F < 0.87
700	+21	+14	+12	0.52 < F< 0.9
600	+23	+14	+11.5	0.5 < F < 1.0

where: F is the fraction of total sulfur contributed by Ordovician marine sulfate sulfur. The limiting values at 800°C\*, for example, were obtained from mass balance calculations as follows:-

(+23) F + (0) 1-F = > +12.5%, F = > 0.54%, (+23) F + (0) 1-F = < +20.0%, F = < 0.87%,Therefore 0.54 < F < 0.87

It is evident from the F values in Table 8-10 that Ordovician marine sulfate sulfur would have contributed at least 50 to 60% of the total sulfur in hydrothermal vent fluids. This would be reduced by about 10% if the magmatic sulfur had a composition of +5%. These minimum proportions presume of course that  $S^{-}$  was by far the most abundant sulfur species but this may be an unrealistic presumption. While it is obvious that the bulk isotopic composition was closest to that of the most abundant sulfur species or sulfur compound present, it is uncertain what this might have been especially since much of the connate water sulfate could have been reduced by hydrogen at high temperatures. If either  $SO_h^{-}$  or  $SO_2$  was by far the most abundant sulfur compound present, the bulk isotopic composition would need to have been about+20%, or heavier. Such a composition may be more realistic since  $SO_2$  is found to be the most abundant sulfur compound in high temperature fumarolic gases (Mizutani, 1962a). In any event, it is evident that at least a large proportion of the total sulfur must have been contributed by connate water sulfate in order to generate  $H_2S$  of suitable composition.

The equilibrium temperatures corresponding to the 65<sup>34</sup> extremes and the mean value for the B-1 orebody would be approximately 700, 500 and 560°C, respectively, if it is assumed that the bulk isotopic composition of the vent fluids was close to that of Ordovician marine sulfate (+23%,) and that isotopic equilibrium was maintained throughout. It is interesting and perhaps fortuitous that the highest temperature agrees well with the probable temperature of a water-saturated granitic source magma (Turner and Verhoogen, 1960, p. 55). It is apparent that the general parallelism observed between the mean  $\delta S^{34}$  values of "volcanic" type stratiform deposits and evaporite sulfates of similar age can probably be accounted for by this model provided the  $\delta S^{34}$  value of sulfate in connate waters was not appreciably different from marine sulfate of the same age. If this condition has been generally satisfied, such a parallelism should be produced since most of the sulfur is probably derived from connate sulfate and the exchange processes occurring in sub-volcanic systems should be in the 500 to 700°C range.

# 8-11. <u>A suggested explanation for the isotope trends and across</u> <u>deposit base metal zoning in the B-1 orebody</u>

The proposed model postulates that the sulfur and the base metals in the B-1 orebody were derived from hydrothermal fluids that were discharged at the sediment-water interface, and consequently it should be possible to reasonably account for the isotope and base metal trends in terms of a single mechanism.

There appears to be strong evidence that the base metal zoning in the B-1 orebody was dependent on changing P/T conditions in hydrothermal fluids in contact with the source magma. The following observations support the view that copper-rich ores form at high temperatures and zinc-lead and lead-rich ores form at lower temperatures:

- i) copper-rich, zinc-rich and finally lead-rich ores occur in this order moving progressively further away from closely associated intrusive igneous source rocks (Bateman, 1958, p. 314-315), e.g. deposits of Cornwall, England and Bingham, Utah.
- ii) hydrothermal copper and copper-zinc deposits are characteristically associated with basic intrusive rocks and lead-zinc and lead-rich deposits are associated with acid igneous rocks (Wilson and Anderson, 1959; Kilburn, 1960). A similarity is evident in the base metal ratios in both the ores and the related igneous rocks (Kilburn, 1960).
- iii) the findings of Mizutani (1962b) indicate that the absolute abundances of lead and zinc as well as Pb/Zn ratios are higher in volcanic incrustations formed at lower temperatures.

