A SOLUBILITY MODEL FOR DEPOSITION OF STRATIFORM MASSIVE SULPHIDE DEPOSITS, NEW BRUNSWICK, AND ITS RELATION TO THE DISTRIBUTION OF GOLD AND PALLADIUM

By

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ABSTRACT

Gold and palladium concentrations have been determined in sulphide ores and host rocks of the Caribou, Brunswick No. 12 and Heath Steele mines, New Brunswick, by neutron activation analysis. Gold contents vary from 100 to 6000 ppb in the ores. Gold correlates positively with lead and zinc in the Caribou and Brunswick No. 12 deposits, but is uncorrelated with base metals in the Heath Steele B-1 orebody. Palladium contents range from 3 to 0.1 ppb and, in contrast with gold, show no correlation with base metals in any of the mines. Thus, transport and depositional processes controlling palladium distribution remain obscure. An analysis of the variation of gold content of separated minerals found in replicate analyses, suggests that the dominant mode of occurrence is the native metal.

Based on work by Sato (1972b, 1973), a comparison with the Kuroko deposits and analytical data collected by the author, a syngenetic model for metal distribution in the New Brunswick ores has been developed. On the basis of such features as shape, lamination, initial grain size and metal ratios, it is suggested that these latter ores were formed at lower temperatures and from solutions of higher density than the Kuroko deposits.

The correlation of gold with lead and zinc is similar to that found in the Kuroko and is inexplicable in terms of chlorocomplexing (Helgeson, 1969) for either Kuroko or New Brunswick stratiform deposits. It is concluded that gold sulphide complexes are the most likely species responsible for gold solubility and transport in the ore solutions which formed these deposits.

The zoning of gold from low concentrations in copper-rich ore to higher concentrations in lead-zinc ore is thought to reflect gradual saturation of an ore solution with respect to gold in the waning states of sulphide precipitation. Decreasing temperature, fugacity of oxygen and molality of aqueous sulphide, together with increasing ore solution pH, are primarily responsible for attainment of saturation with respect to metallic gold.

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CHAPTER 1

PURPOSE OF STUDY

This study was undertaken to determine the concentration and distribution of gold and palladium in the stratiform base metal deposits of New Brunswick. Gold is present at economic levels, but the nature of its zoning is poorly established and much less well known than that of zinc, lead, copper or silver.

In other studies (Krauskopf, 1951; Kakovskii and Tyurin, 1962; Helgeson, 1969; Weissberg, 1970; Seward, 1973; Henley, 1973) a number of possible gold complexes, important for transport in hydrothermal solutions, have been investigated. From knowledge of the stabilities and solubilities (Helgeson, 1969) of the sulphides of iron, zinc, lead and copper, it should be possible to delineate the physicochemical conditions necessary for formation of massive sulphide deposits. By consideration of these physicochemical conditions it is anticipated that limits can be placed on the gold solubilities required to explain the gold distribution in the New Brunswick deposits. A choice between prospective aqueous gold complexes can then be made.

Palladium, as a representative of the platinum group, was expected to show some similarities to gold as far as solubilities in hydrothermal solutions are concerned. Almost no data, however, are available concerning its concentration in geothermal solutions, sediments or non-magmatic ore deposits. By determining its abundance in the stratiform base metal deposits and comparing this with gold, knowledge of the behaviour of palladium in the geochemical cycle, and particularly in hydrothermal ore deposition, is increased.

Table 1-1. List of Symbols and Abbreviations

$$d^{34}S = \frac{(S^{32}/S^{34})_i - (S^{32}/S^{34})_s}{(S^{32}/S^{34})_s} \times 1000$$

E = Oxidation potential of reaction

f = Faraday constant

ΔF^o = Free energy of reaction at 25°C

$\Delta H_r^o(T_r)$ = Enthalpy of reaction at reference temperature (T_r)

$K(T)$ = Equilibrium constant at temperature T

m = Molality

M = Molarity

n = Number of electrons transferred in reaction

pKa_1 = First dissociation constant of H_2S

R = Gas constant

$\Delta S_r^o(T_r)$ = Entropy of reaction at reference temperature T_r

T_r = Reference temperature, 25°C

CHAPTER 2

REGIONAL GEOLOGY

2-1 Geology of the Tetagouche Belt

2-1-1 Stratigraphy

All the ore deposits investigated are contained within one area of mixed sedimentary and volcanic rocks of Ordovician age in central New Brunswick (Fig. 2-1, after Davies, 1972). The supposed middle Ordovician age is indicated by two fossil localities (Alcock, 1935, Helmstaedt, 1971). The rocks, which have been termed the Tetagouche group, have been intensely deformed and this, coupled with the lack of outcrops or marker beds, has prevented elucidation of the stratigraphic succession. This problem is discussed in some detail by Helmstaedt (1971).

Until recently a four-fold classification of the Ordovician rocks as shown by Davies (1972), was followed by most authors (Fig. 2-1, Table 2-1). However, Helmstaedt (1971), from mapping of the western part of the area covered by Fig. 2-1, has presented a slightly different grouping of the rocks and a different stratigraphic succession (Table 2-1). Table 2-1 shows the author's suggested relations between the classifications of Davies and Helmstaedt. These should only be

Fig. 2-1 Geology of the Tetagouche Area, Northern New Brunswick. (Davies, 1972).

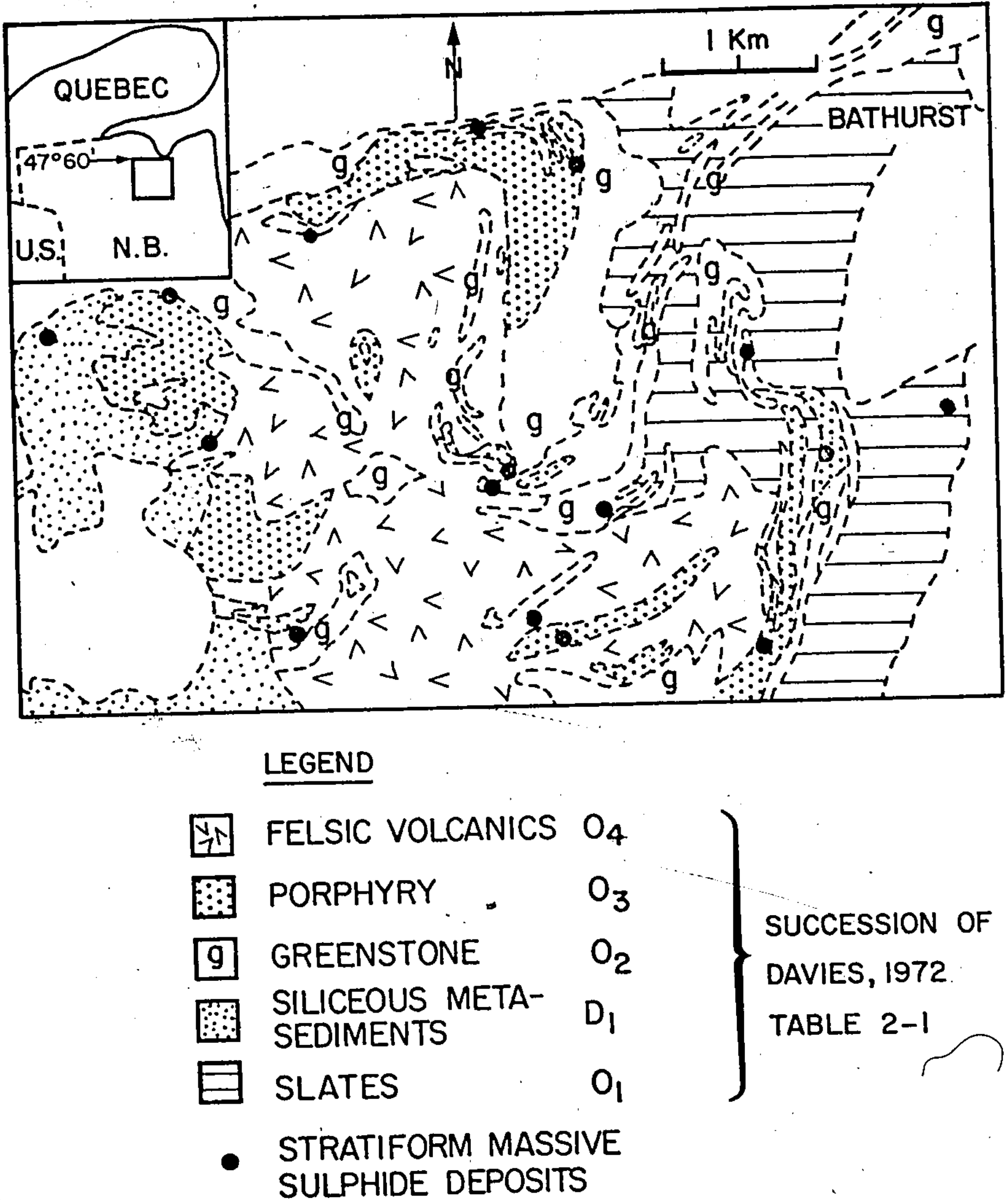
QUEBEC
47°60'
U.S.
N.B.
N
1 Km
BATHURST
g
LEGEND
FELSIC VOLCANICS O4
PORPHYRY O3
GREENSTONE O2
SILICEOUS META-SEDIMENTS D1
SLATES O1
STRATIFORM MASSIVE SULPHIDE DEPOSITS
SUCCESSION OF DAVIES, 1972 TABLE 2-1

Table 2-1. Stratigraphic Succession in the Tetagouche Area*
(Helmstaedt, 1971; Davies, 1972)

Correlation between two sets of units not certain

	Units of Helmstaedt	Description	Units of Davies	Description
Youngest	Unit 5	Massive mafic volcanic rocks	O_2	Mafic volcanic rocks
	Unit 4	Slate, chert and andesitic volcanic rocks	O_4	Felsic volcanic rocks
	Unit 3	Rhyolite volcanic rocks both massive and schistose	O_3	Porphyry
	Unit 2	Slate, siltstone and greywacke	(part of) D_1	Siliceous metasediments
Oldest	Unit 1	Quartzite and phyllite	O_1	Slates

* In Fig. 2-1 only the units of Davies are shown.

taken as suggested relations.

Poole (1967, 1973) suggested that the tectonic regime is consistent with formation of an initially stable platform (Unit 1 of Helmstaedt), which developed into a eugeosyncline during deposition of Unit 2. The range of the volcanic rocks from felsic to mafic with considerable volumes of intermediate rocks, also supports the idea of the development of a eugeosynclinal environment.

The Silurian-Devonian rocks to the north and the Pennsylvanian rocks to the south, are far less deformed and metamorphosed than the Tetagouche group. As no stratiform massive sulphide deposits occur in these younger rocks, they will not be discussed further.

The area is intruded by a number of batholiths of variable composition, mainly granitic, which are post-tectonic and Devonian (Tupper and Hart, 1961).

2-1-2 Structure and Metamorphism

A number of phases of deformation have occurred, and some authors differ on the details and which ones to assign to the Taconic and Acadian orogenies (Davis, 1972; Helmstaedt, 1971, 1972; McAllister, 1973). In general the first phase probably involved isoclinal folding and formed the regional schistosity. The broad flexures of the region seem to have developed considerably later, as they affect the Siluro-Devonian rocks also.

The main period of metamorphism was synkinematic with respect to the first phase of folding and was accompanied by penetrative deformation, with development of cleavage and schistosity. The metamorphic assemblages are summarized below:

(1) phyllites; quartz-muscovite-chlorite

(2) rhyolites; quartz-muscovite-chlorite-sericite-albite

(3) basic volcanics; albite-chlorite-epidote-leucoxene-stilpnomelane.

The assemblages found in the phyllites and rhyolites are consistent with the quartz-albite-muscovite-chlorite subfacies of the greenschist facies. Helmstaedt (1973) has suggested that a biotite-chlorite isograd is present in the area. Further south in Maine the contemporaneous metamorphism is of biotite grade. These facts suggest a decrease in metamorphic grade southwest to northeast (McAllister and LaMarche, 1972).

2-2 Geological Setting of the Ore Deposits

2-2-1 Introduction

The rhyolitic volcanic rocks described above as Unit 3 occur in a number of forms which include massive rhyolite flows, ashfall tuffs, ignimbrites and intrusions. The differing origins are suggested by the varying degrees to which schistosity has developed in the rocks. The stratiform sulphide deposits of the area are all contained within or near one rock type characteristic of this unit - the so-called "Bathurst Porphyry".

The porphyry has been described as quartz-feldspar-muscovite schists containing variable amounts of quartz and alkali feldspar augen. The high potassic nature of these rocks is well-established (Loudon, 1960; Davies, 1966; Cavalero, 1970; Roscoe, 1971). Detailed petrographic and chemical studies have been carried out by Loudon (1960) and Jones (1964). These volcanic schists are interlayered with graphitic schists, greywackes and pelitic quartz-muscovite-chlorite-sericite phyllites. Occasionally the latter rock type is gradational into the "Bathurst Porphyry".

The proposed geological environment, which is of island arc-eugeosynclinal type (Helmstaedt, 1971; Poole, 1973) is a typical setting for the occurrence of ignimbrites and rhyolite tuffs. As noted by Helmstaedt (1971), typical eugeosynclinal sequences are characterized by stratigraphically older basic volcanic rocks and younger acidic volcanic rocks. In the case of the Tetagouche area, however, the rhyolitic rocks appear to be older than the basic rocks.

There are many massive sulphide deposits in the area, especially if those of low grade and/or small size are included. Rather than present a generalized description, each of the deposits investigated will be described in some detail. In Fig. 2-1, the major deposits are shown in relation to the felsic and porphyritic volcanics.

2-2-2 Anaconda Caribou Deposit

Three phases of folding in the Caribou area have been recognised by Davis (1972). The first, F_1, produced isoclinal folds and the formation of the regional schistosity. The formation of kink folds occurred during the second phase, F_2, while the final period, F_3, produced the broad regional folds. The Caribou deposit lies within a synformal fold known as the "Caribou" fold, probably of F_3 age. The regional geology and a detailed plan (Cavalero, 1970) showing the location of the drill holes investigated in this research are presented in Fig. 2-2.

Outcrops are sparse, though I.P. resistivity defines continuity well (Cavalero, 1970). The "Caribou" fold is delineated by a sequence of interbedded metasediments and metavolcanics, mainly of rhyolitic and andesitic composition. The orebody is situated at the contact of one belt of metasediments with quartz-feldspar augen schist. The succession has been described in some detail by Cavalero (1970) and is presented in Table 2-2.

The primary sulphide minerals include pyrite, sphalerite, galena and chalcopyrite with minor arsenopyrite, marcasite, pyrrhotite, bornite and tetrahedrite. Magnetite and accessory hematite also occur in the ore horizon. The ore is often banded parallel to the regional schistosity and bedding. Various compositional and textural properties of the ore give rise to banding, including the nearly monomineralic bands in the

Fig. 2-2. Geology of the Caribou Mine Area (after Cavalero, 1970)

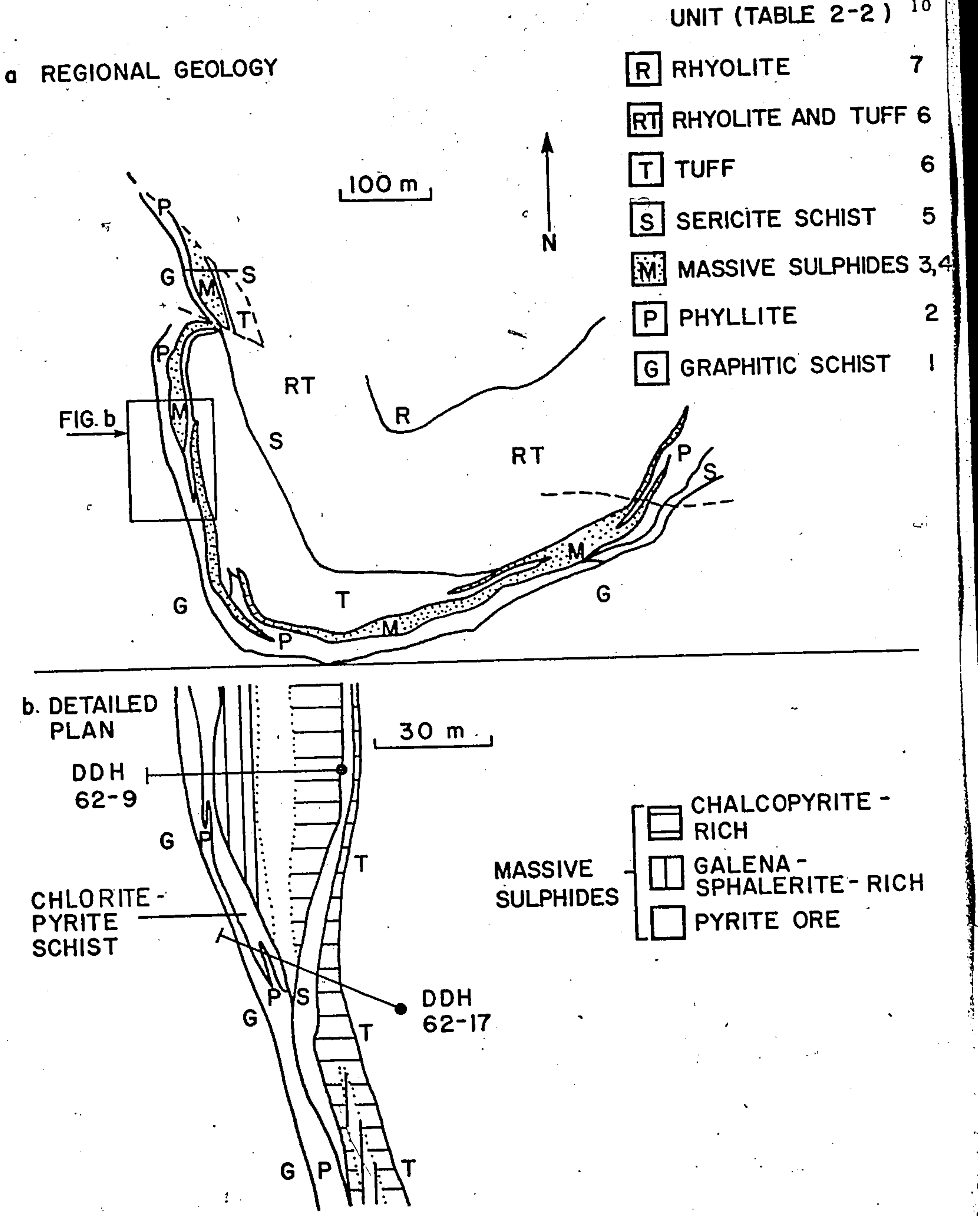
a REGIONAL GEOLOGY
UNIT (TABLE 2-2)
R RHYOLITE 7
RT RHYOLITE AND TUFF 6
T TUFF 6
S SERICITE SCHIST 5
M MASSIVE SULPHIDES 3,4
P PHYLLITE 2
G GRAPHITIC SCHIST 1
100 m
N
FIG. b
P
G
S
M
T
P
RT
M
R
S
RT
P
S
M
G
T
G
M
P
b. DETAILED PLAN
30 m
DDH 62-9
G
P
T
CHLORITE-PYRITE SCHIST
P
S
G
DDH 62-17
T
G
P
T
MASSIVE SULPHIDES
CHALCOPYRITE-RICH
GALENA-SPHALERITE-RICH
PYRITE ORE

Table 2-2. Geological Succession at the Anaconda Caribou Deposit (Cavalero, 1970)

Unit /Age	Thickness	Rock Name	Mineralogy[1]	Description
7/Youngest	30m	Potash-rhyolite porphyry	M-O-Q-S	Competent, foliated as repetitive units
6	40-20m	Hanging-wall schist	Q-S-O-minor C-Pl	Texture varies with quartz content
5	3-1m	Hanging-wall phyllite	S-Q	Only on west limb, sharp contact with ore with 0.3 to 0.1m chloritic envelope
4		Ore Horizon		
3	8m	Chlorite-pyrite schist	Hard Black with Py	Adjacent to south part north sulphide body, type of iron formation?
2	3-20m on limbs 35m on nose	Phyllite zone	i. 0.3m from orebody, S-C schist, ii. then M-C-Q with Py iii. heterogeneous M-C-Q to quartzite to M-C	Well-developed schistosity
1/Oldest	30m	Graphitic zone	Q-M-Graphite with Py (framboidal)	Blackish with well-developed crenulation

Note 1. C=chlorite, M=muscovite, O=orthoclase, Pl=plagioclase, Py=pyrite, Q=quartz. S=sericite.

zinc- and lead-rich ore, laminations with differing pyrite grain sizes in the chalcopyrite ore and laminations with local magnetite enrichment.

The minerals are very fine grained, with typical sulphide grains exhibiting a maximum dimension of about 0.05mm. (Tempelman-Kluit, 1970). The pyrite occurs in colloform, framboidal, anhedral, euhedral and grain aggregate textures. It shows various stages of recrystallization according to Roscoe (1971). Sphalerite and galena often occur as "atoll" like structures in the pyrite. There are numerous textures suggestive of deformation and metamorphism of the sulphides (Davis, 1972) including internal fracturing of the pyrite, "foliation" of chalcopyrite, sphalerite and galena, and fracture-filling of pyrite by the "softer" sulphides.

Despite a number of contentious issues (Helmstaedt, 1973) concerning the dating of the various periods of folding, the structural analysis of Davis (1972, 1973) shows that the orebody was emplaced before the formation of the "Caribou" fold. In addition, the textures suggest that the ore was deposited before the metamorphism, and thus was deposited prior to F_1 stage folding.

It should be noted that small stratiform sulphide occurrences as inferred from geophysical methods, are to be found some distance away on the same stratigraphic horizon.

2-2-3 Brunswick Mining and Smelting No. 12 Orebody

The stratigraphic succession, as described by Stockwell and Tupper (1966), is presented in Table 2-3. Three phases of deformation have been recognised in the area (McAllister and LaMarche, 1972). F_1* produced isoclinal folds and the regional schistosity and F_3 large-scale, broad regional folds. F_2 is manifest as crenulation cleavage. The orebody occurs in tight isoclinal F_1 folds which are thought to have considerably shortened and thickened the deposits (Fig. 2-3).

The sulphides form two lenses known as the Main Zone and the West Zone (Rutledge, 1971). The Main Zone has lead-zinc rich ore, copper rich ore and barren pyrite. Fig. 2-3b (from Company maps) shows the distribution of the different ore types and the location of the drill holes analysed in this study.

The West Zone is far more complex than the Main Zone and shows greater evidence of deformation. It converges on the Main Zone with depth. The distribution of copper suggests that the two ore zones are related by a sheared out, isoclinal fold (Rutledge, 1971). The Main Zone ore is banded parallel to the regional schistosity; however, in the West Zone, the regional schistosity is at an acute angle to banding and to the sulphide-wallrock contact (Rutledge, 1971).

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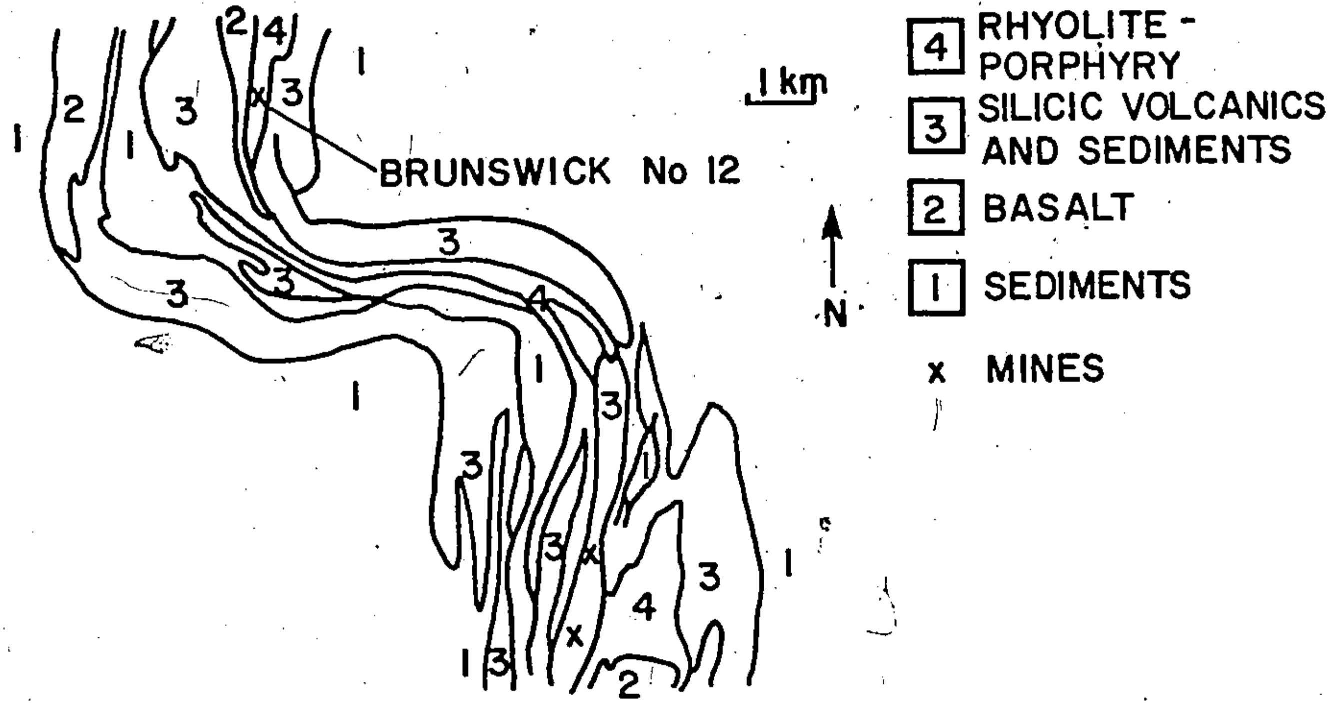
* Equivalent to D_1 of McAllister and LaMarche.

Fig. 2-3. Geology of the Brunswick No. 12 Mine (from Brunswick Mining and Smelting Company Maps and Stockwell and Tupper, 1966) a REGIONAL GEOLOGY



b MINE GEOLOGY

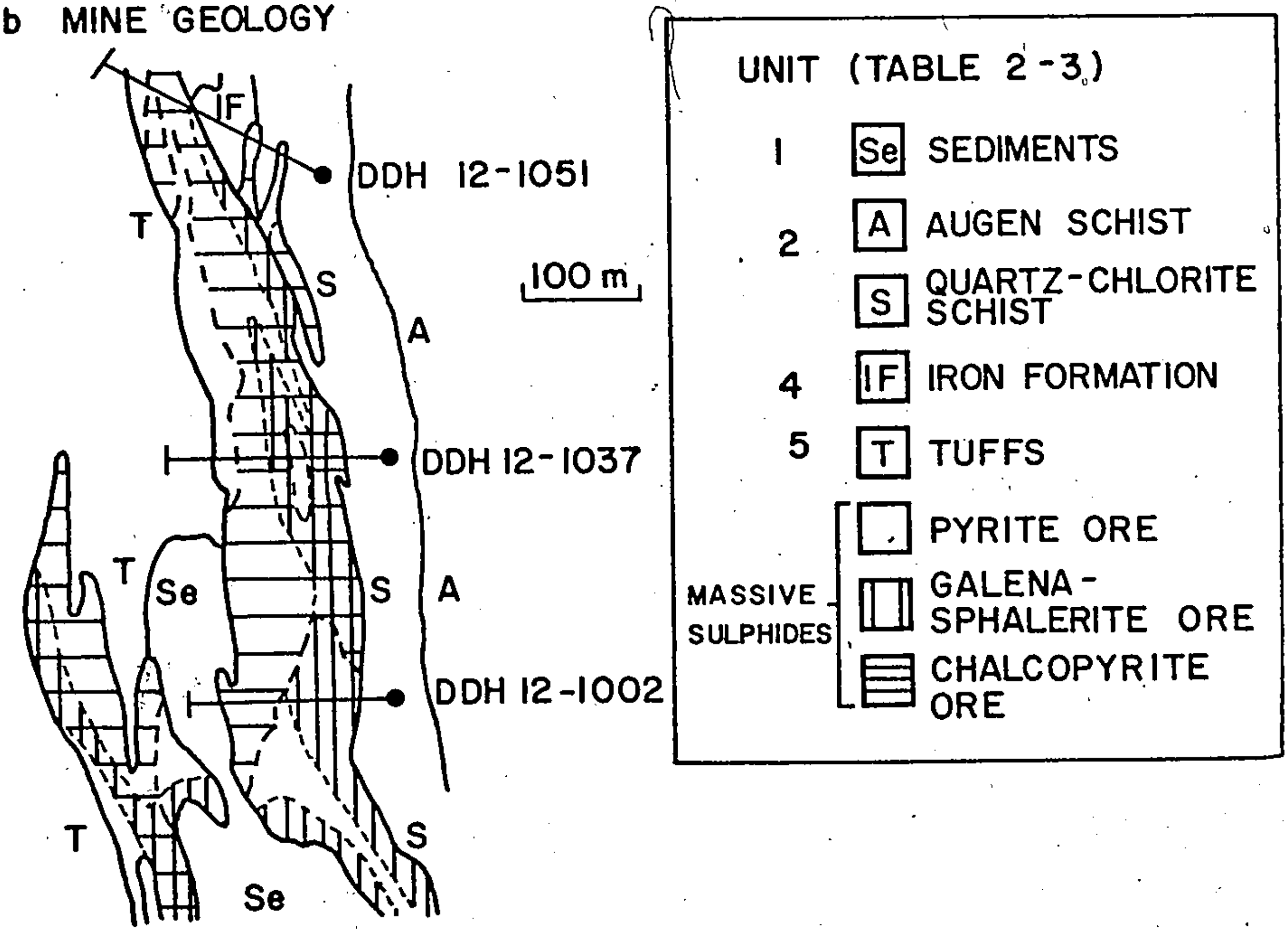


Table 2-3. Geological Succession at the B.M. and S. No. 12 Orebody (Stockwell and Tupper, 1966)

UNIT[2]	MINERALOGY[1]	DESCRIPTIVE NOTES
5 Upper volcanics (Youngest)		Metasediments with volcanogenetic constituents, followed by mafic meta-tuffaceous rocks
4 Iron Formation	M-Si-C-Q	Banded rock, laterally continuous with the ore
3 Ore Horizon		
2 Augen Schist	Q-F-S-C-B	Augen make up 20% of rock; matrix is crudely layered, relic feldspars and quartz suggest ash flows and tuffs
1 Metasediments (Oldest)	Q-C-S-F	Thinly bedded, gray-green contorted greywacke, phyllites argillites, schists and minor graphitic phyllites

Note 1. B=biotite, C=chlorite, F=feldspar, M=magnetite

Q=quartz, S=sericite, Si=siderite

Note 2. Numbers refer to the units noted in the legend to Fig. 2-3(b).

The sulphides are predominantly pyrite, sphalerite, galena, chalcopyrite, tetrahedrite and bornite, with numerous minor minerals including silver sulphosalts (Boorman, 1968). Deep in the Main Zone there is a pyrrhotite-rich lens on the footwall. The nearby footwall schists are strongly chloritized, and heavily veined with pyrite-pyrrhotite and variable amounts of chalcopyrite. The gangue minerals of the deposit are largely quartz and some chlorite-sericite-carbonate-graphite, typical components of metsediments and metavolcanics of low grade metamorphism.

The sulphides are generally fine grained and intimately intergrown. Pyrite forms euhedral crystals or aggregates of anhedral grains, and may have a collomorphic or spheroidal appearance (Fuller, 1968). Sphalerite is the next most abundant mineral. Rounded inclusions of a "soft" mineral within a "harder" one are frequently observed. Colloform and concentric structures can often involve a number of minerals.

In the West Zone the ore is strongly laminated and coarse grained. Pyrite is frequently brecciated or recrystallized. On occasion, "flames" of coarse galena, 1m. long, occur at the contact of the ore with the wall rocks.

The nearby Brunswick No. 6 orebody with its associated iron formations, and the Austin Brook Iron Formation, are on the same stratigraphic horizon as the Brunswick No. 12 mine.

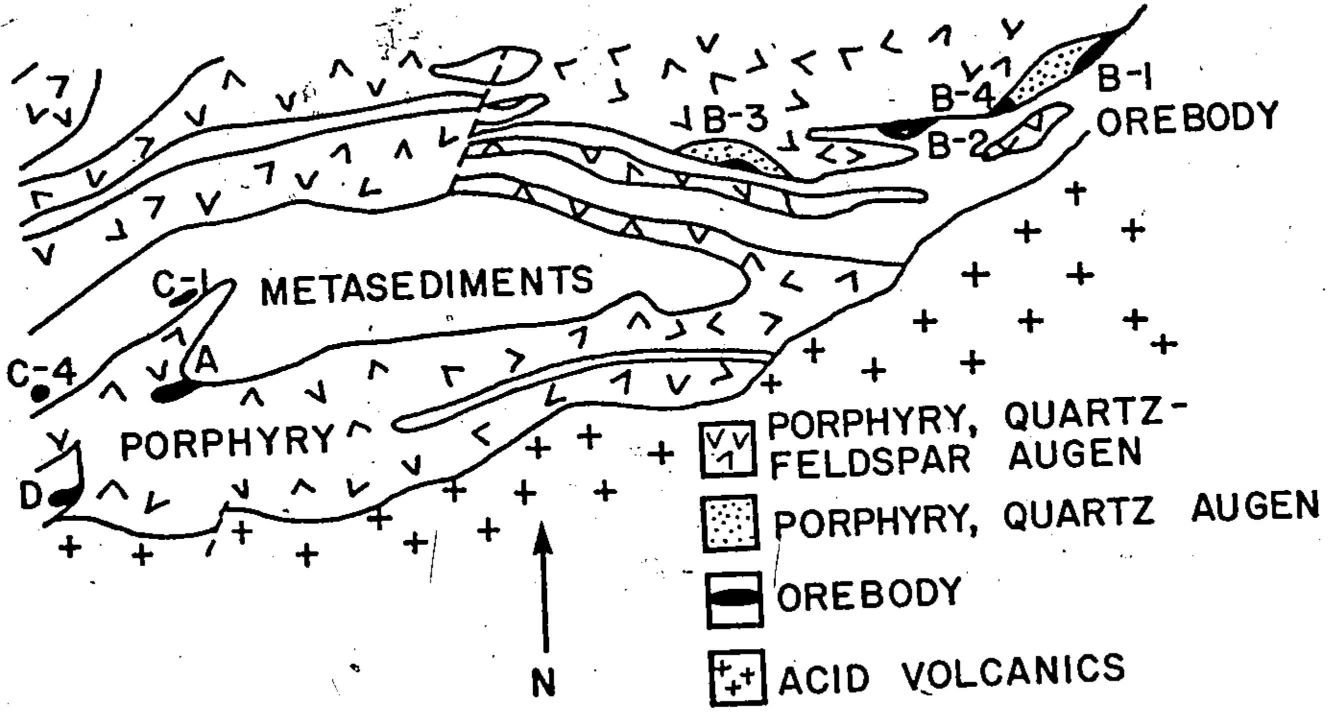
2-2-4 Heath Steele B-1 Orebody

The distribution of ore deposits in the Heath Steele locality is shown in Fig. 2-4a (from Gates, 1970). The gross zonation of galena-sphalerite and chalcopyrite ore on the 8600 level of the B-1 deposit, together with the location of the analysed drill hole B138, are presented in Fig. 2-4b. The stratigraphic succession for the Heath Steele district has been described by McMillan (in Whitehead, 1973) and is presented in Table 2-4.

There are a number of distinct ore zones which vary considerably in degree of deformation and which are arranged around a broad anticline of porphyry and tuff some 3 km. across. Three groups may be recognised including: (i) B-zones, (ii) the A-, C- and D-zones and (iii) the E-zone (Gates, 1970). The B-zone consists of a continuous massive sulphide body divided into the B-1, B-2, B-3 and B-4 blocks. The orebody shows undulations and tight folds with depth which often do not have expression in the enclosed rocks.

The B-zone, which is the least deformed, shows typical ore zoning with galena-sphalerite ore on the hanging wall and chalcopyrite-pyrrhotite ore on the footwall. These two zones are commonly separated by barren pyrite, and the chalcopyrite-pyrrhotite ore is often disseminated in the footwall metasediments adjacent to the massive sulphides. The A-, C- and D-zones are very complex structurally, with less zoning

Fig. 2-4. Geology of the Heath Steele Area (after Gates, 1970) a REGIONAL GEOLOGY



b. HEATH STEELE B-1 OREBODY PLAN

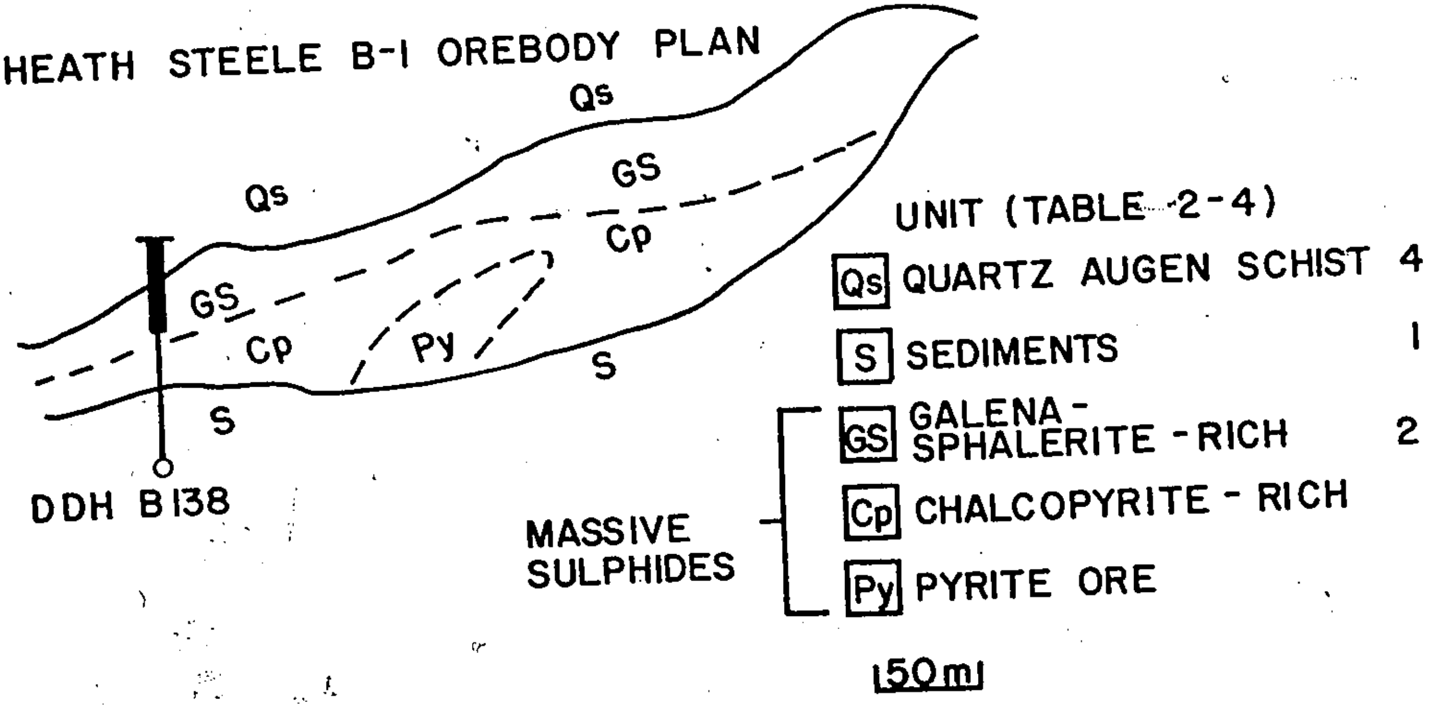


Table 2-4. Geological Succession at Heath Steele B-1 Orebody (Whitehead, 1973)

	UNIT[2]	MINERALOGY[1]	DESCRIPTIVE NOTES
	Acid volcanics with interbedded sediments	Q-O-C	Finer-grained than porphyry
4	Quartz-feldspar porphyry	Q-O-Pl-S-C-Cc	Quartz augen abundant immediately above ore; shows graded bedding.
	Iron Formation	C-Mg-Si-Q	Black banded rock on ore horizon; not shown in Fig. 2-4.
2	Ore Horizon		
1	Metasediments or tuffaceous horizons with porphyry lenses (oldest)	Q-S-C	Schistose and highly contorted

Note 1. C=chlorite, Cc=calcite, Mg=magnetite, O=orthoclase,
Pl=plagioclase, Q=quartz, S=sericite, Si=siderite

Note 2. Numbers refer to the units noted in the legend to Fig. 2-4(b).

across the layering and more lateral zoning. The E-zone has more chalcopyrite-pyrrhotite ore than the other deposits.

