

The Boss Mountain Molybdenum Deposit, B.C. : Fluid Inclusion evidence for H₂O-CO₂ Phase Separation and Light Stable Isotope Geochemistry

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Abstract

Molybdenite mineralisation at Boss Mountain is hosted by a Triassic quartz monzodiorite batholith and is associated with a Cretaceous monzogranite stock. Ore has been mined from subvertical breccia pipes that emanate from the stock and from a sheeted vein complex that describes a partial annulus centred upon the apical region of the stock.

Three groups of fluid inclusions in quartz associated with molybdenite ore are present throughout the deposit: (a) inclusions containing a low salinity aqueous fluid and both liquid and gaseous CO₂, with molar percentages: 94.5% H₂O, 3.6% CO₂ and 1% NaCl, (b) inclusions with just low salinity aqueous fluids (96% H₂O, 4% NaCl), and (c) inclusions with variable H₂O and CO₂ content, up to 100% CO₂. A complete spectrum exists between group (2) and (3) inclusions in the upper levels of the deposit, while only group (1) inclusions are present in the lower. Coexisting inclusions homogenise into both the CO₂ and H₂O phases over the same temperature range (250° to 370°C), indicating that the inclusions were trapped on a solvus in the H₂O-CO₂-NaCl system. Homogenisation temperatures are therefore trapping temperatures. Phase relationships indicate that the fluids were trapped at a pressure of approximately 350 bars, interpreted to be greater than or equal to the lithostatic load and equivalent to a depth of 1.3 Km or less. The hydrothermal fluid underwent CO₂ effervescence as it passed upwards through the deposit. The molybdenite zone at Boss Mountain coincides with CO₂ phase separation in the veins and breccia pipes, suggesting a possible relationship between mineralisation and effervescence.

Compositions of light stable isotopes ($\delta^{13}\text{C}$ in carbonate: -8.0‰ to -15.6‰; $\delta^{34}\text{S}$ in pyrite and molybdenite: -3‰ to +1‰; $\delta^{18}\text{O}$ and δD (calculated) of the hydrothermal fluid: +4‰ to +5‰ and -73‰ to -142‰, respectively) indicate that at least some components of the hydrothermal fluid (C and S) are derived from an igneous source in the lower crust or upper mantle. The isotopic composition of water in the hydrothermal fluid oxygen is consistent with a magmatic origin, with modification of the δD composition due to either (a) incorporation of a small quantity of meteoric water or (b) hydrogen isotopic fractionation due to separation of a hydrogen-bearing gas species, such as H₂S, from the hydrothermal solution.

Introduction

The chemical and thermal constraints on molybdenum transport and deposition to form molybdenum ore deposits are not well understood. Hence, the objective of the work described here was to contribute to the problem by examining the fluid inclusion and light stable isotope characteristics of a specific case-history in detail (Macdonald, 1983). Boss Mountain in Central British Columbia was chosen as a relatively small and simple example of a Cordilleran MoS₂ deposit. It is situated on the northeast slope of Takomkane Mountain, 10 Km to the west of the community of Hendrix Lake (N.T.S. 93A/2W; 52°06'N, 120°56'W). Access is from 100 Mile House by nearly 90 km of road, the first 50 of which are paved. The history of the deposit has been described by Soregaroli (1975).

Between 1965 and 1971 a total of 2,968,740 tonnes of ore were milled, at an average grade of 0.26% Mo. Between 1974 and 1980 a further 3,603,440 tonnes of ore were milled at an average grade of 0.188% Mo. Mining commenced with breccia bodies and progressed to a larger tonnage, but lower grade, sheeted vein complex. The mine closed indefinitely in November, 1982 due to adverse market conditions.

Regional Geology

The Boss Mountain deposit is situated on the eastern flank of the Intermontane, or Interior Structural Belt (Sutherland Brown, 1969; Sutherland Brown et al., 1971). In the Boss Mountain area, the Intermontane Belt is an elevated plateau at approximately 5000ft or 1500m characterised by Mesozoic eugeosynclinal volcanic and sedimentary strata (Sutherland Brown et al., 1971). Boss Mountain occurs within the Quesnel Trough (Campbell and Tipper, 1970), defined by the occurrence of Upper Triassic and Lower Jurassic volcanic and sedimentary rocks which were invaded by intermediate and later acidic intrusions.

The molybdenum deposit is contained in the Takomkane Batholith (Figure 1) that intrudes the Upper Triassic Nicola Group volcanic rocks, suggested by Campbell and Tipper (1970) to be its extrusive equivalent. The batholith is in fault contact with Lower Jurassic volcanic and sedimentary rocks to the east.

Middle Cretaceous monzogranite to granodiorite bodies intrude all older units. A belt containing these intrusions extends for 130 km to the southeast. The most northerly body known within the belt, the Boss Mountain Stock (Figure 2), intruded the Takomkane batholith within a kilometre of its fault bounded eastern flank (Figure 1) and is associated with molybdenum mineralisation at Boss Mountain (Soregaroli, 1968).

The post mineralisation Tertiary geology of the area is described by Campbell (1963), Wilson (1977) and Fujii and Scarfe (1981), and Pleistocene geology by Tipper (1971).

Local Geology

Ore at Boss Mountain is within the Takomkane Batholith (Figure 2), a composite intrusion comprised of at least four rock types: monzodiorite, quartz monzodiorite, biotite porphyry and hornblende porphyry (Soregaroli, 1968; Macdonald, 1983). All other rock types in the immediate mine area are younger than the Takomkane batholith. Quartz-orthoclase-plagioclase-tourmaline (+ magnetite, sphene) pegmatites cut the batholith. Their age relationship with respect to mineralisation was not established by the authors, although Soregaroli (1968) considers them to be older.

Intrusion of a mafic and felsic igneous complex accompanied mineralisation. Basaltic and basaltic-andesitic dikes were considered by Soregaroli (1968) to be pre-mineralisation but recent mining developments on the surface and underground have revealed that both mafic and felsic intrusion took place during the mineralising event. Mafic intrusion during mineralisation include both tholeiitic and alkali basaltic dikes (Macdonald, 1983). The Boss Mountain Stock, an adamellite or monzogranite (classification of Streckeisen 1973), intrudes the Takomkane Batholith and is considered by Soregaroli and Nelson (1976) to be responsible for the molybdenum mineralisation. Dikes of alkali basaltic composition, related to the Quaternary volcanic centre on Takomkane Mountain, cut all rock types related to the period of mineralisation.

The detailed petrography, petrology and hydrothermal alteration of the lithologies exposed at Boss Mountain are described by Soregaroli (1968) and Macdonald (1983). Minor and trace element (including rare earth) geochemistry of the Boss Mountain Stock and the minor felsic and mafic intrusives are described by Macdonald et al. (in prep.).

Molybdenite Mineralisation

Introduction

Economic and sub-economic sulfide mineralisation at Boss Mountain formed in two morphologies :

- (1) Veins;
- (2) Breccias.

Economic mineralisation has been extracted from breccia bodies and a sheeted vein complex. Both ore types describe partial annuli centred upon the Boss Mountain Stock (Figure 3). In both ore types, molybdenite, with or without gangue minerals, is found as fill, either in fractures in host rock forming veins, or between clasts in rubble piles forming breccias. Molybdenite rarely replaced any rock, with the local exception of biotitised mafic material in the breccia ore.

Vein Paragenesis and Classification

There are three principal vein types at Boss Mountain, defined on textural grounds :

- A. Fine grained, 'sugary';
- B. Fine grained, 'ribbon';
- C. Coarsely crystalline.

There are at least three sets of type A and two each of types B and C, as presented in Table I. Each set is defined by texture, attitude, mineralogy and cross-cutting relationships in the mine. The paragenetic scheme modifies that of Soregaroli (1968).

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Sets (vi) and (vii) are of most importance, not only for economic considerations, but since they are also developed most extensively throughout the deposit and comprise approximately 90% of the vein material.

Sets (i), (ii) and (iii) are essentially identical in character, except for structural attitude. They are found throughout the mine, except in the breccia bodies and the monzodiorite intrusion. They contain pyrite, scattered throughout quartz and local magnetite and molybdenite. When cut by later molybdenite-bearing veins, molybdenite may be deposited within the quartz of the earlier vein for up to 1 cm. A 5 mm selvedge of chlorite-sericite +/- clay is frequently developed in quartz monzodiorite adjacent to vein sets (i), (ii) and (iii).

An early breccia (Phase I Breccia, Soregaroli, 1968) with a comminuted rock flour matrix, contains a number of veins of this type within breccia clasts. Whether the clasts contain veins from set (i), (ii) or (iii) is not clear, but none of the sets cut the Phase I Breccia, indicating that brecciation commenced after set (iii) developed. Set (iv) is identical in every way to set (vii) (described below) except that it is cut by, and therefore predates, set (v).

Set (vi) is horizontal and contains quartz, orthoclase and calcite. The footwall to the vein is, in places, intensely brecciated and overlain by banded, cryptocrystalline quartz and coarsely crystalline calcite.

Late chlorite seams (set (viii)) and calcite (+ quartz, zeolites, set (ix)) veins cut all molybdenum-bearing structures and are considered by Soregaroli (1968) to be unrelated to the ore-forming process.