To ascertain whether the proposed model can satisfactorily account for a sulfur isotope trend favouring an overall enrichment in  $S^{32}$  with decreasing temperature, it is first necessary to consider whether the bulk isotopic composition of hydrothermal fluids is likely to have changed in response to a progressive temperature lowering. A progressive temperature decrease of the source magma would result in a decrease in pressure in the vent system and this in turn may favour introduction of larger proportions of connate sulfate. It can therefore be expected that the bulk isotopic composition would either remain essentially constant or become heavier. If it became heavier, an opposite trend would be favoured.

There appear to be two possible explanations for the overall sulfur isotope trends on the basis of this model

- i) the bulk isotopic composition was lighter than that of the H<sub>2</sub>S and the equilibrium temperature progressively increased during ore formation
- ii) the bulk isotopic composition was heavier than that of H<sub>2</sub>S and the equilibrium temperature decreased during ore formation.

Unfortunately it is uncertain whether the bulk isotopic composition would have been heavier or lighter than the  $H_2S$ . It is evident, however, that the first possibility contradicts the proposal that the temperature progressively decreased during ore formation. The second possibility seems reasonable and is consistent with a progressive decrease in temperature. It is therefore concluded that across deposit base metal zoning is consistent with a progressive temperature lowering of the source magma

and that the overall sulfur isotope trends can be reasonably accounted for in terms of such an effect. The fluctuations in the isotope patterns can probably be explained in terms of temperature variations in the hydrothermal fluids produced by non-uniform cooling during transportation to the sea floor. Cooling due to mixing with connate water and adiabatic effects accompanying pressure release are probable causes.

#### 8-12. Explanation of the occurrence of pyrrhotite, pyrite and magnetite in the ores in terms of a volcanic origin for the sulfur

It was mentioned earlier that the association of pyrite and minor magnetite throughout most of the deposit favours the view that the overall Eh conditions were probably moderately reducing and that the association of these minerals does not necessarily require that The controlling factor may they formed under equilibrium conditions. rather have been the availability of sulfur species, in which case ferrous/ferric iron may have precipitated as hydroxides together with FeS and later formed magnetite when there was insufficient sulfide ion present for their subsequent conversion to sulfides. The fact that pyrrhotite is often the only iron sulfide represented in the copper-rich ores, and occurs with pyrite in varying proportions with or without other sulfides may be due to the fact that there was insufficient elemental sulfur available to convert FeS to pyrite. Berner (1964) proposed that this might be an explanation for the rare occurrence of pyrrhotite rather than pyrite in some marine sediments.

Sakai (1957) suggested that native sulfur from fumaroles is deposited through the interaction of two moles of  $H_2S$  to one of  $SO_2$ so that the isotopic composition of the sulfur produced is the weighted mean of these two gases:

$$2H_{2}S + SO_{2} = 3S^{\circ} + 2H_{2}O$$
 i)

Elemental sulfur is also readily formed in solution containing the two gases. Kaplan et al. (1963) and Berner (1964) attributed the formation of pyrite in marine sediments to the interaction of FeS and elemental sulfur. The reaction proposed by Kaplan et al. is:

$$FeS + S^{\circ} = FeS_2$$
 ii)

It is therefore apparent that pyrite would be represented in stratiform ores where there was sufficient elemental sulfur available for reaction with FeS to form pyrite and pyrrhotite would be represented where there was not. As mentioned earlier, it is observed that pyrrhotite is more abundant in copper-rich ores and therefore tends to be more abundant towards the stratigraphic bottoms of stratiform deposits. It now remains to examine this feature in terms of the proposed model.