According to McBride (1974) there have been as many as five periods of deformation, of which the first two (F_1 and F_2) formed major structures and the third and fourth (F_3 and F_4) cleavages only. This seems at variance with studies of other areas (Davis, 1972; Helmstaedt, 1971).

A few detailed geochemical studies have been made of the B-zone ore mass including rock geochemistry (Whitehead, 1973) and sulphur isotopes (Dechow, 1960; Lusk, 1968).

It has long been known that fractionation of manganese and iron during sedimentation (Krauskopf, 1957) depends in part on the oxidation potential of the environment. Whitehead found a higher manganese-to-iron ratio in the iron formations above the orebody than in the orebody itself. This implies an increase in the oxidation state of the environment - hydrothermal fluid or sediment pile - towards the top of the iron formation.

Dechow (1960) established that sulphide sulphur was characterized by positive $d^{34}S$ values with a narrow range of about 5‰. This was confirmed by Lusk (1968) who was able to measure sulphur isotopic fractionation between minerals and thereby deduce a metamorphic temperature. Lusk (1968) also found a very slight decrease in $d^{34}S$ stratigraphically across the orebody from copper-rich to lead-zinc-rich ore.

The genetic significance of this observation will be discussed in section 2-3-6.

2-3 Comparison of the Bathurst-Newcastle Deposits with other Stratiform Massive Sulphide Deposits

2-3-1 General

The massive pyrite deposits of the Bathurst-Newcastle district are examples of the type called variously volcanogenic stratiform (Canavan, 1973; Stanton, 1972a), pyritic deposits (Smirnov, 1970), massive sulphide deposits (Anderson, 1969) or different combinations of these (e.g. Sangster, 1972).

It has been suggested that two principal ore-host rock associations characterize such deposits; namely, copper-zinc deposits with basic volcanic successions and zinc-lead-copper deposits with acidic successions. Poole (1973) and Sillitoe (1972), in attempting to generalize, have inferred that in the Phanerozoic era the copper-rich deposits originate in environments of oceanic rifting, while the zinc-lead-copper deposits are genetically related to subduction processes in an island arc environment. They cite, for example, the Cyprus deposits and the Kuroko deposits, respectively, as representatives of these two associations. However, as pointed out earlier by Anderson (1969), there are exceptions to the above associations of ore and host rock compositions.

The Bathurst-Newcastle sulphide deposits are predominantly of the copper-lead-zinc type, with the latter two metals usually more abundant than copper in individual deposits (Douglas, p. 321, 1970). This is particularly true for the larger deposits of the area, for example the Brunswick No. 12 deposit and the Heath Steele B-1 orebody. In addition, they are consistently near rocks of intermediate or acidic composition. Thus, Bathurst deposits have affinities with, for example, the Kuroko deposits in terms of ore composition, general composition of host volcanic rocks and inferred tectonic environment.

A revolution has occurred in thinking concerning the zinc-lead-copper class of deposits. Their geological and chemical properties may be considered in relation to the two prevalent dogmas of the early 1960's, the epigenetic replacement and syngenetic theories. An excellent review of the history of these theories is presented in the first chapter of "Ore Petrology" by R. L. Stanton (1972a)

Briefly, the epigenetic replacement theory proposes that the sulphides are replacements of pre-existing rocks (Boyle, 1965) though in certain cases this has been modified to encompass replacement of unconsolidated sediments (Wilson, 1967). The origin of the fluid is not important, though in the period of the 1940's to 1950's it was often ascribed to post-tectonic granitic rocks which are so often present in this tectonic environment.

The syngenetic sedimentary theory holds that the sulphides were precipitated on the ocean floor as part of the stratigraphic succession within which they are contained. Usually the metals are thought to have been transported to the surface by a hydrothermal solution and ejected from submarine hot springs or fumaroles.

Study of the unmetamorphosed massive sulphides, such as Kuroko ores, has led to a gradual change of opinion, from a consensus in favour of an epigenetic origin to a syngenetic origin. A similar change has developed for the origin of metamorphosed massive sulphide deposits, such as those in Bathurst or the Caledonides of Norway. It was recognised that if these deposits were syngenetic with the enclosing rocks, then, where the latter were metamorphosed, the sulphides must also be metamorphosed. The inevitable conclusion was that the mineral textures of many deposits could be explained, not in terms of replacement, but by metamorphism and in some cases deformation (Emmons, 1909; Stanton, 1960; Kalliokoski, 1965; Vokes, 1968).

The following account of the general features of stratiform sulphide deposits owes much to review accounts by Anderson (1969), Smirnov (1970), Gilmour (1971), Stanton (1972a), Sangster (1972, 1973) and Mannard (1973).

2-3-2 Form

Volcanogenic stratiform sulphide deposits have their larger dimensions in the plane of stratification of the surrounding rocks. The resultant shape is that of a lens which usually interfingers or displays gradational relations with the laterally contiguous rocks. The deposits are often gradational from a disseminated zone stratigraphically upwards through massive ore. This can be seen clearly in Cyprus-type, Kuroko-type and many Canadian Precambrian deposits. The disseminated zone is often present in the Bathurst deposits but limited in extent both vertically and laterally. The upper contact of the ore with the country rock is usually quite sharp. It has been suggested that the form of the deposit reflects the form of the enclosing rocks (Sangster, 1973). Near a volcanic vent deposits are thick and wedge-shaped (Millenbach and Lake Dufault deposits in the Canadian Precambrian; Kuroko-type deposits), whilst further away they are thinner and more widespread (McArthur, Australia; Sullivan, British Columbia). These have been termed proximal and distal exhalites by Ridler (1974).

Iron formation, often containing magnetite and hematite, is commonly associated with the sulphides. These rocks may be laterally continuous with the sulphides (for example, Brunswick No. 12 mine; some Cyprus deposits), or directly above (for example, Kuroko deposits). The replacement theorists postulate that the form of the sulphide mass is due to incomplete replacement of the iron-rich rocks. In the syngenetic theory the two are integrated as sediments formed from similar hydrothermal solutions under differing conditions of Eh and pH.

In the case of the Bathurst deposits the ores and host rocks have been subjected to complex deformation, suggesting that the occurrence of sulphides in fold crests is due to preferential emplacement in a tensional zone. In fact, a large mass of sulphides could affect the local style of folding. Many deposits, however, are in open folds (e.g. Anaconda Caribou) or are not related to fold structures (e.g. Orvan Brook). The grade of regional metamorphism in Bathurst is low in contrast to the great amount of deformation, and a mobilization of the ore in response to such metamorphism is expected to cause only local changes in metal distribution. Much higher grades of metamorphism, amphibolite facies and above, are required to cause the changes in metal distribution found in deposits such as the Bleikvassli, Norway (Vokes, 1968).

2-3-3 Alteration Haloes and Host Rocks

It has long been recognised that unmetamorphosed massive sulphides, such as the Kuroko-type, have areas of alteration around them. Copper-rich mineralization, which is frequently present at the base of such deposits, is spatially associated with this alteration and often is of discordant character, occurring in a stockwork of veins or a zone of brecciation. This alteration may define volcanic vents or fissures in Kuroko- or Cyprus-type deposits, and is considered to mark the channelways utilized by mineralizing solutions.

Such alteration has not been identified in the Bathurst district. It is possible that intense shearing has obscured this feature (Helmstaedt,

1973) or that it is absent due to the distal character of the deposits. Some evidence of a geochemical change near the orebodies is suggested by studies of changes in the chemistry of chlorites and sericites in the vicinity of the orebodies (Roscoe, 1971; Sutherland, 1967). Alteration above the Bathurst deposits is rare, weak and somewhat problematical (Whitehead, 1973).

Boyle (1965) suggested that the alteration around the Bathurst deposits is indicative of a hydrothermal replacement origin for the sulphides. An approach similar to that of Stanton (1966) for the Mount Isa deposit might provide a test of this suggestion. If selective replacement of lithophile elements took place to form an orebody, an increase in sulphide relative to lithophile elements should be accompanied by a compensating decrease in amount of at least one lithophile element. If the sulphides represent an addition of material, as expected in the syngenetic theory, the ratio of lithophile elements should remain relatively constant. In fact, Stanton's evidence indicates that at Mount Isa the sulphides are an addition to, and not a replacement of a normal sedimentary sequence.

Study of the iron formations in the Bathurst district suggests that they contain unusually high contents of base metals (Enriques, 1973), and that they are characterized by fractionation of iron and manganese relative to the orebodies (Whitehead, 1973). Stanton (1972b) has found unusual contents of some elements in iron formations associated with sulphides at Broken Hill. Most authors explain this in terms of a genetic connection between sulphides, iron formations and submarine hot springs. The occurrence of iron-rich sediments in modern oceans demonstrates a close spatial arrangement with submarine volcanic activity (Honnorez, 1969).

2-3-4 Metal Concentrations and Zoning

The deposits associated with acidic volcanism tend to have a complex assemblage of metals. There is usually iron with zinc, lead and copper, as well as economic quantities of silver, gold, cadmium, selenium and many other metals. The significance of this complex metal assemblage is obscure. It is recognised that certain associations of the four major metals are characteristic (Stanton, 1972a): iron, iron-copper, iron-copper-zinc, and iron-copper-zinc-lead. For example, the assemblage iron-lead is never found.

It has been suggested by Sangster (1972) that there has been an increase in the lead content of volcanic massive sulphide deposits since Precambrian time. Stanton, however, (1972a, p. 520) has emphasized that this may apply in Canada, but Australian Precambrian deposits tend to have fairly high lead contents.

Metal zoning is often present in stratiform sulphides, with the base of such deposits consistently copper-rich. Occasionally, the copper-rich sulphides and the lead- and zinc-rich sulphides are geographically separate, as at Mount Isa, and in some deposits there is lateral zoning of the copper and lead-zinc "facies". Stratigraphic zoning seems to hold even in regimes of considerable deformation.

The zoning is also expressed by varying ratios of lead to zinc, as in the Sullivan deposit (Freeze, 1966), and by systematic variation of minor elements in the Kuroko (Tatsumi and Oshima, 1966) and McArthur deposits (Croxford and Jephcott, 1972). Silver and gold are concentrated towards the stratigraphic top of the Kuroko deposits in the form of tetrahedrite and electrum, respectively (Sato, 1972a). In contrast, silver in the Bathurst deposits occurs as sulphosalts, generally associated with galena (Boorman, 1968) and consequently, is concentrated towards the stratigraphic top of the deposits. Prior to this work the distribution of gold in the Bathurst ores was unknown.

Until recently no attempts had been made to explain the metal zoning in these deposits, despite great advances in the understanding of vein deposit zoning. There seems to be no explanation inherent in the replacement theory. Numerous possibilities are suggested by the syngenetic theory including the following:

i) change in composition of the exhaled solution with time which may or may not be independent of physical factors such as temperature (Lusk, 1973, with respect to the Bathurst deposits).

ii) change in composition of ponded brine in a submarine depression resulting from either gradual cooling with selective precipitation of constituents, or from mixing of sea water with resultant oxidation and cooling of the brine (Red Sea hot brine sediment, Craig, 1969).

iii) transport of copper, lead and zinc to different distances from submarine orifices due to differing solubilities in the exhaled solution, and gradual mixing with sea water (Sato, 1973, for Kuroko deposits).

A number of authors have suggested investigation of certain trace elements to clarify the origin of sulphides. Sulphur: selenium ratios (Goldschmidt, 1954; Yamamoto, Oyushi and Sakai, 1968), selenium and vanadium in pyrite (Anderson, 1969) and selenium and cobalt in pyrite (Loftus-Hills and Solomon, 1967) have been studied. These attempts have met with varying success. The sulphur to selenium ratios in many volcanogenic stratiform massive sulphides suggest an igneous source according to Stanton (1972a). For the New Brunswick deposits (Anderson, 1969) the vanadium and selenium contents of pyrite are more compatible with a sedimentary origin.

2-3-5 Mineralogy

In the majority of massive sulphide deposits the main mineral constituents are pyrite, sphalerite, galena, chalcopyrite and sometimes pyrrhotite. Two consistent features of pyrrhotite-bearing ores occurring in the Bathurst district are worthy of note: firstly, they are most often found in the copper-rich parts of orebodies and secondly, there is an increase in the incidence of pyrrhotite with increased metamorphic grade. Helmstaedt (1973) has suggested that pyrrhotite occurs in Bathurst ores that have been metamorphosed to the biotite subfacies of greenschist metamorphism. This is similar to the proposals of Carpenter (1974) for the Appalachians in general.

A spectrum of deposits is now known from regions of variable metamorphic grade, ranging from deposits in the high grade metamorphics of the Norwegian Caledonides to the Japanese Kurokos, which typically occurs in rocks subjected only to low grade regional metamorphism. Although not identical, these deposits are similar enough to evaluate the changes in mineralogy resulting from increasing metamorphic grade. It is apparent that the mineralogy of the ores is not a sensitive indicator of the temperatures attained during metamorphism. This is due to two main factors. Firstly, many sulphides are stable over wide temperature ranges and secondly, sulphides tend to recrystallize readily and to react (retrogress) at low temperatures. Consequently, sulphide assemblages may equilibrate with decreasing metamorphic temperatures and thereby fail to preserve a record of high temperature metamorphic events. This is in contrast to the characteristic behaviour of many silicate mineral assemblages.

With the exception of pyrrhotite, reliable sulphide index minerals are not available. Vokes (1968) has suggested that pyrite-chalcopyrite is a low temperature and pressure assemblage, while pyrrhotite-chalcopyrite and pyrite-bornite represent high temperatures and high pressures, respectively.

Evidence of metamorphism is more obvious in the textures of the minerals. It had long been believed by many North American and Australian geologists that relative euhedralism is an indication of paragenesis (Edwards, 1954). Norwegian and German geologists, recognising the the metamorphic nature of the host rocks of many massive sulphide deposits deduced that large pyrite porphyroblasts were not the first grains to grow, but developed because of the inherent crystallographic properties of the mineral itself (Berg, 1927).

It is now recognised that in metamorphosed stratabound ores a "silicate-oxide-sulphide crystalloblastic series" can be observed. In order of decreasing idiomorphism the sequence is garnet, magnetite-arsenopyrite, pyrite, dolomite, tremolite, muscovite, chlorite, pyrrhotite, sphalerite, chalcopyrite, galena (Stanton, 1964). Geology has benefited much from metallurgy in the understanding of sulphide textures. The formation of grain boundaries is disucssed in detail by Stanton (1972a). Suffice it to say that the inter-relations of the various minerals seem explicable in terms of interfacial free energy.

An example of the above-mentioned control is the formation of "atoll" structures, such as unsupported nuclei of sphalerite in pyrite, which has some parallels with quartz inclusions in garnets of metamorphic terrains. This is ascribed to negligible differences in free energy between positions within and at the grain boundaries of the host mineral (Stanton, 1964, p. 70).

A variety of textural features may result from various temporal relations of deformation and metamorphism. Deformation at low temperatures will cause cataclasis of "hard" minerals such as pyrite. At higher grades elongation of pyrite grains parallel to the regional schistosity can occur. The "softer" minerals such as pyrrhotite, chalcopyrite and sphalerite show glide or translation twinning, and together with galena, exhibit various gneissic textures, most of which can be found in the Bathurst deposits.

2-3-6 Sulphur Isotopes

The principal sources of original data on the sulphur isotopic composition of Bathurst ores are the papers of Tupper (1960), Dechow (1960), Lusk and Crocket (1969) and Lusk (1973). Tupper (1960) and Dechow (1960) considered the isotopic data to favour an epigenetic origin for the sulphur whereas Lusk (1973) contended that a syngenetic origin was supported by sulphur isotope data.

The genesis of volcanogenic stratiform sulphides as interpreted from sulphur isotope data has been reviewed by Stanton (1972a) and is summarized here:

a) The mean $d^{34}S$ value, in general, is between sea water sulphate and meteroritic sulphur. Some deposits, especially those of Precambrian age, are very close to the meteoritic average. This applies to both Australian and Canadian examples.

Sangster (1971) notes that fractionation between contemporaneous sea-water and massive sulphides has remained roughly constant since the Cambrian, averaging * $\Delta d^{34}S = 15.5‰$ for some one hundred ore-bodies. Deposits associated with volcanic rocks seem to be more fractionated (average $\Delta d^{34}S = 17.3$) than those associated with purely sedimentary rocks (average $\Delta d^{34}S = 13.6$).

The $d^{34}S$ value of Ordovician sea water sulphate was of the order of + 28 according to Thode and Monster,(1965). Using this value and mean $d^{34}S$ for various deposits reported by Tupper (1960) we obtain the following $\Delta d^{34}S$ values:

i) for the Caribou deposit, $\Delta d^{34}S = 19$,

ii) for Brunswick No. 12 deposit, $\Delta d^{34}S = 10$,

iii) for Heath Steele B-1 orebody, $\Delta d^{34}S = 14$.

It can be concluded that the Bathurst deposits show a wide range in mean $\Delta d^{34}S$ values and that no simple fractionation pattern with respect to contemporaneous sea water is obvious.

b) The range in $d^{34}S$ within a single deposit is usually very small, less than ± 5‰. This can be seen with reference to Fig. 2-5.

c) Often there is marked similarity in $d^{34}S$ over large distances within one or a few beds in contrast to a marked dissimilarity across beds.

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* $\Delta d^{34}S = d^{34}S_{\text{sea water}} - d^{34}S_{\text{deposits}}$

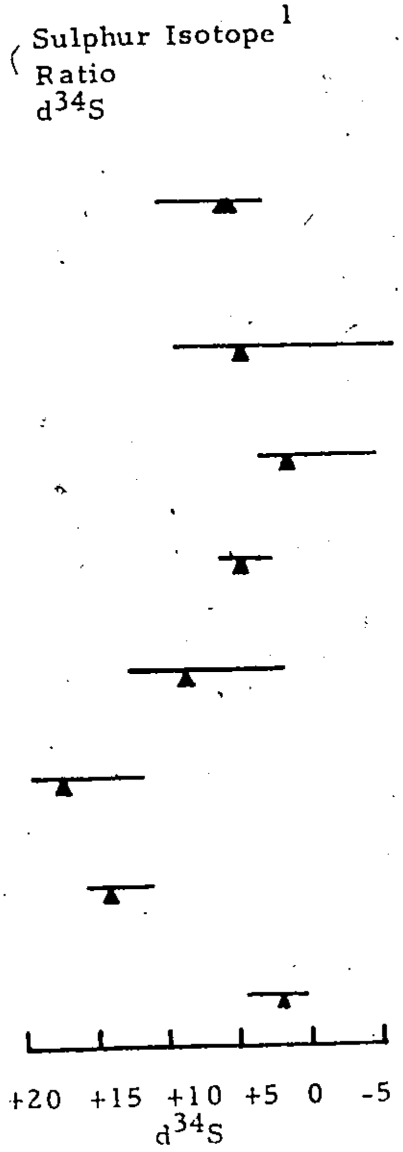
d) Systematic variation across the layering is present in some cases; for example, at Rammelsberg $d^{34}S$ of galena and sphalerite becomes heavier from stratigraphic bottom to top (Anger et al. 1966), whilst in the Heath Steele (Lusk and Crocket, 1969), the Kuroko deposits (Kajiwara, 1971) and the Cyprus deposits (Constantinou, 1974) $d^{34}S$ appears to decrease in the same direction. More complex trends are found in the McArthur deposit, Australia (Smith and Croxford, 1973) and the Millenbach deposit, Canada (Coomer and Schwarcz, 1974).

e) Sulphur isotope fractionation between minerals is found to be consistent in certain cases and in conjunction with experimentally derived partition coefficients can give palaeotemperatures. Unfortunately there is some disagreement as to the values of partition coefficients at different temperatures, as varying experimental techniques give varying fractionations (Czamanske and Rye, 1974).

Kajiwara (1971) used the galena-sphalerite $d^{34}S$ fractionation in Kuroko deposits to deduce temperatures of formation and suggested a decrease in temperature from 250°C to 180°C stratigraphically upwards. Lusk and Crocket (1969) interpreted fractionations for the Heath Steele B-1 sulphides in terms of equilibration at a regional metamorphic temperature of approximately 300°C.

A comparison of mean values, ranges and trends of sulphur isotope ratios of volcanogenic massive sulphide deposits is presented in Fig. 2-5. Several interpretations of the sulphur isotopic parameters of volcanogenic stratiform deposits have been offered.

Fig. 2-5. Sulphur Isotopic Ratios of Selected Stratiform Massive Sulphide Deposits of Various Ages.



Deposit	Sulphur Isotopic Zoning	Age	Reference
Red Sea hot brine deposits	None	Recent	Kaplan et al. (1969)
Kuroko, Japan(Pyrite)	Present	Miocene	Kajiwara (1971)
Besshi-type	None	Permian	Yamamoto et al. (1968)
Cyprus-type	Present	Cretaceous	Hutchinson and Searle (1970)
Caribou, N.B.	Not known	Ordovician	Tupper (1960)
Brunswick No. 12	Not known	Ordovician	Tupper (1960)
Heath Steele B-1	Present	Ordovician	Lusk and Crocket (1969)
Millenbach, Quebec	Present	Archaean	Coomer and Schwarcz (1974)

Note 1: —▲— Mean and range of sulphur isotope ratios.

a) The average value is due to mixing of two sources of sulphur, such as sea water sulphate and unfractionated igneous sulphide (Lusk, 1973).

b) Equilibration of sea water sulphate and sulphide at high temperatures may result in lighter $d^{34}S$ in precipitated sulphides than in the original sulphate. A systematic variation in $d^{34}S$ across layered stratiform deposits is then due to precipitation of sulphides within the stability field of sulphate under varying fugacity of oxygen (Ohmoto et al. 1970). Equilibrium between sulphate and sulphide throughout the formation of the ore deposit is implied.

c) The initial sulphur isotope ratios of the ore solution may be produced as in (b) but subsequent isotopic fractionation is due to precipitation of sulphides from a finite reservoir of reduced sulphur. If the minerals are lighter than the solution, they will become slightly heavier higher up in the succession (Sato, 1974). Lack of equilibrium between ore fluid sulphide and sulphate during sulphide precipitation is implied.

d) Inorganic fractionation of magmatic sulphur by boiling with release of H_20, CO_2 and H_2S leads to loss of lighter sulphur in H_2S and a heavier mean $d^{34}S$ in the fluid phase.

e) Organic precipitation of sulphides occurs by reduction in an "infinite" sea water sulphate source with diagenetic re-equilibration causing a narrow spread.

Sulphur isotopes, then, provide no simple answer to the genetic problems of this class of ore deposits. Whether equilibration between aqueous sulphate and sulphide can occur at temperatures below about 250°C is a fundamental question. The possibility of biogenic origin of the sulphide as in (e) above is unlikely in deposits that are unmetamorphosed and show signs of equilibration between metallic sulphides at high temperatures (Kajiwara, 1971) such as the Kuroko.

2-3-7 Lead Isotopes

The lead isotopic composition of the majority of volcanogenic stratiform orebodies, including the Bathurst deposits, (Tupper, 1960) lies close to a single-stage growth curve and usually shows no detectable variation within a single deposit. This property of such "ordinary leads" was once believed to indicate an upper mantle origin for the lead. Leads of conformable deposits that deviate significantly from the single-stage growth curve are termed "anomalous leads", and are explained on a basis of mixing of two ordinary leads.

An alternative explanation of the "ordinary leads" is that a large number of mixing events have produced a lead which appears to be ordinary (Alpher and Herman, 1951; Shaw, 1957; Brown, 1965).

The latter hypothesis has gained increasing acceptance. One important reason is the improvement in lead isotope measurement. The initial studies of stratiform lead isotopes were largely on Precambrian and Palaeozoic deposits and any deviations from the single-stage curve were too small to be measured precisely. It has been found, however, that some stratabound deposits give younger model ages by lead isotopes than by other geochronological methods, with the deviations increasing for younger deposits (Sato and Sasaki, 1973).

It has been pointed out by Brown (1965) that the range in lead isotope ratios of oceanic sediments duplicates much of the range of volcanogenic stratiform deposits. As a result many authors (e.g. Armstrong and Cooper, 1971) have attempted to link the anomalous lead in Kuroko and other comparatively modern island arc deposits with subduction processes. They compare the lead isotopes in the sediments in a particular oceanic crustal segment with those of nearby ore deposits and it is suggested that the process which fused the downgoing oceanic crust to form magmas during subduction, can cause homogenization of the lead isotopes in large segments of the crust giving pseudo-ordinary lead isotope ratios.

In conclusion, the lead in stratiform volcanogenic sulphide deposits originates from a very homogeneous source. Whether that source is the mantle, crust or both, cannot be determined at present. Certainly the origin of the ore lead cannot be separated from the origin of the host igneous rocks.

CHAPTER 3

THE CHEMISTRY OF ORE FORMING FLUIDS

3-1 Introduction

To model the formation of the Bathurst massive sulphide deposits the composition and physicochemical conditions of the ore solutions must be determined. In many ore deposits (for example, Kuroko) the composition of the ore forming fluid and the temperature of ore deposition have been inferred from fluid inclusions. Unfortunately, due to metamorphism, this is not feasible for the Bathurst deposits. The composition of the ore-forming fluid must be deduced by inference from analogy with unmetamorphosed deposits of similar type and by study of modern hydrothermal fluids.

Hydrothermal fluids occur in marine and terrestrial environments both of which can be instructive as to the reactions of hot water with hot rock. As stratiform massive sulphide deposits are generally accepted as being of syngenetic origin, the characteristics of geothermal waters on land and in oceans are pertinent for analogy with the postulated ore-forming solution.

Initially, this chapter summarizes present knowledge of ore-solution systems and hydrothermal solutions in order to define the approximate range of physicochemical conditions under which the Bathurst deposits may have formed.

There has been considerable debate in the literature of mineral deposit geochemistry as to whether base and precious metals are carried in hydrothermal solutions as chlorocomplexes or bisulphide complexes. Frequently, authors have assumed that either chlorocomplexing (Sato, 1973) or bisulphide complexing is dominant. The only detailed comparison of the two forms of complexing for a wide range of metals is that of Barnes and Czamanske (1967). This work suffers from an inadequate thermodynamic treatment of the data available and is not adequate to evaluate the relative stabilities of chloride and bisulphide complexes of the base and precious metals at pH values, compositions and temperatures (up to 300°C) relevant to hydrothermal ore formation.

There is a consensus among authors that chlorocomplexing is the most important mechanism for hydrothermal transport of base and precious metals in ore-forming processes. Nevertheless, the relative stabilities of chloride and sulphide complexes are poorly established for solutions of mildly acid to neutral pH, a region which may be extremely significant for base and precious metal transport. A quantitative comparison of the stabilities of the two sets of complexes is the object of the second half of this chapter.

3-2 Review of the Physicochemical Properties of Geothermal Waters

3-2-1 Geothermal Waters from Continental Environments

Generalizing from the large amount of information available on hot springs and geothermal waters (Zies, 1929; Grindley and Williams, 1965; Ellis, 1967; Skinner et al. 1967) the following properties characterize such fluids at the earth's surface:

1) the temperature of geothermal waters varies from the ambient surface temperature to 400°C

2) solution pH usually lies in the range of 5 to 9 though in certain cases it is lower

3) chloride is omnipresent at concentrations varying from 3M to 0.1M

4) bicarbonate is perhaps the next most common anion

5) the sum of the concentrations of Na^+, K^+ and Ca^{2+} is approximately equal to total chloride

6) the $SO_4^{2-}:H_2S$ ratio is usually more than unity and highly variable

7) total sulphur ($SO_4^{2-} + H_2S$) varies between 0.0X and 0.00XM

Geothermal fluids are complex systems which undergo continuous readjustment to new conditions as they rise and fall in conduits or reservoirs. Changes commonly occur in the internal equilibria. Reaction with the wall or reservoir rocks, pH and redox equilibria are the variables most likely to be altered by near-surface phenomena.

The relative importance of magmatic and meteoric sources for the cations and anions of geothermal waters is the cause of some dispute. Oxygen and deuterium ratios indicate that the bulk of the water itself is not magmatic (Craig, 1969). The sulphur isotope ratios of pyrite from the Wairakei and Waiotapu geothermal areas are distinctly heavier than normal igneous sulphur, indicating either considerable fractionation or a non-igneous source (Steiner and Rafter, 1966). The isotopic composition of the lead in the Salton Sea brines is not of single-stage type indicating an origin not directly related to igneous processes.

3-2-2 Geothermal Waters from Oceanic Environments

(a) The Island Arc Environment

As already noted volcanogenic massive sulphide deposits of Phanerozoic age containing significant lead and zinc levels are found in island arc-type environments. Areas of submarine island arc volcanicity are the best localities to search for modern analogues of these deposits.

The Hellenic and Calabrian areas of volcanicity have been described as island arc type (Ninkovitch and Hays, 1971) on the basis of the chemistry of the lavas and earthquake foci depths. The volcanic centres are islands in the Mediterranean whose lavas vary from basalt to rhyolite and show potassium enrichment.

The hydrothermal activity of these volcanoes has been studied for some considerable time. Bernauer (1940) investigated submarine iron sulphide formation around Vulcano and discussed the possibility of an iron monosulphide intermediate reaction product. He noted the pseudomorphism of magnetite by pyrite. The activity of Vulcano has been described in great detail by Honnorez (1969) and Honnorez *et al.* (1971).

The visible submarine exhalations of Vulcano consist of water vapour with large amounts of carbon dioxide and some hydrogen sulphide and sulphur dioxide. The highest submarine temperatures are 65°C (100°C on land) and the most acid pH between 3.0 and 3.5. The mineralization on the sea floor consists of marcasite, pyrite, alunite, opal and native sulphur. There is a notable contrast between the subaerial springs which are depositing numerous base metals and the submarine hot springs which are not. Sedimentary deposition in the area has been dominated by four factors: explosive eruptions, wave erosion, rain and wind erosion, and sea current activity. This last factor is believed to cause dilution of any geochemical anomalies of zinc, copper or silver.

Similar hot springs and sediments have been described at other Mediterranean volcanoes by Butuzova (1966), Puchelt (1971) and de Bretizel and Foglierini (1971). The dominant precipitates are iron and manganese and there is no significant base metal deposition.

Hydrothermal activity from the submarine andesite-dacite volcano, Banu-Wuhu in the Celebes has been described by Zelenov (1964). Hot water (40° to 50°C), similar to sea water except for concentrations of carbon dioxide, silica, iron and manganese, is being emitted from fissures in freshly erupted lava. Some 140 mg/l of iron and manganese precipitate from the water on cooling and it is estimated that 10^3 to 10^4 tons of iron are precipitated each year.

Ferguson and Lambert (1972) have investigated a sedimentary exhalative environment at the foot of two andesite-dacite volcanoes in the Bismark archipelago on the island of New Britain. Hot spring waters are enriched in trace elements but not in chloride as compared to ocean water. The sediments forming in the area have high iron and manganese content but low zinc and total sulphur. The absence of significant metal concentrations can be ascribed to high dilution by detrital material, no mechanism to separate the metals and no source of significant amounts of sulphur.

(b) Mid-ocean Ridge Environment

An analogy has been postulated between processes now forming metal-rich sediments on the ocean floor and processes responsible for the formation of stratiform massive sulphide deposits (Corliss, 1974).

There is evidence in Pacific and Indian Ocean sediments that the distribution of certain metals, notably iron and manganese, has a causal relationship with submarine volcanism. Active oceanic ridge sediments are enriched in iron and manganese, and certain trace elements, including vanadium, arsenic, uranium, cadmium, zinc, boron, mercury and to a lesser extent, barium and phosphorous (Boström et al. 1972).

Many authors have considered ways of producing the metalliferous sediments including magmatic differentiation (Corliss, 1971), circulating groundwaters reacting with hot rocks (Bonatti and Joensuu, 1966 and Boström, 1973) and surface reaction of hot lava with sea water (Corliss, 1971 and Dymond et al. 1973).

Such sediments have much lower base metal concentrations than massive sulphide deposits and the author considers that this fact eliminates these sediments as analogues for volcanogenic massive sulphides.

Two localities have been found in the deep ocean with sediments showing high concentrations of some base metals as well as iron and manganese. One is a succession of multi-coloured clays in the Atlantic in the north part of the Hatteras Abyssal Plain (Site 105, Leg 11, Deep Sea Drilling Project, Ewing et al. 1970). These are lower Cretaceous to early Tertiary in age and comprise 50 meters of thin (0.1 to 100 cm) layers of multi-coloured clays (Lancelot et al. 1972). The beds consist largely of variable amounts of goethite, montmorillonite and micas with appreciable pyrite and clinoptilolite in the lower parts. Sphalerite is present in places, with zinc reaching 3.6% overall and up to 50% locally. There is a very small proportion of terrigenous material and an absence of calcareous and siliceous microfossils. The environment must have been very calm to permit the accumulation of such metal-rich beds.

The second site of important metal deposition is the Red Sea, which at present appears to be an area of active sea floor spreading (Phillips et al. 1969). The southern half of the sea shows evidence of on-going volcanism of basaltic character and metal deposition is occurring in deep depressions where saline warm brines have ponded.

Some twelve deeps contain sediments of hydrothermal origin, brines or both (Bäcker and Schoell, 1972). Those that have been most intensely studied are the Atlantis II and Discovery Deeps. These show an interesting contrast in physical and chemical features. Ross et al. (1969) reported that the Atlantis II Deep contained a 56°C brine with an overlying 44°C layer transitional to sea water. The Discovery Deep has brines of comparable salinity but at a temperature of 44°C. The evidence from a number of expeditions is that the Atlantis II Deep brines are in dynamic state and are increasing in temperature. Oxygen and deuterium isotope studies (Craig, 1969) indicate that the brine water is most likely Red Sea water, with the high salinity resulting from the leaching of evaporites. The sedimentation rate in the hot brine deeps is as high as 20 to 50 cm/1000 years.

The sediments within the Atlantis II Deep consist of varying proportions of iron and manganese oxides, iron sulphides and pelagic detritus. There is a vertical and lateral separation of the oxides and sulphides into distinct facies (Bischoff, 1969; Hackett and Bischoff, 1973). Individual facies show great chemical variations, but in general zinc, copper, iron, silver and barium co-vary with sulphur.

The Red Sea hot brine sediments are more similar to stratiform massive sulphides than any known modern sulphide sediment. Unfortunately the reason for the vertical changes in the facies and the absence of sulphides in the present precipitates in the Atlantis Deep is not totally understood. It may be due to insufficient sulphide in the brine. The mechanism of precipitation of the metals in the sediments is extremely complex (Craig, 1969) and this must be borne in mind when developing simple models of volcanogenic massive sulphide deposits which assume equilibrium conditions.

The precipitation of sulphide in the Atlantis Deep has no clear explanation. Sulphur isotopes of the sulphide sediments range from +6 to +3 $d^{34}S$ and show some resemblance to volcanogenic massive sulphides. The sulphur isotope ratios, however, are problematical in that they do not lend themselves to a unique explanation. A possible explanation is that high temperature equilibrium of sulphide with sea water sulphate may be preserved metastably. Alternatively, disequilibrium fractionation may occur between sulphide and sulphate at the ambient brine temperature. Consequently, genetic processes applicable to ancient stratiform base metal deposits cannot be simply inferred from Red Sea hot brine sulphur isotope data.

The Red Sea Brine deposits are interesting as an example of a chemical ore-forming process and because of the chemical and physical nature of the brines. They cannot; however, be used as a general model for the formation of massive sulphide deposits, due to the fact that the brine composition responsible for deposition of the sulphide facies is not known. Also, the tectonic environment is not similar to that of volcanogenic massive sulphide deposits such as Kuroko and the New Brunswick massive sulphide deposits.

3-3 Experimental and Theoretical Limitations on Ore Fluids

3-3-1 Introduction

Prevalent thinking concerning the composition of ore fluids and mechanisms of ore transport has been summarized by Krauskopf (1967), Barnes and Czamanske (1967), Stanton(1972a) and Helgeson (1964) among others. Despite a great increase in information available in the last decade, there are areas of considerable contention. There appears, however, to be a consensus among the authors cited above on the following points:

1) Volatile metal species must be considered as important agents for transport of economically significant amounts of metal at temperatures above about 400°C, but they are not adequate for ore transport

below this temperature.

2) Colloidal or disequilibrium transport would involve too many unpredictable parameters to allow for the consistent metal zoning that is seen in many deposits of contrasting origins.

3) For many metals aqueous solution transport of sufficient concentration to form an ore deposit requires that solutility be due to complex ion species. Because of the great insolubility of most metal sulphides, transport as simple ions is unrealistic except in very acid ore solutions.

General agreement seems to exist that the solutions are 0.5 to 3M in chloride ion and range in pH from 3 and 8. There are, however, two current views on the sulphur content of the fluid. One is that summarized by Barnes and Czamanske who, pointing out the common occurrence of "sulphidized" iron in wall rocks of metal deposits, estimate that the ratio of total sulphur to total heavy metals in ore solutions must be large.

On the other hand, Helgeson (1964), arguing from analogy with hot springs, the Salton Sea brines, and the Red Sea brines, maintains that the sulphur content of an ore fluid never exceeds about 10^{-3}M. Within these limits of chloride and sulphur contents and pH, there is considerable room for disagreement about transport mechanisms. Two groups of complex ion species, sulphides and chlorides, have been considered as the critcial agents in ore metal solubility and transport.

The first model recognises that, while simple sulphides have very low solubilities, the presence of excess reduced sulphur leads to the formation of highly stable sulphide and bisulphide complex ion species for many metals. This concept is consistent with the observation of Barnes and Czamanske (1967) that a high ratio of total reduced sulphur concentration to ore metals concentration is characteristic of hydrothermal vein deposits

The alternative model suggested by Helgeson (1964) is that the sulphur content of the ore fluid is low whereas the chloride content is fairly high leading to chloride complex ion formation for many metals.

The debate does not rest solely on the chloride or sulphide content of the fluid but is also contingent upon fugacity of oxygen and the pH. Briefly, chloride complexing is favoured by low pH and high fugacity of oxygen, conditions under which sulphur is stable largely as sulphate or hydrogen sulphide species. Sulphide complexing is favoured by alkaline pH values and by low oxygen fugacity, conditions under which sulphur is stable as bisulphide.

Hot springs are usually viewed with distrust by geologists as representatives of fluids from which parameters relevant to conditions of ore deposition can be measured. However, fluid inclusions within ore and gangue minerals have certain properties in common with hot spring waters. Thus, chloride is the most common anion in many fluid inclusions. High chloride content is commonly accompanied by high sodium, potassium and calcium contents. Of special interest is the low sulphur content and the fact that sulphur is largely oxidized. It is not possible to state categorically that the properties of sulphur in fluid inclusions are a good approximation of an actual ore fluid. The total sulphur might be low due to removal by sulphide mineral deposition, and due to hydrogen diffusion through mineral lattices which could cause oxidation of the anions. The most reliable measurements from fluid inclusions are temperatures of homogenization and the concentrations of the non-volatile species.

The remaining approach to these problems is to obtain experimentally the necessary thermodynamics data to test the solubilities and stabilities of the metal sulphides under diverse chemical conditions. These solubilities and their variation with the fugacity of oxygen, pH and temperature can be used to predict metal distributions. Comparison with the observed distribution of metals and other components in well-studied deposits can then be carried out to see if a self-consistent model is available.

3-3-2 Comparison of Theoretical and Experimental Solubilities of Ore Metals

The general range of physicochemical parameters considered applicable in a broad sense to hydrothermal base metal ore deposition has been briefly discussed in light of both terrestrial and submarine geothermal waters. The inferred conditions of stratiform massive sulphide deposition are enlarged upon in Chapter 7. To facilitate understanding of the significance of the following calculations on metal solubility it can be stated here that the limiting values of variables relevant to stratiform massive sulphide deposition are probably:-

1. pH in the range 2 to 6
2. Chloride content of ore solution in the range of 0.5 to 3m.
3. Temperature in the range of 50°C to 300°C.
3. Sulphide content of the ore solution in the range 10^{-4} to 10^{-2}m.

The above are the necessary parameters for comparisons of various possible metal complex stabilities. To avoid unnecessary repetition, the solubilities will be considered at fixed chloride and sulphide concentrations of 1m and 10^{-3}m respectively, over a range of temperatures and pH. The presentation below consists of a comparison of the stability of chlorocomplexes of zinc, lead, copper and silver (Helgeson, 1969) with the stability of bisulphide complexes of the same metals, recalculated by this author using experimental data from a variety of sources and the method of Helgeson (1969). The solubility of gold is discussed in Chapter 4.

(a) Zinc

Zinc occurs in deposits of the stratiform type as sphalerite.

The solubility of zinc chloride complexes as a function of temperature has been calculated by Helgeson (1969) and is presented in Fig. 3-1. The only experimental data available for zinc chloride complexes are those of Federov _et al._ (1970). The dissociation constants are presented in Table 3-1, recalculated to 100°C for comparison with those of Helgeson. It is significant that order of magnitude differences exist in many cases. Although it is not possible to reach conclusions as to the quantitative magnitude of this discrepancy at higher temperatures, it seems that significant errors in Helgeson's equilibrium contants may be expected. This should become clear as more experimental data become available.