Set (v) : Coarse Grained Molybdenite Veins

Vein set (va) comprises a sheeted vein complex of parallel to sub-parallel, bifurcating, gently dipping Qz-Mo-Or veins with accessory carbonate (calcite and siderite) and minor fluorite, zeolites, chlorite, sericite and rutile and very minor biotite, amphibole and topaz. A second phase (set vb) is locally developed within the same structure, with an identical mineralogy except that molybdenite is absent and the accessory mineralogy includes a complex sulfide and oxide assemblage : aikinite ($PbCuBiS_3$), bismuthinite (identified by x-ray powder photography; Soregaroli, 1968), chalcopyrite, sphalerite, galena, scheelite and anatase. These are the first veins to cut the Boss Mountain Stock, an indication of relative time of crystallisation. Wallrock alteration adjacent to sets va and vb veins varies from minor sericitisation to intense K-feldspathisation and sericitisation for up to 50 cm. Coarse grained Qz +(Or-Py) veins (set vc), are near vertical and are sub-parallel to the long axis of the breccia ore zone (N35°W). Soregaroli (1968) states that these veins can be traced into the Quartz (or Phase II) Breccia matrix without disruption. Wallrock selvedge alteration is limited to sericitisation of plagioclase feldspar in the quartz monzodiorite host rock.

The set (va) is the most voluminous of the veins in Table I, outcropping within a partial annulus whose external diameter exceeds 1200 m. Veins may be up to 1 m thick, but are typically between 5 and 10 cm, with coarse grained molybdenite selvedges up to 4 cm thick (average 1 cm). The remainder of the vein is filled by coarse grained quartz and, locally, the accessory minerals. Pyrite, where present, may be extremely coarse, developing euhedral cubes with sides up to 8 cm. Vugs are common, filled by zeolites (predominantly stilbite clusters), calcite, clay and, rarely, fluorite. There is textural evidence to indicate that the fractures have filled by crystallisation in open space : the coarse

molybdenite selvages are comprised of aggregates of euhedral molybdenite rosettes or sheafs, exhibiting perfect crystal terminations within the body of the vein (Figure 4); quartz is also coarse grained with no evidence of later quartz introduced after refracturing. Growth planes developed in large (5 cm width) euhedral quartz crystals are locally well preserved, providing additional evidence of open space filling of the veins (Figure 4). Calcite-filled fractures are developed within the quartz, perpendicular to the vein walls.

Set (va) veins, like set (vc), may be traced into the Quartz Breccia without disruption of the minerals. For example, pink K-feldspar selvages in the vein continue into the breccia matrix indicating contemporaneous fill of vein set (v) and the quartz breccia pore space. Apart from differing structural attitudes, there is little difference between veins of set (vc) and set (va). Both contain coarse grained quartz, pyrite + potassium feldspar, although set (vc) ^{veins} are more restricted in space and lack molybdenite.

Molybdenite tenor is commonly variable along strike over short distances within a single vein. It is often apparent that molybdenite is concentrated preferentially in constrictions within veins.

Coarse grained Qz-Mo mineralisation, identical to that found in vein set (va), is in places hosted within relatively steep (>50°), altered dike structures typified by the 'High Grade Vein' of Soregaroli and Nelson (1976, p.440). Field relationships indicate that the minerals deposited during hydrothermal precipitation pass from these structures into the veins of set (v), and not set (vii) as described by Soregaroli (1968); his conclusion was based upon alteration mineralogy, ignoring the similarity in the nature of the quartz-molybdenite mineralisation. The relationship with vein set (v) was suggested initially by Pollmer (1976).

Ribbon Molybdenite Veins

The Qz-Mo ribbon veins of set (vii) are developed throughout the zone of mineralisation, and locally contribute to the ore reserve. The veins are generally steeply dipping (>60°) and have been interpreted by Soregaroli (1968, p.89) to represent sets of conjugate shear planes, with random orientation in a sub-horizontal plane of maximum and intermediate stress axes but a consistent subvertical minimum stress axis. Such a stress distribution is in good agreement with Anderson's (1936) model for structural development of ring dike structures above an intruding pluton. The veins are characterised by fine grained quartz, pyrite and molybdenite with frequent chlorite screens of wall rock incorporated within the vein adjacent to the hangingwalls and footwalls. Molybdenite is typically distributed along thin seams parallel to the vein walls, giving a ribbon-like appearance to the veins when viewed perpendicular to the walls. The veins may be found coincident with mafic dike structures. On the lower levels of the mine, porphyritic felsic dikes cut, and are therefore younger than vein set (vii).

Fluid Inclusion Petrology and Microthermometry

Introduction

Approximately 40 doubly-polished 60µm thick sections from Boss Mountain were studied in detail. Where possible inclusions were investigated in quartz intergrown with molybdenite, based upon the premise that the fluid ^{inclusions} trapped in quartz deposited soonest after molybdenite crystallisation are most likely to reflect the properties of fluids

responsible for the sulfide deposition. In a typical section, inclusions were selected from quartz that crystallised between blades of molybdenite. The euhedral platy molybdenite crystals tended to grow perpendicular to vein walls, sealed by subsequent quartz crystallisation.

Operation of the LINKAM TH600 heating-cooling stage is described by Shepherd (1981). Calibration methods and the chemicals used are discussed by Macdonald and Spooner (1981).

Primary Fluid Inclusions : Petrology

In order to characterise the nature of the fluid responsible for introduction of molybdenite, primary fluid inclusions in vein sets (v) and (vii) were investigated. Roedder (1979, Table 14-1) has described the criteria for the recognition of primary and secondary inclusions, which have been followed in this work. Mineralogical growth zones are rare in Boss Mountain quartz (an example is shown in Figure 4) and did not aid in routine determination of the age of inclusions relative to the quartz host. The principal criteria used in this study to distinguish primary inclusions are :

- (1) occurrence as a single inclusion or a small three-dimensional group, in an otherwise inclusion-free crystal;
- (2) isolated occurrence away from other inclusions for a distance of >5 times the diameter of the inclusion.

At room temperature, the primary fluid inclusions at Boss Mountain can be divided into four groups :

- (1) 2 phase, liquid rich;
- (2) 3 phase, liquid rich;
- (3) 3 phase, vapour rich;
- (4) 2 phase, vapour rich.

The three principal groups (1,2,3) are shown diagrammatically in Figure 5, and examples of each are shown in Figures 6 to 8. Only two inclusions were observed that are two phase, vapour rich (group 4), and are discussed below. It will be demonstrated that groups (2) and (3) are end members of a continuum. Inclusions containing three phases are found ubiquitously in the relationship shown : $H_2O(L)$ wets the inclusion walls and $CO_2(L)$ always surrounds $CO_2(V)$.

None of the inclusions studied from Boss Mountain contain any solid phases. Inclusion abundance is variable from less than 50 in 0.4 mm^2 (a typical field of view) to in excess of a thousand. Negative crystal shapes are present but rare. The fluid inclusions show a wide range in shape and size, from perfect negative crystals (Figure 9) to highly irregular (Figure 10); from the limits of microscope resolution, $<1 \mu\text{m}$, to greater than $50 \mu\text{m}$, with typical size around $15 \mu\text{m}$. The highly irregular inclusions commonly contain considerable quantities of liquid carbon dioxide.

H_2O-CO_2-NaCl Phase Equilibria

In this study, the facilities for selective extraction of fluid inclusion waters for

cation and anion analysis were not available. All further consideration of fluid inclusion compositions, therefore, express the contained salts in terms of equivalent weight % sodium chloride. The effects of the addition of NaCl to the phase equilibria of water are twofold :

- (1) the melting temperature of ice is depressed as a function of NaCl concentration (X(NaCl));
- (2) the pressure and temperature of the critical point is raised as a function of X(NaCl).

The temperature at which carbon dioxide liquid and vapour homogenise is a function of the CO₂ density. A second order least squares curve was fitted to the data of Angus et al. (1973) in the temperature range 26°C-31°C :

$$\text{Density} = 3.69249 - 0.26037T + 0.00495T^2 \dots\dots\dots(1)$$

(correct to five decimal places)

where, T = the CO₂ homogenisation temperature.

The value of CO₂ density is required to calculate mole fraction of CO₂ in an inclusion (see below).

The salinity of inclusions containing both CO₂ and H₂O is obtained from the freezing point depression of CO₂-clathrate (Bozzo et al., 1975; Collins, 1979). For clathrate fusion at the invariant point in the presence of H₂O(L), CO₂(L) and CO₂(V), a least squares fit is derived from the fusion temperature data:

$$\text{Wt. \% NaCl} = 0.05286(10-t)(t+29.361) \dots\dots\dots(2)$$

where t=the final clathrate melting temperature in °C. The equation is valid for 0<wt.% NaCl<16 (Bozzo et al, 1975). The effects on the phase changes described above of addition of other components (e.g. CH₄) will be considered below.

Microthermometric Results

Appendix I contains temperature data on individual fluid inclusions : observed temperatures of phase changes and features such as volume percentage CO₂, and whether an inclusion homogenises into the H₂O-rich or CO₂-rich phase, or by critical homogenisation.