Equation i) above indicates that precipitation of elemental sulfur in sea water would be favoured by high  $H_2S/SO_2$  ratios in the hydrothermal fluids contributed to the marine environment. Mizutani (1962a) reported fairly consistent volumetric  $H_2S/SO_2$  ratios of about  $\frac{1}{10}$  at 700°C and  $H_2S/SO_2$  ratios of approximately 10 at temperatures of 460°C in fumarolic gases of volcano Showashinzan over a three year period. The fact that some of these gas relationships can be extended

to hydrothermal fluids which undergo isochemical cooling is evident from their general agreement with the theoretical predictions of Ellis (1957) and Holland (1965). Both writers suggested that H<sub>2</sub>S/SO<sub>2</sub> ratios should increase with decreasing temperature, but Holland (1965) suggested that the fugacity of H<sub>2</sub>S should remain roughly constant during isochemical cooling. Ellis' calculations suggest that there should be a slight increase in the abundance of H<sub>2</sub>S with cooling whereas SO<sub>2</sub> shows a pronounced decrease. The effect of a large decrease in pressure (e.g. 1000 to 10 atm.) appears to be just the reverse but seems to be relatively small at high temperatures compared with changes due to temperature lowering. It is clear, however, that the decrease in abundance of H<sub>2</sub>S with increasing temperature of Showashinzan fumarolic gases is very much greater than those predicted. The H<sub>o</sub>S content at about 100°C is about 0.15 ml/10001 while the content at 700°C is approximately 0.01 ml/10001 and it is evident that these contents remained fairly uniform over a three year period (Mizutani, 1962a). It therefore appears reasonable to presume that H2S/SO2 ratios in hydrothermal fluids will be higher at lower temperatures and that the absolute abundance of H<sub>2</sub>S is slightly higher at lower temperatures, and possibly very much higher if the situation observed in fumaroles is representative.

It is therefore proposed that the relatively greater abundance of pyrrhotite towards the stratigraphic bottom of the B-1 orebody and other deposits were ultimately caused by the higher temperatures of early contributed hydrothermal fluids which did not generally favour the

formation of elemental sulfur in the marine environment due to low  $H_2S/SO_2$  ratios.

The association of magnetite with varying proportions of pyrite is attributed to the fact that although  $H_2S/SO_2$  ratios were probably high, the absolute abundance of  $H_2S$  was relatively low favouring formation of oxides rather than sulfides. The occurrence of magnetic iron formation alone is attributed to the fact that these gases were essentially absent in fluids which contributed the iron in these rocks.

## 8-13. A suggested relationship between the Heath Steele sulfide deposits and the "porphyry"

The proposed model requires that the bottoms of submarine volcanic vent systems were in direct contact with acid magmas which occurred at unknown depths below the sediment-water interface. While the presence of some "porphyry" below the B-1 and a few isolated lenses within it suggest that some magma escaped prior to and during ore formation, the occurrence of voluminous accumulations above the B-1 and other Heath Steele deposits suggests that the main period of explosive vulcanism succeeded ore formation. It is therefore apparent that the sulfides formed during an early degasing phase of vulcanism.

The localization of the quartz "porphyry" above the B-1 and several other Heath Steele deposits suggests that this was the first deposited fragmental material and therefore probably representative of the magma occurring in contact with the vent systems. It is also apparent that the location of the vents were probably nearby in order to account for the spatial relationships. The fact that disseminated lead-zinc mineralization and a few minor ore lenses occur in the hanging wall "porphyry" suggests that perhaps the source which gave rise to the B-l deposit continued to contribute metals and sulfur for some time while explosive submarine or perhaps even terrestrial vulcanism associated with volcanic islands contributed "porphyry" to the depositional environment. The "plug-like" developments of "porphyry" which appear to project into the massive sulfides at the bottom of the B-l together with the coarse grained quartz-feldspar "clots" in the ores are probably related to this post-ore activity.

The relative heaviness of the sulfide sulfur in the "porphyry" above the B-l is suggestive of some significant change at the source which apparently coincided with the onset of explosive vulcanism. It is uncertain, however, why this should be heavier than the sulfur in the B-l.