Melent'yev _et al._ (1968) have investigated the solubility of sphalerite between 100° and 180°C in 0.1M chloride solutions saturated with hydrogen sulphide from pH 1.0 to 8.0. The variation in total Zn^{2+} solubility as a function of pH is shown in Fig. 3-2. Using the methods described by Gubeli and Ste-Marie (1967), the slopes of the zinc solubilities as a function of pH and pS_{total} for complexes involving zinc and sulphur are shown in Table 3-2. The variation of solubility with pS_{total} is required to fully characterize the stoichiometry of the dominant complex present.

The results suggest a neutral complex from pH 3.0 to 5.0 because there is no change in solubility with pH. Solubility then increases with pH through the point of equal activity of hydrogen sulphide and bisulphide

Fig. 3-1. Zinc (Sphalerite) Solubility as Chlorocomplexes (after Helgeson, 1969). 10^{-3}m sulphide.

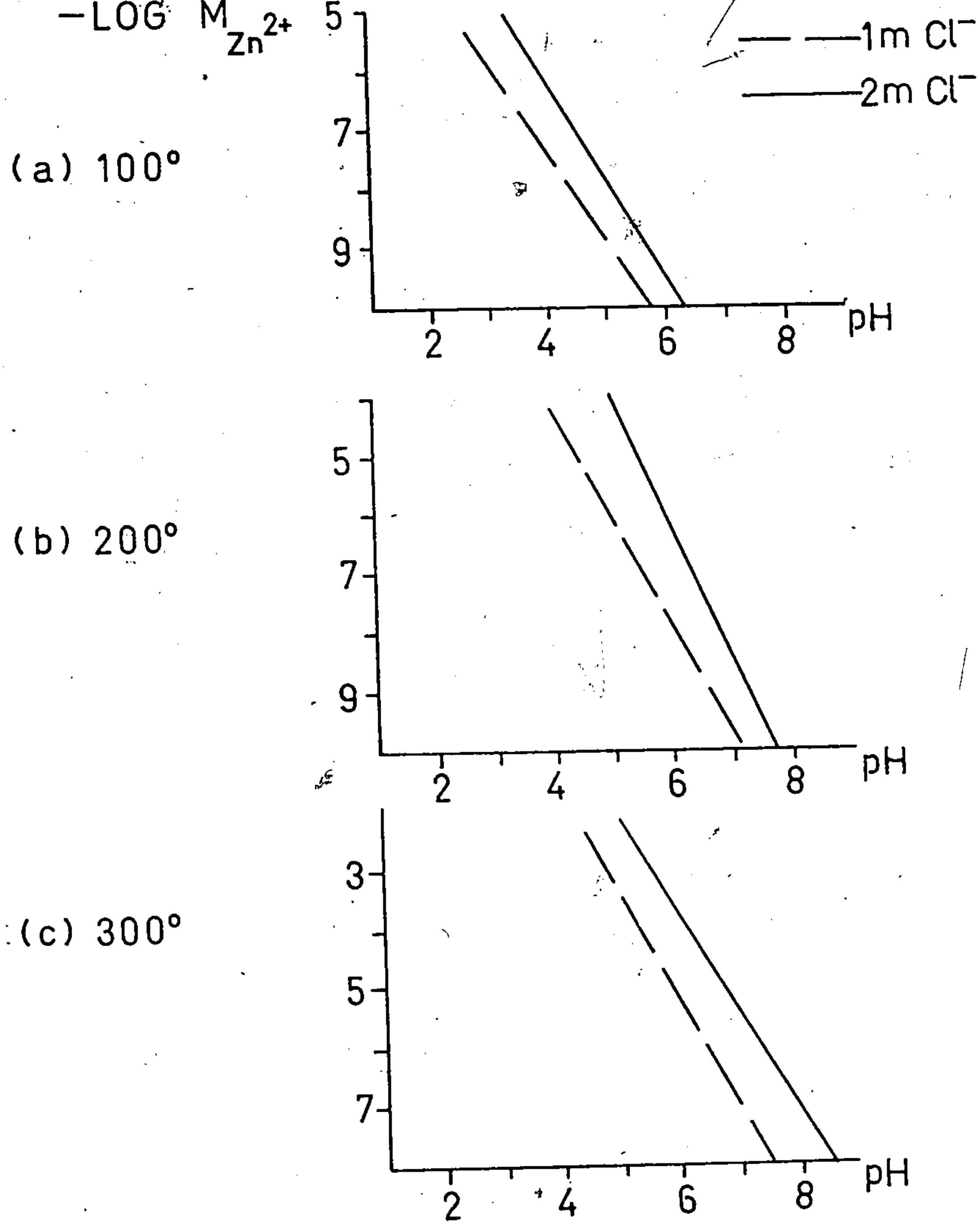

−LOG $M_{Zn^{2+}}$
1m Cl⁻
2m Cl⁻
(a) 100°
5
7
9
2
4
6
8
pH
(b) 200°
5
7
9
2
4
6
8
pH
(c) 300°
3
5
7
2
4
6
8
pH

Table 3-1. Equilibrium Constants for Dissociation of Zinc Chloride Complexes

Reaction	$\Delta H^o_r(T_r)$ cal/mole/deg	$\Delta S^o_r(T_r)$ cal/mole/deg	log. K(T°C) 25	100	200	300	Reference
$ZnCl = Zn^{2+} + Cl^-$	-7790	-28.1	-0.43	-1.82	-3.9	-6.0	1
$ZnCl^o_2 = Zn^{2+} + 2Cl^-$	-8500	-31.3	-0.61	-2.13	-4.4	-6.9	1
$ZnCl^-_3 = Zn^{2+} + 3Cl^-$	-9560	-34.5	-0.53	-2.23	-4.8	-7.7	1
$ZnCl^{2-}_4 = Zn^{2+} = 4Cl^-$	-10960	-37.7	-2.00	-2.14	-5.0	-8.3	1
$ZnCl = Zn^{2+} + Cl^-$	-3570	-11.9	-0.00	-0.61*			2
$ZnCl^o_2 = Zn^{2+} + 2Cl^-$	-5890	-19.8	-0.12	-1.05*			2
$ZnCl^-_3 = Zn^{2+} + 3Cl^-$	-10100	-35.0	-0.36	-2.00*			2
$ZnCl^2_4 = Zn^{2+} + 4Cl^-$			-0.00				2

Note: * calculated with the use of equation 3-5.

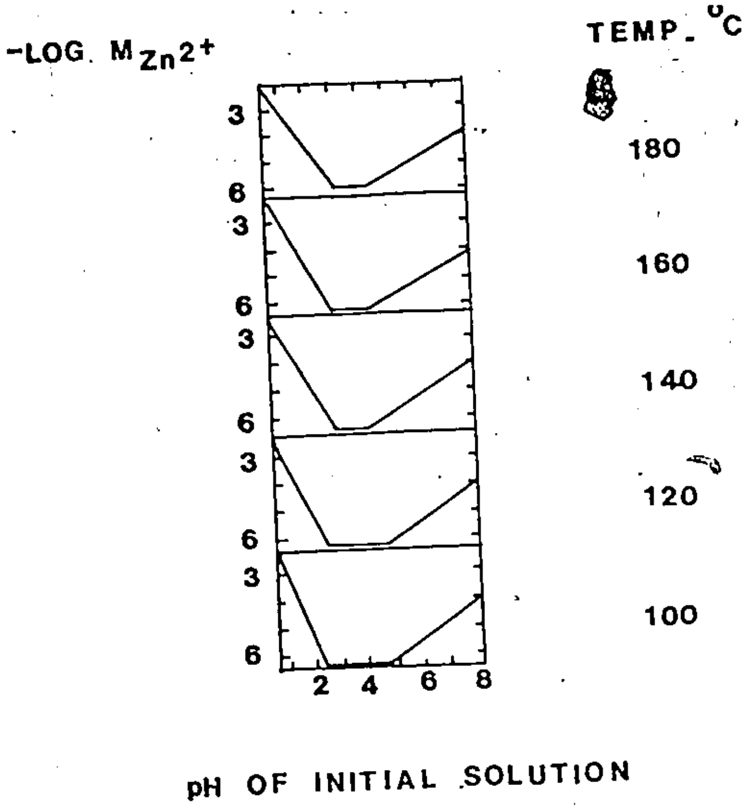
References: 1. Helgeson, 1969, 2. Federov *et al.*, 1970

Table 3-2. Calculated Slopes for Solubility Curves for Selected Zinc Complexes

COMPLEX	$d \log m_{Zn} / d\,pH$		$d \log m_{Zn} / d\,pS_{total}$
	$pH < pKa_1^*$	$pH > pKa_1^*$	
Zn^{2+}	-2	-1	1
$Zn(HS)^+$	-1	-1	0
$Zn(HS)_2^o$	0	-1	-1
$Zn(HS)_3^{2-}$	1	-1	-2
ZnS_2^{2-}	2	1	-1
ZnS_3^{4-}	4	2	-2
$Zn(HS)(S)^-$	1	0	-1

Note: * pKa_1 is the first dissociation constant of H_2S.

Fig. 3-2. Zinc (Sphalerite) Solubility in H_2S Saturated Solution (after Melent'yev _et al._ 1968)


$-\mathrm{LOG}\ M_{Zn^{2+}}$
TEMP. °C
180
160
140
120
100
3
6
3
6
3
6
3
6
3
6
2
4
6
8
pH OF INITIAL SOLUTION

ion at about pH 7. Here a change in slope of the solubility curve does not occur. This contrasts with many other metals. In the pH range 5.0 to 8.0 solubility is probably due to ZnS_2^{2-} or a mixture of complexes, but the data are not sufficient to be sure.

In order to apply the data of Melent'yev et al. to other temperatures and activities of hydrogen sulphide, an equilibrium constant for complex formation is required. Melent'yev et al. (1968) do not calculate equilibrium constants except for the temperature conditions of their experiments. The equilibrium constant can be calculated if the entropy and enthalpy of reaction are known. These quantities are computed below.

Assuming that the complex is ZnS_2^{2-} between pH 5.0 and 8.0 the formation reaction may be represented by:

$$ZnS\ (s) + H_2S\ (aq) = ZnS_2^{2-}\ (aq) + 2H^+ \qquad 3\text{-}1$$

$$\text{with } \log K = \log \left[\frac{(ZnS_2^{2-})\ (H^+)^2}{(ZnS)\ (H_2S)} \right] \qquad 3\text{-}2$$

The equilibrium constant is calculated for a temperature of 100°C from the solubility data of Melent'yev et al. (1968) with,

$\log m_{ZnS_2^{2-}} \equiv \log m_{Zn(total)} = -4.17$, pH = 8 and

$\log m_{HS^-} = -1.05$.

Log m_{H_2S} is calculated from the equation for the first dissociation of H_2S,

$$H_2S\ (aq) = HS^-\ (aq) + H^+ \qquad 3\text{-}3$$

With pH = 8, log m_{HS^-} = -1.05 and pKa_1 (100°C) = -6.63 (Helgeson, 1969), log m_{H_2S} = -2.42.

Substituting these values in 3-2 above,

$$\log K\ (100^\circ C,\ 373^\circ K) = \log \left[\frac{(10^{-4.17})\ (10^{-8})^2}{(10^0)\qquad (10^{-2.42})}\right] \qquad 3\text{-}4$$

$$= -17.75$$

Similarly,

$$\log K\,(453^\circ K) = \log \left[\frac{10^{-4.09}\quad (10^{-8})^2}{10^{0.0}\quad 10^{-2.19}}\right] = -17.90$$

Calculation of equilibrium constants over wide ranges of temperatures which involve the assumption of constancy or zero value of the heat capacity can lead to serious errors at elevated temperatures. Helgeson (1967, 1969) has derived an equation for the temperature dependence of the equilibrium constant for complexes in terms of functions involving the dielectric constant of water - the electrostatic component - and a power series consistent with non-electrostatic interaction.

It is found that many dissociation constants can be approximated by assuming:

$$\frac{\Delta C^{o}_{p,r}\,(T)}{\Delta C^{o}_{p,e}\,(T)} \quad = \quad \text{a constant}^{*}$$

This leads to the following expression (Helgeson, 1967):

$$\log K(T) = \frac{\Delta S^{o}_{r}\,(T_r)}{2.303\ RT}\left[\ T_r - \frac{\theta}{w}\left[\ 1 - \exp\left(\exp\left(b+aT\right) - c + \frac{(T - T_r)}{\theta}\right)\ \right]\ \right] - \frac{\Delta H^{o}_{r}\,(T_r)}{2.303\ RT} \qquad 3\text{-}5$$

where K(T) = equilibrium constant at temperature T in K°.

Then, $\Delta H^{o}_{r}\,(T_r) = \Delta S^{o}_{r}\,(T_r) \times 387.9 + 17.75 \times 2.303 \times 1.99 \times 373$

and $\Delta H^{o}_{r}\,(T_r) = \Delta S^{o}_{r}\,(T_r) \times 528.8 + 17.90 \times 2.303 \times 1.99 \times 453$

Simultaneous solution gives $\Delta H^{o}_{r}(T_r) = 11{,}170$ cal/mole

and $\Delta S^{o}_{r}(T_r) = -49.43$ cal/mole/deg.

Helgeson (1967) finds empirically that equation 3-5 yields log K(T) values which are in close agreement with the experimental dissociation constants for many reactions from 150° to 250°C. This applies especially in cases when $\Delta H^{o}_{r}(T_r)$ and $\Delta S^{o}_{r}(T_r)$ are both negative but also when $\Delta H^{o}_{r}(T_r)$ is large and positive and $\Delta S^{o}_{r}(T_r)$ is small and negative. This is due to the dominance of log K(T) by the $\Delta H^{o}_{r}(T_r)$ term.

Equilibrium constants at elevated temperatures for reaction 3-1 were calculated from equation 3-5 using the $\Delta S^{o}_{r}(T_r)$ and the

---

* $\Delta C^{o}_{p,r}$ (T) is the total heat capacity

$\Delta C^{o}_{p,e}$ (T) is the heat capacity due to electrostatic interaction

$\Delta H_r^o(T_r)$ values given above. The results are tabulated in Table 3-3.

As discussed above, in the pH region 3.0 to 5.0 the solubility data of Melent'yev et al. (1968) is consistent with the presence of a neutral complex. The reaction of formation can be represented by:

$$ZnS\ (s) + H_2S\ (aq) = Zn(HS)_2^o\ (aq) \qquad 3\text{-}6$$

For equation 3-6,

$$\log K\ (373) = \log \frac{(Zn(HS)_2^o)}{(ZnS)(H_2S)} = \frac{10^{-6.43}}{10^{0.0}\ 10^{-1.05}} = -5.38$$

$$\text{and } \log K(453) = \log \frac{10^{-6.11}}{10^{-1.05}} = -5.06$$

where solubility of zinc at pH 3.8 and temperatures of 100° and 180°C is $10^{-6.43}$ and $10^{-6.11}$m respectively (Melent'yev et al.)

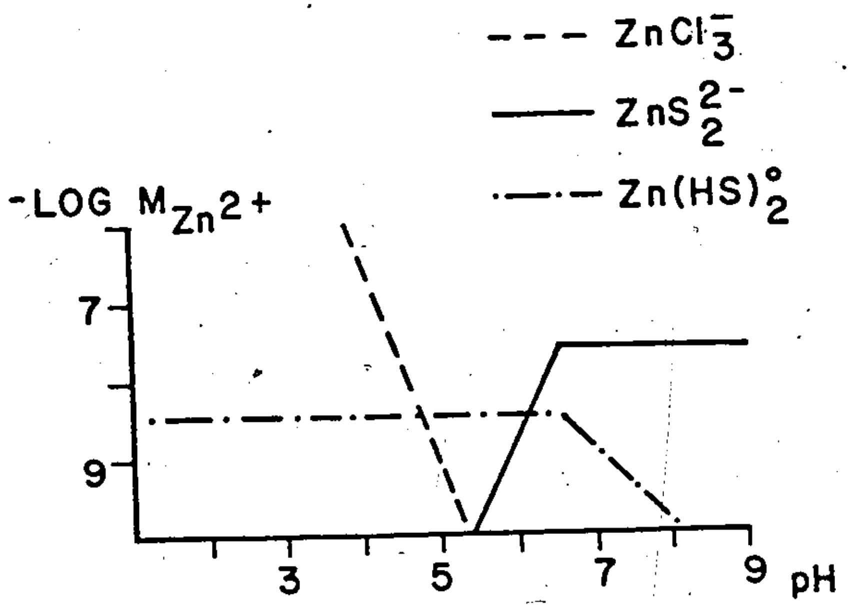
From equation 3-5 and the equilibrium constants for equation 3-6 $\Delta H_r^o(T_r)$ and $\Delta S_r^o(T_r)$ values of 5592 cal/mole and -9.29 cal/mole/deg. respectively are calculated. The calculated equilibrium constants at elevated temperatures are given in Table 3-3.

From the equilibrium constants of Table 3-3 and others given by Helgeson (1969) and Barnes and Czamanske (1967), the solubility of zinc under various conditions has been calculated and is presented in Fig. 3-3. The figures show that pH must be greater than 6 for sulphide complexes to play a dominant role in the solubility of zinc under "average" ore depositional conditions taken as 1m chloride, total reduced sulphur of

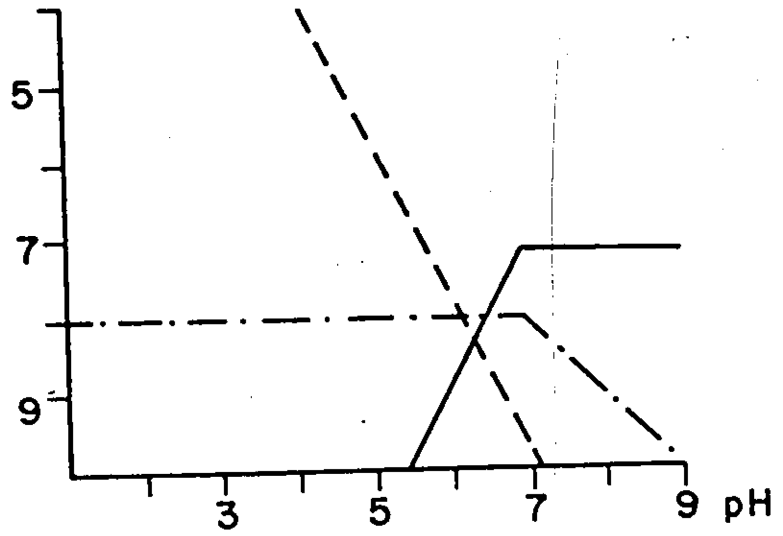
Table 3-3. Equilibrium Constants of Sulphide Complexes

Reaction	$\Delta H_r^o(T_r)$ cal/mole/deg	$\Delta S_r^o(T_r)$ cal/mole/deg	log K(T°C) 25°	100°	200°	300°
$ZnS + H_2S = ZnS_2^{2-} + 2H^+$	11166	-49.4		-17.8	-18.3	-22.3
$ZnS + H_2S = Zn(HS)_2^o$	5592	- 9.3		- 5.38	- 5.04	- 5.51
$PbS+H_2S+HS^-=Pb(HS)_3^-$			-2.72	- 2.5	- 2.22	- 2.42
$CuS+H_2S+2HS^-=Cu(HS)_4^{2-}$			-3.2	- 2.6	- 2.0	- 1.7
$Ag_2S + H_2S = 2Ag(HS)^o$	11072	-23.0		-11.7	-11.3	-12.7
$Ag_2S + 3H_2S = 2Ag(HS)_2^- + 2H^+$	22959	-28.0		-19.8	-18.1	-19.0
$Ag_2S + H_2S = 2AgS^- + 2H^+$	24839	-33.0		-22.1	-20.1	-21.6

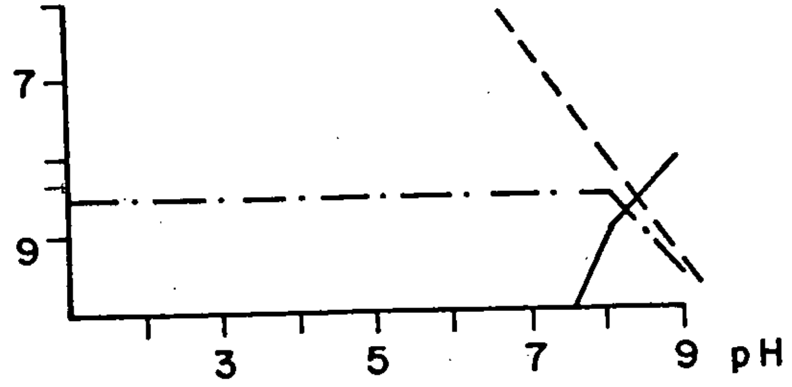
Fig. 3-3. Zinc (Sphalerite) Solubility (after Helgeson, 1969, Melent'yev *et al.* 1968)



(a) 100° C, 1m Cl$^-$, 10^{-3}m TOTAL SULPHIDE



(b) 200°C, 1m Cl$^-$, 10^{-3}m TOTAL SULPHIDE



(c) 300°C, 1m Cl$^-$, 10^{-3}m TOTAL SULPHIDE

10^{-3}m, and temperature between 200° and 300°C. Thus under the conditions of massive sulphide formation inferred in Chapter 7, zinc chloride complexes would be more stable than zinc sulphide complexes.

(b) Lead

The solubility of lead due to chloride complexing has received considerable attention by Helgeson (1964 and 1969, Chapter 3).

Nriagu (1971) has experimentally determined the solubility of galena in chloride solutions saturated with hydrogen sulphide. The solubility curve presented in Fig. 3-4 shows a relationship to pH similar to that of other transition metals. In the pH range 3 to 6 solubility is due to a neutral complex, either $Pb(HS)_2^o$ or $PbS.H_2S$ according to Nriagu. The solubility then increases with pH towards pKa_1 for H_2S with a slope of +1, probably due to $Pb(HS)_3^-$.

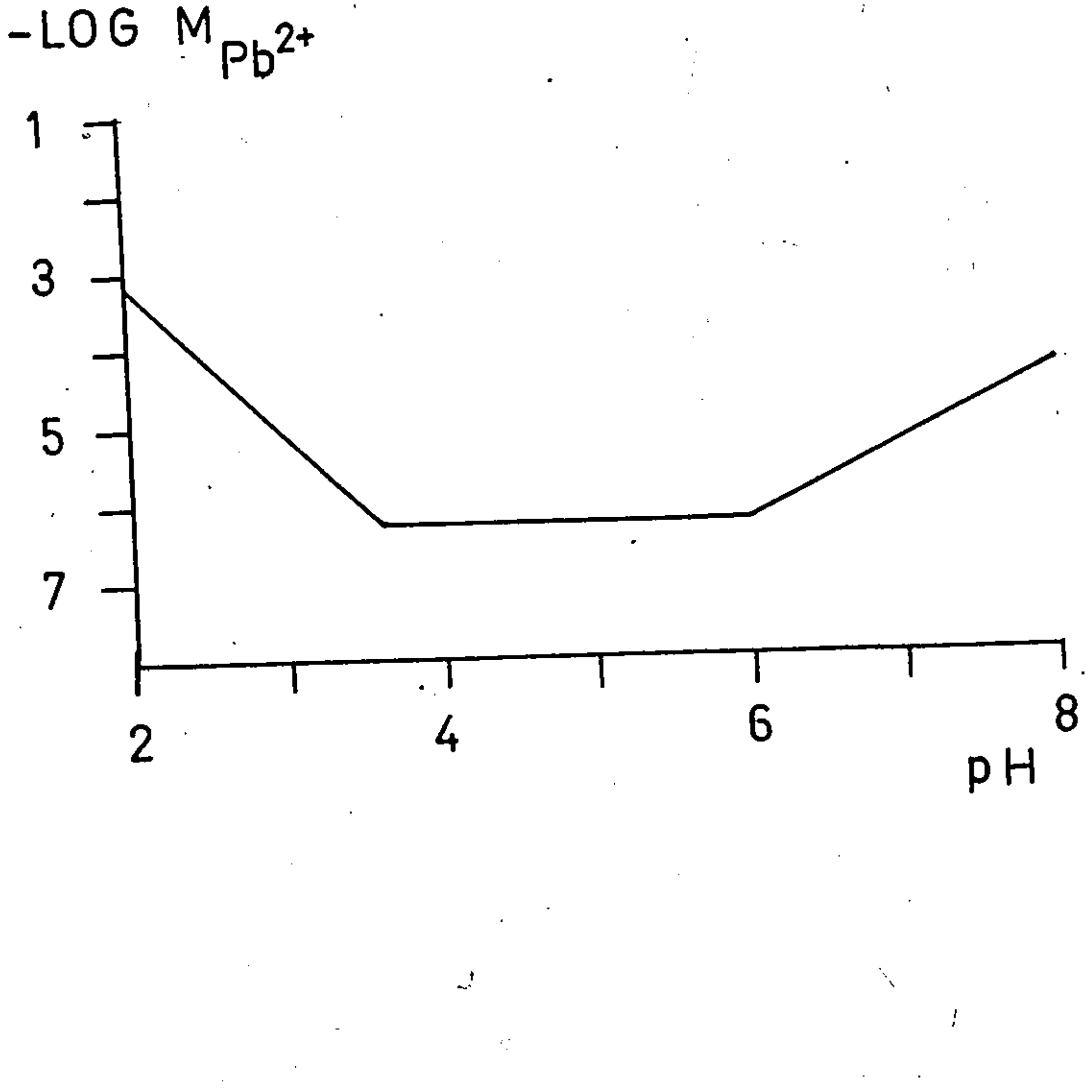
It is not possible to use equation 3-5 to calculate the entropy and enthalpy of the formation reactions for lead bisulphides as the values for at least two temperatures are required. There also seems to be some controversy as to the value of the equilibrium constant for the pertinent reaction:

$$PbS + H_2S + HS^- = Pb(HS)_3^- \qquad 3\text{-}7$$

(see Nriagu, p. 304, 1971 and Anderson, p. 480, 1973).

Solubilities were calculated for $Pb(HS)_3^-$ to 300°C assuming that

Fig. 3-4. Lead (Galena) Solubility (after Nriagu, 1971) 3m NaCl, Saturated with H_2S, 90°C, 1 Atmosphere.



-LOG M Pb2+
1
3
5
7
2
4
6
8
pH

the free energy of reaction ($\Delta F = \Delta H - T\Delta S$) is constant (Table 3-3, Fig. 3-5 (a) to (c)). The assumption of constant ΔF leads to significant errors, but should give a maximum for the solubility provided the entropy change for reaction 3-7 is negative as is the case for zinc and silver (see Table 3-3). This follows from the observation that ΔF will increase with increasing temperature if ΔS is negative and ΔH is positive. Consequently, as

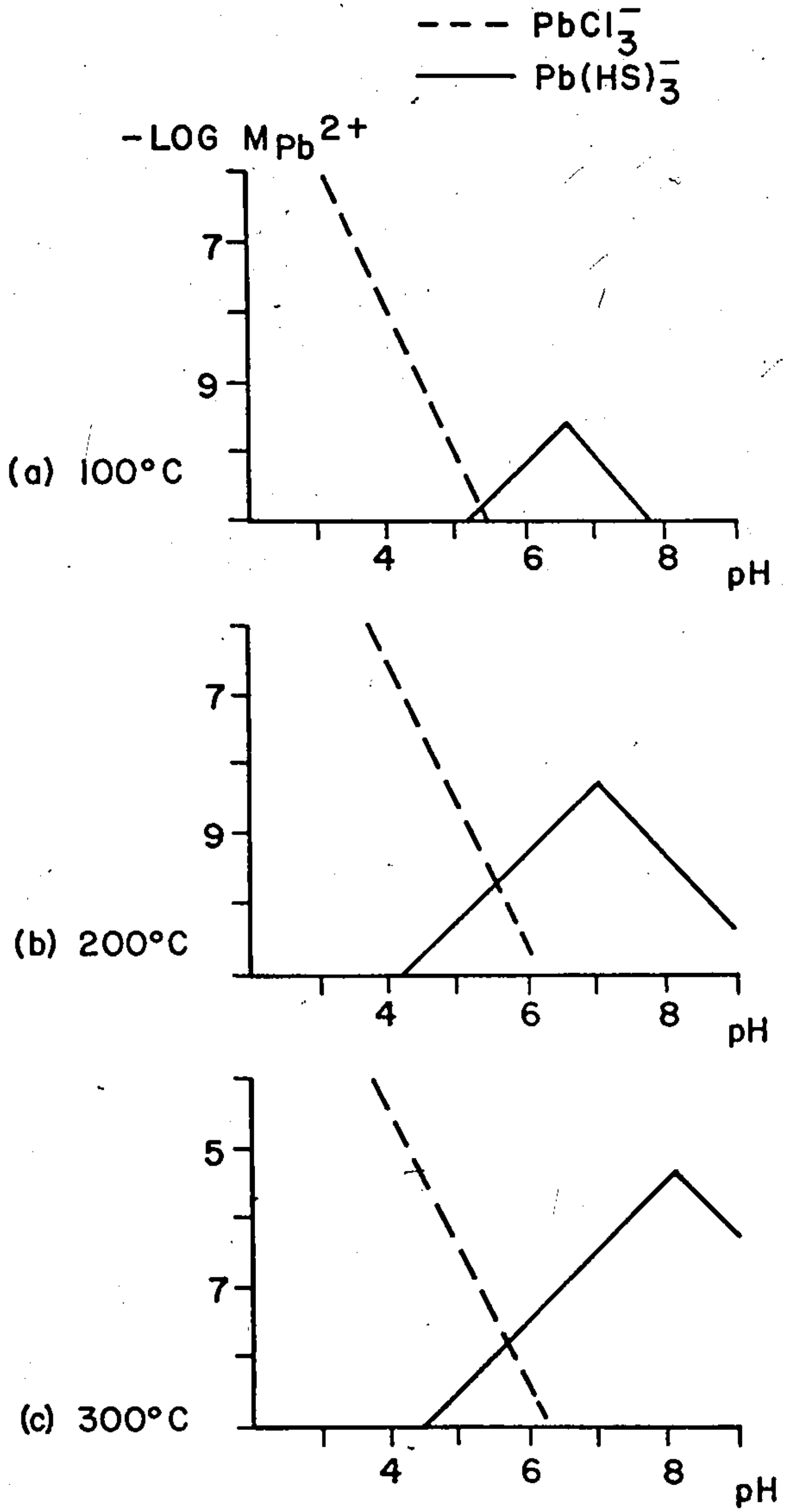
$$\log K\ (T) = - \frac{\Delta F}{2.3RT}$$

increasing ΔF requires that log K(T) becomes more negative. Thus, the metal (lead) becomes more soluble in the case where the solubility is governed by reaction 3-7.

The experimental work of Nriagu and Anderson (1971) on chlorocomplexes of lead gives dissociation constants up to an order of magnitude smaller than those of Helgeson (1969).

From Fig. 3-5 (a) to (c) the relative importance of chlorcomplexes and sulphide complexes of lead can be inferred as was done above for zinc. It is concluded that when pH is less than 5.5 chlorocomplexing is the dominant mechanism for hydrothermal transport of lead. Lead solubility in the ore solutions responsible for stratiform base metal sulphide deposits is attributed primarily to chlorocomplexes.

Fig. 3-5. Lead (Galena) Solubility (after Helgeson, 1969, Nriagu, 1971) 1m Cl^-, 10^{-3} m Total Sulphide



$PbCl_3^-$
$Pb(HS)_3^-$
$-LOG\ M_{Pb^{2+}}$
7
9
(a) 100°C
4
6
8
pH
7
9
(b) 200°C
4
6
8
pH
5
7
(c) 300°C
4
6
8
pH

(c) Copper

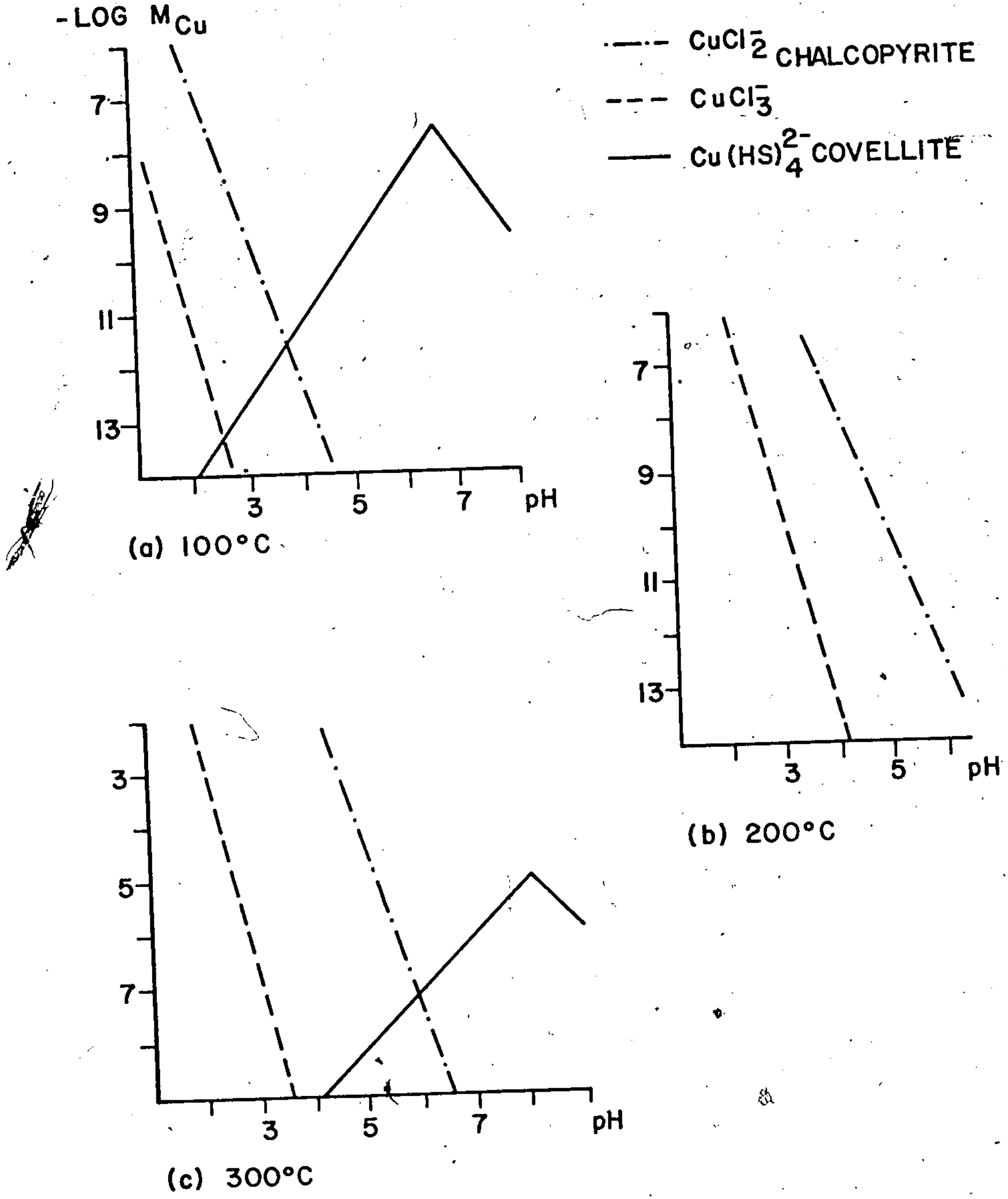
Solubility data for copper complexes are not readily available. Helgeson (1969) has calculated dissociation constants for chlorocomplexes of cuprous and cupric ions.

The only other information available is an estimated dissociation constant of $10^{3.2}$ for $Cu(HS)_4^{2-}$ (Barnes and Czamanske, 1967). This constant has been estimated to 300°C in this work assuming that the free energy change is constant with temperature. Values are tabulated in Table 3-3. They may be seriously in error but, as argued for lead above, give a maximum value if $\Delta S_r^o (T_r)$ is negative.

Melent'yev et al. (1968) attempted to measure the solubility of chalcocite (Cu_2S) in H_2S- saturated solutions. The applicability of copper solubilities pertinent to equilibrium with chalcocite is of doubtful applicability to stratiform ore deposits where copper occurs dominantly as chalcopyrite. Solubility was undetectable in very acid solutions and small (10^{-6}m at 200°C, pH 5.5) in the near-neutral pH range.

From Fig. 3-6 (a) and (c) it can be seen that at pH less than 4 and 6 at temperatures of 100°C and 300°C respectively copper is more soluble as a chlorocomplex than as a sulphide complex. Thus, once again, the chlorocomplex seems to be the most likely species accounting for copper solubility in the hydrothermal solutions responsible for stratiform massive sulphide deposits under the conditions inferred in

Fig. 3-6. Copper Solubility (after Helgeson, 1969, Barnes and Czamanske, 1967) 1m Cl^-, 10^{-3}m Total Sulphide.



(a) 100°C

(b) 200°C

(c) 300°C

(d) Silver

Helgeson's (1969) equilibrium constants for argentous chloro-complexes were utilized to determine silver solubilities in equilibrium with argentite and are presented in Fig. 3-7 (a) to (c).

Melent'yev _et al._ (1968) present data for the solubility of argentite in solutions saturated with hydrogen sulphide. Where applicable their results agree with those of Ol'shanskii _et al._ (1959) implying attainment of equilibrium. The results show three distinct levels of solubility similar to zinc. (Fig. 3-8).

The most probable complex in the acid region is $Ag(HS)^o$. Using Melent'yev _et al._ 's solubility results for the reaction:

$$Ag_2S + H_2S = 2Ag(HS)^o \qquad 3\text{-}8$$

the enthalpy and entropy of reaction were estimated using equation 3-5 and are summarized in Table 3-3. For the steep right-hand portion of the solubility curve (Fig. 3-8) two possible complexes may be relevant:

$$Ag_2S + 3H_2S = 2Ag(HS)_2^- + 2H^+ \quad \text{or}$$

$$Ag_2S + H_2S = 2AgS^- + 2H^+$$

as presented in Table 3-3. In fact AgS^- seems the most likely in view of the increase in solubility at pH greater than 7.

Fig. 3-7. Silver (Argentite) Solubility (after Helgeson, 1969, Melent'yev et al. 1968) 1m Cl^-, 10^{-3}m Total Sulphide.