1. Carbon Dioxide Fusion

Upon cooling a three phase inclusion (i.e. either group 2 or 3) the order of observable phase changes is :

- (a) clathration (rarely visible);
- (b) ice formation;
- (c) CO₂ solidification.

The temperatures at which the solid phases form are not useful phenomena for quantitative interpretation, as such small liquid volumes frequently require tens of degrees of undercooling before crystallisation can be initiated (Roedder, 1972). It was qualitatively

observed, however, that ice formed in the -30 to -40°C range (cf. final melting at approximately -6°C) and that CO_2 froze at between -94° and -97°C compared with final melting at approximately -57°C .

The final fusion temperature of CO_2 is a measure of the purity of the phase. In the fluid inclusions at Boss Mountain, fusion of CO_2 was invariant, i.e. at the triple point as solid CO_2 melts to liquid CO_2 in the presence of vapour. It was noted that CO_2 fusion was extremely rapid (virtually instantaneous) even at a low heating rate (0.4°C per minute). This contrasts with H_2O fusion (see below).

The results of the measurement of carbon dioxide fusion measurements are shown in Figure 11. The mean value of -56.9°C (± 0.8 , $n=85$) is in good agreement with the invariant (triple point) melting temperature of pure CO_2 (-56.6°C) confirming that the phase is CO_2 . Of more interest are the values of fusion temperature that depart from the mean value. The LINKAM TH600 is accurate to $\pm 1\%$ (or $\pm 0.6^{\circ}\text{C}$ at this temperature), (Macdonald and Spooner, 1981); i.e. temperatures measured between -56.0° and -57.2°C are not considered to be significantly different to -56.6°C . Temperatures outside this range may, on the other hand, signify impurities in the carbon dioxide. These data indicate 8 measurements between -55.2° and -55.6° and 19 measurements between -57.4° and -59.0°C (out of a total of 85).

The effect of incorporation of an additional component into CO_2 has been described elsewhere for several compounds. For example, the effects of addition of CH_4 to CO_2 have been discussed by Hollister and Burruss (1976). The depression of the temperature of invariant melting is a function of $X(\text{CH}_4)$. The data of Donnelly and Katz (1954) indicate that a freezing point depression of 2.4°C (i.e. -59°C) equates with approximately 10 mole % CH_4 incorporated within the CO_2 . A freezing point of -182.5°C would correspond with pure CH_4 . The same calculations can be performed for other phases (SO_2 , H_2S , SO_2 , etc.). It is not apparent from microscopic observation which phase is responsible for the freezing point depressions - this problem will be addressed below.

Most of the commonly encountered phases in fluid inclusions have triple points less than CO_2 , making it difficult to account for the eight CO_2 fusion temperatures on the high temperature side of the analytical error window (i.e. at temperatures greater than -56.0°C). One exception is water with a triple point of 0.015°C . It is suggested that minute quantities of H_2O dissolved in solid CO_2 may be responsible for the elevated temperatures. That CO_2 and H_2O are somewhat mutually soluble has been documented by Wiebe and Gaddy (1939): "the molal volume of CO_2 in H_2O at 0°C and atmospheric pressure is 28.9 cc/mole." Solubilities at the temperature in question are not reported. No other component reported from fluid inclusions (Roedder, 1972) possesses a triple point that could account for the high fusion temperature.

A single inclusion from sample B-79-193 (Appendix I), that appeared optically identical to a vapour rich CO_2 -bearing (group 3) inclusion did not freeze until -140°C , contrasting with the typical CO_2 undercooling required (to approximately -96°C). The phase was observed to melt at -86°C . Melting was extremely rapid (even at a slow heating rate, 0.4°C per minute) suggesting that only a single component is present. If the melting takes place over a range of temperatures, a mixture of phases may be expected (such as CH_4 and CO_2). We suggest that the inclusion contained H_2S , which has a quoted triple point of -85.5°C (Weast, 1974).

Fusion of Ice

The invariant fusion temperature of pure water is depressed by the addition of another component such as a polar salt, reducing the chemical potential of the solvent. The H_2O - NaCl binary system has been described by Linke (1965) and Potter et al. (1978). Fusion

commences at the eutectic (-20.8°C). The final fusion temperature of ice is related to the weight percent NaCl in solution or the molality of NaCl in solution by the following equations (from Potter et al., 1978) :

$$W_s = 1.76958T - 4.2384 \times 10^{-2}T^2 + 5.2778 \times 10^{-4}T^3 + 0.028 \dots (3)$$

$$M_s = 0.30604T - 2.8598 \times 10^{-3}T^2 + 4.8960 \times 10^{-6}T^3 + 0.007 \dots (4)$$

where W_s = Wt. % NaCl in solution;
 M_s = Mole % NaCl in solution;
 T = Freezing point depression in °C.

If the fluid is carbon dioxide bearing, the formation of the clathrate (which incorporates water and not solutes - see above) raises the apparent salinity of the remaining water in the inclusion that is not bound up by clathration. Fusion temperatures of ice in H₂O-CO₂ - bearing inclusions, therefore, give erroneously high salinity values (Collins, 1979). Figure 12 shows the calculated equivalent weight percent NaCl for the aqueous inclusions using equation (3) above. For comparison, Figure 13 shows apparent salinity calculated from ice melting temperatures in CO₂ - bearing inclusions, giving a higher mean value than for CO₂-free inclusions (8.2 compared with 6.2 equiv. wt. % NaCl).

Clathrate Fusion

The invariant fusion temperature of carbon dioxide clathrate is a function of the salinity of the aqueous fluid in which it is melting (see above). Figure 14 is a histogram of the observed clathrate melting temperatures and Figure 15 shows the calculated salinities using equation (2). The mean value calculated in this way (5.8 equiv. wt. % NaCl) is in good agreement with that calculated from aqueous inclusions (6.0 equiv. wt. % NaCl, Figure 12).

It is often not possible to confirm that fusion is invariant, i.e. in the presence of CO₂(V), CO₂(L), H₂O(L) and clathrate. The principal difficulty is the inability to observe the small quantities of CO₂(L) as a discrete phase, separating CO₂(V) and H₂O(L) in the inclusions. It is possible that sublimation of the clathrate, forming CO₂(V) may occur; i.e. a univariant phase change. The effect of this on the melting observations would be to record a 'fusion temperature' lower than the invariant point for the particular system. Therefore, some of the higher salinity values calculated from clathrate melting temperatures (i.e. from the observed fusion temperatures with the greatest depressions) may be erroneous, but cannot be quantified due to the limited resolution of the optical system of the microscope.

Carbon Dioxide Homogenisation

Figure 16 shows the temperatures at which CO₂ homogenises either into the vapour phase or into the liquid phase. It is apparent that the bulk of the inclusions containing CO₂ homogenising into the vapour phase, do so close to the critical temperature (31.06°C). After taking possible instrumental error into account (+ 0.3°C, Macdonald and Spooner, 1981a), a small number homogenise at $T > 31.1^\circ\text{C}$, indicating that an additional gas component must be present within the CO₂, a phase that has a higher critical temperature, such as H₂S or SO₂.

Two inclusions were observed containing solely CO₂ and homogenised into the liquid phase at significantly lower temperatures (approx. 20°C). The implications of these two inclusions will be discussed below.

Figure 17 shows the CO_2 densities calculated from equation 1 of CO_2 in inclusions when CO_2 homogenisation was observable. The bulk of the data fall around 0.35 g/cc (equivalent to 0.008 mol/cc).

Final Homogenisation Temperature

349 fluid inclusion homogenisation temperatures are shown in Figure 18 for the main stage of vein and breccia mineralisation. The bulk of the data fall between 300 and 350°C. A small number of inclusions gave homogenisation temperatures above 400°C and below 200°C. None of these inclusions differed optically from other inclusions. In Figures 18 and 19 the data are subdivided in two ways :

(1) by composition, i.e. CO_2 -free or H_2O - CO_2 -bearing;

(2) by type of homogenisation, i.e. into the liquid or vapour phases, or critically.

Note (a) that the CO_2 -bearing inclusions are absent from the high and low end members of the measured homogenisation temperatures and (b) that all the lower temperature homogenisations were into the aqueous phase. The lower temperature homogenisations may either (1) reflect the waning stages of quartz crystallisation or (2) be unrecognised secondary inclusions or (3) be unrecognised leaked or necked inclusions. The three higher temperature homogenisation recordings (453°, 516° and 520°C) were found in a sample from the quartz breccia, are CO_2 -free (Figure 18), and homogenise into both the liquid and vapour phases. The relative paucity of data at the higher end of the homogenisation temperature spectrum does not permit much importance to be placed on them. It is possible that the inclusions have leaked, although the occurrence of all three in one sample may be significant.

Although the mean homogenisation temperature is approximately 310°C, the sudden appearance of observed homogenisations at approximately 350°C is of more geological significance, as inclusions with higher homogenisation temperatures are those trapped earliest as the hydrothermal fluid cooled and will most closely reflect conditions under which molybdenite crystallised. The data have a modal class of 300°C and declining frequencies at lower temperatures. The bulk of the inclusions homogenise by aqueous phase homogenisation, the remainder homogenising into the CO_2 -vapour phase over the same temperature range. Individual samples commonly contain adjacent inclusions, some of which homogenise into the CO_2 -vapour phase, the others into the H_2O -liquid phase at the same temperature (Appendix I, Figure 19).