#### 8-14. Summary and conclusions

Prior to the present investigation it was known that the stratiform deposits of the Bathurst-Newcastle area, including the Heath Steele B-l deposit, have features similar to many stratiform deposits in other parts of the world and most of these features render these deposits unique as a group. Among these features are included their form, occurrence in eugeosynclinal settings, consistencies in base metal ratios, lead isotope abundances and their generally small range of sulfur isotopic variation and enrichment in  $S^{34}$  relative to vein-type deposits of unequivocal igneous hydrothermal origin occurring in older rocks. The grain size of the ores can be correlated in a general way with the grade of regional metamorphism in the enclosing rocks and recent find-

ings suggest that the textural relationships between the constituent sulfides have probably been caused by recrystallization of the sulfides in response to regional metamorphism. There is a lack of clear spatial relationships with intrusive igneous source rocks, a lack of consistent relations with structural features, an apparent absence of "at-depth" feeder channelways extending below the steeply oriented deposits and an absence of clear wallrock alteration effects. Consistencies in the character of the base metal zoning were recognized with relation to the stratigraphy in the Matagami deposits of Quebec and the relationships were interpreted to indicate that the deposits were emplaced when the enclosing strata were in a sub-horizontal position. Furthermore, it has been found that rocks which overlie some of the deposits are unaltered and unmineralized and in these respects are different from rocks occurring in immediate contact with the massive sulfides of the stratigraphic bottoms of these deposits.

While some writers believe that the deposits can be generally related to igneous intrusive rocks, it does not appear that there is any foundation for such claims since the evidence appealled to has been shown to be either ambiguous or inconsistent. A recognition of these deficiencies has led some writers, and notably R.L. Stanton, to postulate a sedimentary origin for this class of deposit. There do not appear to be any serious difficulties in explaining the observed features in terms of a sedimentary origin. The only generally recognized features of the stratiform deposits which had not been satisfactorily accounted for by any of the models relate to the abundance of sulfur isotopes.

Very recently, Sangster (1967) proposed that bacterial reduction of marine sulfate might explain the narrowness of variation, the general heaviness of the sulfur and the parallelism of the mean values of the deposits with evaporite sulfur of similar age.

The findings and conclusions reached in the present study are summarized as follows:

i) sulfur isotope fractionations between coexisting pyritesphalerite, sphalerite-galena and pyrite-galena pairs are fairly uniform for given pairs from a total of six deposits and those from the B-1 orebody were found to be independent of location and  $65^{34}$  values of respective pyrites.

This strongly supports the view that isotopic equilibrium was at least closely approached at a fairly uniform temperature in these deposits and can only be reasonably explained in terms of metamorphism at the lower to middle Greenschist grade of regional metamorphism.

- ii) three across deposit profiles in the B-l orebody exhibit overall sulfur isotope trends which favour enrichment in S<sup>32</sup> towards the stratigraphic top of the deposit. Pyrites from two of these profiles gave similar patterns. It was shown that the trends cannot be attributed to mineralogical variation nor can they reasonably be attributed to regional metamorphism.
- iii) the sulfur isotope ratios in sulfides of Fe, Cu, Pb and Zn precipitated from solution with  $H_2S$  at 25°C were found to be consistently lighter than the source  $H_2S$  by up to about

1%. Sulfur isotope exchange occurs between sulfides in slightly acid solution and the  $H_2S$  reservoir gas in contact with the solution. The isotope effect favours a progressive enrichment in  $S^{32}$  in sulfides but does not seem likely to exceed an estimated equilibrium value of 4%, for PbS at 25°C.

These findings strongly favour the view that if the Heath Steele sulfides were precipitated in sea water, the isotopic composition of the source  $H_2S$  must in any event have been heavier than the  $\delta S^{34}$  values of the ore sulfides.

iv) the Heath Steele B-l orebody exhibits across deposit base metal zoning which is characterized by an overall increase in zinc, lead and silver abundances and a decrease in the abundance of copper moving from the bottom towards the stratigraphic top of the deposit. A remarkable worldwide consistency in the stratigraphic positions of zinc-lead-rich and copper-rich ores has been found so far for "volcanic" type stratiform deposits similar to those in the Bathurst-Newcastle camp.