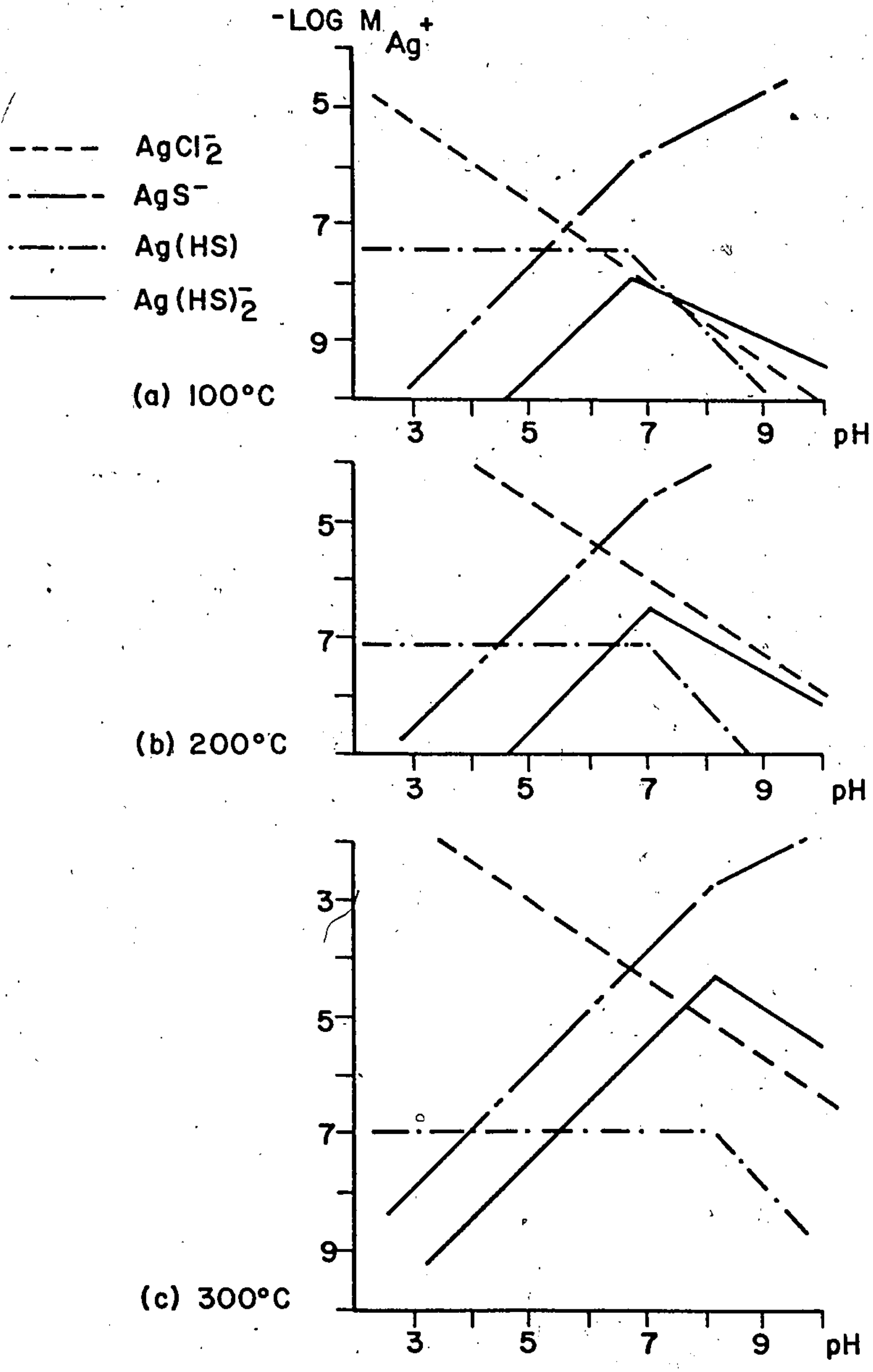
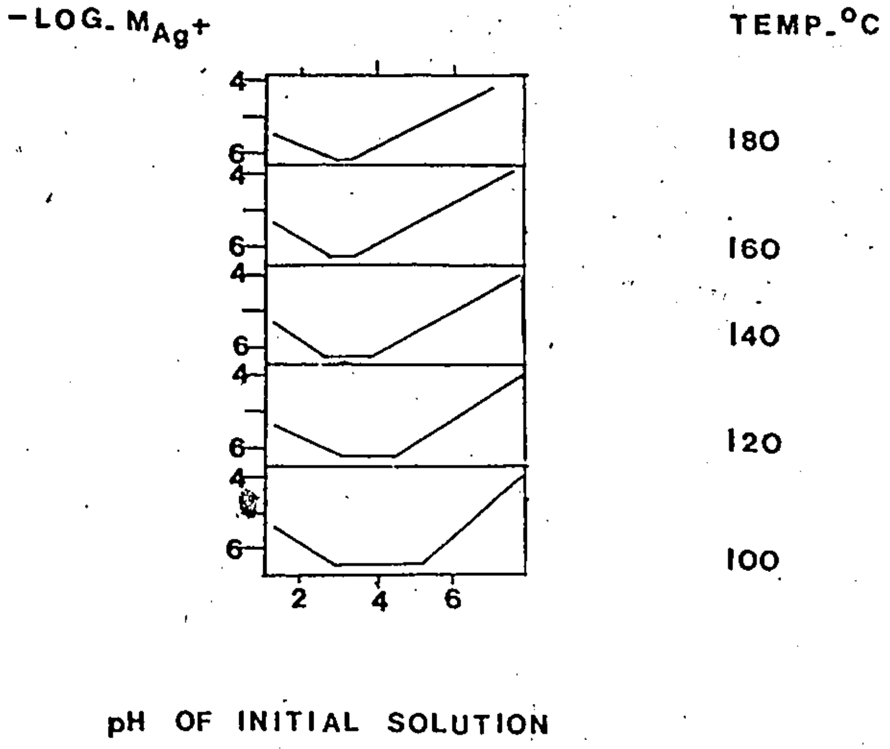

-LOG M$_{Ag^+}$
$AgCl_2^-$
AgS^-
Ag(HS)
$Ag(HS)_2^-$
5
7
9
(a) 100°C
3
5
7
9
pH
5
7
(b) 200°C
3
5
7
9
pH
3
5
7
9
(c) 300°C
3
5
7
9
pH

Fig. 3-8. Silver (Argentite) Solubility in H_2S Saturated Solution.
(after Melent'yev et al. 1968)


−LOG. M$_{Ag^+}$
TEMP. °C
4
6
180
160
140
120
100
2
4
6
pH OF INITIAL SOLUTION

The solubilities of the various complexes at specified conditions are shown in Fig. 3-7 (a) to (c). The chloride complexes of silver are considerably more soluble than any sulphide complexes for pH less than 6.

Unfortunately all the above data for silver are for equilibrium with argentite, whilst silver in New Brunswick stratiform massive sulphides is present as sulphosalts contained within galena. Consequently the above results are possibly inapplicable to the formation of many stratiform massive sulphide deposits. Should silver sulphosalts not greatly affect the relative stabilities of chlorocomplexes and sulphide complexes then silver may be carried as a chlorocomplex in hydrothermal solutions for the conditions inferred for stratiform massive sulphide deposition.

3-3-3 Summary of Relative Solubilities of Ore Metals

Barnes and Czamanske (1967) maintained that ore metals must be transported as complexes involving HS^- or H_2S, stressing that weakly acidic to alkaline solutions are relevant to base metal transport. They suggest that chloride complexes have insufficient stability to account for ore transport at low temperatures.

The analysis of the limited available data presented in this chapter suggests that at temperatures of 100 to 300°C, pH must be greater than 6 for significant transport of base metals and silver as complexes involving sulphur. With increasing temperature in the range of 100 to 300°C the neutral point of pure water moves to lower pH; for example, at 300°C a pH of 6 is alkaline. It has been argued for the Kuroko deposits that the pH of ore solutions was between 3 and 6 (Sato, 1973; Kajiwara, 1973a) and in Chapter 7 (this work) it is suggested that similar pH's may characterize ore solutions relevant to the New Brunswick stratiform sulphide deposits. Under these pH conditions base metals would be more soluble as chlorocomplexes than sulphide complexes.

CHAPTER 4

GEOCHEMISTRY OF GOLD AND PALLADIUM

4-1 Introduction

The geochemical properties of gold in rocks have been recently reviewed by Shcherbakov and Perezhogin (1964), Jones (1969), Gottfried et al. (1972) and Crocket (1974). Palladium geochemistry has been reviewed along with the other platinum metals by Crocket (1969). Many terrestrial abundance data are available for gold, whereas the abundance of palladium in terrestrial materials is very poorly known.

The average concentration of gold and palladium in common rocks of the earth's crust is usually in the range of 1 to 5 parts per billion or less. This low concentration and the poor sensititivy of conventional methods of analysis have prevented detailed investigation of their rock geochemistry until recently. Neutron activation analysis has enabled accurate determination of sub-part per billion levels of these two elements and consequently, has become an important analytical tool for geochemical studies of both metals.

4-2 Igneous Rocks

The concentration of gold and palladium in common igneous rocks is summarized in Table 4-1. Pre-1960 data (see Jones, 1969) are excluded on the grounds of low reliability. The uncertainty of pre-1960 palladium data has been discussed in some detail by Crocket (1969). The salient generalizations are that:

1) The range in average gold values is approximately 2 to 7 ppb and that of palladium 0.5 to 15 ppb.

2) There is a trend of decreasing gold content from ultramafic to felsic rocks (see also Tilling et al. 1973) although the difference is only a factor of 4 approximately.

The average gold contents of rock-forming minerals as estimated by Crocket (1974) are presented in Table 4-2. There is a sympathetic trend compared with the whole rock data, in that minerals of high modal proportion in felsic rocks (quartz and feldspar) are lower in average gold than minerals, such as biotite and hornblende, which are more abundant in intermediate rocks.

4-3 Sediments and Sedimentary Rocks

Data obtained by reliable neutron activation analyses for gold and palladium in sediments and sedimentary rocks are very few. Atomic absorption data for gold in near-shore and coastal sands of the western USA have been presented by Clifton (1968) and Moore and Silver (1968). Estimates from Crocket (1974, 1969) and Crocket et al. (1973) of average gold and palladium contents in sediments and sedimentary rocks

Table 4-1. Concentration of Gold and Palladium in Igneous Rocks

ROCK TYPE	GOLD(ppb)[1]	PALLADIUM(ppb)
Ultramafic	6.6 (149)	8.5(5)[2,3,5]
Gabbro	4.8 (580)	15 (2)[2,4]
Basalt	3.6 (696)	4.8(29)[2,5,6,7]
Diorite	3.2 (261)	0.5(1)[5]
Granite	1.7 (310)	1 (2)[2,5]
Acid Volcanics mainly rhyolite	1.5 (188)	-

References of Table 4-1:

1. Crocket (1974), 2. Crocket and Skippen (1966), 3. Chyi (1972)

4. Vincent and Smales (1956), 5. Rowe and Simon (1971),

6. Crocket et al. (1968), 7. Crocket et al. (1973)

The figure in parentheses is the number of analyses.

Table 4-2. Average Gold Content of some Rock-Forming Minerals

MINERAL	GOLD, ppb[1]
Quartz	1.7(75)[2]
Feldspar	2.0(105)
Biotite	6.0(175)
Hornblende	3.7(94)
Magnetite, Ilmenite	6.7(89)

[1] Crocket (1974)

[2] Figure in parentheses is the number of analyses.

are summarized in Table 4-3. The available data indicate that the major classes of sedimentary rocks differ little in average gold content,and the average values fall within the range of igneous rocks. Palladium data are too limited to make any significant comparisons between average concentration levels in igneous and sedimentary rocks.

4-4 Ore Deposits of the Platinum Group Metals and Gold

4-4-1a Principal Types of Platinum Deposits

The economic geology of platinum deposits has been surveyed by Mertie (1968). Recent contributions on their geochemistry and genesis have been presented by Cousins (1973), Cabri (1974) and Stumpfl (1974). Economic concentrations of primary platinum metals are associated with magmatic mafic and ultramafic rocks. There are three distinctive associations, including : 1) an association with nickel-copper sulphides in mafic rocks exemplified by the Merensky Reef of the Bushveld Complex, the Sudbury Nickel Irruptive and the Noril'sk-Talnakh area of the USSR; 2) native metal disseminations in ultrabasic rocks as at Nizhniy Tagilsk (Urals, USSR), the Inaglinsky massif (Aldan Shield, USSR), Choco district (Columbia) and the Tulameen River area (Canada); 3) an association with chromite horizons in layered gabbros (Upper Group chromite, Merensky suite, Bushveld and the Ultramafic Zone, Stillwater Complex, USA). By far the most important economic host of platinum metals is the Merensky Reef. The author is not aware of any

Table 4-3. Average Gold and Palladium Contents of Sediments and Sedimentary Rocks

ROCK TYPE	GOLD (ppb)[1]	PALLADIUM(ppb)
Sandstone	3.0(105)	-
Shale	2.5(28)	0.1 - 200[2]
Limestone	2.0(20)	-
Deep-Sea and Shelf Sediments	3.4(28)	3.7 (30)[3]

References: 1. Crocket (1974) 2. Crocket (1969)

3. Crocket et al. (1973)

Number in parentheses is number of analyses economically significant platinum metal recovery from Cu-Zn-Pb ores. This is in marked contrast with economic sources of gold.

4-4-1b Principal Types of Gold Deposits

Recent world gold production is dominated by output from the fossil placers of the Witwatersrand district, Republic of South Africa which has annually produced about two-thirds of the world's total output (Simons and Prinz, 1973). Excluding placer production, the most important sources of gold are gold-quartz veins or lodes and by-product production from Cu-Zn-Pb and porphyry copper mining. Several distinctive types of deposits can be recognised including the following:

1) auriferous-quartz veins in Precambrian (Archaean) terrain dominated by mafic volcanic rocks commonly metamorphosed to green-schist facies. Ridler (1970) has ascribed some deposits of this type from the Kirkland Lake area, Canada, to a dual "volcanic-syngenetic plus late-metamorphic lateral secretion" origin.

2) auriferous-quartz veins in Tertiary volcanic terrain exemplified by the epithermal veins of the North American Cordilleran region (Tonopah, Cripple Creek, Ouray, USA). Representatives from the Tertiary of Japan commonly carry silver and may be continuous with base metal mineralization at depth (Hunahashi and Akiba, 1970).

3) auriferous-quartz veins of Palaeozoic and later age represented by the Berezovskoye deposit, USSR (Koltun, 1965a).

4) by-product gold from porphyry copper and Cu-Zn-Pb deposits. Investigation of the porphyry copper-type by Meshchaninov and Azin (1972) indicates that gold occurs both with the copper mineralization and in distinctive auriferous-quartz veins about the periphery of porphyry stocks. Gold in base metal deposits is characteristic of stratiform types including Kuroko (Sato, 1972) and various lead-zinc deposits of the USSR (Koroleva, 1971). Gold from base metal ores averaged 16.5% of total Canadian production from 1960 to 1969 (Hogan, 1971).

5) disseminated gold in carbonate bed rock. Examples of this type include the Carlin, Cortez, Getchell and Gold Acres occurrences in Nevada, USA where very fine-grained gold (0.01 to 10 microns) occurs in carbonaceous, dolomitic limestone.

In summary, gold occurs in economic quantities in a wide variety of host rocks and structural settings. This aspect of gold occurrence prompted Shilo (1971) to term gold a "cosmopolitan" element.

4-4-2 Mineralogy

There are a number of minerals containing palladium and various other platinum metals. Microscopically visible platinum metal minerals are very scarce. They may occur as minute, discrete mineral grains or in solid solution within the major sulphide minerals, as suggested by Cabri (1974) and Chyi (1972) respectively.

Gold is most frequently present as the native metal often alloyed with greater or lesser amounts of copper (auricupride), silver (electrum) and other metals. The second, most important group of economic gold minerals are the tellurides, calaverite ($AuTe_2$) and sylvanite ((Au.Ag) Te_4). Gold sulphide is unknown.

The possibility of solid solution of gold in sulphide minerals has been considered by a number of investigators. Chyi(1972) concluded that gold could be carried in such a manner up to concentrations of 300 ppb in sulphides from the Sudbury Nickel Irruptive.

Selected data for gold in sulphides of various deposits are presented in Table 4-4. The data, as a whole, give no evidence of consistent partition of gold between minerals. There is only a general tendency for gold to increase in the series galena, sphalerite, chalcopyrite, pyrite and arsenopyrite.

An electron microprobe study of gold in the Cortez and Carlin deposits (Wells and Mullens, 1973) has shown an uneven distribution of the metal within arsenopyrite and pyrite, the distribution in the latter mineral correlating with arsenic. These authors observed no discrete gold mineral but suggested that the metal probably occurs as submicron particles of native gold or as a gold mineral.

As will be discussed in Chapter 6, native gold at levels less than 1 ppm can lead to extremely erratic analytical results due to inhomogeneous distribution of very small grains.

Table 4-4. Gold and Silver Content of Hydrothermal Sulphide Minerals

Type of Deposit	Mine or Area	Mineral	Gold ppm	Silver ppm	Reference
Vein	Middle Asia(USSR)	Arsenopyrite	17-704		Koroleva (1971)
		Pyrite	0.6-833		
		Chalcopyrite	0.0-60		
		Galena	0.0-38		
	Karamazar USSR	Pyrite	40-200	20-1000	Badalov and Badalova(1967)
		Galena	0.0-30	1000-1500	
Porphyry Copper	Karamazar USSR	Pyrite	3	37	Badalov and Badalova(1967)
		Chalcopyrite	14.5	71	
		Sphalerite	0.0	170	
		Galena	11	500	
Lead-Zinc in Carbonates	Tien-Shan (USSR)	Pyrite	0.0	4-22	Maksudov (1969)
		Galena	0.0	0.0-2600	
		Sphalerite	0.0	20-1500	
Lead-Zinc (Strataform ?)	Middle Asia(USSR)	Pyrite	0.19-11	0.08-410	Koroleva (1971)
		Arsenopyrite	1.5-114	0-260	
		Galena	0.0	200-18000	
		Chalcopyrite	0.04-0.2	80-439	
	Transbaykal USSR	Pyrite	0.02-16		Vakrushev and Tsimbalist (1967
		Galena	0.01-1.9		
		Sphalerite	0.004-0.01		
Tin-Tungsten	Middle Asia (USSR)	Arsenopyrite	0.4-8		Koroleva (1971)
		Pyrite	0.0-11		
		Galena	0.0-2.4		
		Chalcopyrite	0.0-10		
Disseminated Gold	Cortez	Arsenopyrite	0.0-6800		Wells and Mullens (1973)
		Pyrite	0.0-3500		
	Carlin	Pyrite	2100-8100		
		Sphalerite	0.0-1500		
		Chalcopyrite	0.0-1700		

4-5 Hydrogeochemistry of Palladium

No data on the palladium content of hot spring waters or sinters are available, and no experimental studies of its solubility under hydrothermal conditions have been carried out. Palladium is known to form stable chloride complexes. Data presented by Sillen and Martell (1964) suggest it should have similar solubility to gold but high temperature solubilities would be speculation at this stage.

4-6 Hydrogeochemistry of Gold

4-6-1 Natural Hydrothermal Fluids

Studies of gold in hot spring waters and their precipitates have been summarized by Crocket (1974). Thermal waters analysed for gold (Table 4-5) seem to fall into two groups in terms of pH, those between 0.0 and 4.0 and those between 6.0 and 8.5. There appears to be a significant absence of thermal springs within the range 4.0 to 6.0 as may be seen by examination of the tables of thermal spring pH's of Ellis (1967) or White (1967).

Thermal waters approach equilibrium with their reservoir rocks at depth and on rising to the surface may become more acid if oxidation occurs or more alkaline if carbon dioxide is boiled off and the water cooled (Ellis, 1967).

The range of gold contents of thermal waters is 0.0 to 2.2 ppb.

Table 4-5. Gold and Silver Contents of Hot Spring Waters

Name, Area	Temp. °C	pH	Character or Composition/ ppm	Gold ppb	Silver ppb	Reference
Broadlands DH2 New Zealand	276	8.3	Cl/1700, H_2S/120	0.04	0.6	1
Ohaki Pool New Zealand	95	7.0	Cl/1000, H_2S/1	0.04	0.06	1
Broadlands DH7 New Zealand	270	8.6	Cl/1800,	1.0-0.1	2.0	2
Beppu, Kyushu Island, Japan	57	2.6	Acid H_2S	0.55	20.9	3
	77	2.2	Glaubers salt - NaCl	1.57	28.9	3
	73	2.8	NaCl-Acidic	1.15	21.2	3
	96	3.8	NaCl-Borate	0.5	12.4	3
	53	7.1	Weak NaCl	0.3	1.5	3
	55	6.8	Alkali Earth-NaCl	0.35	0.8	3
	54	6.9	NaCl-$NaHCO_3$-Alk. Earth	0.25	6.6	3
	58	7.2	NaCl-$NaHCO_3$	0.30	5.4	3
	51	7.0	Simple Hot Spring	0.27	4.9	3
	59	6.2	Simple H_2S Spring	0.0	2.2	3
Kamchatka, USSR	7	5.2	Cold CO_3^{2-} Spring	0.1		4
Kuril Isles, USSR	92	0.65	Fumarole	1.6		4
Kuril Isles, USSR	35	2.6	Hydrosolfatara	0.02		4
Angren, USSR	35	7.5	Sulphate/CO_3^{2-}/Chloride Spring	0.07		4
Yellowstone, USA				0.004-0.04		5

References: 1. Weissberg, 1969, 2. Browne, 1969, 3. Koga, 1961, 4. Goleva et al., 1970, 5. Gottfried et al., 1972.

The average concentration in waters of pH 6.0 to 8.0 is 0.3 ppb and in waters of pH 0.0 to 4.0, 0.9 ppb. Work of Koga (1961) and Tilling <u>et al.</u> (1973) demonstrates that sinters precipitated from either group may contain 1.0 to 200 ppm of gold (Table 4-6).

Very small quantities of gold in solution are capable of forming economic deposits given favourable conditions, but any theories of transport and deposition must take into account the range in pH over which transport can occur. It is of interest to note that Weissberg (1969) finds that lead, zinc, and copper are apparently precipitated at depth at Broadlands and Waiotapu, New Zealand, possibly due to boiling and loss of carbon dioxide, whereas arsenic, antimony, mercury, gold and silver seem to be carried to the surface.

4-6-2 Thermodynamics

The aqueous solubility of gold at 25°C has been calculated by Krauskopf (1951) from standard electrode potentials and free energies (Latimer, 1952). Equilibrium constants can be calculated from the relationship:

$$\Delta F^{o} = n\,f\,E^{*} \quad \text{and}$$

$$\log K = \frac{-\Delta F^{o}}{2.303RT_{r}}$$

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* American Electrochemical Society sign convention

Table 4-6. Gold and Silver Contents of Hot Spring Precipitates

Country	Name	Properties of Hot Spring Water					Precipitates		Reference
		Temp. °C	pH	Composition			Gold ppm	Silver ppm	
				Cl ppm	SO_4 ppm	H_2S ppm			
USA	Old Faithfull	ND	ND	ND			0.0055		1
	Beryl Springs	ND	ND	ND			5.5		1
	Steamboat	60	6.1	1000	100	10	200.0		1
	Steamboat						0.11		1
	Steamboat						10.0	400.0	1
New Zealand	Broadlands	280	8.3	1800	8	120	55.0	200.0	2
	Waimangu	67	3.8	762	320	0.2	1.0	5.0	2
	Waiotapu	280	8.8	1500	520	100	80.0	175.0	2
	Rotokawa	290	7.8	3000	125	1000	70.0	30.0	2
	Ohaki	95	7.0	1000	100	1.0	85.0	500.0	2
Beppu, Kyushu Island, Japan	Unohaha	65	2.5	Acid-H_2S			500.0	69.0	3
	Umijigoku	84	2.0	Glaubers-NaCl			22.4	406.0	3
	Jiyumani-jigaku	96	3.8	Borate-NaCl			56.5	933.0	3
	Raienjigoku	83	2.9	NaCl-Acidic			26.9	418.0	3
	Shibaishi	63	2.7	NaCl-Acidic			11.7	331.0	3
	Chinoikejigoku	60	2.1	Glaubers-NaCl			23.3	383.0	3
	Honbozujigoku						7.5	190.0	3
	Average for Japan						21.3	390.0	

References: 1. Gottfried et al. (1972), 2. Weissberg (1969), 3. Koga (1961)

ND: Not determined.

Gold is commonly characterized by two stable oxidation states, +1 and +3. Krauskopf, with Cloke and Kelley (1964), considered only the auric state to be important in the natural environment and his results must be viewed in that light.

Krauskopf's conclusions were that:

1) In order to dissolve gold in acid solutions a strong oxidizing agent such as MnO_2 is required, although O_2, Fe^{3+}, and Cu^{2+} might have some dissolution effect.

2) In acid solution gold is significantly soluble as $AuCl_4^-$ and in alkaline solution as AuS_2^- if sufficient sulphide is present.

3) Qualitative results suggest a large increase in solubility with temperature.

A different approach to gold solubility was taken by Helgeson and Garrels (1968) who, from premises of the formation of gold-quartz veins by replacement of country rock and of the metastable precipitation of cristobalite, computed a "geologic" solubility for gold. Helgeson and Garrels (1968) showed that a solution with $\log m_{HSO_4} = -2.5$, $\log m_{S^{2-}} = -3.0$, chloride = 3m, pH = 2.5 and at a temperature of 300°C could carry sufficient gold to form an economic gold quartz-alunite vein deposit.

The approximations behind these and similar calculations are discussed in Helgeson (1967, 1968, 1969). The main deficiency in the thermodynamic data is lack of heat capacity values especially for ions, at elevated temperatures. Helgeson obtained entropies of dissociation for ionic species by assuming an approximately linear relation between the entropy of dissociation of complexes involving a common ligand. Average heat capacities were then derived over a specified temperature range from the relationship:

$$C_p \Big]_{T_r}^{T} = \alpha'' (T) + \beta'' \ (T) \ S_{i(abs)} \ (T_r) \qquad 4\text{-}1 \ *$$

The equilibrium constants for reactions involving the formation or dissociation of relevant gold complexes were calculated for 25°C from the free energy data of Latimer (1952). Computation of equilibrium constants at elevated temperatures involved an assumption of average heat capacity over the required temperature range or an assumption that the total heat capacity change was proportional to that of the electrostatic heat capacity (Helgeson, 1967). The first approximation is useful where sufficient heat capacity data are available or can be estimated from absolute entropies. The second approximation is useful for geochemical problems where no heat capacity information of any kind is available. In the latter case equation 3-5 is used:

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* (α'') and (β'') are coefficients in equation 4-1 (Helgeson, 1969, p. 734)

$$\log K(T) = \frac{\Delta S_r^o (T_r)}{2.303RT} \quad T_r - \frac{\theta}{w} \quad 1 - \exp (\exp (b + aT)$$

$$- C + \frac{(T - T_r)}{\theta}) \quad - \frac{\Delta H_r^o (T_r)}{2.303RT}$$

The relevant equilibrium constants for gold complex ion stabilities from Helgeson (1969) are shown in Table 4-7. It is difficult to judge the accuracy of these numbers.

The work of Helgeson and Garrels has been criticized by Boyle (1969) for a number of reasons largely concerned with the pH of the solutions and the role of temperature. Helgeson and Garrels stressed the acidic and oxidized nature of the ore solutions. Boyle points out that hot springs carrying gold are frequently neutral or alkaline, that alumina is not commonly transferred to any degree during vein formation and that carbonates are frequently present in gold-quartz veins.

Boyle states that the occurrence of gold-quartz veins in seemingly dilatant features and the evidence of reaction between most rocks and fluid, belie the predominant role of temperature called for by Helgeson and Garrels.

Gold-quartz veins with alunite ($KAl_3(OH)_6(SO_4)_2$), the type discussed by Helgeson and Garrels, are not common. It is relevant to note the experimental work of Hemley et al. (1969) on alunite which indicates very acid pH (about 3.0) for the ore-forming solution in

Table 4-7. Equilibrium Constants for Reactions Involving Formation or Dissociation of Gold Complex Ion Species

Reaction	log K(T°C)						References
	25°	100°	150°	200°	250°	300°	
$AuCl_2^- = Au^+ + 2Cl^-$	- 9.0	- 7.5	- 6.9	- 6.4	- 6.2	- 6.2	1
$AuCl_4^- = Au^{3+} + 4Cl^-$	-26.0	-22.4	-21.0	-20.2	-21.2	-21.1	1
$Au^o + \frac{3}{4} O_2 + 3H^+ = Au^{3+} + \frac{3}{2} H_2O$	-13.61	-13.91	-12.59	-12.35	-12.17	-12.02	1
$Au^o + \frac{1}{4} O_2 + H^+ = Au^+ + \frac{1}{2} H_2O$	- 7.81	- 5.89	- 4.94	- 4.17	- 3.52	- 2.97	1
$Au^o + HS^- = AuS^- + \frac{1}{2} H_2$	- 4.3 to -3.9						2
$Au^o + HS^- = AuS^- + \frac{1}{2} H_2$	- 6.0						3
$Au^o + HS^- = AuS^- + \frac{1}{2} H_2$	- 5.6						4
$Au(HS)_2^- = Au^+ + 2HS^-$				-21.1	-19.5		5
$Au_2(HS)_2S^{2-} = 2Au^+ + 2HS^- + S^{2-}$				-50.7	-47.9		5
$Au^o + H_2S + HS^- = Au(HS)_2^- + \frac{1}{2} H_2$				- 1.28	- 1.19		5
$2Au^o + H_2S + 2HS^- = Au_2(HS)_2S_2^{2-} + H_2$				- 2.40	- 2.55		5

References: 1. Helgeson, 1969, 2. Weissberg, 1970, 3. Krauskopf, 1951, 4. Kakovskii and Tyurin, 1962

5. Seward, 1973.

deposits, such as Goldfields, Nevada and Butte, Montana, both of which have alunite as gangue. Gold chloride complexes are almost certainly important in this class of deposits, but the role of these complexes in Precambrian gold-quartz veins and epithermal gold-silver veins of the Japanese type is less certain. Conditions of metal deposition seem to have involved solutions more alkaline than pH of 3.0.

4-6-3 Experimental Studies on Gold Solubility

Early experimental studies of Ogryzlo (1935), Lindner and Gruner (1939) and Zviagincev and Paulsen (1940) established two important aspects of gold solubility. These are that gold is soluble as a chloride complex in weak hydrochloric acid solution and that gold is soluble in NaHS solution at high temperatures and pressures.

Among the most important of the modern studies on gold solubility in fluids of potential ore solution composition (Chapters 3 and 7 of this work) are those of Weissberg (1970) and Seward (1973). Seward, developing previous experimental techniques of Weissberg, determined gold solubility under conditions of variable m_{H_2S}, m_{NaCl}, total sulphur, pH and temperature with f_{H_2} buffered against the pyrite-pyrrhotite couple. By comparison of the expected acid-base dependence of suspected complexes with observed solubility he concluded that $Au(HS)^o$, $Au(HS)_2^-$ and $Au_2(HS)_2S^{2-}$ are the complexes responsible for solubility in acid, neutral and alkaline conditions, respectively. No evidence was found for AuS^-, a complex suspected by Krauskopf (1951) and Weissberg (1970) to be responsible for gold solubility in alkaline solution. The formation constants for the pertinent complex ion reactions are shown in Table 4-7.

It was argued by Seward that wall-rock alteration, fluid inclusions, sulphide-oxide equilibria and the observed content of gold in hot springs all strengthened the likelihood that gold deposits form from near-neutral pH solutions. Under such conditions the experimental gold solubility due to the bisulphide complex, $Au(HS)_2^-$, is greater than that calculated for the chlorocomplex from Helgeson's data.

The chemistry of gold in potassium chloride solutions from 300° to 500°C was investigated by Henley (1973). The pH and fugacity of oxygen were buffered at about 3.0 and 10^{-29} atm. respectively at 300°C. The total solubility curve was steep for temperatures greater than 480°C and solubility of 200 ppm was obtained at 1000 bars at this temperature. However, gold solubility was only 20 ppm at 300°C.

Considering the stoichiometries of known gaseous gold chloride compounds Henley deduced that Au_2Cl_6 is the most likely species but theoretically calculated solubilities are 10^{-7} lower than those obtained experimentally. Two possibilities for the discrepancy between calculated and experimental solubilities are that:

1) Au_2Cl_6 is not the relevant complex, or

2) extensive hydration of the simple gold chloride species may involve sufficient solvation free energy to account for the higher experimental solubilities.

4-6-4 Fluid Inclusions in Gold Vein Deposits

Fluid inclusions of gold-quartz veins provide important data on the chemistry of gold-bearing solutions and the temperature of gold deposition in gold-quartz veins. Russian geochemists have described in detail the fluid inclusions from a variety of minerals from Palaeozoic hydrothermal gold-quartz veins (Koltun, 1965a, 1965b; Moiseenko and Fatyanov, 1972).

Carbon dioxide is a major constituent of fluid inclusions in gold quartz veins. A positive correlation between the abundance of carbon dioxide-rich fluid inclusions and free gold has been noted by Machairas (1970). It is significant that the highest molarity of chloride found by Moiseenko and Fatyanov was 0.364M which is considerably lower than that called for in the chlorocomplex models of ore-deposition. However, fluid inclusions in epithermal gold-silver veins in Japan have chloride concentrations up to 3M (Sato, 1972).

Moiseenko and Fatyanov found a highly significant positive correlation between fineness of gold and the ratios of $Na^+:Na^+ + K^+$ and $Cl^-: Cl^- + HCO_3^-$ in fluid inclusions from hydrothermal gold-quartz veins of the USSR.

The homogenisation method for temperature determination of fluid inclusions in quartz, associated with various generations of sulphides and gold, has revealed a wide range of temperatures associated with gold deposits (Koltun, 1965a, 1965b; Moiseenko and Fatyanov, 1972), but a relatively narrow temperature interval for gold precipitation. Typically, sulphides, such as arsenopyrite, sphalerite, and chalcopyrite, are deposited between 400° and 200°C but gold, pyrite, quartz and silver in Japanese epithermal ores are deposited between 200° and 130°C. The final stages of precipitation, with associated carbonates, may occur from 130° to 30°C.

Evidence shows that major gold precipitation takes place at much lower temperatures than suggested by the studies of Helgeson and Garrels (1968) and Henley (1973).

4-6-5 Gold Solubility - Summary

1) Experimental and theoretical work demonstrates significant solubility for gold in solutions of both acidic (pH less than 4) and neutral to mildly alkaline (pH between 6 and 8) character.

2) In acidic solutions gold is significantly soluble as a chlorocomplex given a high fugacity of oxygen and sufficient chloride. In neutral to alkaline solutions in the presence of reduced sulphur, gold is soluble as a sulphide complex.

3) Hot springs transporting gold have a wide range of pH but the majority fall into the two pH groups noted in 1) above.

4) Fluid inclusions from gold deposits suggest that the temperature of gold precipitation is fairly low and the molarity of chloride is often of the order of 0.4 M or less.

5) It has been postulated by Sato (1973) that Kuroko deposits formed from hydrothermal solutions with pH between 3 and 5. This acidity coincides with a minimum in the solubility of gold between the chlorocomplexes of Helgeson (1969) and the sulphide complexes established by Seward (1973). On the other hand, the pH of Kuroko deposition suggested by Kajiwara (1973a, 1973b) is between 5 and 6, where gold solubility is dominated by sulphide complexes.

Taking into account the geochemical similarities of the Kuroko and Bathurst stratiform sulphide deposits (Chapter 7, this work), it is thus of paramount importance to establish the solubility of gold at pH 3 to 6 in the presence of both sulphide and chloride ions. This topic is discussed in detail in Chapter 7.

CHAPTER 5

METHOD OF ANALYSIS

5-1 Sample Preparation

Four types of sample were used in this research including:

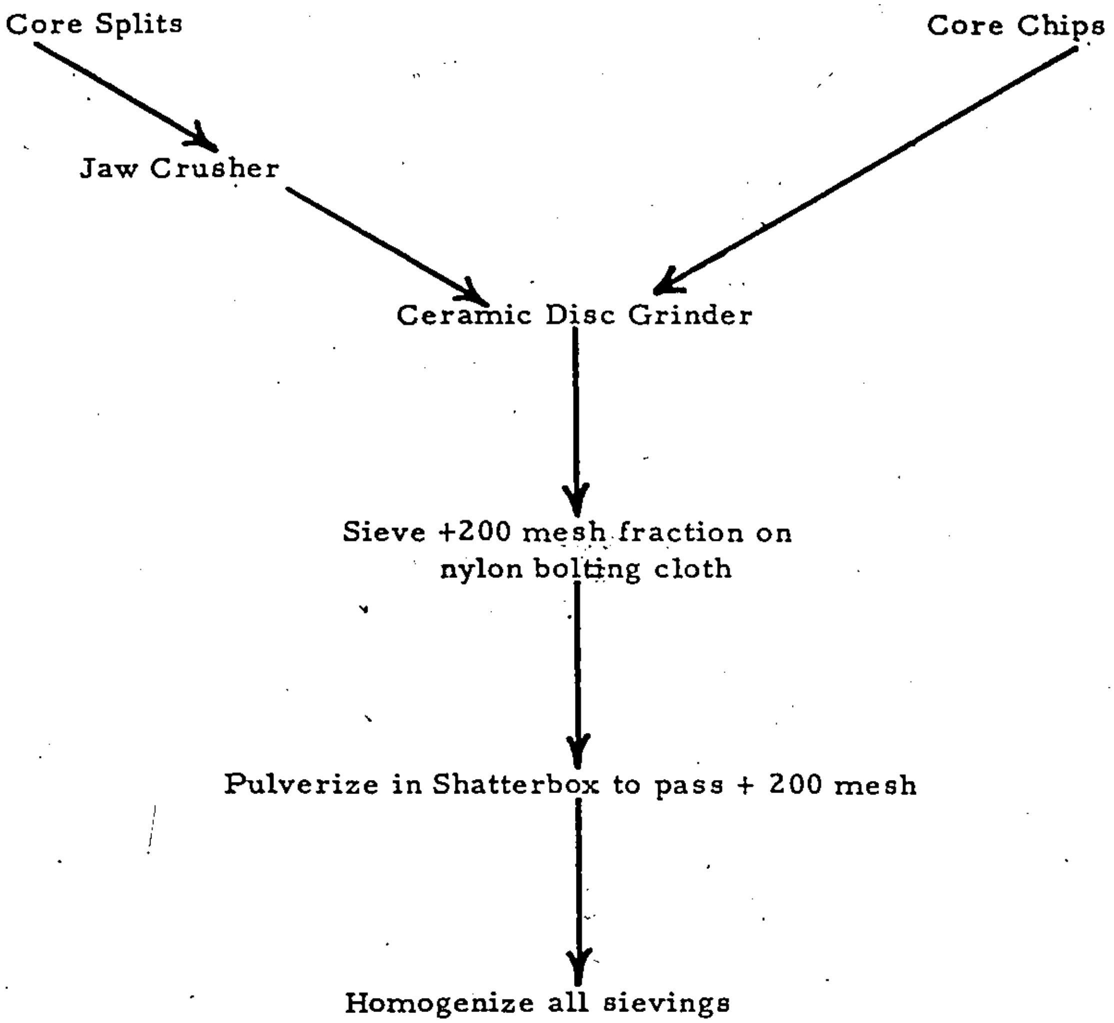
1) diamond drill core pulps (Heath Steele Mines),
2) split diamond drill core (Brunswick No. 12 Mine),
3) chipped diamond drill core (Anaconda Caribou Mine), and
4) hand specimens (Brunswick No. 12 and Caribou).

The drill core pulps required no further processing. The treatment of split drill core and drill core chips is shown in Fig. 5-1. The hand specimens were used for mineral separations which were carried out in the following manner.

Banded hand specimens were cut with a diamond saw parallel to the lamination to obtain sections rich in one mineral. The individual slices were then pulverized by hand in a steel percussion mortar, sieved between -200 and +300 mesh and washed with distilled water and acetone.

Mineral separation was then carried out using a Franz Isodynamic Separator after removal of pyrrhotite and magnetite with a hand magnet.

Fig. 5-1 Flow Sheet for Preparation of Drill Core Splits and Chips



Settings on the Franz were those used by Lusk (1968). In addition to magnetite and pyrrhotite the separates produced were pyrite, chalcopyrite, sphalerite and galena.

Galena and sphalerite were easily identified with a binocular microscope and the purity of concentrates was estimated visually as better than 80%. Pyrite usually had no visible impurities under the binocular microscope. Chalcopyrite was obtained in very small quantities and was difficult to distinguish from pyrite. Thus, the purity of the chalcopyrite separate (sample 14265, Chapter 6) is difficult to establish but probably better than 70%. The separations were all very difficult to obtain due to the fine grain size of the ores (3mm to 0.001mm). The mineral separates were ground to a powder in an agate mortar.

The mineral separates and bulk ore samples were weighed into high purity quartz ampoules for irradiation.

5-2 Analytical Procedure

5-2-1 General

A wet chemical, carrier-based neutron activation procedure, involving separation and purification of gold and palladium activities, was used. Samples and standards were irradiated together in a high flux position in the McMaster Nuclear Reactor. The pertinent induced nuclear reactions are:

$^{197}Au\ (n,\gamma)\ ^{198}Au\ (T_{1/2} = 2.695 \text{ days})$, and

$^{108}Pd\ (n,\ \gamma)\ ^{109}Pd\ (T_{1/2} = 13.46 \text{ hours})$

The induced activity for such n, γ reactions follows the relationship

$$A(d/s) = \phi\ \sigma\ N\ (1 - e^{-\lambda t})$$

where A = neutron induced activity in disintegrations per second

ϕ = neutron flux in neutrons/cm^2/sec.

σ = the activation cross-section in units of $10^{-24}cm^2$

N = number of atoms of target nuclide

λ = decay constant of the induced radioactivity

t = irradiation time

The method is a comparitive one in which the unknown weight of the desired element in the sample C_s is given by,

$$C_s = \frac{A_s \quad C_{std}}{A_{std}}$$

where A_s = activity of the desired element in the sample

A_{std} = activity of the desired element in the standard

C_{std} = the known weight of the desired element in the standard.

The use of carriers, milligram amounts of normal (inactive) palladium and gold, added to samples after irradiation and intimately mixed with the radioactive palladium and gold of the sample in a high temperature fusion, permit the use of analytical procedures in which recovery of the analysis element need not be quantitative.

5-2-2 Carrier Preparations

Carrier solutions were prepared from Johnson, Matthey and Mallory gold and palladium sponges. The pure metals were dissolved in aqua regia, converted to chlorides and diluted in 2N HCl to give solutions containing 5 mg/ml of palladium and 10 mg/ml of gold. One ml. of each solution was taken as carrier for each sample.

5-2-3 Irradiation

The normal irradiation unit consisted of 3 to 4 standards and 4 to 8 samples packaged together in an aluminium radiation can. During the progress of this work the power of the McMaster Reactor was increased from 1.5 to 2.0 and finally, to 5.0 megawatts/hr. Irradiation times were selected to give 15 to 20 megawatt-hours at these power levels (12, 10 and 3hrs respectively) in high flux positions. After decay for a period of 10 hours following irradiation the samples were at a safe radiation level to begin the chemical processing.