In the same manner, at approximately the same temperature (350°C) CO_2 -bearing inclusions become prominent (Figure 18) with a modal class of 350°C, and declining frequencies at lower temperatures. The bulk of the inclusions homogenising into the vapour phase are CO_2 -bearing inclusions (26 out of 33). Of the small number of inclusions that are aqueous and homogenise into the vapour phase, 5 come from one sample (B-79-193, Appendix I) and will be considered below.

To summarise, the final homogenisation temperature data indicate :

(1) the bulk of the fluid inclusions at Boss Mountain homogenise between 300°C and 350°C;

(2) two fluid composition types were trapped simultaneously, simple H_2O - and H_2O - CO_2 -bearing;

(3) coexisting inclusions may homogenise into both the vapour and liquid phases;

Volume Percentage of Carbon Dioxide

In order to calculate the mole percentage of CO₂ in the fluid inclusions (groups 2 and 3), it is necessary to obtain an estimate of the volume percentage of the gas in an inclusion. The method used is as follows :

- (1) at a temperature slightly in excess of the CO₂ homogenisation temperature (e.g. 40°C) the inclusion is photographed or accurately drawn;
- (2) using a chart of inclusions with various gas to liquid ratios (e.g. Roedder, 1972, p. JJ14) the volume percentage of the gas phase is estimated visually.

The volume percentage estimate for the gas bubble may commonly be in error by as much as 20% as a result of (a) the assumption of spherical shape and (b) a small inaccuracy in estimation of bubble radius has a large effect on the ensuing volume estimate (volume being a function of the cube of the radius). If a more accurate determination of volume percentage of a gas bubble is essential, it is necessary to use a universal stage to examine the inclusion.

Calculation of mole percentage of vapour in an inclusion requires knowledge of the following parameters :

- (1) water salinity;
- (2) density of the aqueous solution;
- (3) volume percentage of CO₂;
- (4) density of CO₂.

Derivation of all the parameters has been discussed in earlier sections, with the exception of (2). Crawford (1981 Figures. 4.1, 4.12) indicates that the value for the density of a solution of 6 weight percent NaCl has a density at the temperature of interest of approximately unity. The uncertainty at this value is approximately 1%, considerably less than the error in estimation of volume percentage CO₂, and may be ignored.

Figure 20 is a histogram of the values of volume percentages determined in the manner described above. Note the considerable variability. The graph includes two inclusions containing 100% CO₂, discussed below.

The calculation of mole % CO₂ is described in Appendix II and is modified from Tourret (1977). Further consideration of the mole % CO₂ is given below.

Gas Analysis of Fluid Inclusions

Six samples of quartz were analysed at the Institute of Geological Sciences, London, for non-condensable gases (N.C.G., e.g. H₂, CO, CH₄, N₂) and CO₂. One gram of hand picked vein quartz is outgassed at 100°C and then heated to 600°C, which is above the temperature at which most inclusions have decrepitated. The fluids from the decrepitated inclusions are removed in vacuo, and analysed by a Vacuum Generators SUPAVAC quadrupole mass spectrometer. The results of the analyses are give in Table II. The optically determined presence of CO₂ is confirmed (Table II) by gas analysis. The measured mole % of CO₂ (1.3% to 3.7%) in the decrepitated fluid inclusions is not quantitatively significant due to the vagaries of trapping immiscible phases. N.C.G. are in all cases below detection limit

(6.28×10^{-4} torr). One sample, B-78-206, was re-analysed, using 10 grams to increase yield. A ratio of N_2 to CH_4 of 23 was determined. No H_2S was found, even though the unmistakable smell of the gas can be detected as Boss Mountain vein quartz is crushed. The nose has a minimum H_2S detectability of 0.025 ppm (Patty, 1962) equivalent to a release from fluid inclusions of approximately 10^{-10} g of H_2S (Roedder, 1972), which in turn is equivalent to 1.4×10^{-6} cc. H_2S is subject to rapid absorption on the stainless steel tubes that pass from the sample chamber in to the mass spectrometer. This is considered to be the reason for the lack of detection.

There is one serious disadvantage with the method described here. All inclusions in the specimen will be subject to decrepitation, regardless of origin. Therefore the analyses of all primary inclusions will be somewhat diluted by secondary inclusions. Optical examination of all the specimens indicates that secondary inclusions are not abundant, although present in places along fractures. The data, however, can only be considered to give a qualitative indication of fluid compositions.

Spatial Variability in Fluid Inclusion Properties

1. Homogenisation Temperature

Investigation of the variability found in homogenisation temperatures (Appendix I) indicates that any particular 2mm diameter chip may contain a range in temperatures that spans the range over which the bulk of the data are found. For example, sample B-78-10 contained 28 inclusions that homogenised between 255° and 344°C. The mean standard deviation of homogenisation temperatures for the samples is 44°C, i.e. two standard deviations equals 88°C, which encompasses over 75% of the data. It is therefore apparent that no well defined spatial variability in homogenisation temperatures can be determined and statistically accepted. The inference is that the veins throughout the deposit (and the breccia bodies) formed over approximately the same temperature range (at least, not over statistically detectable different ranges). Two vein samples were taken at a considerable distance from the centre of molybdenite mineralisation:

(1) B-78-8, from the ridge to the west of the mine, at an elevation of approximately 5700' - approximately 1.2km west of the ore zone;

(2) B-78-104, from a vein cutting the adamellite stock, in Molybdenite Creek, at 7770E, 4950N (mine grid) - approximately 800m east of the ore zone.

Neither of these veins contained molybdenite, but both are texturally and structurally identical to the principal MoS_2 -bearing veins in the mine (i.e. coarse grained quartz, in shallow dipping veins). In addition, both samples are CO_2 -bearing, which it has been noted earlier is characteristic of the main ore forming stage at Boss Mountain. The means (and standard deviations) of homogenisation temperatures for each of the two samples are:

(1) B-78-8 328°C (+ 13);

(2) B-78-104 329°C (+ 40), omitting one anomalously low value;

These samples were each from locations over 1000 m from the bulk of the ore at Boss Mountain (and the bulk of the other samples investigated by microthermometry) indicating no great lateral temperature variations during the principal mineralising stages. Similarly, no variation is found with depth.

2. Variation in Fluid Composition

No spatial variability could be detected for fluid salinity, expressed in terms of equivalent weight % NaCl. A spatial variation was observed, however, in the number of CO₂-rich inclusions (those that homogenise into the vapour phase, in general equivalent to group 3 inclusions) in the quartz from the levels below the 5045' elevation (the 'main' level).

Veins of Stage (v) are sparse and poorly mineralised on the lower levels. They are identified on the basis of coarse grained quartz + K-feldspar, with local MoS₂ selvages, in a structural attitude concordant with the partial annulus described earlier (Figure 3).

Quartz from 11 vein and breccia samples was investigated from these lower levels and it was found that in the breccia pipe CO₂-bearing inclusions (that are vapour-phase homogenising) are rare to absent on the 4440 level, but present above; in the vein inclusions of this type (group 3) are present in samples from the 4686 level, rare on the 4636 level and rare to absent on the 4440 level. The transition is summarised and shown diagrammatically in Figure 21. Nearly all inclusions observed on these lower levels (4636 and 4440 elevations) contained minor quantities of CO₂(L+V), but do not homogenise into the vapour phase, indicating that they were not trapped as a CO₂ vapour phase, but rather as a single phase mixed H₂O-CO₂ fluid.

Composition of the Gas Phase

Microthermometric analysis indicates the presence of almost pure CO₂, with a small number of measurements indicating dissolved H₂O (i.e. those with a carbon dioxide fusion temperature >-56.6°C). Another subset of CO₂-bearing inclusions contains an additional dissolved component that depresses the fusion temperature by as much 2.4°C, to -59°C. The additional component(s) must therefore possess a triple point less than that of CO₂, e.g. H₂S, CH₄, CO, N₂. Methane is a common component of fluid inclusions (Roedder, 1972), especially in low-grade metamorphic rocks (Mullis, 1979), graphite-bearing high grade metamorphic rocks (Touret, 1974; Swanenburg, 1980) but only very rarely in the gangue minerals of ore deposits (e.g. Renison Bell tin deposit, Patterson et al., 1981). The single fluid inclusion sample analysis producing a quantitative yield for CH₄ gave an N₂/CH₄ ratio of 23, suggesting that CH₄ is not a significant component of the gas phase at Boss Mountain. One inclusion was found to contain H₂S, which is also detectable, by smell, upon crushing vein quartz. This may indicate that H₂S is the component responsible for CO₂ fusion depression.

Three adjacent inclusions were found that homogenised into the liquid phase at between 20 and 21°C, corresponding to a density of approximately 0.8 g/cc (Angus et al., 1973). These contrast considerably with the bulk of the CO₂-bearing inclusions which homogenise into the gaseous CO₂ phase, with densities around 0.35 g/cc. From Angus et al. (1977), the isochore of the 3 anomalous inclusions is considerably different from that of the bulk of the data, being much steeper, indicating entrapment at a higher pressure. If these inclusions are not some artifact of an unrecognised secondary process, they must have a different history from the bulk of the CO₂-bearing inclusions.