These consistencies strongly favour the view that the deposits were formed while at least the underlying rocks were in a sub-horizontal position as was suggested by Roscoe (1965) for the Matagami deposits. A comparison of the pattern of zoning with features observed in zoned hydrothermal deposits occurring in close association with intrusive igneous rocks and the abundances of copper, zinc and lead in volcanic incrustations formed at various temperatures indicate that the copperrich ores formed from higher temperature hydrothermal solutions than the lead-zinc ores and this is interpreted to reflect a temperature decrease at the magmatic source.

> v) the B-l orebody is essentially a stratiform pyritic body containing two principal funnel-shaped "centers" of higher grade zinc-lead-silver ore. The axes of the "centers" are essentially normal to the stratification in the steeply inclined enclosing rocks. "Porphyry" occurs in immediate contact with the massive sulfides in the vicinity of the "centers" and in places has "plug-like" forms which project into the massive sulfides. Minor copper-rich mineralization occurs in the metasediments below the deposit.

It is considered that all these features are genetically related and they suggest that the base metals were transported through the footwall sediments and discharged at the sediment-water interface from vents whose positions remained fairly constant during deposition. The base metals are interpreted to have rapidly precipitated with available  $H_0S$  from sea water above the sediment-water interface.

It is concluded that the findings of the present study strongly support a volcanic origin for the base metals in the B-1 orebody and probably also in other "volcanic" type deposits where similar base metal zoning is evident. While a biogenic origin for the sulfur might account for the narrow range of variation and the general heaviness of the sulfur in these deposits, it does not appear to satisfactorily account for the across deposit sulfur isotope trends, the widespread

association of pyrite and minor magnetite and the greater abundance of pyrrhotite in the lower parts of the B-1. A further difficulty is to explain why there is no evidence to suggest that abundant organic material, which is necessary as a food source for sulfate reducing bacteria, might have existed.

A model has been proposed which genetically relates the metals The model proposes that large quantities of connate and the sulfur. water entered submarine volcanic vent systems and the connate sulfur exchanged with magmatic sulfur compounds at temperatures of 500 to 700°C thereby generating H<sub>2</sub>S of the required composition. The principal justification for the model is that it seems inevitable that hydrothermal fluids would communicate with connate waters contained in permeable sediments which formed the walls of at least the upper portions of volcanic vent systems. There are many uncertainties involved in the model, however. The most critical uncertainty is whether the isotopic composition of sulfate sulfur in Ordovician connate waters varied appreciably from Ordovician marine sulfate. If it is assumed, however, that this was not appreciably different and that it accounted for at least 60% of the total sulfur in the hydrothermal fluids, it appears that the overall isotopic trends and the greater abundance of pyrrhotite in the lower parts of the B-1 can be satisfactorily explained in terms of a progressive temperature decrease in the source magma. A temperature decrease at the source is indicated by the across deposit base metal zoning. The generally greater abundance of pyrrhotite in the stratigraphically lower parts of some stratiform deposits appears to constitute fairly strong evidence in favour of a volcanic-exhalative

origin for the sulfur. Low  $H_2S/SO_2$  ratios in higher temperature fumarolic gases and presumably also in higher temperature magmatic fluids are believed to be less likely to precipitate elemental sulfur from sea water than lower temperature fluids having high  $H_2S/SO_2$  ratios. The greater abundance of pyrrhotite in the lower parts of some zoned stratiform deposits is thus attributed to a lack of initially precipitated inorganic elemental sulfur which prevented precipitated FeS from forming pyrite. The association of pyrite and magnetite is attributed to generally low temperature fluids having high  $H_2S/SO_2$  ratios but having relatively low  $H_2S$  contents.

It is concluded that the base metals in the Heath Steele B-1 orebody and probably also in deposits of similar kind, can be most satisfactorily accounted for in terms of a volcanic-exhalative origin. While it seems equally probable that the sulfur is also of sedimentary origin, there is uncertainty as to whether it was made available by organic or inorganic processes.

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256

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257

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