5-2-4 Standard Preparation

Gold-palladium standard solutions were prepared from Johnson, Matthey and Mallory high purity gold and palladium metal sponge (JMM Catalogue Nos. JM74 and JM940). About 700 mg. of each metal was weighed to ± 0.025 mg., dissolved in aqua regia, converted to chloride form by repeated evaporation and addition of hydrochloric acid. The solution was then diluted with 2M HCl to a final concentration of approximately 5 mg/ml of gold and palladium. Dilution was carried out by weighing, using a top loading Mettler Model P 1200 balance.

About 50 mg of standard solution were weighed into quartz ampoules and sufficient +200 to -100 mesh quartz powder added to absorb the solution. The ampoules were then taken to complete dryness in an oven at 75°C.

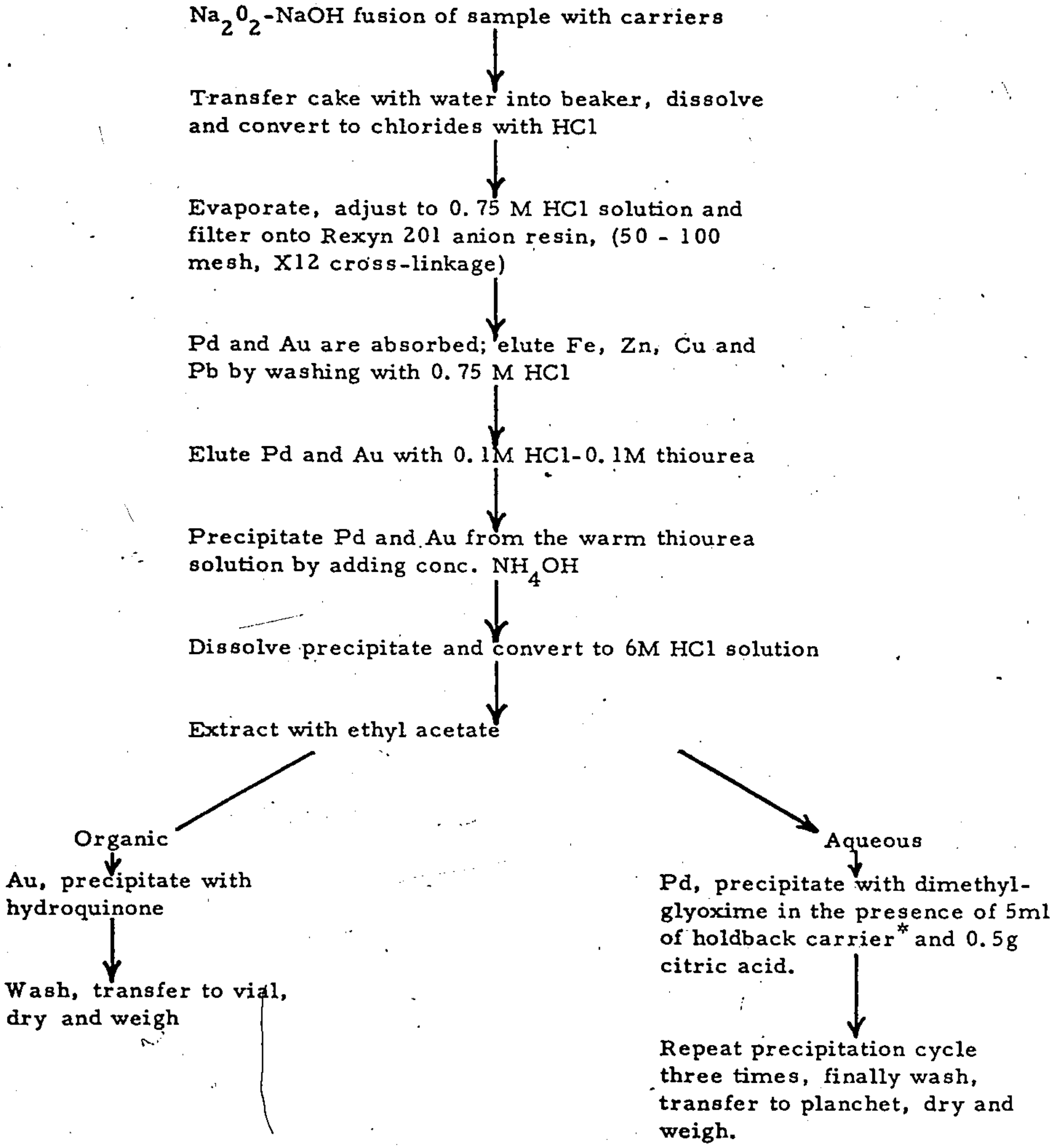
5-2-5 Chemical Procedure

The chemical procedure was taken with minor modifications from Crocket et al. (1968). A significant improvement in the purity of the final palladium precipitates, as compared with the above procedure, was obtained by use of a holdback carrier of the type employed by Smales et al. (1967) in activation analysis of iron meteorites. The essential details of the procedure are shown in the flow sheet presented in Figs. 5-2 (a) and 5-2 (b).

5-2-6 Measurement of Activity

The palladium precipitates were counted on aluminium planchets in a Nuclear Chicago gas flow proportional counter with coincidence shielding and background of about 2.5 counts per minute. The equipment

Figure 5-2. (a) Chemical Procedure for Samples



Na_2O_2-NaOH fusion of sample with carriers

Transfer cake with water into beaker, dissolve and convert to chlorides with HCl

Evaporate, adjust to 0.75 M HCl solution and filter onto Rexyn 201 anion resin, (50 - 100 mesh, X12 cross-linkage)

Pd and Au are absorbed; elute Fe, Zn, Cu and Pb by washing with 0.75 M HCl

Elute Pd and Au with 0.1M HCl-0.1M thiourea

Precipitate Pd and Au from the warm thiourea solution by adding conc. NH_4OH

Dissolve precipitate and convert to 6M HCl solution

Extract with ethyl acetate

Organic

Au, precipitate with hydroquinone

Wash, transfer to vial, dry and weigh

Aqueous

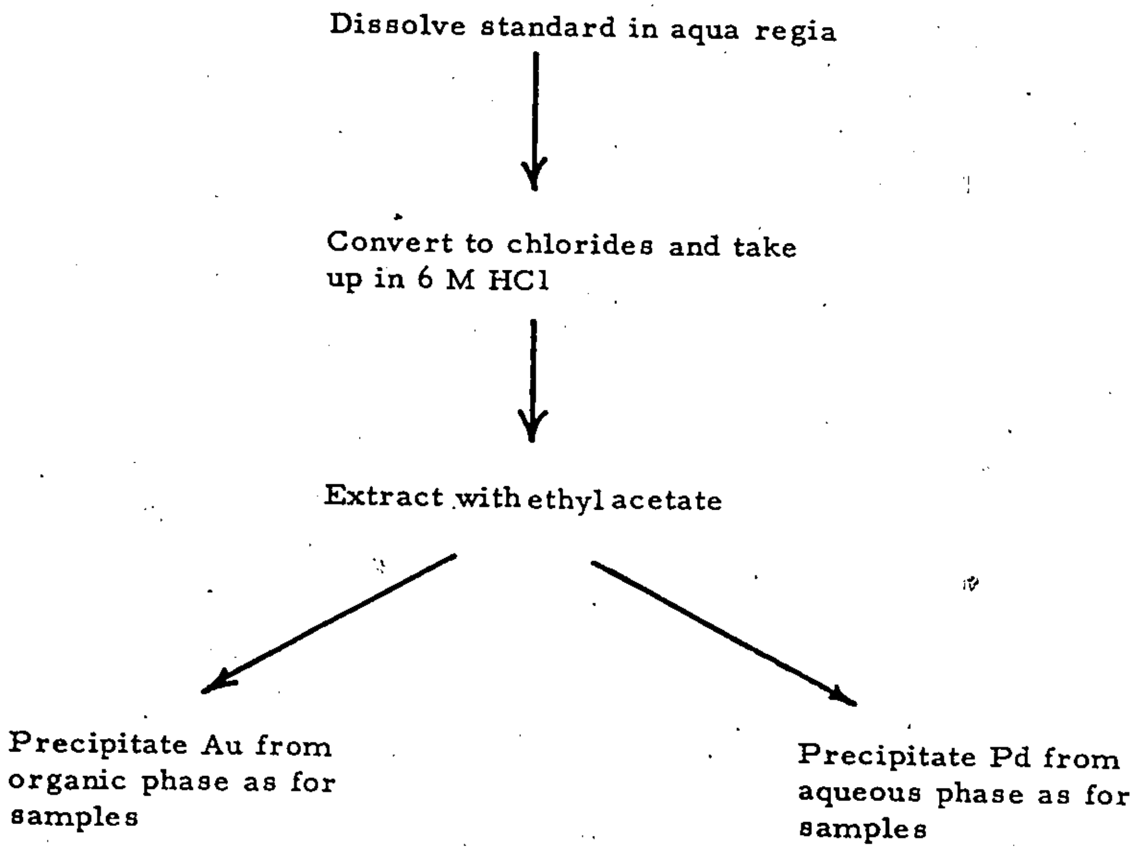
Pd, precipitate with dimethylglyoxime in the presence of 5ml of holdback carrier* and 0.5g citric acid.

Repeat precipitation cycle three times, finally wash, transfer to planchet, dry and weigh.

---

* The holdback carrier contained 2mg/ml of Fe, Co, Cr, Ca, Zn, Mn, Mo and As (Smales et al. 1967)

Fig. 5-2. (b) Chemical Procedure for Standards



consisted of an automatic sample changer, scaler with time and total counts selection, proportional counting tube, and typed paper tape output giving sample number, duration of count and total counts.

The palladium beta activity was followed for as many half-lives as possible. Usually each sample was counted three times a day for the first few days and then less frequently for one or two weeks. Decay curves (plots of count rate vs. time) were then plotted on semi-logarithmic graph paper.

Under ideal conditions the decay curve resolved into two linear components consisting of a short-lived member with a half-life fairly close to that of ^{109}Pd and a second component of very long half-life. By extrapolation of the latter, and subtraction from the composite curve, a resolved curve for pure ^{109}Pd was obtained.

The palladium content of the sample was then calculated from:

$$\text{metal (parts per billion)} = \frac{N \times 10^9 \times Y_1}{M \times W \times Y_2}$$

where N = sample counts at time t

M = mean activity of standards per gram of palladium

W = weight of sample in grams

Y_1 = yield of standard in weight fraction

Y_2 = yield of sample in weight fraction

The gamma radiation from gold was counted in a well-type 3" X 3" NaI (Tl) scintillation detector linked through an analog to digital converter to a 1600 channel memory (Nuclear Chicago Corp.). Output was on teletype, using both punched paper tape and typed paper roll.

The gold spectra were invariably pure and calculation was straight forward. For samples with 500 ppb or more the activity level was high enough to permit counting periods of approximately 5 minutes. Calculation of the gold content was by computer programme. The method of calculation is that of Wasson (Baedecker, 1971) which compares favourably with other methods according to Baedecker. A representation of the Wasson method is shown in Fig. 5-3. The peak area is calculated by the following expression:

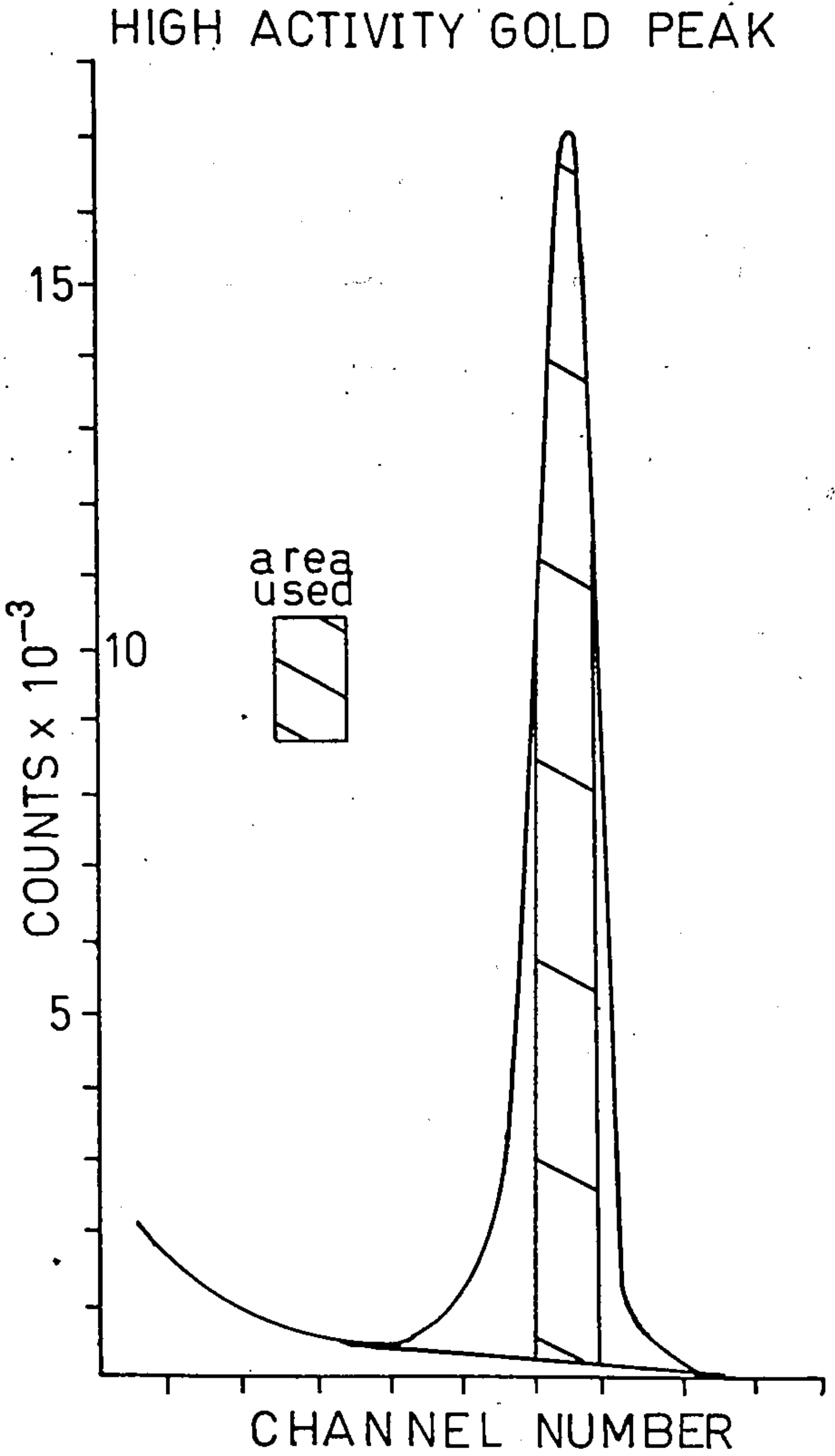
$$\text{area} = \sum_{i=-n}^{i=+n} a_i - (n + \tfrac{1}{2})(b_n + b_{-n})$$

where n = the number of channels on the left side and right side of channel zero (the centremost channel) at half peak height

a_i = the number of counts accumulated in channel i

b_n = the background in channel n as determined from a straight line drawn between channels at the left- and right-hand limits of the peak.

Fig. 5-3. Wasson Method of Peak Calculation (after Baedecker, 1971)


HIGH ACTIVITY GOLD PEAK
15
10
5
COUNTS × 10^{-3}
area used
CHANNEL NUMBER

5-3 Precision, Accuracy and Sensitivity

5-3-1 Precision

(a) Discussion

In the following account σ % is to be read as "percentage standard deviation due to . . . ". All error limits are for one standard deviation. Errors are random or systematic, with random errors reflected in precision and systematic errors in accuracy. Four components of random error can be distinguished: σ % (sample inhomogeneity), σ % (irradiation), σ % (chemical method) and σ % (counting statistics).

The weight of the sample taken is a major factor in determining the percentage standard deviation due to sample inhomogeneity, because larger samples are more likely to be representative and show the characteristics of homogeneity.

Variations in neutron flux across and along the samples account for most of the standard deviation due to irradiation. De Soete et al. (1972) suggest that this may amount to 10%/cm in a small-core water-moderated reactor. Skippen (1963) found a flux variation of 2.5%/cm for the McMaster University Reactor for an irradiation position at the core margin. The standard irradiation container is 2.5 cm in diameter by 4.5 cm in length.

The expected standard deviation attributable to the chemical method is difficult to determine, but should be small as the use of a carrier eliminates the need for quantitative recovery of the element of interest. Each of the numerous stages has a possibility of small error. It is expected that this error is less than 2% (De Soete et al. 1972).

The count rate measurements are affected by sample geometry, electronic drift and counting statistics. For gamma-counting of the gold in a well-type detector, geometry probably does not generate significant error. This was verified by counting standards and samples at different positions with respect to the detector. Errors due to electronic drift are minimal because of the short counting times involved. The error due to counting statistics, given by $\sqrt{N}/N \times 100\%$ where N is the total number of counts, is usually less than 1%.

An additional source of error in counting the 0.96 MeV beta radiation of ^{109}Pd is self-absorption which may become significant when sample and standards differ in weight by more than 10%. A self-absorption correction curve was estiablished by Chyi (1972) and was used in this study to correct all palladium count rates for self-absorption effects.

Variations in the texture of palladium precipitates could also cause differences in counting geometry. Sufficient washing with alcohol to remove any traces of unreacted dimethylglyoxime and slow drying were usually sufficient to ensure an even, smooth precipitate.

The electronic drift of the beta-counting equipment was monitored by uranyl acetate standards. Short-term (periods of 1 to 2 days) corrections of palladium activity were not required.

The random errors may be summarized by the following expression:

$$\sigma\,\%\,(\text{total}) = \sigma\,\%\,(\text{sample inhomogeneity}) + \sigma\,\%\,(\text{analytical}) \qquad 5\text{-}1$$

where $\sigma\,\%\,(\text{analytical}) = \sigma\,\%\,(\text{irradiation}) + \sigma\%\,(\text{chemical}) +$

$$\sigma\,\%\,(\text{counting}) + \sigma\,(\text{calculation}) \qquad 5\text{-}2$$

with the last term in equation 5-2 applicable to Pd only.

(b) Error Analysis

1) The pooled variance estimate (Dixon and Massey, 1951) of the percentage standard deviation of duplicate analyses for gold and palladium was found to be 34%* and 52% respectively (see Table 6-7 for data used to compute pooled variance). The corresponding values for the standards were 6% and 10%.

2) The error for the standards is considered to be σ % (irradiation) = σ % (counting). σ % (counting) can be found from $\sqrt{N}/N$. Hence for gold, σ % (irradiation) = 6% - 1% = 5%, and for palladium, σ % (irradiation) = 10% - 1% = 9%.

---

* One value, exceeding 4 standard deviations from the mean, was neglected.

3) The error due to the chemical method, σ % (chemical) is taken to be less than 2%.

4) The total error due to the analytical technique is calculated from equation 5-2. A summary of error components is presented in Table 5-1. For gold we have that σ % (analytical) = 5% + 2% + 1% = 8%, and for palladium σ % (analytical) = 9% + 2% + 10% + 10%* = 31%.

5) Finally, from equation 5-1, the error due to sample inhomogeneity is given by σ % (sample inhomogeneity) = σ % (total) - σ % (analytical). This error, 26% for gold and 24% for palladium, is approximately the same for both metals.

5-3-2 Accuracy

There is no internal method of closely defining the accuracy of the method. The usual approach is to compare the results on standard rocks with those of other laboratories, methods or analysts. No systematic contamination of the samples is expected from the crushing procedures or from quartz irradiation tubes.

Possible systematic errors of a nuclear nature are:

1) self-shielding of the neutron flux by the element of interest causing neutron attenuation at certain energies,

2) products from competing reactions of the (n, p) or (n, α) type,

3) uranium fission products.

---

* Graphic errors could cause up to 10% error in the calculation of palladium activities for samples.

Table 5-1. Summary of Random Errors for the Analytical Method

	GOLD % standard deviation	PALLADIUM % standard deviation
Sample Total	34	55
Standard Total	6	10
Counting	1	10 (samples) 0 (standards)
Calculation	-	10
Irradiation	5	9
Chemical	2	2
Analytical	8	31
Sample Inhomogeneity	26	24

Self-shielding may be significant for gold because of a very large resonance peak at a neutron energy of about 5eV. To minimize this effect the standard gold should be well dispersed as in the preparation used here. A well-thermalized neutron flux is also advantageous as is apparent from the cross-section vs. neutron energy curve for gold (See Fig. 5-4).

Products from reactions such as (n, p), (n, α) or fission of uranium are unlikely to be of any significance for gold. Possible interferences for palladium involving (n, p), (n, α) and (n, fission) reactions on Ag, Cd and U have been discussed by Crocket and Skippen (1966). For 1% interference, silver/palladium, cadmium/palladium or uranium/palladium ratios must be greater than 10,000:1, 10,000:1 and 190:1 respectively. The uranium content of massive sulphides is not expected to be significant, although that of sediments and volcanics may cause some degree of inaccuracy. The maximum silver content of the massive sulphides is approximately 30 to 60 ppm resulting in a maximum interference of 10% for 0.5 ppb palladium. The cadmium content of the sulphides may be of the order of 100 ppm giving a maximum interference of 20% for 0.5 ppb palladium.

The accuracy of the analytical method was tested by analysing the U.S. Geological Survey standard diabase W-1 and the D. E. M. R. (Mines Branch) standard nickel-copper matte PTM - 1(A). The latter standard was analysed for gold only. The results are shown in

Fig. 5-4. Relationship of Neutron Flux and Cross-Section of Gold to Neutron Energy.

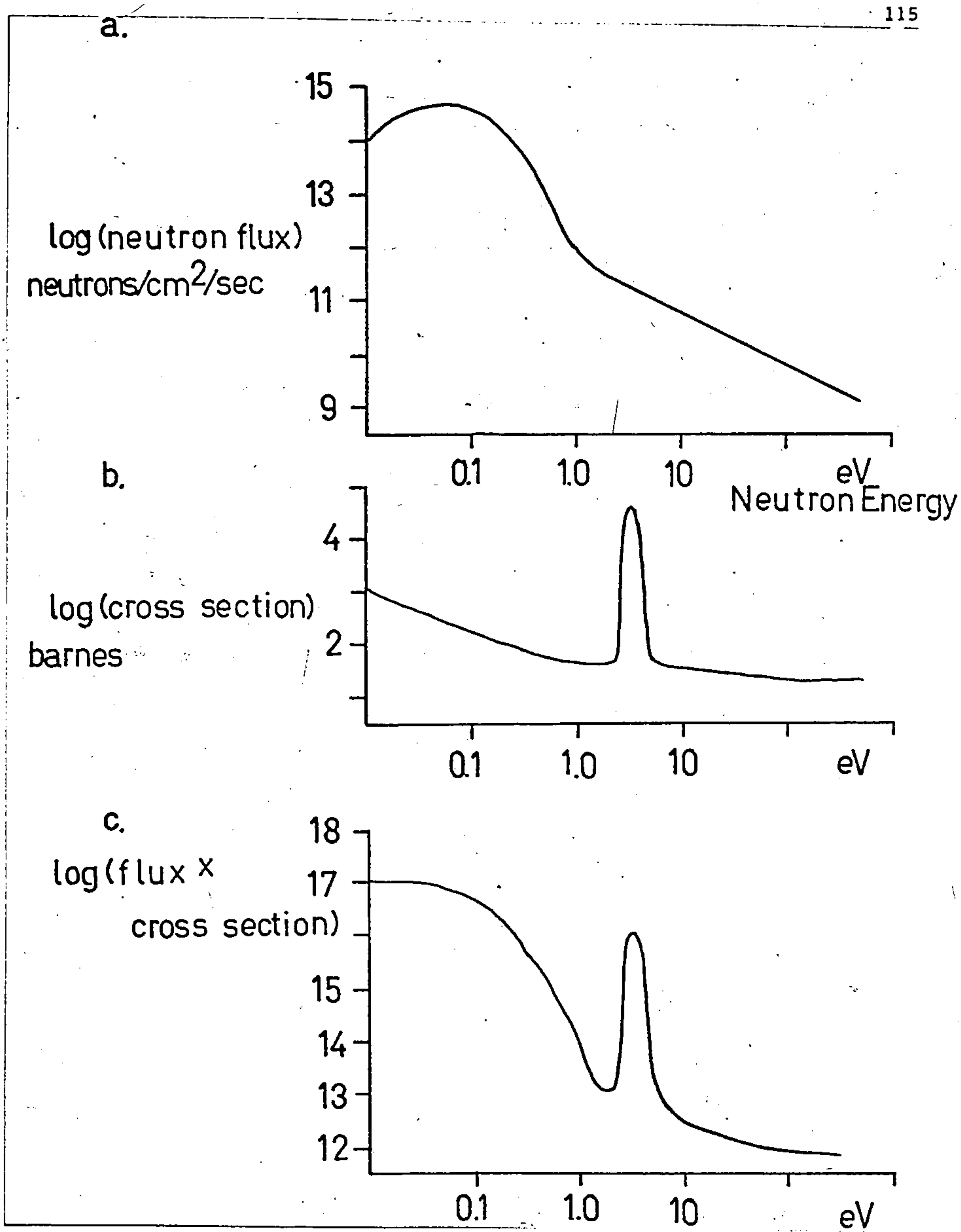

a.
15
13
11
9
log (neutron flux)
neutrons/cm2/sec
0.1
1.0
10
eV
Neutron Energy
b.
4
2
log (cross section)
barnes
0.1
1.0
10
eV
c.
18
17
15
14
13
12
log (flux x cross section)
0.1
1.0
10
eV

Table 5-2.

During the progress of the work four standard solutions were prepared for gold and palladium. These were periodically compared to provide an internal check on the accuracy of preparation and to detect possible deterioration with time.

5-3-3 Sensitivity

Crocket (1971) calculated a sensitivity limit of 0.5 ppb for gold by gamma-spectrometry. All samples analysed in this study contained gold contents well above this level. For palladium determination by beta-counting, it must be recognised that the definition of a sensitivity limit must include provision for nuclide characterization by half-life determination.

If the usual practice of assigning the detection limit at a signal-to-background ratio of 2:1 is followed, a palladium content equivalent to a count rate of 4 counts per minute (cpm) is required. The background count rate was 2 cpm. If a decay period equivalent to 3 half-lives is required for characterization of the radiation, the initial count rate must be 4×2^3 or 32 cpm. If graphical subtraction of long-lived contamination is required, somewhat higher count rates are needed. The count rate required for adequate characterization in the presence of minor contamination is taken as 40 cpm which is equivalent to 0.5 ppb although the detection limit, 4 cpm, is equivalent 0.05 ppb of palladium.

Table 5-2. Gold and Palladium Analyses of Standard Samples

(a) Analyses of W-1 (Standard Diabase)

Experiment	Gold ppb	Palladium ppb	Note
BRA-1	4.2	14.8	
BRA-2	4.6	8.7	
BRA-3	6.1	10.9	
BRA-5	12.0	15.8	
TEST-1	6.1, 4.1	-	
CM-3	-	9.9	
	5.0 ± 0.8	12.0 ±3.1	Mean for this work (excluding BRA-5 value for gold)
		12.0 ± 1.7	Rowe and Simon, 1971 (12 determinations)
		11.5 ± 0.3	Crocket <u>et al.</u> 1968 (17 determinations)
	4.6 ± 0.69		Gottfried <u>et al.</u> 1972 (8 determinations)

(b) Analysis of PTM-1(A) (Ni-Cu Matte)

Experiment	Gold ppb	Palladium ppb	Note
	2045		This work
	1810 ± 220		McAdam <u>et al.</u> 1971

Inspection of the palladium analyses performed in this work showed that, in general, most problems with decay curve analysis are not due to insufficient counts but to contaminants of intermediate half-life. This is evident in the fact that the best decay curves were obtained for samples having low initial count rates. The opposite would be expected if the errors were due to statistical counting factors. Improvement of sample purity by increasing the number of purification steps is of limited usefulness however, due to attendant decrease in the yield.

In the tables of results those palladium analyses whose decay curves were followed for three half-lives or more are distinguished from those where significant contamination was present.

CHAPTER 6

ANALYTICAL RESULTS

6-1 Sampling

6-1-1 Metal Profiles on Diamond Drill Holes

Variations in lead, zinc, copper, gold and silver are presented in a series of figures, Fig. 6-2 to Fig. 6-7, showing metal profiles and lithologies along the six diamond drill holes studied. These diagrams are preceded by Fig. 6-1 which is a key to the lithological symbols and mineralogical notations used in the metal profile diagrams.

Samples from the Heath Steele B-1 orebody were pulps prepared from 5 ft. (1.5 m) intervals of core from diamond drill hole B138. The location of this hole is shown in Fig. 2-4 and a log of the lithology and character of sulphides is given with the metal profiles in Fig. 6-2. The analysed samples provide continuous metal profiles across 10 ft. of footwall metasediments and 140 ft. of ore, an almost complete section of the orebody. In Fig. 6-2 and all other metal profile diagrams, zero footage is taken at the diamond drill hole collar.

Selected samples representative of various ore types and host rocks were taken at discontinuous intervals along three diamond drill holes through the Brunswick No. 12 orebody. The samples consisted of split drill core representative of various core lengths. The drill hole locations are plotted in Fig. 2-3. Logs of the core lithology, the core intervals sampled and the metal profiles are presented in Fig. 6-3 to 6-5.

The Anaconda Caribou Mine is represented by two diamond drill holes intersecting two orebodies as shown in Fig. 2-2. Both holes are mainly in massive sulphide but they do intersect some non-ore grade schist and tuff (Figs. 6-6 and 6-7). In massive sulphides a continuous sequence of samples was taken. Each sample is an aliquote taken from a pulp prepared by the Company and represents on the average 5 ft. (1.5 m.) of split core. Wallrock schists and tuffs were sampled on a discontinuous basis to represent the main host rock types distinguished by Dr. R. Cavalero, mine geologist. Samples were aliquots of pulps prepared from split core representing on average 2 ft. (0.5 m.) of core.

6-1-2 Separate Mineral Samples

Samples of separated sulphide minerals from each of the three deposits were analysed for gold and palladium. The preparation of mineral separates from the Heath Steele B-1 orebody was described by Lusk (1968), and the mineral separates from the Brunswick No. 12 and Anaconda Caribou deposits prepared by the author were discussed in

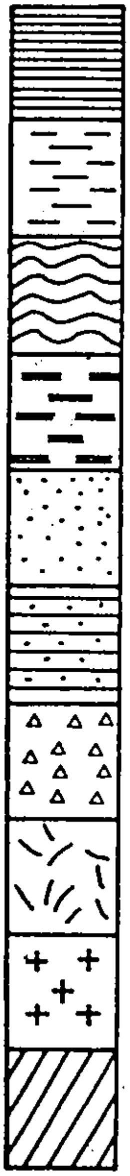
Chapter 5. Mineral separates from 22 Heath Steele, 5 Brunswick No. 12 and 4 Caribou Mine samples were analysed. The mineral separates prepared were pyrite, sphalerite, galena, chalcopyrite and pyrrhotite, although in the majority of cases samples were represented by pyrite and sphalerite only.

Three of the samples from the Brunswick No. 12 Mine, 16136, 16141 and 14265, were diamond drill core chosen because of their high metal contents as indicated by company assays. Samples WMCB011 (Caribou Mine) and WMCB018 (Brunswick No. 12 Mine) were hand specimens of banded lead-zinc sulphides which could be selectively sawn to obtain slices rich in galena, sphalerite or pyrite. Sample WMCB017 (Caribou Mine) was a hand specimen of massive pyrite ore. The Heath Steele separates were obtained from both drill core and hand specimens.

6-2 Results

The results of the drill core activation analyses for gold and palladium together with the lead, zinc, copper and silver assays kindly provided by the mining companies, are presented in Tables 6-1 to 6-6. The gold and palladium values are means where more than one analysis was made. Individual gold and palladium values of samples analysed in duplicate are given in Tables 6-7 (a) and 6-7 (b) respectively.

Fig. 6-1. Key to Lithological Symbols and Mineralogical Notations used in Figs. 6-2 to 6-7.



SEDIMENTS

GRAPHITIC SCHIST

IRON FORMATION

BANDED SULPHIDES

MASSIVE SULPHIDES

DISSEMINATED SULPHIDES

TUFF

RHYOLITE

"VOLCANIC SCHIST"

PORPHYRY DYKE

P	PYRITE
Po	PYRRHOTITE
C	CHALCOPYRITE
S	SPHALERITE
G	GALENA
Si	SIDERITE
Ch	CHLORITE
Mt	MAGNETITE
+	GOLD ASSAY POINT (FIG 6-3, 6-4, 6-5)

Fig. 6-2. Metal Profiles and Lithology for Diamond Drill Hole B138, Heath Steele B-1 Orebody.

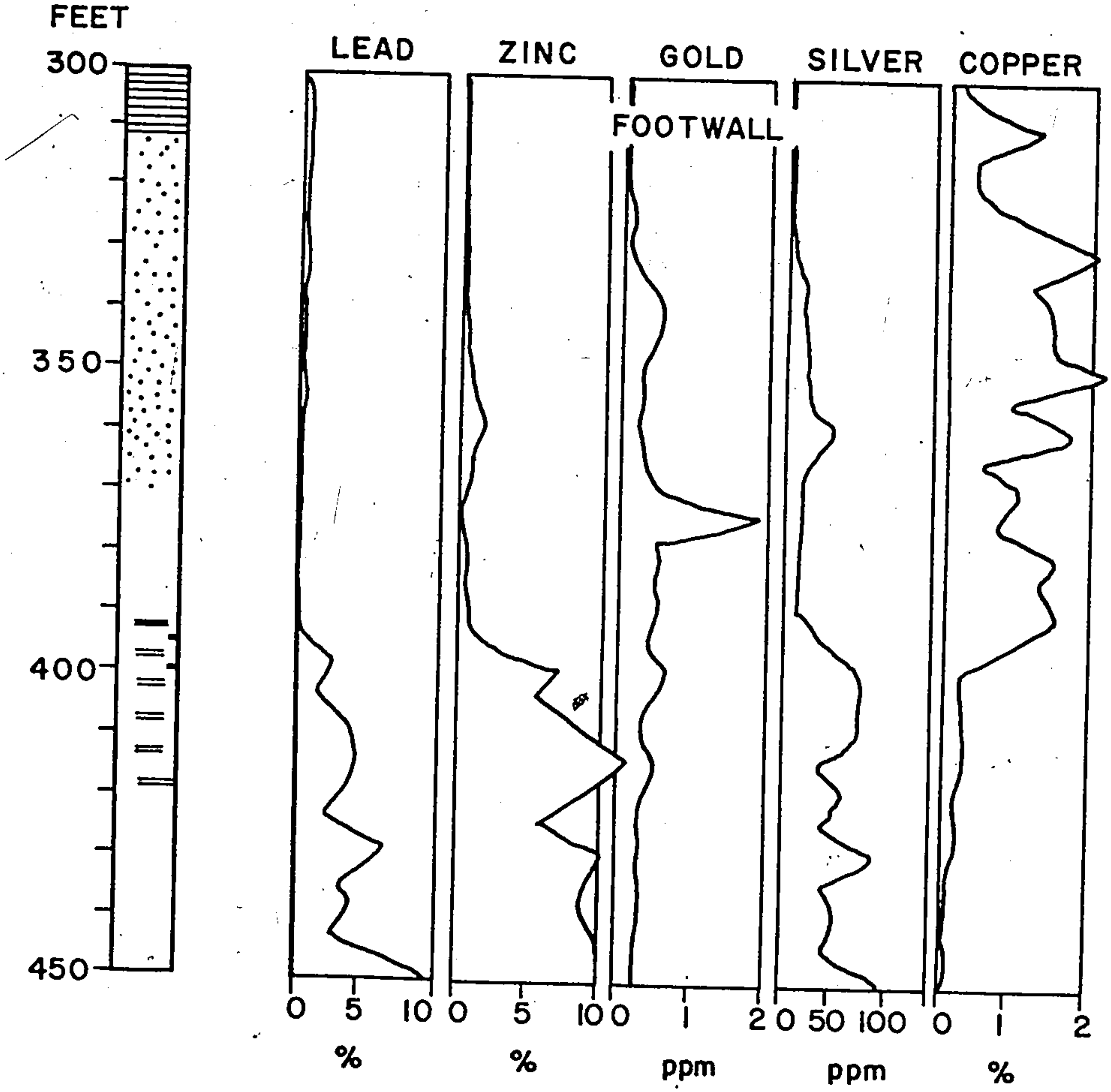

FEET
300
350
400
450
LEAD
ZINC
GOLD
FOOTWALL
SILVER
COPPER
0
5
10
%
0
5
10
%
0
1
2
ppm
0
50
100
ppm
0
1
2
%

Fig. 6-3. Metal Profiles and Lithology for Diamond Drill Hole 12-1037, Brunswick No. 12 Mine.

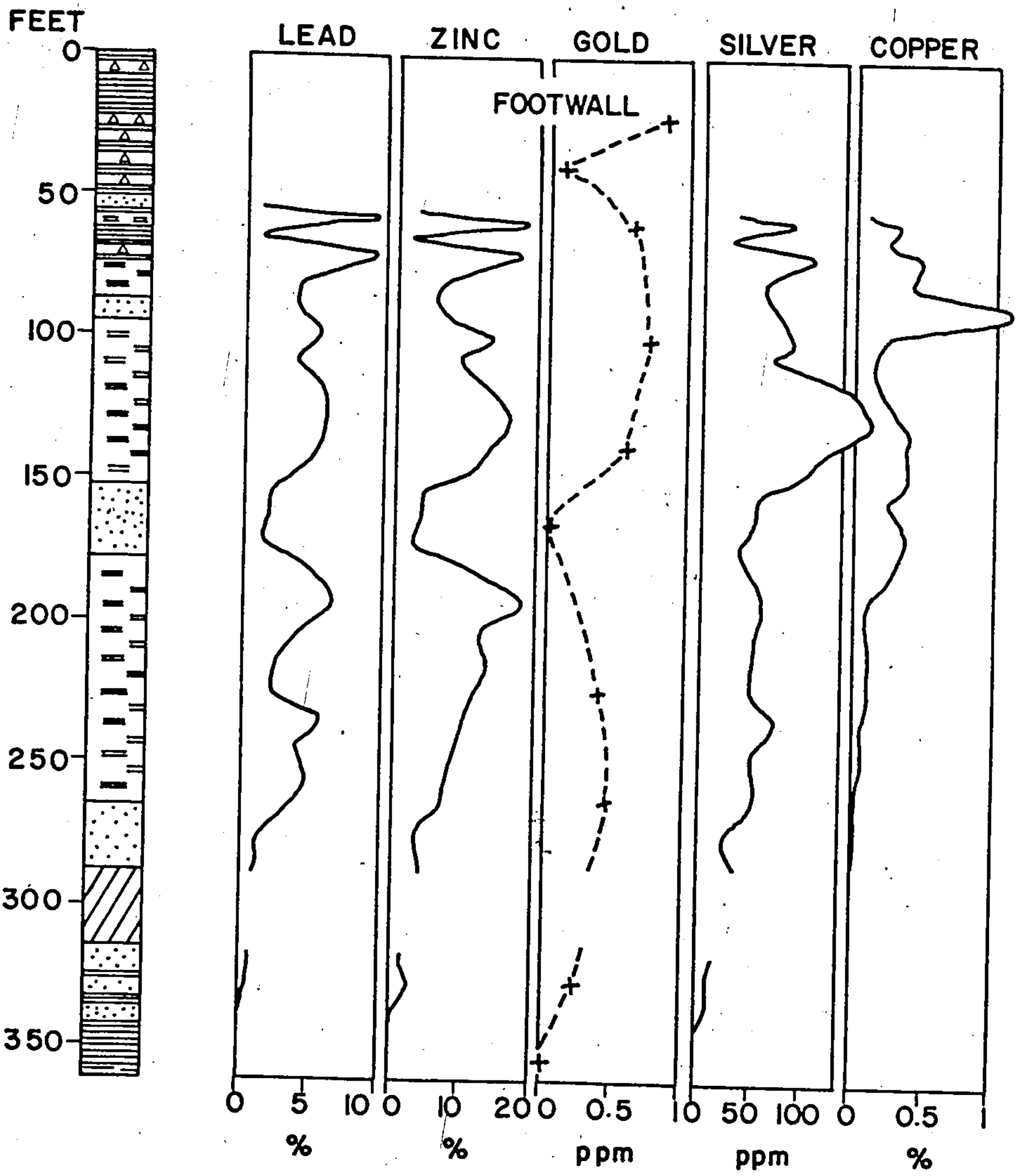

FEET
0
50
100
150
200
250
300
350
LEAD
ZINC
GOLD
SILVER
COPPER
FOOTWALL
0 5 10
%
0 10 20
%
0 0.5 1
ppm
0 50 100
ppm
0 0.5 1
%

Fig. 6-4. Metal Profiles and Lithology for Diamond Drill Hole 12-1002, Brunswick No. 12 Mine.