Carbon Dioxide Effervescence

Several observations, described earlier in this chapter, are pertinent to an understanding of the phase chemistry of the hydrothermal fluid responsible for molybdenite mineralisation:

- (1) the variable volume percentage CO₂ found in the inclusions (Figure 20);
- (2) coexisting inclusions above the 4440' level homogenising into both the vapour and liquid phases;
- (3) the spatial proximity of both sets of coexisting inclusions in (2);
- (4) the same homogenisation temperature ranges of both sets of inclusions in (2);

These data indicate that, above the 4440ft (1353m) level two phases coexisted; CO₂ and an aqueous fluid of low salinity. Hence, the single phase fluid from depth underwent CO₂ separation (effervescence). The process is analogous to boiling in the purely aqueous system, but in addition to phase separation involves component removal. Inclusions in quartz that crystallised in a two phase, polycomponent fluid may therefore trap variable proportions of the phases and components over a particular temperature range.

An important consequence of the interpretation is that the hydrothermal fluid deposited quartz whilst upon a solvus in the CO₂-H₂O-NaCl system. Hence, (i) homogenisation temperatures are equal to trapping temperatures and, (ii) if the immiscibility relations are known accurately as f(T,P,X), a particular temperature has one unique corresponding pressure.

A corollary of the observation that effervescence has been prominent throughout the upper part of the deposit, coincident with random trapping of variable ratios of the components during crystallisation, is that measurements of volume % CO₂ in an inclusion after effervescence has occurred, bear little relationship to that in the original hydrothermal fluid. Volume percent CO₂ (and hence volume % H₂O+NaCl) is a crucial value in the calculation of mole % CO₂ in the primary hydrothermal fluid, which in turn is necessary for the use of the solvus to place constraints upon pressure as a function of temperature. It is singularly fortunate that at Boss Mountain a horizontal plane has been determined at the 4440ft (1353m) level below which effervescence is extremely rare to absent and above which it is common, i.e. such a plane approximates to the level at which the hydrothermal fluids encountered the solvus in the H₂O-CO₂-NaCl system. We infer that the physical and chemical properties exhibited by fluid inclusions on the 4440ft level (Figure 21) are a good approximation to the properties of the single phase hydrothermal fluid prior to effervescence.

Estimation of the H₂O:CO₂:NaCl composition of the single phase hydrothermal fluid

The following is a synthesis of the pertinent fluid inclusion data from the 4440ft level, for the calculation of X(CO₂):

| | m. s.d. | n |
|--------------------------------|------------|----|
| vol % CO ₂ | 15 (+11) | 12 |
| density CO ₂ (g/cc) | 0.35 | 1 |
| Salinity (ew% NaCl) | 6.7 (+1.5) | 18 |

Volume % CO₂ was optically determined from 12 inclusions and is subject to considerable error as described above. The density of CO₂ was calculated from the homogenisation temperature of CO₂(L+V) in one inclusion, the only inclusion where the measurement could be determined reliably. The determined density agrees well with the densities calculated throughout the deposit. Salinity was calculated from the depressions of CO₂ clathrate fusion temperatures. The value agrees, within uncertainty, with the calculated salinity throughout the remainder of the deposit of 6 weight % equivalent NaCl. Using the equation,

modified from Tourret (1977) described in Appendix II, the mole percentages of the three principal components (H₂O, CO₂ and NaCl) are :

- X(H₂O) : 94.5%
- X(CO₂) : 3.6%
- X(NaCl) : 1.9%

The error on the calculated mole fractions may be considerable, particularly due to the difficulty in estimating volume percent CO₂ in a fluid inclusion.

Estimation of Fluid Pressure

As there is no detectable temperature variation throughout the deposit, either laterally or vertically, the fluid intersected the solvus in the CO₂-H₂O-NaCl system by decompression, as it flowed upwards.

From the data of Franck (1977) a unique pressure exists at which effervescence will occur if (a) the temperature is known, (b) if the mole fractions of the components have been determined and (c) if it can be assumed that the physical process involves either decompression or pressure increase. In this case, decompression is considered to be most likely (Toulmin and Clark, 1967). Figure 22 shows the trace of the phase boundary for a fluid of composition : 94.1 H₂O, 4.0 CO₂, 1.9 NaCl (mole percentages). A temperature of 350°C (from homogenisation temperature data) corresponds to a pressure of 350 bars.

It is estimated, therefore, that the hydrothermal solution at Boss Mountain underwent effervescence at a temperature and pressure of approximately 350°C and 350 bars, respectively. Knowledge of the formation pressure permits calculation of the possible depth of formation, depending upon whether the quartz in the veins and breccia pipes crystallised under lithostatic or hydrostatic pressure or an intermediate pressure.

Pressure is related to depth by:

$$P = \rho \cdot g \cdot H \dots\dots\dots(5)$$

- where P = pressure, in Nm⁻²
- ρ = density of the medium in kg m⁻³
- g = acceleration due to gravity = 9.81 m sec⁻²
- H = depth in m.

A rock of the composition of the Takomkane batholith has a density of approximately 2700 kg m⁻³ (Daly et al., 1966). Assuming that this rock type continued up to the palaeo-surface during mineralisation, a depth corresponding to lithostatic pressure conditions is given by:

$$H = \frac{350 \times 10^5}{2.7 \times 10^3 \times 9.81}$$

$$= 1.3 \text{ km.}$$

If on the other hand, the pressure is due to a hydrostatic column, assuming $\rho(\text{water}) = 700 \text{ kg m}^{-3}$, H is similarly calculated to equal 5.1 km calculated using the data of Potter and Brown (1977), assuming a linear variation in temperature with depth .

The relative merits of the two possible models may be assessed by considering how each can

be related to the structure of the mineralised zones shown in Figure 3.

Scenario I : Lithostatic Pressure

If the hydrothermal fluid was under lithostatic pressure, it did not vent to surface, at least directly. This implies that both the sheeted vein complex and breccia bodies were not connected to surface through large openings. From knowledge of the sheeted vein complex, this is quite reasonable. The complex is less than 200 m thick, an inverted saucer shape, and would not be predicted to intersect the surface if mineralisation occurred at a depth of 1.3 km. There is not such good geometric control on the main breccia pipe which breaches present-day surface. The South Breccia pipe, which formed contemporaneously with the main breccia pipe (Soregaroli and Nelson, 1976) does not however, reach present surface, but gradually passes into Phase I Breccia. It can be reasonably suggested that the main breccia pipe could have shown a similar impersistency with elevation.

It was noted that the depth of 1.3 km is only a maximum. If the depth were greater than 1.3 km and pressure was lithostatic, the pressure due to the overlying rock would be greater than that within the veins (350 bars) and the veins could not remain open. On the other hand, it is possible that pressure in the veins was 350 bars at a depth of less than 1.3 km, but not at a sufficiently shallow depth such that the fluid overpressure greatly exceeded the tensile-strength of the rock. It should be noted that under this scenario, opening of the veins could be aided by hydraulic fracturing, superimposed upon the stress field caused by the Boss Mountain Stock, or by thermal contraction due to cooling.

Scenario II : Hydrostatic Pressure

Under the hydrostatic pressure scenario, the veins and breccia pipe were connected to the surface from 5.1 km. The sub-horizontal sheeted vein complex would then be subjected to a lithostatic load of approximately 1.35 kbar (from equation 5). It is unreasonable to expect shallow dipping veins to remain open, filling with molybdenite and gangue minerals at a fluid pressure of approximately 350 bars in the presence of a lithostatic over-pressure of 1 kbar. The vein fractures, upon forming, would be expected to re-close in response to this pressure differential. There is no evidence of extensive pinch and swell structures in the veins, which could provide effective 'room and pillar' support. In addition, blocks of wall rock that could bridge open the veins are absent.

On the basis of these considerations, a model of mineralisation with fluids venting directly to surface may not be totally rejected. Scenario II, however, is the least acceptable as subhorizontal veins in the sheeted complex could not remain open at a depth of 5.1km.

Aqueous Phase Boiling

As described earlier, a number of coexisting, single component, aqueous phase fluid inclusions were observed that homogenised into both the liquid and vapour phases. These were found in two samples :

- (a) B-79-193(H.W.) : vein;
- (b) B-78-118 : quartz breccia.

The four inclusions in (a) were found in a chip taken from the hanging wall of the vein and homogenised at temperatures between 270° and 313°C, with normal salinities (i.e. approximately 6 wt.% equiv. NaCl). From the data of Sourirajan and Kennedy (1962), boiling under these conditions would occur at a pressure of less than 150 bars, differing

considerably from the 350 bar estimate derived from H_2O-CO_2-NaCl phase equilibria. There are two explanations of this phenomenon :

- (1) the inclusions have leaked or necked;
- (2) a sudden drop in pressure initiated boiling.