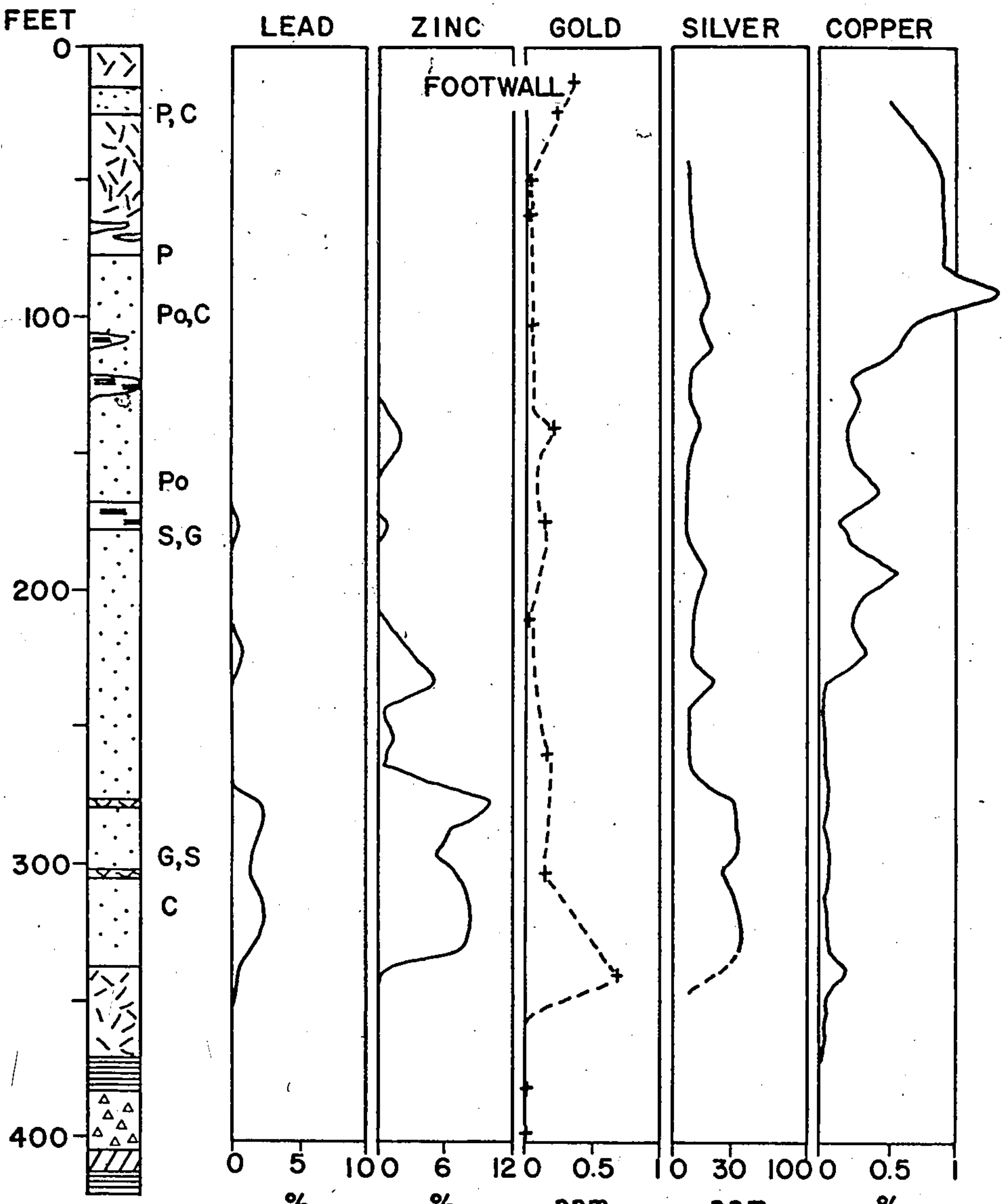

FEET
0
100
200
300
400
P, C
P
Po, C
Po
S, G
G, S
C
LEAD
ZINC
GOLD
SILVER
COPPER
FOOTWALL
0
5
10
%
0
6
12
%
0
0.5
1
ppm
10
30
100
ppm
0
0.5
1
%

Fig. 6-5. Metal Profiles and Lithology for Diamond Drill Hole 12-1051, Brunswick No. 12 Mine.

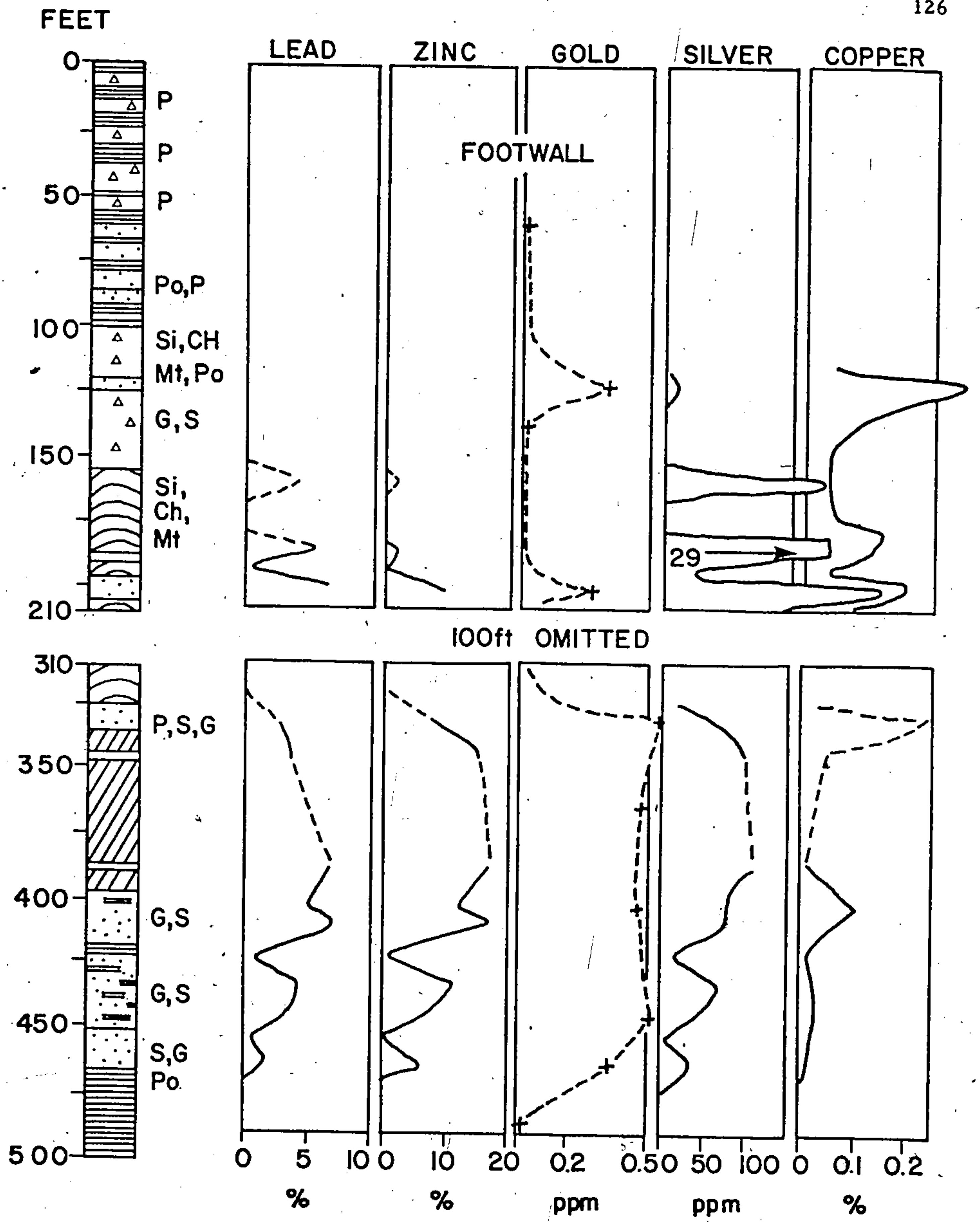
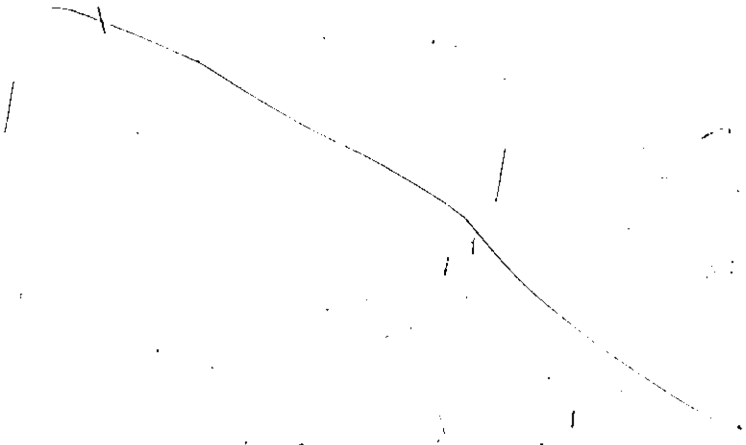

FEET
0
50
100
150
210
310
350
400
450
500
P
P
P
Po,P
Si,CH
Mt,Po
G,S
Si,
Ch,
Mt
P,S,G
G,S
G,S
S,G
Po
LEAD
ZINC
GOLD
SILVER
COPPER
FOOTWALL
29
100ft OMITTED
0
5
10
0
10
20
0.2
0.5
0
50
100
0
0.1
0.2
%
%
ppm
ppm
%

Fig. 6-6. Metal Profiles and Lithology for Diamond Drill Hole 62-9, Caribou Mine,



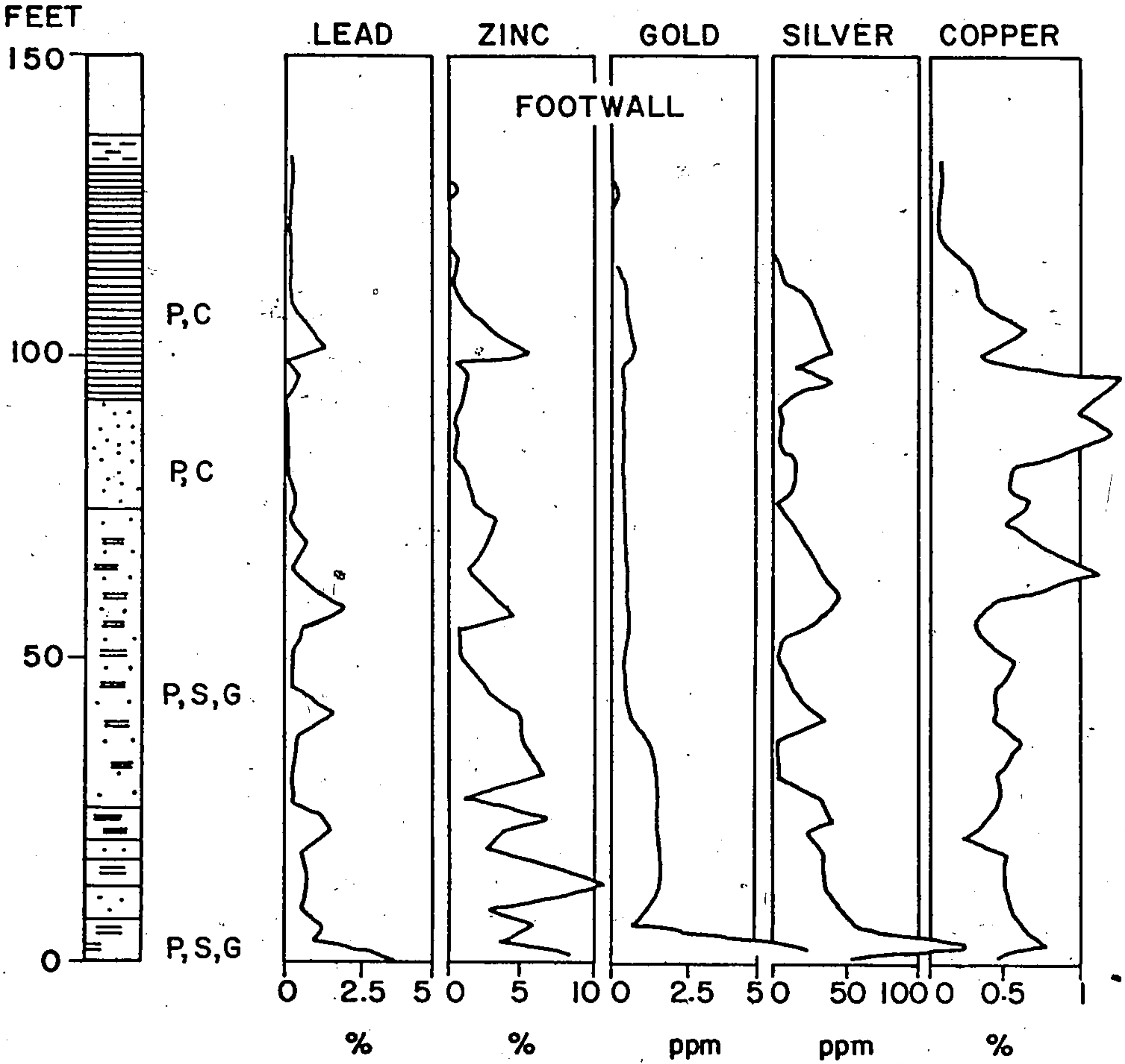

FEET
150
100
50
0
P, C
P, C
P, S, G
P, S, G
LEAD
ZINC
GOLD
SILVER
COPPER
FOOTWALL
0
2.5
5
0
5
10
0
2.5
5
0
50
100
0
0.5
1
%
%
ppm
ppm
%

Fig. 6-7. Metal Profiles and Lithology for Diamond Drill Hole 62-17, Caribou Mine.

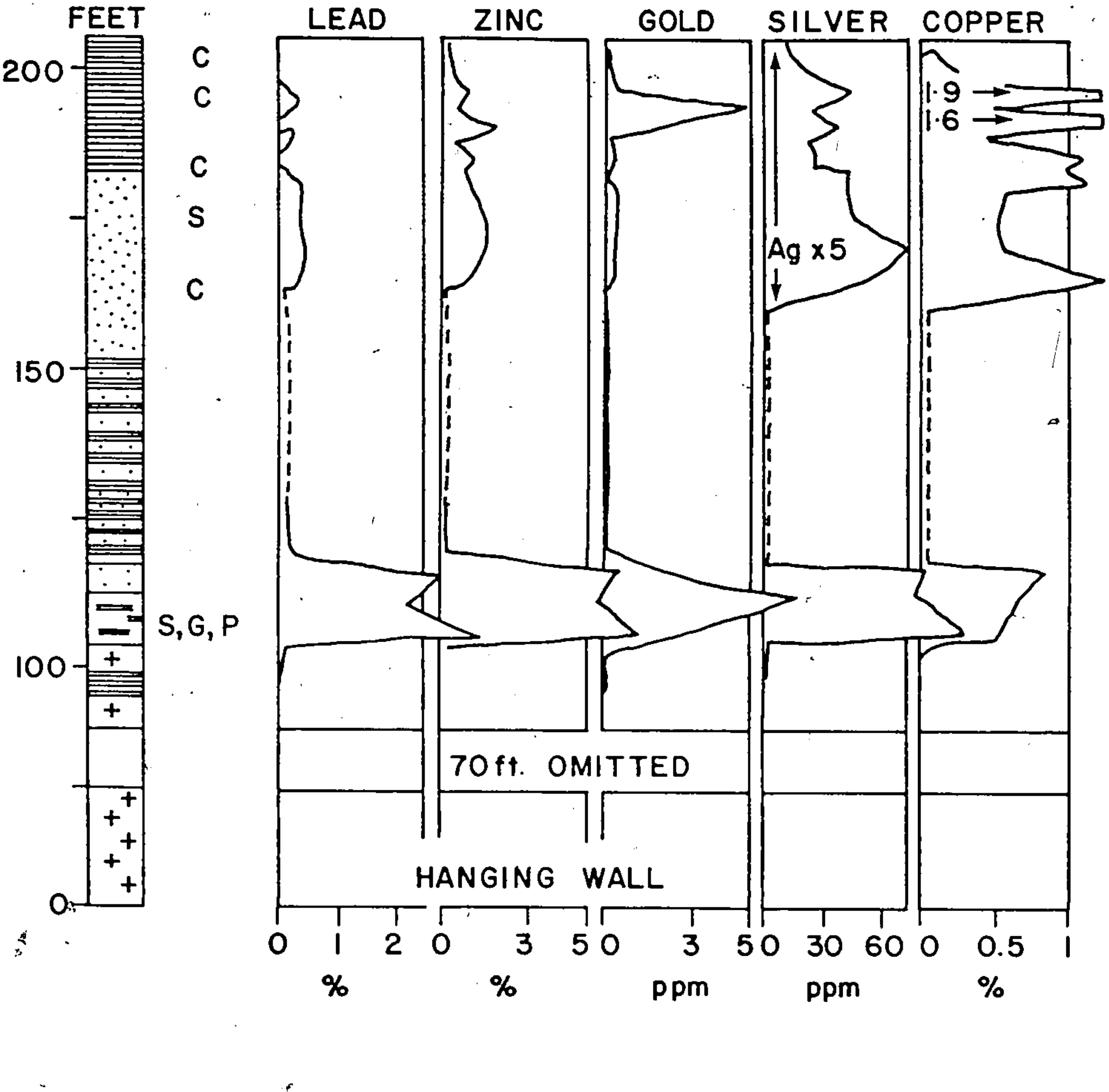

FEET
200
150
100
0
C
C
C
S
C
S,G,P
LEAD
ZINC
GOLD
SILVER
COPPER
Ag x 5
1·9
1·6
70 ft. OMITTED
HANGING WALL
0 1 2
%
0 3 5
%
0 3 5
ppm
0 30 60
ppm
0 0.5 1
%

Table 6-1. Diamond Drill Hole B138, Heath Steele B-1 Orebody.

Company Assays for Lead, Zinc, Copper and Silver and Neutron Activation Analyses for Gold and Palladium

SAMPLE	FOOTAGE	LEAD %	ZINC %	COPPER %	SILVER		GOLD		PALLADIUM
					oz/ton	ppm	oz/ton	ppb	ppb
A4078	300-305	0.09	0.10	0.33	0.068	2.33	0.0005	15.9	0.75
A4079	305-310	0.05	0.10	1.53	0.192	6.58	0.0010	35.2	0.72*
A4080	310-315	0.12	0.10	0.45	0.166	5.69	0.0016	55.2	9.5*
A4081	315-320	0.05	0.10	0.45	0.130	4.46	0.0025	86.6	1.3*
A4082	320-325	0.06	0.07	1.35	0.152	5.21	0.0014	46.6	1.3
A4083	325-330	0.05	0.07	2.43	0.204	7.00	0.0060	206.0	4.9
A4084	330-335	0.15	0.30	1.45	0.590	20.24	0.0022	77.0	1.1*
A4085	335-340	0.07	0.15	1.70	0.435	14.92	0.010	340.0	2.2*
A4086	340-345	0.15	0.25	1.78	0.748	25.66	0.019	662.0	1.2*
A4087	345-350	0.20	0.70	2.65	0.770	26.41	0.016	535.0	3.0
A4088	350-355	0.40	1.00	1.18	0.940	32.24	0.008	280.0	23.7
A4089	355-360	0.35	1.95	2.10	1.594	54.67	0.010	348.0	1.5*
A4090	360-365	0.25	1.15	0.65	0.910	31.21	0.007	247.0	1.3*
A4091	365-370	0.20	1.05	1.25	0.588	20.17	0.011	374.0	10.3*
A4092	370-375	0.25	0.30	0.80	0.672	23.05	0.015	526.0	0.54*
A4093	375-380	0.16	0.28	1.86	0.550	18.87	0.067	2300.0	2.8*
A4094	380-385	0.09	0.33	1.55	0.532	18.25	0.020	670.0	1.0
A4095	385-390	0.09	0.39	1.91	0.600	20.58	0.016	532.0	0.52*
A4096	390-395	0.61	1.06	1.18	1.306	44.80	0.017	593.0	0.46*
A4097	395-400	2.93	7.05	0.35	2.600	89.18	0.012	414.0	1.6
A4098	400-405	1.75	5.95	0.35	2.700	92.61	0.023	800.0	164.0
A4099	405-410	3.75	8.75	0.45	2.624	90.00	0.014	489.0	2.0
A4100	410-415	4.64	11.35	0.40	1.116	38.28	0.011	362.0	1.0
A4101	415-420	4.00	9.05	0.28	2.050	70.32	0.017	598.0	1.0*
A4102	420-425	2.75	5.45	0.30	1.382	47.40	0.013	452.0	2.2*
A4103	425-430	6.80	9.85	0.25	3.016	103.4	0.009	310.0	0.67*
A4104	430-435	3.25	8.70	0.10	1.508	51.72	0.010	351.0	0.38
A4105	435-440	4.40	8.75	0.05	1.960	67.23	0.010	343.0	0.34*
A4106	440-445	3.15	9.25	0.07	1.430	49.05	0.010	344.0	0.53*
A4107	445-450	8.80	9.70	0.10	3.050	104.6	0.013	440.0	0.86*

Note: * signifies sample whose palladium decay curve was followed for three half-lives or more.

Table 6-2. Diamond Drill Hole 12-1037, Brunswick No. 12 Mine

Company Assays for Lead, Zinc, Copper and Silver and Neutron Activation Analyses for Gold and Palladium

SAMPLE	FOOTAGE	LEAD %	ZINC %	COPPER %	SILVER		GOLD		PALLADIUM
					oz/ton	ppm	oz/ton	ppb	ppb
	20-24	-	-	-	-	-	0.024	832.0	-
	38-40	-	-	-	-	-	0.004	132.0	1.6*
16136	54-61	9.15	19.64	0.32	3.15	108.4	0.018	602.0	1.1
16141	93-103	5.57	13.96	0.17	3.12	107.0	0.020	682.0	1.0
16145	133-143	4.90	13.92	0.31	4.56	156.4	0.016	559.0	0.39
16148	160-169	1.51	3.93	0.34	1.88	64.5	0.0004	12.4	0.55
16154	218-228	1.98	10.54	0.08	1.93	66.2	0.012	395.0	0.55*
16158	258-265	3.90	7.63	0.03	1.83	62.8	0.013	440.0	-
16174	323-331	0.38	3.29	0.01	0.39	13.4	0.007	256.0	0.60
	350-354	-	-	-	-	-	0.0001	5.0	-

Note 1. * signifies sample whose palladium decay curve was followed for three half-lives or more.

Note 2. - signifies "not determined"

Table 6-3. Diamond Drill Hole 12-1051, Brunswick No. 12 Mine

Company Assays for Lead, Zinc, Copper and Silver and Neutron Activation Analyses for Gold and Palladium

SAMPLE	FOOTAGE	LEAD %	ZINC %	COPPER %	SILVER		GOLD		PALLADIUM
					oz/ton	ppm	oz/ton	ppb	ppb
	60-61	-	-	-	-	-	0.0005	18.6	1.1*
16708	120-125	0.08	0.10	0.33	0.48	16.5	0.010	343.0	2.1*
	140-141	-	-	-	-	-	0.0004	12.1	3.1*
16712	197-209	6.34	9.33	0.20	8.78	301.2	0.009	294.0	1.6*
	219-220	-	-	-	-	-	0.0004	12.2	2.3*
	224-225	-	-	-	-	-	0.0004	13.9	2.5*
16718	325-337	2.69	6.43	0.23	2.19	75.1	0.015	528.0	0.29
	360-361	-	-	-	-	-	0.00005	1.82	1.1*
16738	398-405	5.15	11.82	0.11	2.68	91.9	0.014	464.0	0.91
16742	438-450	3.97	7.29	0.03	1.69	58.0	0.017	600.0	0.62
16744	455-468	1.56	5.76	0.02	1.23	42.2	0.001	389.0	1.8
	480-481	-	-	-	-	-	0.002	60.0	1.3*

Note: * signifies sample whose palladium decay curve was followed for three half-lives or more

- signifies "not determined"

Table 6-4. Diamond Drill Hole 12-1002, Brunswick No. 12 Mine

Company Assays for Lead, Zinc, Copper and Silver and Neutron Activation Analyses for Gold and Palladium

SAMPLE	FOOTAGE	LEAD %	ZINC %	COPPER %	SILVER		GOLD		PALLADIUM
					oz/ton	ppm	oz/ton	ppb	ppb
	18-22	-	-	-	-	-	0.007	248.0	1.6*
	38-42	-	-	-	-	-	0.0008	27.0	-
	58-62	-	-	-	-	-	0.002	53.2	0.86
14265	95-105	0.10	0.09	0.76	0.52	15.2	0.003	102.0	0.33*
14269	135-145	0.27	1.89	0.21	0.52	15.2	0.006	196.0	0.38
14289	176-186	0.15	0.11	0.21	0.28	8.2	0.005	157.0	0.72
14297	216-226	0.18	2.45	0.34	0.30	8.7	0.001	47.2	0.49*
14321	256-266	0.12	0.43	0.04	0.32	9.4	0.005	182.0	0.22
14326	297-307	1.69	5.46	0.03	0.94	27.4	0.004	144.0	-
14330	332-342	0.22	0.26	0.19	-	-	0.020	672.0	0.98
	378-382	-	-	-	-	-	0.00003	1.04	-
	408-412	-	-	-	-	-	0.00003	1.36	-

Note: * signifies sample whose palladium decay curve was followed for three half-lives or more

- signifies "not determined"

Table 6-5. Diamond Drill Hole 62-9, Anaconda Caribou Mine

Company Assays for Lead, Zinc, Copper and Silver and Neutron Activation Analyses for Gold and Palladium

SAMPLE	FOOTAGE	LEAD %	ZINC %	COPPER %	SILVER		GOLD		PALLADIUM
					oz/ton	ppm	oz/ton	ppb	ppb
6361	0.0-3.4	2.14	5.78	0.61	2.34	80.26	0.20	6760.0	0.76*
6363	3.4-11.7	0.73	7.18	0.57	1.14	39.10	0.029	983.0	8.5
6365	11.7-15.5	0.74	10.15	0.51	0.88	30.18	0.044	1500.0	5.3
6366	15.5-20.5	0.55	2.55	0.49	0.60	20.60	-	-	-
6367	20.5-30.1	0.90	3.80	0.37	0.64	21.95	0.039	1340.0	7.6
6370	30.1-39.0	0.20	5.51	0.51	0.20	6.46	0.033	1130.0	-
6372	39.0-48.0	0.91	3.38	0.41	0.67	22.98	0.018	610.0	-
6374	48.0-53.0	0.18	0.77	0.55	trace	3.4	0.012	424.0	1.9
6375	53.0-57.5	0.52	0.92	0.31	0.92	31.56	-	-	-
6376	57.5-67.2	1.56	3.33	0.42	0.96	32.93	0.017	592.0	0.51
6378	62.2-67.2	0.38	1.31	1.13	0.68	23.32	-	-	-
6379	67.2-74.8	0.41	2.76	0.63	0.18	6.17	-	-	-
6381	74.8-81.1	0.16	1.58	0.57	0.42	14.41	0.017	332.0	0.15
6383	81.1-86.0	0.08	0.55	0.57	0.20	6.46	0.011	370.0	2.1
6384	86.0-91.0	0.21	0.72	1.21	0.24	8.23	-	-	-
6385	91.0-94.4	0.25	0.74	0.98	trace	3.4	0.011	373.0	9.9
6386	94.4-97.0	0.33	1.20	1.18	0.64	21.95	0.011	368.0	3.5
6387	97.0-97.7	0.42	1.70	1.31	1.00	34.29	-	-	-
6388	97.7-100.0	0.18	0.68	0.42	0.36	12.35	0.011	369.0	3.9
6389	100.0-103.8	1.50	5.50	0.29	1.00	34.29	0.011	394.0	8.0
6290	103.8-107.8	0.70	3.05	0.63	0.84	28.81	0.014	480.0	0.62*
6391	107.8-112.8	0.04	1.10	0.32	0.68	23.32	-	-	-
6392	112.8-114.0	0.01	0.09	0.28	trace	3.4	0.012	428.0	0.10*
6393	114.0-119.3	0.07	0.38	0.20	trace	3.4	0.006	220.0	0.46*
	121.0-126.0	-	-	-	-	-	0.0009	33.0	1.9*
	126.0-131.0	-	-	-	-	-	0.003	120.0	3.4*
	131.0-136.0	-	-	-	-	-	0.0001	2.9	2.9*

Note: * signifies sample whose palladium decay curve was followed for three half-lives or more
- signifies "not detetermined"

Table 6-6. Diamond Drill Hole 62-17, Anaconda Caribou Mine

Company Assays for Lead, Zinc, Copper and Silver and Neutron Activation Analyses for Gold and Palladium

SAMPLE	FOOTAGE	LEAD %	ZINC %	COPPER %	SILVER		GOLD		PALLADIUM
					oz/ton	ppm	oz/ton	ppb	ppb
	15.0-17.0	-	-	-	-	-	0.00003	0.88	1.6*
	32.0-33.0	-	-	-	-	-	0.00003	0.96	1.4*
	45.0-46.0	-	-	-	-	-	0.0001	4.08	1.1*
	57.0-69.0	-	-	-	-	-	0.00008	2.94	1.5*
	83.0-95.0	-	-	-	-	-	0.0005	15.5	1.7*
	96.0-99.0	-	-	-	-	-	0.0006	20.6	0.59*
	100.0-104.0	-	-	-	-	-	0.0004	12.6	0.82*
6528	105.6-110-6	3.40	6.06	0.50	3.30	113.2	0.077	2640.0	1.1*
6529	110.6-115.3	2.20	5.56	0.66	2.60	89.18	0.189	6480.0	2.9*
6530	115.3-118.5	3.02	4.40	0.85	2.75	94.42	0.045	1540.0	0.51*
	119.0-122.0	-	-	-	-	-	0.0001	4.36	20.5*
	133.0-135.0	-	-	-	-	-	0.00002	0.57	0.13*
	143.0-151.0	-	-	-	-	-	0.000001	0.11	0.26*
6531	163.7-168.5	0.19	1.00	1.22	0.38	13.03	0.0097	332.0	3.3*
6532	168.5-173.5	0.33	1.45	0.56	0.47	16.12	0.0090	308.0	0.65*
6533	173.5-178.5	0.26	1.66	0.48	0.31	10.63	0.0121	415.0	0.93*
6534	178.5-181.0	0.29	1.12	0.54	0.28	9.60	0.0157	540.0	0.58*
6535	181.0-183.0	0.17	1.00	1.05	0.28	9.60	0.0054	184.0	0.95*
6536	183.0-185.3	0.03	0.85	0.95	0.16	5.49	0.0071	244.0	1.3*
6537	185.3-187.3	0.03	1.12	1.05	0.18	6.17	0.0063	216.0	1.5*
6538	187.3-189.3	0.02	0.53	0.45	0.16	5.49	0.0033	114.0	1.3*
6539	189.3-193.0	0.08	1.87	1.55	0.24	8.23	0.062	2130.0	1.4*
6540	193.0-196.4	0.04	0.48	0.46	0.17	5.83	0.134	4600.0	2.6
6541	196.4-197.4	0.22	1.00	1.88	0.30	10.29	0.0097	334.0	1.2*
6542	197.4-202.0	0.02	0.41	0.60	0.20	6.46	0.0045	153.0	1.5*
6543	202.0-206.3	0.01	0.13	0.24	0.12	4.12	0.0038	130.0	-
6544	206.3-211.0	0.01	0.10	0.13	0.08	2.74	0.0012	40.0	3.1*

Note: * signifies sample whose palladium decay curve was followed for three half-lives or more
- signifies "not determined"

Table 6-7. (a) Duplicate Analyses of Rocks for Gold

SAMPLE	[1]MINE	GOLD ppb	MEAN ppb	STANDARD DEVIATION %
A4081	H.S.	39.2,134	86.6	±77.
A4085	H.S.	440,240	340.	±42.
A4086	H.S.	800,524	662.	±29.
A4089	H.S.	366, 330	348.	± 7.3
A4090	H.S.	227,267	247.	±11.
A4091	H.S.	219,528	374.	±56.
A4092	H.S.	778,273	526.	±66.
A4093	H.S.	3160,1440	2300.	±52.
A4102	H.S.	560,344	452.	±33.
A4104	H.S.	414,288	351.	±25.
A4106	H.S.	343,366,352 305,358	354.	±15.
A4107	H.S.	520,360	440.	±26.
57'-69'	A.C.	2.39,3.48	2.94	±27.
83'-95'	A.C,	11.8,19.2	15.5	±34.
6533	A.C.	448,381	415.	±11.
6539	A.C.	2060,2190	2125.	± 4.3
6361	A.C.	1960,2600,3200 3160,23000	6785.	±85.
6386	A.C.	363,372	368.	± 1.7
121'-126'	A.C.	36.6,29.4	33.	±15.
126'-131'	A.C.	123,116	120.	± 4.2
131'-136'	A.C.	2.8,3.0	2.9	±44.2
60'-61'	Br.	24.2,20.4,11.4	18.6	±23.
224'-225'	Br.	13.8,14.0	13.9	± 1.0
360'-361'	Br.	0.92,2.73,1.8	1.82	±60.
16141	Br.	740,624	682.	±12.
16145	Br.	501,619	560.	±15.
16174	Br.	272,239	256.	± 8.5

Pooled estimate of standard deviation = 34%

Note: H.S., Heath Steele B-1 Orebody; A.C., Anaconda Caribou Orebody, Br., Brunswick No. 12 Orebody

Table 6-7. (b) Duplicate Analyses of Rocks for Palladium

SAMPLE	MINE	ORE TYPE	PALLADIUM ppb	MEAN ppb	STANDARD DEVIATION %
A4081	H.S.	DO	0.56, 2.1	1.3*	109
A4085	H.S.	MO	3.1, 1.2	2.2*	64
A4086	H.S.	MO	1.2, 1.2	1.2*	0
A4089	H.S.	ZPO	1.7, 0.99	1.3*	44
A4091	H.S.	ZPO	2.0, 10.3	6.2	67
A4092	H.S.	MO	0.77, 0.31	0.54	43
A4093	H.S.	MO	4.9, 0.62	2.8*	110
A4102	H.S.	ZPO	3.1, 1.2	2.2*	58
A4106	H.S.	ZPO	0.58, 1.0, 0.07	0.55	86
A4107	H.S.	ZPO	1.3, 4.1	2.7*	73
6539	A.C.	ZPO	1.1, 4.1	1.3	17
6361	A.C.	ZPO	0.35, 0.42, 0.97 1.5, 1.2, 0.09	0.78	73
6386	A.C.	MO	6.9, 0.15	3.5	136
121'-126'	A.C.	BS	1.7, 2.1	1.9*	15
126'-131'	A.C.	BS	2.5, 4.3	3.4*	37
131'-136'	A.C.	BS	3.5, 2.3	2.9*	29
60'-61'	Br.	BS	1.3, 1.1, 0.92	1.1*	25
224'-225'	Br.	IF	2.5, 2.5	2.5*	0
360'-361'	Br.	Dyke	1.3, 0.90	1.1*	26
16145	Br.	ZPO	0.48, 0.30	0.39	33

Note 1: H.S., Heath Steele B-1 Orebody; A.C., Anaconda Caribou Mine; Br., Brunswick No. 12 Mine.
Note *: Signifies sample whose palladium decay curve was followed for three half-lives or more
Pooled estimate of standard deviation for samples marked thus, *, = 36%
Pooled estimate of standard deviation for all samples = 52%
Note 2: DO, disseminated ore; MO, massive ore; ZPO, Zinc-lead rich ore; BV, barren volcanics; BS, barren sulphides; IF, iron formation.

The gold and palladium contents of individual separated sulphide minerals are presented in Tables 6-8 (a), (b) and (c). Average values for the mineral separates are given in Tables 6-9 (a) and 6-9 (b) for gold and palladium respectively.

The gold and palladium results for host rocks are presented in Table 6-10. The petrographic names used are those employed by the mine geologists in the various deposits. The samples are from the drill holes previously noted and include either hanging-wall or footwall intersections of the various host rock types shown in Figs. 6-2 to 6-7. They are all within 100 ft. of a massive sulphide body. Compared to average values for rocks of comparable composition or petrogenetic type (see Chapter 4) most samples are anomalously high with respect to gold.

Finally Table 6-11 presents the average value and standard deviation for Pb, Zn, Cu, Ag and Au in each of the drill holes investigated from the Heath Steele and Caribou Mines. For the Brunswick No. 12 deposit the same parameters are averaged for the three drill holes from this mine. These averages apply to all samples analysed whether ore grade material or not. A second set of average values is computed for gold and palladium applicable to massive sulphides only.

Table 6-8. Gold and Palladium Content of Separated Sulphide Minerals

(a). Anaconda Caribou Mine

SAMPLE NO.	FINES[1] Gold ppb	FINES[1] Palladium ppb	PYRITE Gold ppb	PYRITE Palladium ppb	SPHALERITE Gold ppb	SPHALERITE Palladium ppb	GALENA Gold ppb	CHALCOPYRITE Gold ppb
WMCB011-G	6990		43000				3.3	
WMCB011-S	5430		205	2.1	187	1.8	10.4	
WMCB014	6520		20600	35.0				
WMCB017	11.5		4020	9.0				

(b). Brunswick No. 12 Mine

SAMPLE NO.	FINES Gold ppb	FINES Palladium ppb	PYRITE Gold ppb	PYRITE Palladium ppb	SPHALERITE Gold ppb	SPHALERITE Palladium ppb	GALENA Gold ppb	CHALCOPYRITE Gold ppb
WMCB018-S	290		16900	3.5	338	1.2		
WMCB018-P	778		632					
16136	1560	1.1	347		301	0.54		
16141	1698	1.1	716	4.6	97	0.39	11478	
14265	555	0.35	354					31.9

Description of samples:

WMCB011: Caribou Mine, west limb, north sulphide body, lead-zinc rich unbanded ore.
WMCB014: Caribou Mine, west limb, south sulphide body, lead-zinc rich banded ore.
WMCB017: Caribou Mine, west limb, north sulphide body, copper-rich ore.
WMCB018: Brunswick Mine, main zone, banded lead-zinc ore.
16136)
16141) Brunswick Mine, from diamond drill holes (see sample analyses in Tables
14265) 6-2 and 6-4).

Note 1: Fines are less than 200 mesh.

Table 6-8. Continued

(c). Heath Steele B-1 Orebody

Sample No.	PYRITE		SPHALERITE		GALENA		CHALCOPYRITE		PYRRHOTITE	
	Gold ppb	Palladium ppb	Gold ppb	Palladium ppb	Gold ppb	Palladium ppb	Gold ppb	Palladium ppb	Gold ppb	Palladium ppb
B78-2	733	3.3	31	0.8						
B78-4-1	918	0.95	31	0.8						
B78-4-2									109	
B78-5	431±3%(2)	6.2±82%(2)	130	1.6						
B78-6	1208	4.0							215±3.3%(2)	30±29%(2)
B78-7	564±16%(3)	2.2±17%(3)	270±8.2%(2)	3.3						
B78-8A-3	257±40%(2)	2.7	165±22%(2)	1.4						
B89-2			170	0.3						
B89-4			420	3.3						
B89-6			16	0.5						
B100-3-1							135	0.72		
B110-3-2							430			
B100-6					1040	3.0	890		393±19%(2)	3.1±26%(2
B101-1									22.0	6.8
B101-2B-1	309	5.0	92	0.8						
B101-7			410	2.4						
B101-8B	534	1.8	93	2.7						
B101-9	271	5.8	75	2.0						
B101-10B	251	2.5	65	2.4						
B104-5-1									71.0±20%(2)	7.0
B109-3-2							1860			
B127-10-1			170	3.2	48.7±4.1% (3)	3.1±27% (2)				

Note: Numbers in parentheses are numbers of analyses.

Table 6-9(a) Average Gold Contents of Separated Sulphide Minerals in New Brunswick Massive Sulphide Deposits in PPB

MINE	PYRITE	SPHALERITE	GALENA	CHALCOPYRITE	PYRRHOTITE
Heath Steele	548(10)	162(13)	544(2)	1578(4)	162(5)
Anaconda Caribou	17000(4)	187(1)	6.9(2)		
Brunswick No. 12	3790(5)	245(3)	11500(1)	32(1)	
Grand Average	4900±224% (19)	178±71% (17)	2516±194% (5)	669±111% (5)	162±91% (5)

Table 6-9(b) Average Palladium Contents of Separated Sulphide Minerals in New Brunswick Massive Sulphide Deposits in PPB

MINE	PYRITE	SPHALERITE	GALENA	CHALCOPYRITE	PYRRHOTITE
Heath Steele	3.5(10)	1.9(13)	3.1(2)	0.72(1)	11.7(4)
Anaconda Caribou	15.4(3)	1.8(1)			
Brunswick No. 12	4.1(2)	0.71(3)			
Grand Average	5.9±140% (15)	1.6±68% (17)	3.1±2% (2)	0.72 (1)	11.7±10.5% (4)

Number in parentheses is number of samples

Errors are given at one standard deviation from mean in percent.