Explanation (1) is preferred, as only four inclusions were found which gave these results. It is unreasonable to suggest that a sudden drop in pressure, by, for example, breaching of the fluid to surface, inducing boiling in response to decompression, would not be recorded throughout the deposit in several samples.

Three coexisting inclusions in B-78-118 homogenised into the vapour (2) and liquid (1) phases at between 450 and 500°C. It is interesting to note that a water containing 6 wt. % equiv. NaCl, at a pressure of 350 bars, would boil at 425°C (Sourirajan and Kennedy, 1962). Once again, however, it is not acceptable to present a hypothesis based upon three data points, and we assume the inclusions have either leaked or necked down.

Relevance of Quartz Hosted Fluid Inclusions to Molybdenite

Throughout the preceding discussion, all fluid inclusion data presented have been from quartz. The validity of extrapolating physical and chemical inferences to molybdenite, when considering solution chemistry, must be evaluated.

Within the scope of the analytical facilities available for this study, no single line of evidence indicates conclusively that the fluids responsible for quartz crystallisation are identical to those from which molybdenite was deposited. A number of facts are, however, consistent with this hypothesis:

(1) Sample B-79-193 consists of a 4 cm vein with 1/2 cm MoS_2 selvages and 3 cm of vein quartz fill. Chips were investigated from the vein foot- and hanging-walls and from the vein centre. In all three cases, fluid compositions (i.e. salinity, presence of CO_2 in some inclusions etc.) and homogenisation temperatures are similar, indicating that during vein filling, the fluid properties did not change appreciably, with the exception of a small number (4) of inclusions in the central portion of the vein with homogenisation temperatures less than 200°C.

(2) In a few localities, MoS_2 not only coats the vein walls as selvages, but is found within the vein as isolated sheafs that have crystallised on quartz. The sulfur isotopic compositions of molybdenite from the hanging- and foot-walls and vein centres are statistically indistinguishable (see below), indicating that there was no change in the sulfur isotopic composition of the fluid between the time of vein wall and vein centre deposition to disturb the isotopic fractionation between it and the crystallising sulfide.

(3) Similarly, hydrogen isotopes were analysed from the fluid inclusions in both molybdenite, pyrite and quartz and are identical (see below) indicating that the hydrogen isotopic composition of the fluid from which both quartz and molybdenite crystallised was the same.

(4) The euhedral crystal terminations of molybdenite sheafs that grew from vein walls into the vein centre are perfectly preserved, as opposed to being corroded. This implies that the fluid responsible for depositing quartz onto molybdenite was in chemical equilibrium with the sulfide. Disequilibrium would be manifested by corrosion of molybdenite euhedra.

Implications for the solution chemistry of the hydrothermal fluid

Smith and Norman (1980) and Smith (written communication, 1981) have calculated the high temperature speciation of oxidised aqueous molybdenum species from thermodynamic properties (at S.T.P.). The calculations were based upon buffering of the O and S fugacities by the magnetite-pyrite-hematite or nickel-nickel oxide-pyrite-pyrrhotite assemblages. The dissociation constants for twelve Mo species were considered, including hydroxy, chloride, sulfide and fluoride complexes of hexavalent Mo and the chloride complex of pentavalent Mo. In addition, the solubilities of molybdenite at 250°, 300° and 350°C were calculated. The conclusions from the thermodynamic analysis are:

- (1) chloride and sulfide complexes are not important in the transportation of molybdenum;
- (2) Mo may be transported in significant quantities as HMoO_4^- , with lesser amounts transported as H_2MoO_4 ;
- (3) the solubility of MoS_2 is temperature dependant; several thousand ppm Mo may be transported at 350°C, with solubility decreasing by over two orders of magnitude upon cooling to 250°C;
- (4) fluorine is not necessary for Mo transportation in hydrothermal solutions although it can have a significant effect at high temperature and low pH.

Conclusion (4) is supported by recent experimental data (Candela and Holland, 1981) on the effect on Mo partitioning between a silicate melt and a fluorine- (or chlorine-) bearing aqueous fluid. Chlorine shows no effect and fluorine causes only a slight increase in the partition coefficient, and only if fluorine is present in high concentrations (e.g. 2.5 wt. % NaF in the charge). As a result, Candela and Holland (op. cit.) consider that "fluorine is probably not very important in the formation of magmatic hydrothermal Mo deposits". The common association of fluorine-bearing minerals with Mo deposits (Wallace et al., 1968; Wallace et al., 1978) is a result of the "geological processes which concentrate Mo also being those that are responsible for concentrating F". Candela and Holland also point out that the "field association of a metal, such as Mo (or W) with an anion (such as Cl^- , F^- , CO_3^{2-}) does not necessarily imply complexing of the metal by that particular ligand."

In summary, both the theoretical and experimental data on the aqueous chemistry of molybdenum, as it pertains to hydrothermal ore solutions, is in a youthful stage of development. Halide and sulfide complexing do not appear to be important contributors to Mo transport in the solutions.

At Boss Mountain it has been noted that, above the 4440 ft elevation, carbon dioxide effervescence occurred. Molybdenite has only been found in the veins above this level and Mo grades in the breccia pipe at the 4440ft level (Figure 21) are low compared with higher levels; i.e. the magnitude of Mo grade exhibits a direct relationship with effervescence in the hydrothermal fluid. This empirical observation may shed some light on molybdenum transport at Boss Mountain, in particular, and Mo-deposits in general.

CO_2 effervescence will cause two principal effects upon the species in the hydrothermal solution :

- (1) pH change, due to the break down of $\text{CO}_2\text{-H}_2\text{O}$ acid species, such as carbonic acid H_2CO_3 ; if CO_2 is lost, pH may increase as free H^+ ions are removed from solution;
- (2) any species that was associated with CO_2 by, for example carbonate complexing, may be

destabilised.

We are not able to assess the effect of CO_2 effervescence at Boss Mountain upon the solubility of Mo in the remaining fluid as the Mo content of the hydrothermal fluid is not known. Smith and Norman (1980) indicate that an order of magnitude change in pH is accompanied by only a factor of two change in molybdenum solubility in their modelled system. We suggest that the spatial relationship between MoS_2 precipitation and CO_2 effervescence may indicate a chemical association between the two. The possibility of Mo transport in hydrothermal solutions as a carbonate complex requires experimental testing. At this stage the hypothesis may only be suggested, but it is interesting to note that the artificial formation of molybdenite in the laboratory is "by heating a molybdate or molybdic oxide with sulfur or hydrogen sulfide and an alkaline carbonate" (Palache et al.: Dana's System of Mineralogy, 1944). Preliminary experimental results suggest that molybdenum solubility may be increased substantially in carbonate-bearing fluids (Richardson, C., personnel communication, 1984).

Carbonate complexing has been considered briefly for other species. Poty et al. (1974) have reported that unmixing of a CO_2 - H_2O solution accompanied pitchblende (plus quartz, marcasite and pyrite) deposition in veins and altered pods at Limousin, in the Saint-Sylvestre granite of the Massif Central, France. Poty et al. (op. cit.) state that this suggests transport of uranium as uranyl carbonate complexes and deposition due to effervescence, although they do not fully understand reduction of the uranyl ion.

Rare earth elements form carbonate complexes, responsible for certain vein and pegmatite bodies deposited from relatively alkaline solutions (Kosterin, 1959). Kerrich and Fyfe (1981) have suggested that gold in hydrothermal fluids may complex with a carbon and oxygen ligand to form a carbonyl complex. Experimental verification of the hypothesis is currently (1983) in progress. Evidence from fluid inclusions led Higgins (1980) to suggest that tungsten is transported in hydrothermal fluids by a carbonate complex.

The likelihood of transition elements forming carbonate complexes has been questioned for some time, as the other C-O complexing ligands, the oxalates, are all more stable (Jorgensen, 1963) and would, it is inferred, form preferentially. Projection of low temperature thermodynamic data to elevated temperatures indicates that formation of metal ion carbonate or bicarbonate complexes is inhibited (Helgeson, 1964). The arguments are uncertain as stability is dependant upon relative atomic sizes and upon which bond angles are amenable to complex formation. Cobalt, for example, does form a bright green carbonate complex ($\text{Co}(\text{CO}_3)_2^{2-}$) that is "an excellent starting material for other cobalt (III) complexes" (Jorgensen, 1963, p.81). From the information of Palache et al. (1944, see above), a molybdeno-carbonate complex may be an excellent starting material for the formation of molybdenite. Molybdenum carbonate complexes are not mentioned in the literature; experimental verification or repudiation of their relevance in hydrothermal transportation is sorely needed.

To conclude this discussion, an hypothesis is presented for transportation and precipitation of molybdenum at Boss Mountain :

- (1) Mo was transported in the hydrothermal fluid as a carbonate complex;
- (2) intersection of the solvus in the H_2O - CO_2 - NaCl system, due to decompression, destabilised the complex with the ligand separating as CO_2 ;
- (3) the cation component of the complex (Mo) combined with reduced sulfur in the hydrothermal fluid to form insoluble molybdenite;

(4) pH increase could also have been a factor in MoS₂ precipitation.