Table 6-10. Gold and Palladium Contents of Host Rocks in the Vicinity of the Heath Steele, Brunswick No. 12 and Caribou Mines

ROCK TYPE	GOLD(ppb)	PALLADIUM(ppb)
Chloritic meta-sediments	5.1(B), 1.0(B), 21.0(C)	0.59(C) 3.1 (C)
Graphic meta-sedimentary schist	2.9 ± 4% (2) (C)	2.9 ± 7% (2) (C)
Iron Formation	13.0 ± 10% (3) (B)	2.4 ± 7% (3) (B)
Tuffaceous sediments	16.0 (H) 130 (B) 19.0(B) 12.0(B) 60 (B)	0.75 (H) 1.6 (B) 1.1 (B) 3.1 (B) 1.3(B)
Intermediate to acidic volcanic schist or tuff	0.88(C) 0.96(C) 4.1(C) 2.4(C) 19.0(C) 12.0(C)	1.4 ± 30% (6) (C)
Rhyolite	27.0(B) 53.0(B)	0.86 (B)
Andesitic porphyry dyke	1.4 (B) 1.8 (B)	1.1 ± 25% (2) (B)

Note: Number in parentheses is number of samples
(H) = Heath Steele Mine, (B) = Brunswick No. 12 Mine
(C) = Caribou Mine.

Table 6-11. Average Metal Concentrations in Diamond Drill Holes

MINE	Heath Steele	Caribou	Caribou	Brunswick No. 12
Diamond Drill Hole No.	B138	62-9	62-17	Combined 12-1037 12-1051 12-1002
Lead %	1.65±140%[1] (30)[2]	0.56+120(17)	0.61±180%(17)	2.50±100%(20)
Zinc %	3.44±120%(30)	2.76±95%(17)	1.69±110%(17)	6.22±90%(20)
Copper %	0.98±79%(30)	0.58±53%(17)	0.91±65%(17)	0.20±90%(20)
Silver ppm	39.5±80%(30)	20.0±80%(17)	27.8±130%(17)	57.5±110%(19)
Gold ppb	428 ±95%(30)	677 ±220%(20)	686 ±230%(27)	249 ±99%(34)
Palladium ppb	2.0±120%(28)	3.4±93%(18)	1.4±70%(25)	1.1±68%(27)
Mean value for massive sulphides only				
Gold ppb	430 ±96%(30)	758 ±190%(17)	1200 ±150%(17)	353 ±60%(20)
Palladium ppb	2.0±120%(28)	3.6±98%(15)	1.7±55%(16)	0.74±75%(20)

Note 1: Limits are quoted at one standard deviation in percent of the mean.

Note 2: Figures in parentheses are number of samples.

6-3 Discussion of Results

6-3-1 Introduction

The relevance of the standard deviation of the gold analyses with respect to sample inhomogeneity has already been discussed in Chapter 5. The overall standard deviation based on a pooled variance estimate is 34% of which some 26% can be ascribed to sample inhomogeneity.

The massive sulphides and the majority of the host rocks show no significant differences in mean palladium content. However, in the Brunswick No. 12 mine the iron formations which average 2.40 ± 7% ppb are significantly higher than the massive sulphides whose average palladium concentration is 0.74 ± 75% ppb.

The sulphide minerals were found to be highly variable in gold content. This is partly due to the smaller sample weights of mineral taken for analyses. Pyrite consistently shows a higher content of gold than sphalerite (Table 6-9). The great variability in the gold contents, especially of pyrite, suggests that gold is present as a discrete phase, probably the native metal. The systematic partition of gold between sulphide minerals from Sudbury Nickel Irruptive ore found by Chyi (1972) presumably occurs only at the ppb level and at magmatic temperatures.

From Table 6-10 it is apparent that the host rocks of the deposits generally show low palladium contents, in the range X to 0.X ppb. On the other hand, gold content of the footwall rocks generally increases towards the orebody. It is also noticeable in DDH 62-17 (Caribou Mine) that six samples from the hanging wall show a gradual, though small, increase in gold as the orebody is approached.

6-3-2 Metal Zoning

Zoning of base metals and silver has been recognised in this class of deposit for some time (Chapter 2, this work). The association of silver with lead is well known, but the degree of correlation of gold with the various base metals is very poorly established. In particular it is not known with any certainty whether gold exhibits a zonation comparable to any of the base metals.

The results obtained in this work were used in factor analysis which attempted to define the zoning of the precious metals in relation to that of the base metals. Correlation coefficients were computed from the abundance data and used as primary input for the factor analysis. The correlation matrices for lead, zinc, copper, silver, gold and palladium for individual drill holes from the Heath Steele and Caribou Mines and for all data from the Brunswick No. 12. Mine are presented in Table 6-12. The weightings for the rotation of three factors are shown in Table 6-13.

In both the Brunswick No. 12 and the Caribou deposits the same three factors can be identified.

Table 6-12. Correlation Coefficients

Drill Core Analyses

(see tables 6-1 to 6-6 for data used)

Brunswick No. 12 Mine (all data)

	Lead	Zinc	Copper	Silver	Gold	Palladium
Lead	1.000					
Zinc	.930	1.000				
Copper	-.084	-.140	1.000			
Silver	.754	.637	.002	1.000		
Gold	.583	.588	-.268	.278	1.000	
Palladium	.188	.108	.035	.287	.259	1.000

Caribou Mine (DDH 62-9)

Lead	1.000					
Zinc	.584	1.000				
Copper	-.137	-.149	1.000			
Silver	.838	.555	.017	1.000		
Gold	.670	.444	-.033	.765	1.000	
Palladium	.100	.358	.254	-.056	-.084	1.000

Caribou Mine (DDH 62-17)

Lead	1.000					
Zinc	.947	1.000				
Copper	-.206	-.204	1.000			
Silver	.784	.711	.246	1.000		
Gold	.506	.629	-.216	.395	1.000	
Palladium	-.073	.019	-.321	-.261	.462	1.000

Heath Steele B-1 Orebody (DDH B138)

Lead	1.000					
Zinc	.910	1.000				
Copper	-.646	-.699	1.000			
Silver	.822	.812	-.530	1.000		
Gold	-.005	.008	.204	.134	1.000	
Palladium	-.276	-.290	.183	-.284	-.034	1.000

Table 6-13. Rotated Factor Loadings

Drill Core Analyses

(see tables 6-1 to 6-6 for data used)

Brunswick No. 12 Mine
Percent of Total Communality-85%

Factor	1	2	3
Gold	-.70	-.65	.31
Silver	-.95	.17	.25
Zinc	-.98	-.20	-.01
Lead	-.99	-.11	.07
Copper	-.01	1.00	.08
Palladium	-.12	.02	.99

Caribou Mine (DDH 62-9)
Percent of Total Communality-87%

Factor	1	2	3
Zinc	-.70	-.66	-.28
Lead	-.97	-.19	-.14
Gold	-1.00	.10	.02
Silver	-1.00	-.00	.04
Copper	.03	-.12	.99
Palladium	.06	-.97	.21

Caribou Mine (DDH 62-17)
Percent of Total Communality-92%

Factor	1	2	3
Gold	-.63	.77	.06
Silver	-.93	-.11	-.34
Zinc	-.97	.15	.16
Lead	-.98	.01	.17
Palladium	.17	.96	.21
Copper	.06	-.18	-.98

Heath Steele B-1 Orebody (DDH B138)
Percent of Total Communality-89%

Factor	1	2	3
Copper	.92	-.40	-.05
Silver	-.96	-.21	.17
Zinc	-.99	-.01	.14
Lead	-.99	-.01	.14
Palladium	.17	.01	-.99
Gold	-.01	-1.00	.02

1. zinc-lead-silver-gold
2. copper
3. palladium

The identification of the three factors obtained from the Caribou and Brunswick No. 12 data with geological and mineralogical properties of the deposits is facilitated by taking into account the correlation coefficients. The four metals making up factor 1 are all positively correlated, with the lead-zinc correlation the strongest by far. Silver correlates strongly with lead and somewhat less strongly with zinc. Although gold correlates positively with lead, zinc and silver, the correlation is weaker than all other correlations involving this group of metals.

The lead-zinc correlation arises largely from the occurrence of these two metals mainly as interbanded, lead-rich and zinc-rich layers. Characteristically both metals show sympathetic variation in concentration along all drill holes. The high lead-silver correlations are compatible with the occurrence of much silver as discrete sulphosalts in very close association with galena (Boorman, 1968). The gold correlation with lead and zinc is weaker than the Pb-Zn-Ag associations and is not significantly biased in favour of either metal. Gold is preferentially concentrated in pyrite relative to coexisting sphalerite. Insufficient gold data were obtained on galena to assess its importance as a gold host relative to pyrite or other sulphides. However, there is very little evidence to suggest that the relatively weak gold-lead-zinc correlations are due to lattice substitution of gold in sphalerite or galena. Rather, saturation of the ore solution with gold (with respect to the native metal), galena and sphalerite at approximately the same stage in the sulphide depositional cycle is regarded as a more plausible explanation.

The second factor identified is copper. Again, the correlation coefficients are compatible with the existence of a separate copper factor in that the metal correlates weakly and negatively with lead and zinc. This reflects the characteristic separation or zoning of copper-rich and lead-zinc-rich zones in these ores. The correlation of gold with copper in both deposits is negative and very weak, a consequence of the preferred association of the metal with lead-zinc rich ore in these deposits.

Palladium constitutes a separate factor and is only weakly correlated with other metals. It does not appear that palladium is strongly influenced by the ore depositional processes controlling the distribution of the base metals.

The factors for the Heath Steele B138 hole are somewhat different:

1. zinc-lead-silver-copper
2. gold
3. palladium

Here copper appears with the lead-zinc-silver factor and gold is isolated as a separate factor. An examination of the B138 profile (Fig. 6-2) indicates that this drill hole is characterized by a local gold enrichment in massive sulphides. This enrichment occurs in the waning stages of copper deposition and just prior to the onset of lead-zinc deposition. There is no obvious explanation for this gold-base metal relationship which differs from that observed in other profiles. Palladium again is weakly correlated with the other metals exhibiting no detectable zoning or significant correlations.

6-3-3 Conclusions

The palladium results show that the metal is not characterized by zoning or systematic spatial distribution within the deposits that correlates with any of the demonstrated base metal trends. Palladium is often lower in concentration within the sulphides than in the host rocks. This indicates that either no significant amount of palladium was transported in the ore solution or that palladium was not precipitated with the other metals but lost to the surrounding environment.

The gold is highly enriched in the massive sulphides compared to the host rocks and shows a zonation towards the lead-zinc-rich ore in the Anaconda Caribou and Brunswick No. 12 deposits. The Heath Steele B-1 deposit shows no correlation of gold with any other element, though this may be due to insufficient analyses to provide a representative suite for this deposit.

It is interesting to contrast these results with trends of gold and palladium in sediments near the East Pacific Rise (Crocket et al. 1973). In this mid-ocean ridge environment palladium is concentrated on the rise crest and correlated positively with elements associated with volcanic emanation, including iron, manganese and arsenic. Gold, although more widely dispersed was also concentrated about the rise crest region. Thus similar geochemical behaviour of gold and platinum is characteristic of these volcanic emanations. This is markedly different to the contrasting geochemistries of palladium and gold in the volcanic fluids from which the Bathurst ores were deposited.

The most probable mineralogical form of gold is the native metal. The following reasons support this contention:

1. There is no obvious mineral host among the major sulphides.
2. Great variation in duplicate analyses of ores and separated sulphides is found.
3. In deposits of similar or analogous type (e.g. Kuroko) native gold has been identified.

If the assumption of the presence of native gold is correct then presumably the ore solutions reached saturation with respect to this phase. Thermodynamic models for the formation of these deposits derived from consideration of lead, zinc, copper and iron abundances should also predict the behaviour of gold in ore solutions if equilibrium of soluble gold complex ions with the native metal is assumed.

The probable gold grains in the New Brunswick stratiform sulphide deposits are too small for characterization with the electron microprobe. The possibility of the occurrence of gold as tellurides cannot be positively ruled out. To evaluate the possibility of gold occurrence as a telluride phase, analysis for tellurium and comparison with gold contents would be required.

CHAPTER 7

FORMATION OF MASSIVE SULPHIDE DEPOSITS AND TRANSPORT OF GOLD

7-1 Introduction

In order to elucidate the significance of the gold data, it is necessary to develop a model or models for the formation of the massive sulphide deposits of New Brunswick. The consistency of the analytical data with conventional theories of metal transport in ore solutions can then be tested.

Modern analogues of massive sulphides would be helpful but are lacking, although the Red Sea hot brines suggest some properties of the behaviour of concentrated solutions on the sea floor (Chapter 3). Unmetamorphosed stratiform massive sulphides are not common, but the Japanese Kuroko deposits afford some parallels. Taking into account the more extensive knowledge of the Kuroko, a comparison with the New Brunswick ores allows some conditions of formation of the New Brunswick deposits to be elucidated.

7-2 Models of Formation of Kuroko Deposits

7-2-1 General Features

Some features of Kuroko deposits have been mentioned in Chapter 2.

These are summarized as follows:

1. The sulphides may occur on top of vent-like stockworks of pyrite and chalcopyrite, characterized by considerable hydrothermal alteration.
2. There is evidence of a direct genetic connection with dacite magma at shallow depth.
3. Massive sulphides are vertically zoned from chalcopyrite-rich ore at the stratigraphic bottom grading upwards to galena-sphalerite-rich ore at the stratigraphic top. Such zoning may occur in a lateral sense as well.
4. In some instances deposition on steep topographic slopes is suggested in that the ore exhibits structure interpreted as resulting from gravity sliding and slumping.

7-2-2 Models of Sato (1972b, 1973)

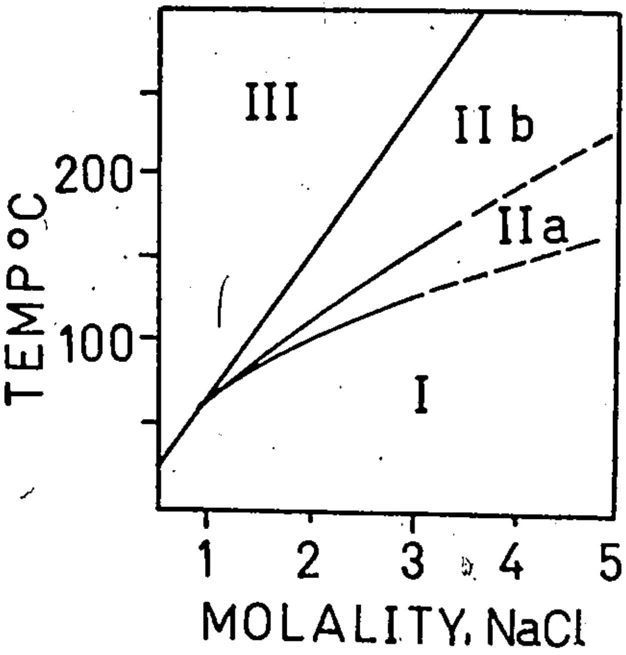
It is apparent that Kuroko ore solutions were saturated with copper and iron before reaching the ocean floor as they commonly precipitate chalcopyrite and pyrite, the "keiko" ore, in vent stockworks. A large proportion of the remaining copper and iron is precipitated on the sea floor to form the yellow ore, the "oko". After this stage the ore solution has apparently cooled sufficiently for lead, zinc and barium to reach saturation and precipitate galena, sphalerite and barite to form the black ore, or "kuroko".

Sato (1972b) has argued that the density of ore-forming solutions is controlled primarily by total molality of sodium chloride and temperature. Depending on ore solution density three types of mixing relations can be expected with sea water. Mixing of sea water with an ore solution of considerably lower density results in a mixture which never attains a density sufficiently high to allow the mixture to sink. Type III solutions, shown in Fig. 7-1, are of this character. Consequently, such solutions are rapidly dissipated. Any dissolved metals will be precipitated and dispersed, possibly forming a base metal geochemical anomaly or an iron formation,

Very different behaviour is shown by Type I solutions which are relatively cool, concentrated and dense (Sato, 1972b). These solutions immediately flow down the palaeoslope until a topographic low is reached. Little mixing with sea water occurs and the brine should cool slowly relative to Type III. Dissolved metals precipitate gradually in areas localized by submarine topography and not necessarily in the vicinity of a volcanic vent. An obvious analogy with the Red Sea brines is recognised.

Sato (1972b) suggests that the features of Kuroko deposits are most consistent with ore solutions which are initially lighter than sea water and therefore flow upward mixing with sea water and cooling. Such solutions, Type IIb, reach a maximum density exceeding that of sea water and subsequently behave like Type I solutions. Much of the metal

Fig. 7-1. Four Types of Salinity-Temperature Relations for Ore Solution Mixing with Sea Water (after Sato, 1972b).


III
II b
II a
I
TEMP °C
200
100
1
2
3
4
5
MOLALITY, NaCl

nearest saturation may initially precipitate on first mixing with sea water, but other metals precipitate later from a settled and relatively quiescent brine.

Other properties of Kuroko ore solutions are inferred from fluid inclusion and sulphur isotope data. Temperatures of formation can be obtained from fluid inclusion homogenization temperatures and sulphur-isotope fractionations between coexisting minerals. In general, suggested temperatures decrease from 250° to 200°C for the "keiko" to less than 200°C for the "kuroko". Sulphur isotope fractionation temperatures leave much to be desired because of uncertainty in the accuracy of experimental curves. This is discussed below, in the context of Kajiwara's (1973a) model of Kuroko formation. Fluid inclusions indicate that the maximum salinity of the ore solution was equivalent to that of 2m sodium chloride solution. Taking into account temperature, concentration of chloride, and general shape of the deposits, Sato (1972b) concluded that Kuroko ore solutions were probably of Type IIb.

Using the molality of chloride, temperature and sea water/ore solution mixing characteristics as inferred from the above considerations, Sato (1973) modelled the formation of the Uchinotai-Nishi deposit making the following assumptions:

1. the ascending ore solution has a constant composition,
2. total metal content of the deposit approximates that of the ore solution,

3. the pH of the ore solution can be estimated from the K:Na ratios for the ore solution which, in turn, is inferred from the wall rock alteration below the ore deposit.
4. dissolved sulphide is sufficient to precipitate all dissolved iron and base metals as sulphides,
5. the initial copper content exceeds 1 ppm, and
6. the ore metals are transported as chloride complexes whose thermodynamic properties can be calculated from Helgeson's (1969) data.

Allowing the reasonable premise that the ore solution is initially in equilibrium with chalcopyrite and pyrite, then ratios of copper to iron define the temperature and fugacity of oxygen of the ore-forming system. The brine is first saturated with respect to pyrite and chalcopyrite. Zoning of metals, particularly later precipitation of ~~galena~~ and sphalerite, is explained by progressive saturation of the ore brine with respect to base metal sulphides in response to changing physiochemical character of a ponded brine. Determination of the initial metal content of the ore solution is critically dependent on assumption No. 2 above. Changes in ore solution metal content during the depositional process are calculated by consideration of metal removed by mineral precipitation in various preceding arbitrarily defined stages. Decreasing temperature and oxygen fugacity as well as changing pH and reduced sulphur content of the ore solution are among the important parameters, whose variation control base metal saturation.

Central to Sato's model is the condition that sea water sulphate and ore solution sulphide coexist metastably in the brine. This condition is required to explain the sulphur isotope ratios of the sulphides and sulphates, and the precipitation of barite.

The necessity that reduced sulphur content of the fluid be sufficient for precipitation of total metal is a consequence of Sato's assumption of disequilibrium between the aqueous sulphide and sulphate species at temperatures below 200°C.

Sato (1973) finds that the variations in base metal content observed stratigraphically across the Uchinotai-Nishi deposit are reasonably well predicted by this type of modelling.

7-2-3 Model of Kajiwara (1973a, 1973b)

Kajiwara (1973a, 1973b) derives the conditions of formation of the black ore, the kuroko, from the rock alteration below the deposits, sulphur isotope partition between coexisting minerals, the lead content of barite and the stability limits in f_{S_2} - temperature space of the sulphide minerals.

Kajiwara then calculates metal content of the ore solution using Helgeson's (1969) data and assuming 1m chloride, chloride complexing of the base metals and saturation with the respective metal sulphides. The solution so derived has a metal content similar to normal sea water.

The low metal content results from the high postulated pH.

Ore deposition takes place with sulphate as the dominant form of sulphur, and sulphate-sulphide equilibrium is required to provide sulphide for precipitation of the metals. According to Kajiwara sulphide-sulphate equilibrium is also required to explain the sulphur isotope ratios of Kuroko deposits.

Kajiwara's model depends critically on the interpretation of the sulphur isotope fractionation between the minerals and there is some indication that his estimated temperatures are 50°C too high (Czamanske and Rye, 1974). If temperatures were 50°C lower fugacities of oxygen determined from the lead content of barite would be similar to those of Sato's model; that is, very much lower than actually assumed by Kajiwara. In fact, lower fugacities of oxygen would place the ore-forming solution in the sulphide field.

There are other problems with the suggestion that sea water or a solution of similar metal concentration had an important role in Kuroko formation. The most serious are the following:

1. Could sufficient fluid be provided to form a sizeable ore deposit?

2. Why, if the metals are at a similar concentration to sea water, are they not easily lost from the ore solution to sea water?

3. What is the process causing zonation of the metals in these deposits?

A possible explanation of the metal zoning compatible with Kajiwara's model is that the ore-solution changed composition with time. However, the stockwork ore is never veined by later galena-sphalerite suggesting that variation in the composition of the ore fluid with time is not a satisfactory explanation of the metal zoning.

In Sato's model the gradual cooling of the brine and precipitation of the metals can occur in space and time. In this way both the lateral and vertical zoning are explained.

7-2-4 Gold and Silver in the Kuroko

Sato's model satisfactorily explains many features of the Kurokos, including zoning of lead, zinc, copper, iron and barium. However, the calculated silver and gold contents of the ore solutions are too high and too low respectively.

Helgeson (1969) gives data only for the solubility of silver in equilibrium with argentite, but silver in the Kuroko is present as sulphosalts. Craig and Barton (1973) give free energies of formation of a number of sulphosalts. Their data show that lower solubilities of silver would prevail if the metal were in equilibrium with sulphosalts. However, rigorous calculations are not possible.

Helgeson's equilibrium constants for gold chloride complexes render gold too insoluble to fit Sato's model. Sato suggests that particulate gold is carried as a colloid from depth, but does not explain the zonation of the metal.

7-3 Formation of the New Brunswick Massive Sulphide Deposits

7-3-1 Comparison with Kuroko

Important points of comparison between the Kuroko and New Brunswick deposits include the following:

1. The New Brunswick deposits are of wider lateral extent (typically 1000m x 1000m) than the Kuroko (largest 700m x 500m) and have larger tonnages (fifty to one hundred million of tons) compared to Kuroko (less than forty million of tons).

2. Excluding localized increases in grain size due to deformation, the average grain size of the Bathurst ores is significantly less (40-50 μ for Caribou and Heath Steele sulphides, Tempelman-Kluit, 1970) than the average grain size of the Kuroko (100-200μ, Lambert and Sato, 1974).

3. Lamination of the lead-zinc ore is common in the Bathurst deposits but rare in Kuroko ores. Pre-tectonic brecciation and slump structures, common in Kuroko, are rare in Bathurst ores.

4. The mineralogy of the Bathurst ores is similar to the Kuroko with the exception that primary barite is rare or absent.

5. The Bathurst ores show close spatial association with felsic volcanics in the field, but do not seem to sit on recognisable volcanic vents as do the Kuroko.

6. There is evidence of interruption of sulphide precipitation by detrital sedimentation or volcanic eruption (presence of tuffs in the Caribou deposit in contrast with apparent rapid deposition of Kuroko sulphides).

7-3-2 Significance of the Form of the Bathurst Deposits

Table 7-1 presents a qualitative summary of some physical and geological characteristics of stratiform base metal deposits expected as a result of ore solution brine-sea water mixing as envisaged by Sato (1972b). A categorization of the Red Sea hot brine deposits, Kuroko deposits and New Brunswick massive sulphides is also included. Certain properties of the New Brunswick deposits, particularly their lateral extent, massiveness and thickness are consistent with deposition from Type I or IIa solution as defined by Sato (1972b)

One difference between the deposits attributed to deposition from the Type I solutions of Sato and the Bathurst deposits is the presence of lamination in the latter. However, the sediments forming from the Red Sea hot brines, which have the physicochemical characteristics of Type I solutions, show lamination. In the opinion of this author there is no reason to expect lack of lamination in deposits from Type I solutions. The presence of lamination in the Bathurst deposits is not considered incompatible with their origin from Type I or IIa solutions.

Table 7-1. Some Probable Features of Mineral Deposits formed in Submarine Environments from Four Types of Mixed Brine (after Sato, 1972b)

	Control of sea bottom topography	Lateral extent of deposits	Thickness of deposits	Grading, Slumping	Lamination	Alternation with mud or tuff
Type I solution	Strong	Wide	Thin	Absent	Absent	Present
Type IIa solution	Weak	Narrow	Thick	Present	Absent	Absent
Type IIb solution	Very weak	Narrow	Thick	Present	Absent	Absent
Type III solution	None	Very wide	Very thin	Absent	Present	Absent
Red Sea hot brine deposits	Strong	Wide	Thin	Absent	Present	Absent
Kuroko deposits	Very weak	Narrow	Thick	Present	Absent	Absent
New Brunswick massive sulphides	?	Wide	Thick	Present	Absent	Absent

If the inference that the Bathurst deposits were formed from Type I or IIa solutions is correct then the temperature of the exhaled solution was lower than that of the Kuroko, or alternatively the chloride content was very high. The low temperature of formation is consistent with the fine grain size of the sulphide minerals and the lack of evidence of proximity to igneous intrusives or explosion vents shown by the New Brunswick stratiform ores.

7-3-3 Inferred Process of Formation of Bathurst Massive Sulphide Ores

The process of formation of the Bathurst deposits is envisaged as broadly similar to that postulated by Sato (1973) for the Kuroko, but differing in detail due to the difference in density of the ore solutions as suggested above.

It is believed that the solutions were exhaled on the ocean floor but maintained their coherency and were ponded in topographic lows due to their high density. All the metals were contained within the ore solution, and zoning of the ore metals is not ascribed to progressive exhalation of an ore solution of varying base metal content. Successive impulses of brine may differ slightly in chemistry, but have little effect on the overall process of ore deposition as they mix with the brine already present.

Precipitation of base metals from a ponded brine occurs in response to changes in physicochemical properties of the brine. Of these, the most significant for sulphide precipitation is decreasing temperature.

7-3-4 Inferred Physicochemical Environment for Precipitation of the Chalcopyrite-Pyrite Ore

To characterize the physicochemical environment of ore deposition, one must assign a value or range of values to certain critical parameters. These include the following: the initial or maximum temperature of the ponded brine, the m_{Cl^-} of the ore solution, the initial concentration of the metals of interest (Cu, Zn, Pb, Fe, Ag and Au) in the ore solution, the range of m_{H_2S} during ore deposition and the range of pH during ore deposition.

(a) Temperature

From the preceding section it is concluded that the New Brunswick stratiform base metal deposits have the geometric characteristics of deposits formed by deposition from Type I or IIa solutions. Thus, from Fig. 7-1, a maximum temperature of the ore solution brine on the order of 200°C and a high initial chloride content are inferred. Alternative values of lower temperature and lower chlorinity are considered unlikely due to the significantly lower metal solubilities that would result. Furthermore, the Red Sea brines and Salton Sea brines suggest that chloride concentration as high as 5m are geologically reasonable.

(b) pH

Deposits of this class in unmetamorphosed terrains show associated chloritic and sericitic alteration in vent stockworks due to reaction with ore solutions. For the Kuroko, chloritic and sericitic alteration has been interpreted by Sato (1973) and Kajiwara (1973) to suggest pH's of approximately 3 to 5.5.

Some sericite and chlorite found characteristically in host rocks at the stratigraphic base of various Bathurst deposits may have been produced by reaction of the host rock with the ore solution according to Roscoe (1969). In view of the problem of distinguishing regional metamorphic assemblages from primary wall rock alteration, however, it is difficult to place limits on ore solution pH based on wall rock mineral assemblages as was done by Sato and Kajiwara. Very general limitations on the pH of ore forming solutions can be inferred from Helgeson's (1967) studies which suggest that the pH of a solution which has reached partial equilibrium with volcanic rocks will be weakly acid (pH = 5.6 at 200°C, Helgeson, 1969). The absence of alunite would suggest that pH was not extremely low though alunite stability is, of course, also dependent on $m_{SO_4{}^{2-}}$ (Hemley et al. 1969). For example, in Sato's model for Kuroko, $m_{SO_4{}^{2-}} = 10^{0}$ and alunite cannot form, while for Kajiwara's model with $m_{SO_4{}^{2-}} = 10^{-2.6}$ alunite would only form at pH less than about 3.0.

Thus, pH values more acid than 3 and greater than neutral

(5.6 at 200°C) are considered unlikely. Narrower limits cannot be strictly justified. However, by analogy with Kuroko ores and geothermal waters (see Chapter 3, and Ellis, 1967) pH's of 3.5 and 4.5 are believed to be representative of the approximate range of values pertinent to stratiform base metal ore solutions. A change of 0.5 pH units would have little effect on the solubilities of the relevant metals. pH values of 3.5 and 4.5 are used in the calculation of model ore solutions to follow (Table 7-3).

(c) Metal Ratios of the Ore Fluid

Sato's assumption of almost complete precipitation of metal from the ore fluid is considered highly probable for the following reasons:

1) Loss of base metal from the ore solution brine to sea water would depend primarily on the degree of mixing and dilution of the brine by sea water. If the density-temperature properties of the brine allow a high degree of mixing, it is improbable that an ore deposit will form in any event.

2) There is little evidence of extensive base metal geochemical anomalies along strike from the orebodies. Iron formation does occur but the volume of iron formation associated with individual base metal deposits is usually small relative to the volume of sulphide. Where extensive oxide iron formations are present the reduced sulphur content of the ore solution must have been insufficient to precipitate the total

base metal plus iron load as sulphides.

It is expected then, that the ratios of metals in the deposits approximate those in the ore fluids at the time of initial extrusion,and that the total reduced sulphur content of the ore fluid is approximately that necessary to precipitate all the metals in solution. To obtain the desired metal ratios for each of the three deposits investigated, the average weight percentage of each metal is recalculated as an atomic ratio with respect to copper, where the weight percentage of this metal is arbitrarily set at 100. These ratios are presented in Table 7-2. Although the values are subject to revision as the deposits are more extensively developed, they should be correct within an order of magnitude.

(d) Mineral Stabilities

The copper-rich ore that frequently lies at the stratigraphic bottom of the New Brunswick massive sulphide deposits is mainly pyrite and chalcopyrite with subsiduary pyrrhotite and trace quantities of other copper minerals. Pyrrhotite is believed to be of metamorphic origin (Chapter 2, this work). Based on the presence or absence of diagnostic mineral assemblages various reactions, presented as equations 7-1 to 7-3, define the stability field of coexisting pyrite-chalcopyrite with respect to temperature and pO_2 of the ore solution. Thus,

Table 7-2. Average Metal Content of the Anaconda Caribou, Brunswick No. 12 and Heath Steele B-1 Mines

Anaconda Caribou Mine

Copper	Lead	Zinc	Silver	Gold	Iron	
0.7%	2%	5%	34 ppm	1 ppm	40%	Amount by weight
100	88	690	9.3	0.0046	6540	Atomic ratio

Brunswick No. 12 Mine

Copper	Lead	Zinc	Silver	Gold	Iron	
0.5%	23%	6.4%	70 ppm	0.35ppm	40%	Amount by weight
100	210	1800	1.1	0.0023	8770	Atomic ratio

Heath Steele B-1 Orebody

Copper	Lead	Zinc	Silver	Gold	Iron	
1.1%	3.0%	7.2%	10 ppm	0.40ppm	40%	Amount by weight
100	80	640	0.6	0.0012	4150	Atomic ratio

Notes: Copper, lead and zinc contents are from Douglas (1970). Silver is estimated from drill core assays and the gold values are from this work. Iron is estimated assuming the orebody is 100% sulphides.

The atomic ratios are calculated with respect to copper taking atoms of copper as 100. For example, the atomic ratio of lead to copper for the Anaconda Caribou Mine is, (2/207.16) x 100 / (0.7/64.54) = 88

$Cu_5FeS_4 + 4\ FeS_2 + 2H_20 = 5\ CuFeS_2 + 2S^{2-} + 4H^+ + 0_2$ 7-1

bornite pyrite chalcopyrite

$FeS_2 + H_20 = FeS + S^{2-} + 2H^+ + 1/2\ 0_2$ 7-2

pyrite pyrrhotite

$3FeS_2 + 6\ H_20 = Fe_30_4 + 6\ S^{2-} + 12\ H^+ + 0_2$ 7-3

pyrite magnetite

Bornite does occur in some very copper-rich New Brunswick ores (C.M. and S. deposit) but is rare in the deposits considered in this study. The absence of bornite is taken as the mineralogical constraint for definition of the upper limit of oxygen fugacity. Pyrrhotite-pyrite and pyrite-magnetite equilibria define the lower limit of oxygen fugacity. The equilibrium constants for reactions 7-1, 7-2 and 7-3 at temperatures of 150°, 200° and 250° are given in Table 7-3. The equations are plotted as functions of temperature and fugacity of oxygen in Figs. 7-2(a) to (d) for fixed values of m_{H_2S}, m_{Cl^-} and pH.

The diagrams define limits of temperature and oxygen fugacity over which the ore fluid may coexist at equilibrium with the assemblage chalcopyrite-pyrite. Inspection of reactions 7-1 to 7-3 indicates that these equilibria are dependent on two other intensive variables, pH and activity of sulphide ion. In Figs. 7-2(a) to (d) reactions are plotted for constant values of pH and m_{H_2S}, the latter parameter being related to $a_{S^=}$ through the reaction $H_2S = 2H^+ + S^=$ and the appropriate activity

Table 7-3. Equilibrium Constants of Reactions Defining the Phase Boundaries in Fig. 7-2.

Reaction	log K(T)*		
	150°C	200°C	250°C
$Cu_5FeS_4 + 4FeS_2 + 2H_2O = 5CuFeS_2 + 2S^{2-} + 4H^+ + O_2$	- 88.8	- 79.1	- 70.5
$FeS_2 + H_2O = FeS + S^{2-} + 2H^+ + \frac{1}{2}O_2$	- 47.58	- 42.53	- 38.33
$3FeS_2 + 6H_2O = Fe_3O_4 + 6S^{2-} + 12H^+ + O_2$	-153.06	-166.36	-151.75

* Calculated from data of Helgeson (1969)

Fig. 7-2(a). Temperature-pO_2 Stability Field of Pyrite-Chalcopyrite in 3m Chloride Solution; pH = 3.5, log m_{H_2S} = -2.

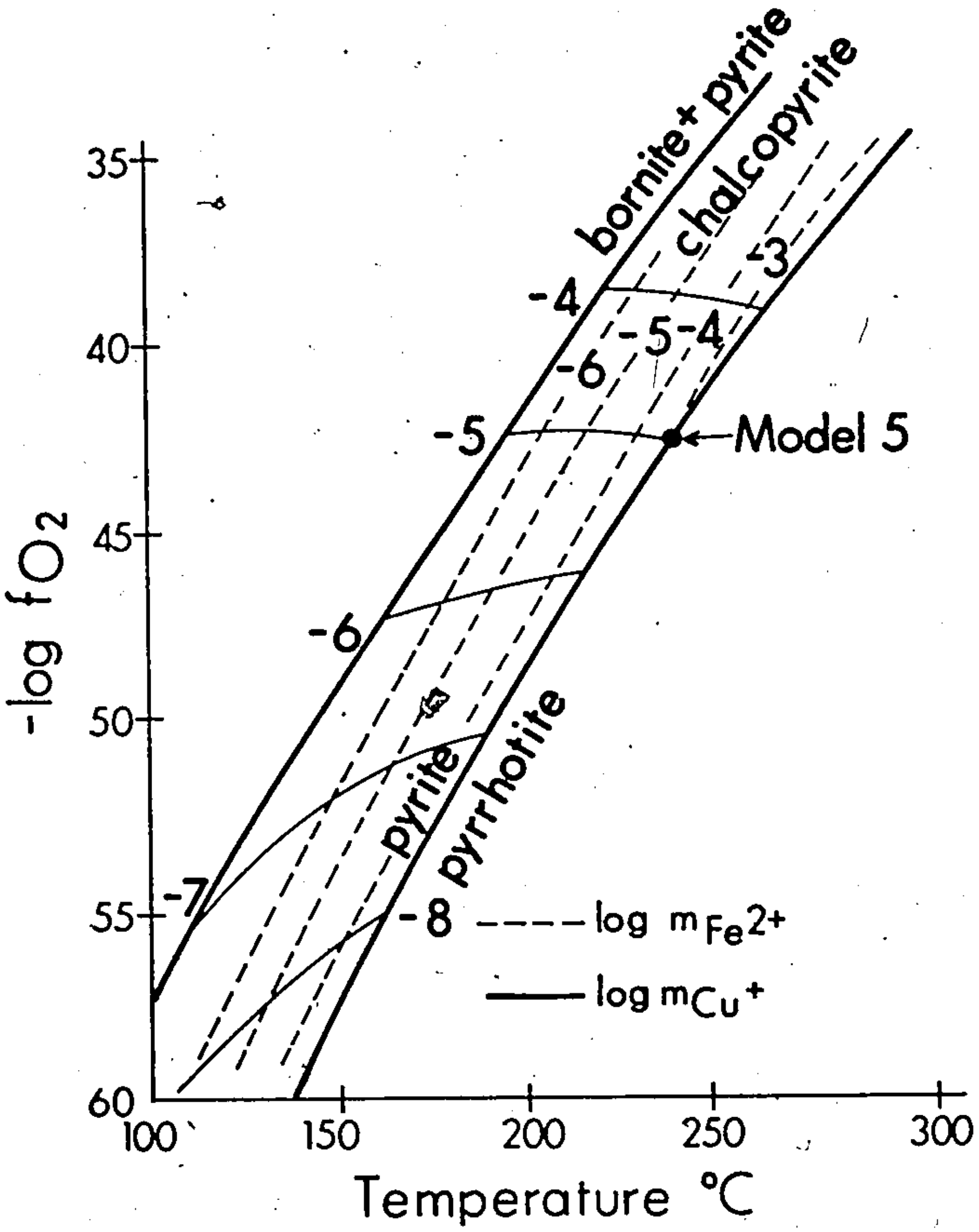

bornite+ pyrite
chalcopyrite
pyrite
pyrrhotite
-3
-4
-5
-4
-6
-5
-6
-7
-8
Model 5
- - - - log $m_{Fe^{2+}}$
—— log $m_{Cu^{+}}$
35
40
45
50
55
60
-log fO_2
100
150
200
250
300
Temperature °C

Fig. 7-2(b). Temperature-pO_2 Stability Field of Pyrite-Chalcopyrite in 3m Chloride Solution; pH = 4.5, log m_{H_2S} = -2.