Comparison with Other Molybdenum Deposits

Temperatures and pressures of formation (estimated principally from fluid inclusion analyses) and fluid compositions for molybdenum deposits described in the literature are given in Table III :

Note that the Boss Mountain data (approx. 350°C, 350 bars, 2 - 8 equiv wt. % NaCl (equivalent) and presence of CO₂) are very similar to those of most of these deposits, with the exception of the Henderson formation temperatures. The temperature range over which the deposits are interpreted to have formed corresponds well with the theoretical calculations of Smith and Norman (1960) that indicate Mo solubility decreases by two orders of magnitude between 350 and 250°C. Carbon dioxide also appears to be a common occurrence in fluid inclusions associated with mineralisation. Although few authors stress the point, it can be interpreted from their descriptions that CO₂ effervescence has accompanied mineralisation at Climax (Hall et al., 1974) and Buckingham (Blake et al., 1979), where CO₂-bearing inclusions homogenise into both the liquid and vapour phases.

The wide variability in CO₂ volume percentages has not been described from other deposits, although Kamilli and Ohmoto (1979) found a wide variation in liquid to vapour ratios in inclusions trapped during H₂O boiling, a physical process analogous to effervescence. Variability in volume percentages of the two components (CO₂ and H₂O) in the case of effervescence, or the two phases (liquid and vapour) in the case of boiling, can only occur if the vapour phase bubbles are smaller than the inclusion volume. Bubbles are only small close to the position of phase separation, above which their size increases by diffusion of the immiscible component (or phase) into the bubble. This is additional evidence for the intimate association between the Boss Mountain mineralising event and the onset of effervescence.

The empirical association of CO₂ with sulfide mineralisation in Mo deposits does not on its own demonstrate a chemical (? complexing) relationship (cf. Candela and Holland, 1981). The correspondence of CO₂ effervescence in the hydrothermal fluid with mineralisation is, however, consistent with Mo-carbonate complexing as a means for hydrothermal metal transport.

STABLE ISOTOPE GEOCHEMISTRY

Introduction

At Boss Mountain, the principal sulfide phases are pyrite and molybdenite, and the most abundant associated gangue minerals are quartz, calcium carbonate and potassium feldspar. Four sets of stable isotopic ratios were investigated with the objective of determining the possible sources of these elements :

- (1) oxygen in quartz, calcite and potassium feldspar;
- (2) hydrogen from fluid inclusions in quartz, pyrite and molybdenite;
- (3) carbon in carbonate;
- (4) sulfur in pyrite and molybdenite.

Oxygen and Hydrogen Isotopes : Introduction

Samples of quartz, calcium carbonate, potassium feldspar, molybdenite and pyrite, were

selected from the main stage of vein mineralisation (set va) and crushed in a pestle and mortar to about 1mm diameter. Approximately 1g of pure mineral separate (3g for D analyses) was hand picked, under a binocular microscope, taking care to avoid any contamination, and sealed in glass vials. Carbonate samples were analysed in two laboratories, the University of Waterloo isotope laboratory in Canada and the Hebrew University of Jerusalem isotope laboratory in Israel. Quartz and potassium feldspar samples were also analysed in Jerusalem for oxygen isotope values. Hydrogen isotopic data were obtained from fluid inclusions in quartz and sulfides at the University of Tübingen isotope laboratory, Germany. D/H ratios were also obtained in Tübingen from sulfide samples.

Oxygen and Hydrogen Isotopic Determinations : Analytical Methods

Standard analytical techniques were employed by each isotope laboratory, described by Clayton and Epstein (1958) and Clayton and Mayeda (1963) for silicate oxygen, and McCrea (1950) for carbonate oxygen. Determination of δD values is performed on H_2 gas obtained from fluid inclusion waters trapped in either sulfides or silicates. The analytical method is described by Bigeleisen et al. (1952). Precision, determined by analysing repeats, averaged $\pm 2\%$, ranging from 0 to $+3\%$. D/H ratios were not obtained from two of the sulfide samples due to insufficient fluid yields.

Results of Oxygen and Hydrogen Isotopic Determinations

Oxygen isotope values for quartz, calcium carbonate and potassium feldspar are presented in Table IV. The isotopic ratios for quartz and feldspar cover a small range, while those for carbonate are considerably more varied, with one particularly light sample ($\delta^{18}O = +4\%$). δD ratios are also tabulated in Table IV. Oxygen and hydrogen isotopic data from individual quartz samples are shown in Figure 23. Fluid inclusions in quartz exhibit a considerable range in δD , from -80 to -120 (40 per mil). The sulfide fluid inclusion δD values also fall within this range. Note the relatively small $\delta^{18}O$ variation, contrasting with a large range in δD in the same samples. Also shown is the primary magmatic water box, defined "somewhat arbitrarily as the calculated H_2O in equilibrium with 'normal' igneous rocks or magmas at $T > 700^\circ C$ " (Taylor, 1979, p.247). The diagram also includes the meteoric water line of Craig (1961) and the approximate range of present day meteoric water in the Boss Mountain region of British Columbia based upon the data of Friedman et al (1964) and Dansgaard (1964). Boss Mountain meteoric waters are presently light due to the fractionation effects of both latitude and altitude. Increases in both latitude and altitude induce lighter (lower δD and $\delta^{18}O$) values in the precipitation.

The meteoric water values for Boss Mountain during the mineralisation period (approximately 100 Ma.) are not well constrained. Margaritz and Taylor (1976) have calculated that the Tertiary to Mesozoic δD of meteoric water responsible for alteration (commonly sericitisation) in the Coast Range Batholith of Central B.C., is -120 ± 20 per mil, assuming $T = 500^\circ$ to $200^\circ C$. These ratios are not significantly different from those found in modern Coast Range meteoric waters (-110 to -130 per mil). It is inferred, therefore, that, within the limitations of the data, the isotopic composition of meteoric water at Boss Mountain has also not significantly changed since the Jurassic.

Hydrogen and oxygen isotopic composition of fluids in equilibrium with crystallising quartz

As the ^{18}O fractionation between quartz and water is temperature dependent, the oxygen

isotopic ratios of waters in equilibrium with quartz at 350°C can be calculated using the experimentally derived equation of Matthews and Beckinsale (1979) to calculate isotopic fractionation factors (α):

$$10^3 \ln \alpha (\text{SiO}_2 - \text{H}_2\text{O}) = 3.05 \times 10^4 T^{-2} - 2.09$$

Using this equation, the oxygen isotopic ratios of waters in equilibrium with quartz at 350°C have been calculated and plotted in Figure 23, with their corresponding δD values.

Interpretation of Oxygen and Hydrogen isotopic composition of carbonate and feldspar

The mean $\delta^{18}\text{O}_{\text{Kfs}}$ = 8.5 \pm 0.2 per mil and the mean $\delta^{18}\text{O}_{\text{Qz}}$ = 9.8 \pm 0.2 per mil; i.e. the Δ (Qz-Kfs) ranges from 1.7 to 0.9 per mil. The effect of oxygen isotopic fractionation between quartz and alkali feldspar has been determined by Bottinga and Javoy (1973). The Δ (Qz-Kfs) range corresponds with a temperature range of approximately 700° to 480°C, which is in excess of the temperature indicated by fluid inclusion investigations. Assuming that the determination of Bottinga and Javoy is correct, there are two possible explanations :-

- (1) Isotopic speciation takes place prior to crystallisation;
- (2) Quartz and alkali feldspar did not crystallise in isotopic equilibrium.

There is no textural evidence to indicate that quartz and feldspar are in disequilibrium (although this is the most plausible explanation for the apparent disparity).

The $\delta^{18}\text{O}$ (carbonate) values show a wide range (+4 to +12.5%) which may, again, be due to disequilibrium, or a re-equilibration with later, isotopically different fluids. The data are unable to distinguish between these options. The carbonate samples were selected, however, from intergrowths with quartz, feldspar or sulfides, in an attempt to obtain the highest probability of equilibrium.

It is worthwhile comparing the $\delta^{18}\text{O}$ values determined for carbonates and silicates in the same specimen (Table IV). Samples B-79-59 and -324 have approximately equal oxygen isotopic values in quartz and coexisting carbonate. According to the extrapolated data of Bottinga and Javoy (1973), if these samples formed in isotopic equilibrium, the formation temperature would be approximately 1000°C. Such a temperature is unreasonably high for a hydrothermal solution that may have derived heat from a granitic source. Sample B-79-0 also indicates disequilibrium between coexisting quartz and carbonate, as the carbonate has preferentially concentrated the heavier isotope, in opposition to the equilibrium fractionation. Only sample B-79-75 gives a formation temperature, based upon oxygen isotopic fractionation, that is consistent with the fluid inclusion data (380°C).

We suggest that even though considerable care was taken to obtain oxygen isotopic values on carbonate and silicate samples that crystallised in close juxtaposition, isotopic equilibrium between phases was not always achieved nor maintained. In addition, the wide range of values exhibited by carbonate, contrasting with the silicates, suggests that carbonate may readily re-equilibrate with other, isotopically distinct fluids.