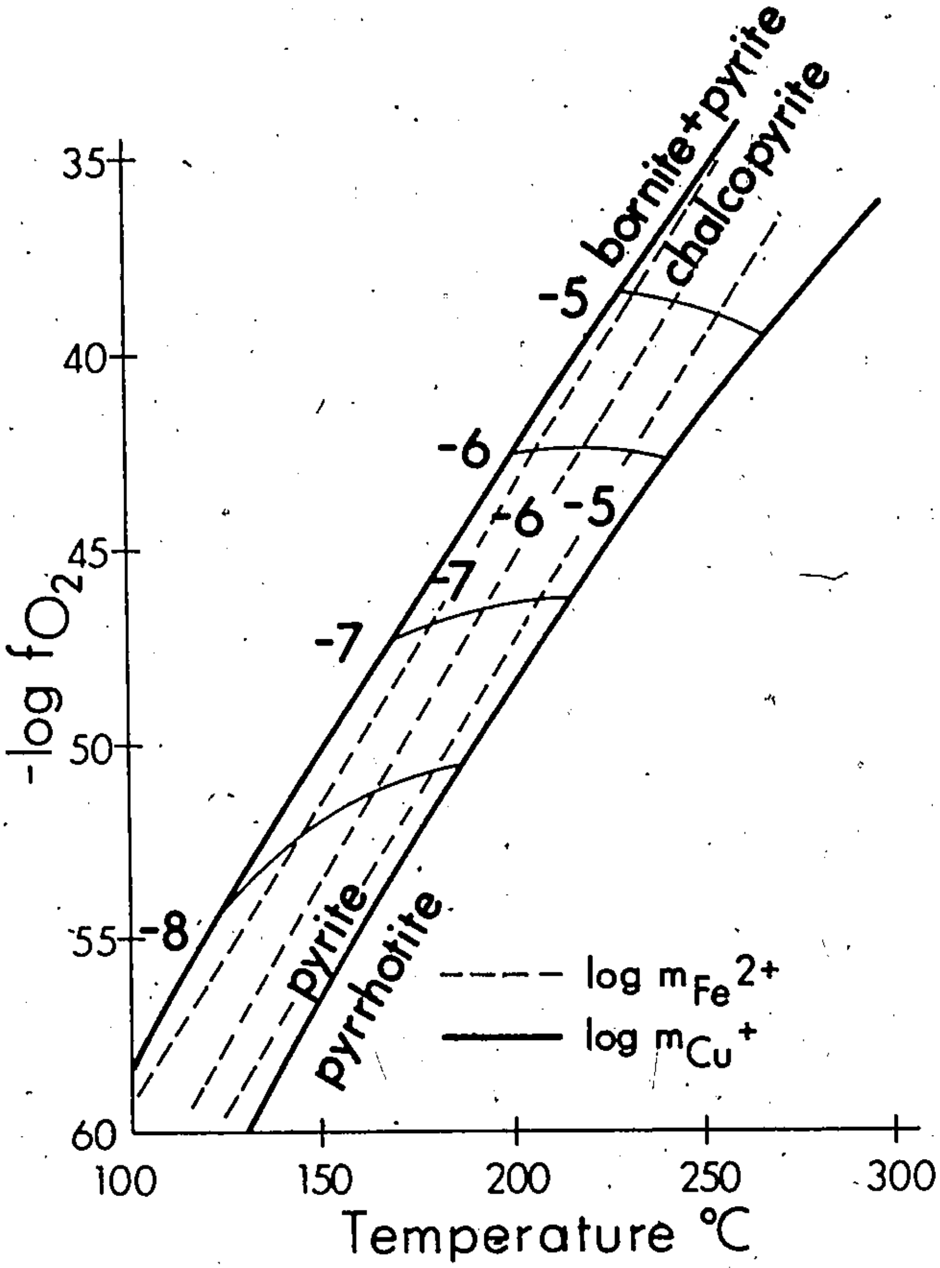

bornite+pyrite
chalcopyrite
pyrite
pyrrhotite
-5
-6
-7
-8
-6
-5
-7
$- - -$ log $m_{Fe^{2+}}$
— log m_{Cu^+}
-log fO_2
35
40
45
50
55
60
100
150
200
250
300
Temperature °C

Fig. 7-2(c). Temperature-pO_2 Stability Field of Pyrite-Chalcopyrite in 3m Chloride Solution; pH = 3.5, $\log m_{H_2S} = -3$.

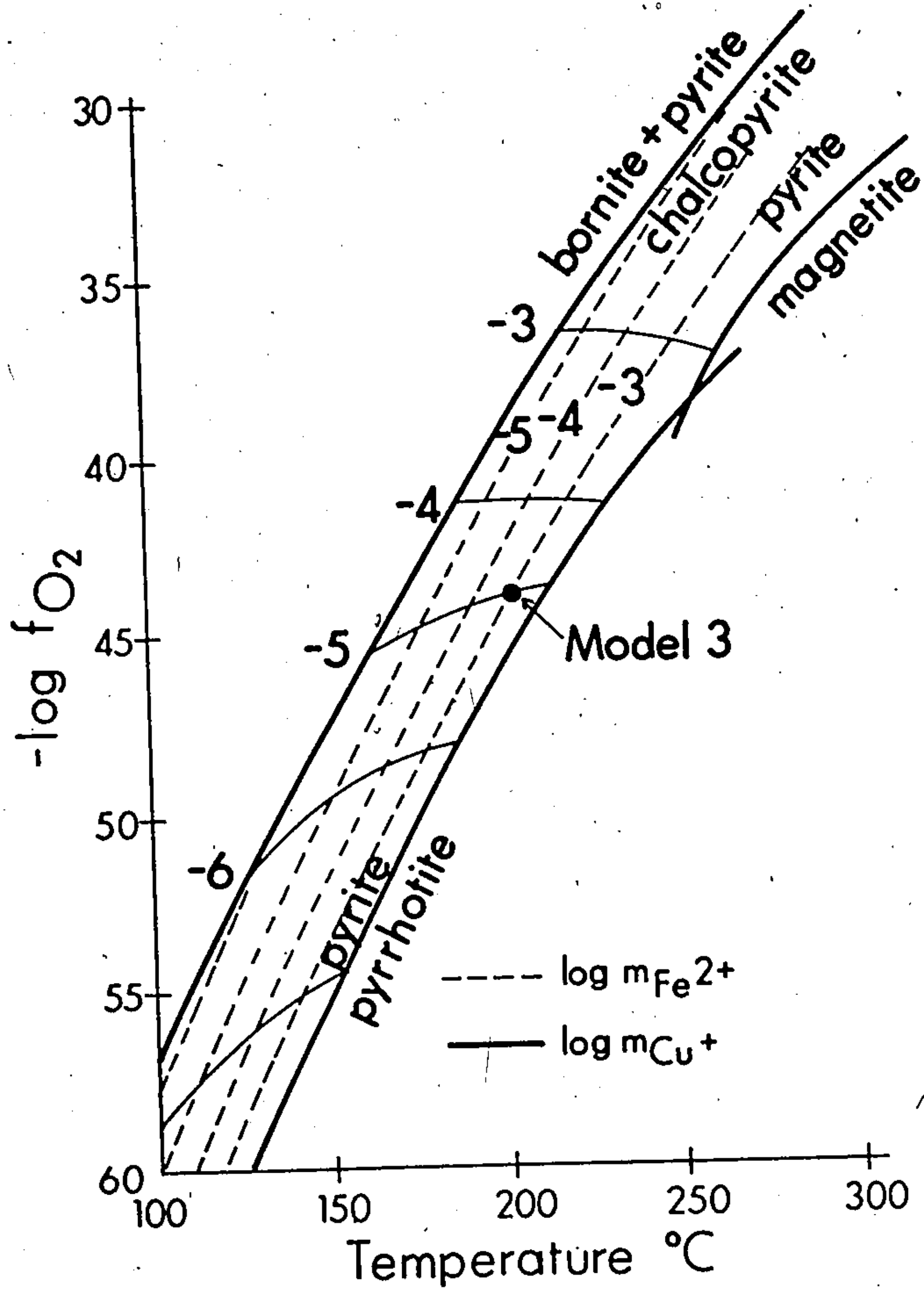
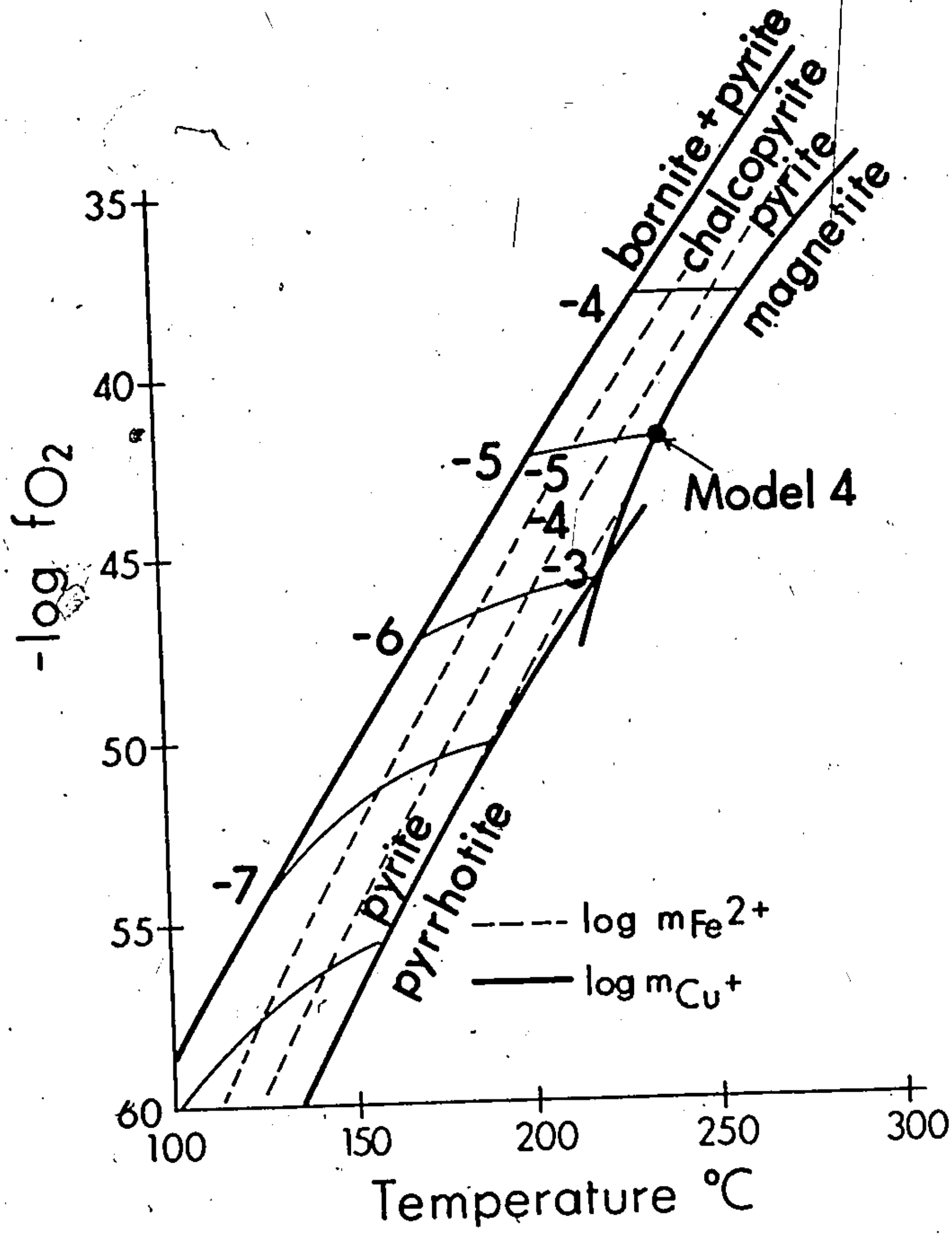

-log f_{O_2}
30
35
40
45
50
55
60
100
150
200
250
300
Temperature °C
bornite + pyrite
chalcopyrite
pyrite
magnetite
pyrite
pyrrhotite
-3
-4
-5
-6
-3
-4
-5
Model 3
log $m_{Fe^{2+}}$
log m_{Cu^+}

Fig. 7-2(d). Temperature-pO_2 Stability Field of Pyrite-Chalcopyrite in 3m Chloride Solution; pH = 4.5, log m_{H_2S} = -3.


bornite + pyrite
chalcopyrite
pyrite
magnetite
pyrite
pyrrhotite
-4
-5
-5
-4
-3
-6
-7
Model 4
log $m_{Fe^{2+}}$
log m_{Cu^+}
-log fO_2
35
40
45
50
55
60
100
150
200
250
300
Temperature °C

coefficients. The values of pH and m_{H_2S} selected represent the limiting values of these parameters considered applicable to the ore solutions. Evaluation of the pH range was discussed in 7-3-3b and the variation in m_{H_2S} will be considered in 7-3-4e. With the pO_2-temperature range of chalcopyrite-pyrite deposition specified, the iron and copper concentrations of the ore solution can be calculated.

(e) Assignment of Metal Solubilities and Molalities of Hydrogen Sulphide

The equilibrium concentrations of iron and copper in the ore solution may be calculated from Helgeson's data (1969, p. 762 and 778) for the range of oxygen fugacities and temperatures required by the stable coexistence of chalcopyrite and pyrite. The reasonable assumption must be made that base metal and iron solubilities are due to chloro-complexes. Other parameters which must be specified are pH, m_{Cl^-} and m_{H_2S}.

Calculated concentrations or solubility contours of Fe^{2+}_{aq} and Cu^{+}_{aq} are plotted on Figs. 7-2(a) to 7-2(d). Values of pH, m_{Cl^-} and m_{H_2S} for which the solubilities apply are noted in the appropriate figure captions. These concentrations represent the full range of copper and iron contents which might exist in the ore solution if equilibrium with the solid phases, chalcopyrite and pyrite, were maintained

There is no direct method (e.g. fluid inclusions) of obtaining the actual concentrations of iron and base metals in the ore solutions and thereby charaterizing their metal contents more exactly than allowed by the thermodynamic calculations. Nevertheless, a consensus of opinion of many geologists concerned with metallogenesis (see discussion by Sato, 1973) is that a minimum concentration of 1 ppm metal is required in solution to produce an economic deposit. The author accepts this premise, in general, and assigns a value of 0.5 ppm copper or 10^{-5}m as the minimum copper content of the Bathurst ore solutions. As discussed in section 7-3-4c the base metal concentrations in the ore solution are considered to be in the same approximate atomic ratios as in the deposits themselves and may be estimated from the data in Table 7-2, the atom ratios of individual metals with respect to copper. Thus, using metal ratios averaged over the Anaconda, Brunswick and Heath Steele Mines, the concentrations of iron, zinc and lead in the ore solution corresponding to various copper contents may be calculated. The range in copper content regarded as relevant is 0.5 to 5 ppm. Iron plus base metal contents expected in an ore solution characterized by this range of copper are presented in Table 7-4.

The remaining variable for which limits must be deduced is m_{H_2S}. With decreasing m_{H_2S} the magnetite stability field expands into the pyrite-chalcopyrite field from the high temperature side of Figs. 7-2. When m_{H_2S} is less than 10^{-4}, concentrations of Fe^{2+}_{aq} greater than 10^{-5} m are impossible in a solution in equilibrium with pyrite-chalcopyrite (not illustrated, but see Fig. 7-2d which approaches this condition).

This iron concentration is much lower than that calculated as minimal in the proposed ore solution (see Table 7-4) and consequently m_{H_2S} in excess of 10^{-4} must prevail. A further constraint is placed on m_{H_2S} if it is required that reduced sulphur for precipitation of iron and the base metals be carried by the ore solution. For an iron concentration in solution of 10^{-3}m, the minimal iron concentration in the proposed ore solution, m_{H_2S} must be approximately $10^{-2.5}$m to give complete precipitation. A maximum hydrogen sulphide concentration of approximately 10^{-2}m is suggested by Figs. 7-2a and 7-2b which show that for $m_{H_2S} = 10^{-2}$ iron solubility at temperatures less than 250°C is approximately 10^{-3}m or less. Thus, it is concluded that the most likely range in m_{H_2S} is 10^{-2} to 10^{-3}m if total iron solubility of 10^{-3}m in the ore solution is required.

(f) Most Probable Values of the Physicochemical Parameters Governing Chalcopyrite-Pyrite Deposition

The physicochemical environment of chalcopyrite-pyrite deposition is delineated by the reaction curves bornite-pyrite-chalcopyrite, pyrite-pyrrhotite and pyrite-magnetite. These reactions were plotted in pO_2-temperature coordinates for the ranges or limits of pH and m_{H_2S} thought to be relevant to the ore solutions under consideration. The resulting diagrams Figs 7-2(a) to 7-2(d), define fields of coexistence of pyrite and chalcopyrite with the ore solution.

Table 7-4 lists various possible combinations of pH and m_{H_2S} represented by upper and lower limits of these parameters. The base metal and iron components of the ore solution are specified as discussed above in 7-3-4e for two selected values of copper content, m_{Cu^+}. Six possible groupings of independent variables or "models" are presented in Table 7-4.

Concentrations of Fe^{2+}_{aq} and Cu^{+}_{aq} calculated from chlorocomplex solubility data (Helgeson, 1969) and for values of relevant variables as specified in Figs. 7-2(a) to 7-2(d) are then superimposed on the diagrams. The models or combination of variables judged most realistic are those for which the inferred copper and iron concentrations (as listed in Table 7-4) fall within the chalcopyrite-pyrite stability field as defined in Figs 7-2(a) to 7-2(d).

On this basis the most probable models are 3 and 5 represented by Figs. 7-2(c) and 7-2(a) with ore solution temperatures of 200 and 250°C respectively. These models provide the only two combinations of variables for which the inferred iron and copper concentrations of the ore solutions lie within the chalcopyrite-pyrite stability field. Both models are characterized by the same pH, iron and base metal values and differ in terms of m_{H_2S}. The lower temperature model, model 3, is preferred (see section 7-3-4a for discussion of ore solution temperature). Thus it is suggested that the ore solution brine is characterized by the following physicochemical parameters at the beginning of

Table 7-4. Calculated Base Metal and Iron Contents of Various Hypothetical Ore Solutions.

Model	pH	MCl^-	log m				
			H_2S	Cu^+	Fe^{2+}	Zn^{2+}	Pb^{2+}
1	3.5	3	-2	-4	-2	-3	-4
2	4.5	3	-2	-4	-2	-3	-4
3	3.5	3	-3	-5	-3	-4	-5
4	4.5	3	-3	-5	-3	-4	-5
5	3.5	3	-2	-5	-3	-4	-5
6	4.5	3	-3	-5	-3	-4	-5

chalcopyrite-pyrite precipitation: temperature = $200^{\circ}C$, $pO_2 = 10^{-44}$ atm., pH = 3.5, $\log m_{H_2S} \sim -3$, $m_{Cu} = 10^{-5}$m, $m_{Fe} = 10^{-3}$, $m_{Pb} = 10^{-5}$ and $m_{Zn} = 10^{-4}$. These initial conditions, referred to as Stage A, are summarized in Table 7-5a. The evolution of this hypothetical ore solution, leading to eventual precipitation of galena and sphalerite, mainly in response to decreasing temperature, can now be considered.

7-3-5 Physicochemical Parameters Relevant to Deposition of Galena-Sphalerite Ore

In the discussion below the terms lower and upper ore are used in a stratigraphic sense for the inferred original zoning of the ore such that the lower ore is copper-rich and the upper ore lead-zinc rich.

Of the three deposits investigated, the Heath Steele B-1 and Anaconda Caribou are characterized by distinctive zoning in the vertical stratigraphic sense. Their copper concentrations usually range from a maximum of 1% in the lower copper-rich ore to a minimum of 0.1% in the lead-zinc rich upper ore. The iron concentration is relatively constant throughout the deposits. To evaluate the changes in the ore solution resulting from precipitation of pyrite and chalcopyrite, the properties of the solution are considered at a stage when approximately half the iron has been precipitated. Formation of the lower half of the orebody is considered to result in removal of approximately 90% of the copper, as well as half the iron, from the ore solution. This stage of evolution is referred to as Stage B (Table 7-5a) and leaves the iron and copper contents of the ore solution at $m_{Fe} = 10^{-3.3}$ and $m_{Cu} = 10^{-6}$. Allowing for a reduction in sulphide content of the ore solution as required for precipitation of iron and copper, m_{H_2S} decreases to approximately 10^{-3}m. The temperature is inferred from Fig. 7-2c for the relevant copper and iron contents as noted above and is approximately 170°C.

The equilibria which govern the precipitation of galena and sphalerite are:

$$Pb^{2+} + S^{2-} = PbS \text{ (galena)} \qquad 7\text{-}4$$

$$Zn^{2+} + S^{2-} = ZnS \text{ (sphalerite)}^{*} \qquad 7\text{-}5$$

$$\text{where } K_{PbS} = a_{Pb^{2+}} \cdot a_{S^{2-}} \qquad 7\text{-}6$$

$$\text{and } K_{ZnS} = a_{Zn^{2+}} \cdot a_{S^{2-}} \qquad 7\text{-}7$$

The temperatures of saturation of the ore solution with respect to sphalerite and galena can be calculated for the zinc and lead concentrations prevailing in the initial ore solution (Stage A, Table 7-5a) and for the sulphide concentration at Stage B. The activity of sulphide ion is calculated from m_{H_2S} at Stage B. Constant pH over Stage A deposition is assumed. Using the appropriate stoichiometric ion activity coefficients and equilibrium constants from Helgeson (1969),

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* Actual sphalerite composition is (Zn, Fe)S but Bathurst sphalerites are low in iron.

saturation temperatures of 135°C and 170°C are obtained for sphalerite and galena respectively. A problem with this observation is that these minerals are often intimately interbanded in many Bathurst area massive sulphide deposits, suggesting nearly simultaneous saturation of the ore solution with respect to lead and zinc. The calculated saturation temperatures suggest prior precipitation of galena. A possible explanation is that the thermodynamic data (Helgeson, 1969) are insufficiently accurate to resolve chemical behaviour where relatively small temperature differences, in this case 35°C, are involved. Anderson (1973) noted that experimental evaluation of lead and zinc chlorocomplex solubilities indicates a similar order of solubility for both metals, an observation more compatible with actual lead-zinc distribution. Nevertheless, if the objective is to model the gross features of metal zoning, as in this study, the thermodynamic data appear adequate. Thus, 170°C is also the temperature of the ore solution at the end of Stage A deposition. Thus, galena and sphalerite are not expected to precipitate in the first half (lower half) of the depositional process. Rather, both minerals should occur in the upper half of deposits as is commonly the case.

The final stage, Stage C, marks the complete precipitation of copper and iron from the ore solution. Their residual concentrations are taken as 1% of their initial concentrations or 10^{-7} and 10^{-5} m respectively. The corresponding temperature and pO_2 from Fig. 7-2(c) are approximately 100°C and 10^{-60} atmospheres and m_{H_2S} is reduced to $10^{-5.0}$m largely due to removal as pyrite in precipitation of the remaining half of the iron. The lead and zinc contents of the ore solution at Stage C are calculated from equations 7-6 and 7-7 using appropriate equilibrium constants and activity coefficients from Helgeson (1969) and sulphide ion activity appropriate to the m_{H_2S} at Stage C ($H_2S = 2H^+ + S^=$).

The complete characterization of the ore solution at the beginning, middle and end of base metal deposition, denoted as Stages A, B and C, is summarized in Table 7-5a.

7-3-6 Characterization of the Ore Solution with Respect to Gold Content

The concentration of gold in the hypothetical ore solution can, in part, be inferred in a manner similar to that used for the base metals. The initial concentration (Stage A) is obtained by assuming that average metal ratios in the deposits themselves approximate average metal ratios of the ore solution at the beginning of metal precipitation. Thus, using the average gold to copper ratio for the three deposits investigated and assigning an initial copper content of 10^{-5}m an initial gold concentration of $10^{-9.7}$m is obtained. However, the change in gold content of the ore solution with cooling cannot be calculated as was done for lead and zinc because the relevant solute species is unkown. Instead, changes in gold content of the ore solution are estimated from the

Table 7-5(a) Hypothetical Model for an Ore Solution Relevant to Formation of New Brunswick Massive Sulphide Deposits.

Stage	Temp. °C	log f_{O_2}, atm	pH	H_2S	Cu	Fe	Pb	Zn	Au
A	200°C	-44	3.5	-2.7	-5	-3	-5	-4	-9.7
B	170°C	-49	3.5	-3.0	-6	-3.3	-5	-4	-9.85
C	100°C	-60	4.0	-5.0	-7	-5.0	-6.5	-4.9	-10.7

Table 7-5(b) Ore Deposits Resulting from Hypothetical Model Described by Table 7-5(a)

	Grams Metal Precipitated per 100 Grams of Solution					
Stage	S	Cu	Fe	Pb	Zn	Au
A→B	32×10^{-3}	0.58×10^{-3}	28×10^{-3}	0	0	1.1×10^{-8}
B→C	32×10^{-3}	0.58×10^{-4}	27×10^{-3}	2.0×10^{-3}	5.6×10^{-3}	2.7×10^{-8}
	Weight Percent of Metal*					
Upper Half	47	0.1	42	3.0	8.3	4.0×10^{-5}
Lower Half	53	1.0	46	0	0	1.9×10^{-5}

* Example calculation of weight percent lead in the upper half of the deposit: Wt. % lead = $((10^{-5}-10^{-6.5})$moles x 208 gm/mole x $100)/\Sigma(S+Fe+Cu+Pb+S)$ where each component of the Σ term is the gram equivalent of the moles

actual gold variations in drill core.

As noted in section 6-3-2 there is a preferential association of gold with the lead-zinc rich ore in most holes investigated. While this association is not regarded as strong and cannot be clearly discerned in every hole, it is quite apparent in the correlation coefficients and by comparison of gold contents of copper-rich and lead-zinc ore. Using the data from the three Brunswick No. 12 holes, the B138 hole from Heath Steele and DDH 62-9 from Caribou, the average gold content of the stratigraphic lower half of these holes (in general the copper-rich portion) is approximately one-third the total gold content. The end of Stage A deposition (A to B) is, therefore, considered to result in precipitation of one-third of the gold from the ore solution. At Stage C, 100°C, most of the remaining gold has been precipitated. Ninety percent precipitation is used for modelling purposes but it would not affect the conclusions if more complete precipitation, say 99%, were in fact the case. The gold contents of the ore solution at the beginning, middle and end of base metal deposition as inferred from the above considerations are listed in Table 7-5(a). In section 7-4 the gold contents of the ore solution calculated by assuming various complex ion gold solutes are compared with the above estimates in an attempt to establish the most likely solute complexes responsible for gold transport.

7-3-7 Summary of the Model

The changes in the physicochemical state of the ore solution required by the model delineate certain changes in metal concentrations during the depositional process. The resulting ore deposit can be calculated by subtracting metal concentrations of Stage A and B solutions to obtain the metal removed during deposition of the lower half of the deposit (200°C to 170°C), and similarly subtracting concentrations of Stages B and C to obtain the metal contents of the upper half of the deposit (170°C to 100°C). The resultant metal contents are the atomic ratios of metals in either half of the deposit. They may be recalculated as weight percentages for comparison with actual drill hole metal profiles. Table 7-5(b) presents results of such a calculation and represents the hypothetical ore deposit resulting from the model ore solution of Table 7-5(a).

The average grades of DDH 62-9 (Anaconda Mine) and DDH B138 (Heath Steele B-1 orebody) are presented in Tables 7-5(c) and 7-5(d) respectively. The holes have been divided into a lower and upper half in terms of inferred stratigraphy. These average metal grades may be compared with the hypothetical model deposit of Table 7-5(b). A high degree of correspondence is not expected. The model considers only a two-stage depositional process and the cumulative error resulting from uncertainty in the estimation of various parameters such as pH and minimum copper content of the initial ore solution may be fairly large. Nevertheless, the sense of the zoning of lead and zinc with respect to copper is correctly predicted and, in the case of the Heath Steele hole, with rather good agreement to the concentrations actually found in the upper half of the hole. Neither copper nor gold are predicted directly from the model although the gold concentration in the Stage A ore solution ($10^{-9.7}$m) is that required by the actual measured gold contents of cores and the assumed equality of the gold/copper ratio of the ore deposit and the initial ore solution. The gold content of the ore solution at Stages A, B and C could have been modelled assuming gold chlorocomplexes as the dominant species in solution. However, as argued in section 7-4 and the solubility data in Table 7-7, gold chlorocomplexes provide grossly insufficient solubilities compared with those required by the measured gold content of cores and the assumed gold/copper equivalence of ore solution and ore deposit.

The main purposes of the model are two-fold: firstly, to determine whether Sato's model for Kuroko deposition yields reasonable physicochemical parameters for the ore-forming solutions of the Bathurst stratiform deposits, and secondly, to obtain the necessary physicochemical parameters to estimate gold solubility in the ore solution. The gross features, at least, of the Bathurst stratiform ores seem to be adequately modelled by Sato's approach. Estimates of the variables important to gold transport are also regarded as adequate. In particular,

Table 7-5(c) Average Metal Grades Through Anaconda Caribou DDH 62-9

	COPPER %	LEAD %	ZINC %	GOLD ppm
UPPER HALF	0.50	0.91	4.6	1.3
LOWER HALF	0.81	0.33	1.6	0.36

Table 7-5(d) Average Metal Grades Through Heath Steele DDH B138

	COPPER %	LEAD %	ZINC %	GOLD ppm
UPPER HALF	0.61	3.1	6.4	0.60
LOWER HALF	1.3	0.2	0.5	0.26

the fugacity of oxygen in the ore solution has a strong effect on the solubility of gold due to the requirement of oxidation of the native metal to effect dissolution. The fugacity of oxygen in the ore solution model above was restricted by requiring equilibrium with chalcopyrite and pyrite. At any one temperature, the range of permissible oxygen fugacities is comparatively small. Thus, changes in the inferred molality of base metals in the model are unlikely to affect the fugacity of oxygen greatly. Most other variables, such as pH, temperature and chloride molality have similar effects on the solubility of the base and precious metals, assuming chloride complexing for all metals. Consequently, it is considered that the model is valid for comparison of possible models of gold solubility by chloride and sulphide complexes.

7-4 Gold Behaviour in the Postulated Model

7-4-1 Total Gold Solubility

It has already been mentioned that gold chlorocomplex solubility is insufficient to account for the average gold contents of Kuroko deposits. From the model for the New Brunswick deposits in Table 7-5(a) the gold solubility can be calculated and compared with that predicted for chlorocomplexes. Chlorocomplex solubility is due to $AuCl_2^-$ and the relevant equilibrium expression,

$$AuCl_2^- + 1/2\ H_2O = Au^o + 2Cl^- + 1/4O_2 + H^+$$

is obtained by subtraction of the two equations in Table 4-8 giving equilibria involving the univalent gold ion (data in Table 4-8 are from Helgeson, 1969). Concentrations of $AuCl_2^-$ are calculated for temperatures of 200°C, 170°C and 100°C using the appropriate pH, m_{Cl^-} and pO_2 values from Table 7-4(a).

The calculations yielding the $AuCl_2^-$ concentrations listed in Table 7-7 indicate insufficient gold chlorocomplex solubility for the variables specified by the model ore solution of Table 7-5a.

The solubility of gold as a bisulphide complex, $Au(HS)_2^-$, was discussed in Chapter 4. It was concluded that this complex is important for gold transport in hot springs with pH's near neutrality. However, solutions with pH less than 4.5 are thought to be relevant to formation of the New Brunswick deposits. For these mildly acid solutions the neutral complex found in Seward's experiments (1973) must be considered.

Due to experimental difficulties Seward could not prove the stoichiometry of the neutral complex but suggested the species $Au(HS)^o$. The formation reaction can be represented by:

$$Au^o + 1/4\ 0_2 + H_2S = Au(HS)^o + 1/2\ H_20$$

with equilibrium constant, K, given as:

Table 7-6. Equilibrium Constants for Dissolution Reactions Producing Gold Bisulphide Complexes

	log K(T)				
	100	150	175	200	250
$Au^{o}+2H_2S+\frac{1}{4}O_2 = Au(HS)_2^{-}+H^{+}+\frac{1}{2}H_2O$				† +3.30	† +0.44
$Au^{o}+H_2S+\frac{1}{4}O_2 = Au(HS)^{o}+\frac{1}{2}H_2O$	* +11.9	* +9.9	† +8.9	† +7.9	† +6.2
$Au^{o}+2H_2S+\frac{1}{4}O_2 = Au(H_2S.HS)^{o}+\frac{1}{2}H_2O$	* +12.8	* +10.1		† +8.2	

Note: * Extrapolated
† Calculated using solubility data of Seward (1973)

Table 7-7. Concentration of Gold Complexes in the Model Ore Solution for conditions of Stages A, B and C of Table 7-5(a).

Temp. °C	Required log m_{Au}	log $m_{AuCl_2^-}$	log $m_{Au(HS)^o}$	log $m_{Au(H_2S.HS)}$
200	- 9.7	-11.8	-5.9	- 8.2
170	- 9.85	-13.9	-7.1	- 8.7
100	-10.7	-16.6	-7.1	-10.2

$$K = \frac{a_{Au(HS)^o} \; a_{H_2O}^{1/2}}{a_{Au^o} \; f_{O_2}^{1/4} \; a_{H_2S}} \qquad 7\text{-}8$$

$$= \frac{m_{Au(HS)^0}}{f_{O_2}^{1/4} \; \gamma_{H_2S} \; m_{H_2S}} \qquad 7\text{-}9$$

The equilibrium constant is evaluated using the oxygen fugacity calculated from equation 7-2 as the experiments were buffered by pyrrhotite-pyrite. The molalities of sulphur and gold used were those found experimentally by Seward (1973). The pH value used varied between 3.5 and 4.0 according to the conditions of Seward's experiments. It should be noted, however, that the effect of pH on the pyrite-pyrrhotite equilibrium (equation 7-2) and on hydrogen sulphide-bisulphide equilibrium cancel out when considering the solubility of gold. Consequently the solubilities of neutral gold sulphide complexes in acidic solutions do not vary with change in pH. The activity coefficient of hydrogen sulphide is obtained from Gamsjager and Schindler (1969) and the calculated equilibrium constants are given in Table 7-6.

The solubility of gold as the $Au(HS)^o$ complex was then calculated from equation 7-9 for the ore solution specified by the model parameters given in Table 7-5(a). The results are presented in Table 7-7 for temperatures of 200°C, 170°C and 100°C. The $Au(HS)^o$ complex leads to solubilities exceeding those indicated by the observed gold contents by three orders of magnitude. Thus gold could not have reached concentration levels sufficient for precipitation as the native metal if solubility was due to $Au(HS)^o$.

Sabin (1971) suggested that $(H_2S.HS)^-$ forms a stable adduct, which might lead to formation of complexes of the type $Au(H_2S.HS)^o$, although Seward comments that such complexes would not be expected to be stable at elevated temperatures. The formation reaction may be represented by:

$$Au^o + 2\,H_2S + 1/4\ O_2 = Au(H_2S.HS)^o + 1/2\ H_2O \qquad 7\text{-}10$$

$$\text{where } K = \frac{m_{Au(H_2S.HS)}}{a_{H_2S}{}^2\ f_{O_2}{}^{1/4}} \qquad 7\text{-}11$$

Equilibrium constants for this reaction calculated from the data used to obtain the K for $Au(HS)^o$ are given for the temperature range 100 - 250°C in Table 7-6.

Calculated gold solubilities due to $Au(H_2S.HS)$ are presented in Table 7-7 and compared with the solubilities required by the observed gold contents of the ores. Because of the dependence of the solubility of $Au(H_2S.HS)^o$ on the second power of the hydrogen sulphide concentration, the solubility is less than $Au(HS)^o$. However, it exceeds that of the chlorocomplex, $AuCl_2^-$, for the relevant parameters of the model, and provides the best agreement with the solubility expected from the observed gold contents of the ore.

In conclusion, three gold complexes, $AuCl_2^-$, $Au(HS)^o$ and $Au(H_2S.HS)^o$, may be important in the pH range considered relevant for formation of this class of deposit. $AuCl_2^-$ and $Au(HS)^o$ give too low and too high solubilities respectively. Due to the failure of Seward's apparatus it must be recognised that the identity of gold sulphide complex ion species in the mildly acid region is very poorly established, and there is no direct experimental evidence to suggest whether $Au(H_2S.HS)^o$ does exist. This complex does, however, give gold solubility most compatible with the model postulated above.

It has been pointed out in the discussion of zinc solubility that there is some disagreement between the available experimental evidence of Federov et al. (1970) and Helgeson's (1969) theoretical zinc solubilities. Helgeson's gold solubility data seem to this author to be based on less reliable source data than his zinc solubilities. It is thus suspected that there may be large errors in the gold solubility data for chlorocomplexes especially at elevated temperatures.

7-4-2 Zonation of Gold

Three properties of the postulated ore fluid may cause decreasing solubility of gold during ore deposition. These factors are independent of the complex involved, and include:

1. decrease in fugacity of oxygen
2. increase in pH

3. cooling

A further property, decrease in molality of hydrogen sulphide, is applicable to sulphide complexes only.

The effect of a decrease in oxygen fugacity is a reduction in the oxidation potential required for dissolution of native gold. The increase in pH decreases chloride complex stability in every case of metal chlorocomplex formation. pH also has an indirect effect on the solubility of sulphide complexes in that hydrogen sulphide-bisulphide equilibrium is shifted toward HS^- with increasing pH thereby promoting formation of the highly soluble $Au(HS)_2^-$ complex. The effect of cooling is apparent in the change of the equilibrium constants with temperature.

To explain the preferential association of gold with lead and zinc in a stratigraphically zoned deposit such as the Anaconda Caribou, the gold must be undersaturated with respect to the native metal upon initial exhalation of the ore fluid. At about 170°C when lead and zinc begin to precipitate, gold must also approach saturation. The complex that, as a result of the changes of fugacity of oxygen, pH, temperature and molality of hydrogen sulphide has the correct change in solubility, is $Au(H_2S.HS)$.

It is worthy of note that the calculated solubility of gold as $Au(H_2S.HS)$ somewhat exceeds that required by the model ore solution at 170°C, the temperature of beginning of zinc-lead precipitation.

A 70°C drop in temperature to 100°C results in a decrease in gold solubility by about one order of magnitude such that the model solubility and that attributable to Au($H_2S.HS$) are in closest agreement at 100°C. It is suggested that gold may be too soluble to precipitate initially with zinc and lead but rather precipitate toward the end of the zinc-lead depositional phase when ore solution temperatures have significantly decreased. The high gold concentrations within a few tens of feet of the hanging wall contact, that is almost at the end of the zinc-lead deposition, as seen in Caribou DDH 62-9 and Brunswick DDH 12-1002, are possible examples of this effect.

7-5 Association of Gold with Pyrite

In Chapter 6 it was noted that, although gold did not show behaviour compatible with solid solution in any sulphide minerals, it nevertheless was concentrated in pyrite relative to other sulphide minerals. This could be due to surface chemistry effects during the precipitation and diagenesis of gold.

Zviagincev and Paulsen (1940) found that gold was preferentially precipitated upon pyrite, arsenopyrite and galena as opposed to chalcopyrite and sphalerite. The concentration of much of the gold on the former minerals was explained as an interaction between the mineral surface and the gold sol which forms at the first stage of precipitation.

CHAPTER 8

CONCLUSIONS

1. The average gold contents of the Bathurst district stratiform base metal ores as inferred from analysed drill cores strongly suggest that these deposits concentrate gold by factors of 10^2 to 10^3 times the crustal average (taken as 1 to 5ppb). In general, the wall rocks stratigraphically below the sulphides are significantly enriched in gold for distances of at least 100 feet. In contrast, the palladium content of these ores is approximately the same as the crustal average and it is inferred that this type of base metal deposit does not concentrate palladium (and probably the rest of the platinum group metals).

2. Although the evidence is not completely consistent, in the majority of holes studied, gold is strongly zoned and enriched in the zinc-lead rich ores. No zoning of palladium was detected. Gold, therefore, is considered a minor constituent of the ore solutions whose geochemical behaviour was controlled by the same physiochemical parameters that governed base metal transport and deposition.

3. Examination of the variability of replicate analyses for both gold and palladium indicates that most of the variability is due to sample

inhomogeneity rather than chemical analytical error. It is tentatively suggested that in the case of gold a discrete mineral phase is present, at least in the lead-zinc ore where higher gold content is generally found.

4. A survey of the literature indicates considerable evidence favouring a submarine exhalative volcanic origin for the Bathurst-Newcastle district stratiform ores. Based on a qualitative assessment of the geometry of the Bathurst camp ores and utilizing a model applied by Sato (1972) to Kuroko deposits, the likely temperature-density characteristics of the ore solution were evaluated. These considerations led to the conclusion that on mixing with sea water the ore solution brines maintained a coherency and sufficiently high density to sink and aggregate or pond as discrete brine pools in submarine topographic depressions.

5. A detailed evaluation of available thermodynamic and experimental data suggests that in chloride-rich solutions containing reduced sulphur ($M_{Cl^-} = 1$, $M_{\text{total sulphide}} = 10^{-3}$), solubility of base metals in the pH-temperature region relevant to stratiform base metal ore deposition is dominantly due to chlorocomplexes of zinc, lead and copper.

6. A model to estimate limiting values of the physicochemical properties of the ore solution relevant to transport and deposition of iron and the base metals can be developed following the approach

of Sato (1973). Equilibrium of the ore solution with pyrite and chalcopyrite is applicable to the Bathurst ores as an initial condition and provides limits of the likely pO_2-temperature profile of the ore solution. The stratigraphic zoning of the base metals can be modelled by progressive saturation of the ore solution with various sulphide minerals in response to falling temperature, changing oxygen fugacity and decreasing reduced sulphur content of the ore brine. A critical assumption required is that complete precipitation of metals is effected by the reduced sulphur carried by the ore fluid. An estimate of the minimum base metal content of the ore solution is also required.

7. From the physicochemical conditions of ore deposition inferred from the base metal distribution, a critical evaluation of gold transport processes can be developed. According to the model values of the important variables deduced from the base metal study, gold chlorocomplexes provide insufficient gold solubility whereas gold bisulphide complexes provide too great a solubility to model the actual gold contents of the deposits. A neutral gold sulphide complex, $Au(H_2S.HS)$, gives gold solubility which agrees best with the observed concentration and distribution of gold in the deposits. The existence of this complex, however, has not yet been substantiated by experimental data.

8. Experimental data on gold solubility in mixed chloride-sulphide solutions over the temperature range 100 to 300°C and pH range 3 to 5 are required to provide a more secure base for thermochemical modelling of gold transport applicable to stratiform base metal deposits and to provide an independent evaluation of Helgeson's (1969) theoretical data.

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