Interpretation of the Oxygen and Hydrogen isotopic composition of Quartz

Any model for the origin of the hydrothermal fluid responsible for quartz and sulphide deposition at Boss Mountain must account for the large range in deuterium data and correspondingly small range in oxygen isotopic ratios with respect to SMOW. Two models are

presented here, based upon two possible end-member compositions of the hydrothermal fluid. Either the fluid was of approximately composition B (Figure 23) and by some mechanism fractionated to heavier δD values, or, vice versa, a fluid of composition A fractionated to lighter, more negative δD values.

Another suggestion could be that the large range in δD may be due to some unknown problem inherent in the analysis of the waters contained within fluid inclusions. This aspect of mineral deposits studies is still in its infancy and it would be premature to assume that the systematics are completely understood.

Possible mechanisms for the two models are :

Model (1) : the hydrothermal water can become preferentially enriched in the heavy isotope by phase separation of a hydrogen-bearing species, such as CH_4 , H_2S or H_2 ;

Model (2) : incorporation of a small volume of isotopically light water (with respect to water with 'magmatic' isotopic characteristics) into the magmatic system can have a pronounced effect upon the D/H ratio but little on the $^{18}O/^{16}O$ ratio.

Model 1. Taylor (1974, p.847) has described some of the fractionation effects of phase separation as a function of temperature. For example, at 400°C, H_2O will be 400 per mil heavier in D than coexisting H_2 gas. For methane-water, the maximum enrichment of the water is 74 per mil (Bottinga, 1969). If carbon is present in the system (as it is at Boss Mountain) under reducing conditions, methane generally will be an enormously more important constituent than H_2 gas (Taylor, 1974, p.847). Little CH_4 was detected in Boss Mountain fluid inclusions, although it could be argued that phase separation was efficient and complete, with CH_4 escaping from the system before being trapped in inclusions. Taylor (1974) shows, however, that +20 per mil change in the δD ratio of the hydrothermal fluid would require that 30% of that fluid reacted with a carbon species to make methane, which may be possible if the fluid encountered abundant hydrocarbons (e.g. Eugster and Skippen, 1967). There is no evidence of such a hydrocarbon source at Boss Mountain.

Model 2. Meteoric water may be incorporated into a magmatic system in two ways:

(a) diffusion;

(b) contamination, by assimilation of altered country rock.

Meteoric water is not able to flow through major conduits into the magma chamber as it is under essentially hydrostatic pressure, contrasting with the magma at lithostatic pressure (2.5 to 3 times higher than hydrostatic). Any major fractures that intersected the magma chamber would be filled by igneous material. Therefore water that passes into a magma chamber can only do so by the rate controlling step of grain boundary diffusion up a thermal gradient, through the hornfelsed contact zone and into the chamber.

Isotopically light water may also be introduced by stoping and subsequent exchange with, or assimilation of, hydrothermally altered roof rock (c.f. Burnham, 1979). Under equilibrium conditions at 200° to 500°C, H_2O strongly concentrates deuterium with respect to hydroxyl-bearing minerals, common to alteration zones (Taylor, 1977). Assimilation of this material during, for example, intrusion of the magma into a higher level by stoping, will add an isotopically light component to the magmatic reservoir.

Both methods described here to introduce a 'light' component into the magmatic system may generate large variations in δD values, but little change in oxygen isotopic ratios, as

the silicate melt contains a large reservoir of oxygen which predominates over any introduced oxygen. On the other hand, the magma contains relatively little hydrogen and is therefore sensitive to the incorporation of small quantities from another source. The variation in δD values will only be apparent if the introduced water has a markedly different isotopic ratio than magmatic values. At Boss Mountain, the proposed meteoric values differ considerably from accepted magmatic values (Figure 23).

Under these two scenarios within model 2, the final δD value of the magma (and ensuing hydrothermal system) may (a) approach the value of the meteoric δD if the introduction of the water is by diffusion, or (b) may even be lower than that of meteoric water if incorporation of considerable volumes of stopped material occurs, owing to the fact that OH-bearing minerals may contain extremely light δD values due to fractionation between the mineral and water, described above.

Taylor (1977, p.526) has indicated that small water:rock ratios (<0.01, by weight) are sufficient to lighten the hydrogen isotopic composition of minerals (i.e. make the δD value more negative) and by inference, coexisting water in a granodiorite by 60 per mil without significantly altering the oxygen isotope ratios, if the introduced water is sufficiently light in deuterium. His model uses a meteoric δD of -120‰, which is similar to that proposed for Boss Mountain, where the observed range is 40 per mil.

There is no direct evidence to support introduction of the fluid by diffusion or by contamination through assimilation, except to point out that xenolithic material, though present in the Boss Mountain stock, is rare and volumetrically insignificant. It is, therefore, suggested that Model 2 represents a scheme consistent with the large range in hydrogen isotopic values, with little variability of oxygen values. Equally possible, however, is a depletion of the liquid phase due to deuterium loss in a gas phase such as H_2S .

Comparison of Oxygen and Hydrogen isotopic data with other deposits

Fluid inclusion hydrogen isotopic compositions have only been investigated in detail for a relatively small number of vein or porphyry mineral deposits: Pasto Bueno (Landis and Rye, 1974); Climax (Hall et al., 1974); Casapalca (Rye and Sawkins, 1974); Butte (Sheppard and Taylor, 1974); Copper Basin (Blake et al., 1979); Panasqueira (Kelly and Rye, 1979); Gonnarow (Bray, 1980). The results of some of these studies and the Boss Mountain data are compared in Figure 24. Data for Panasqueira are not shown as δD and $\delta^{18}O$ values were not determined upon the same samples, but are discussed below. It is apparent that many of the deposits show a considerable isotopic variability. Interpretation of these data have either invoked water-mixing or phase separation models: at Pasto Bueno, Landis and Rye (1974) demonstrated that earliest fluids are of magmatic isotopic composition, and that periodic influxes of a meteoric water (lighter in δD) were coincident with wolframite deposition. Waters of at least two origins were present during the complex history of multiple intrusion and repeated ore mineralisation associated with the Climax intrusions, again brought out by the lower δD of the meteoric water (Hall et al. 1974). At Casapalca, Peru, the latest stage of mineralisation is accompanied by an influx of fluid of lower δD (Figure 24), interpreted to be of meteoric origin (Rye and Sawkins, 1974). There is some doubt as to the composition of meteoric water at Casapalca (and, presumably therefore, at Pasto Bueno as well) during mineralisation as the altitude may have been considerably less during the earlier Pliocene (approx. 10 my b.p.). Extensive recent uplift of the Andes would have caused local meteoric waters to become steadily more depleted in δD with increasing altitude. The extreme variation seen in the O and H isotopic compositions at Butte (Sheppard and Taylor, 1974) during main stage mineralisation is interpreted to result from ore formation by a mixed meteoric-hydrothermal fluid whose $\delta^{18}O$ values varied widely in time and space throughout the Butte ore deposit depending on the detailed

history of wall-rock reactions. Blake et al. (1979) obtained a δD range from -77 to -118 per mil from fluid inclusions in quartz associated with molybdenite at Copper Basin, Lander County, Nevada. Calculated $\delta^{18}O$ values in water in equilibrium with the quartz range from +5.8 to +9.6 per mil. Blake et al. (1979) state that the $\delta^{18}O$ in quartz samples with lighter δD initially contained meteoric values ($\delta^{18}O = -15$ per mil) and have since equilibrated with wallrock oxygen. They conclude that vein quartz at Copper Basin contains a suite of inclusions indicating hydrothermal fluids that comprise magmatic and meteoric water in various proportions. Some interaction between ore forming fluid and the wall rock is also suggested at Panasqueira (Kelly and Rye, 1979). The hydrogen isotopic ratios from fluid inclusions, however, show a range that Kelly and Rye cannot readily account for: -40 to -124. Meteoric water during ore formation was estimated at -49 ± 6 per mil for δD . Kelly and Rye (1979, p.1807) suggest that a second meteoric water may have been present in the system, with very low δD values, acquired possibly in a high elevation recharge area. At Goonbarrow (Bray, 1980), the variability in δD values is toward heavier hydrogen isotopic composition, contrasting with the other mineral deposits. The δD of meteoric water was concluded by Bray (1980) to be too deficient in deuterium to account for the δD values in quartz inclusions, which range up to -14 per mil (Figure 24). Bray (1980) demonstrated that boiling accompanied mineralisation and suggested that the observed range is due to H_2O (gas-liquid) fractionation of hydrogen isotopes. It is also possible that phase separation of a hydrogen-bearing species, such as CH_4 or H_2 , and accompanying isotopic fractionation with the hydrothermal water is responsible. H_2 , particularly, is an efficient scavenger of the heavy isotope, with a fractionation factor (given in terms of $1000 \ln \alpha$) of over 400 at 400°C. A final possibility to explain the Goonbarrow data is a mixing of a small volume of oceanic water with a magmatically derived water, to produce a marked δD shift to heavier values, but little change in $\delta^{18}O$.

The Boss Mountain data are similar to those obtained for several of the deposits described here, showing a large δD range with restricted values for $\delta^{18}O$. In most cases, the δD range can be attributed to a mixing of two fluids, from magmatic and meteoric sources. A small volume of meteoric water, mixed with magmatic, may produce a large shift in hydrogen isotopic compositions, but little change in oxygen, due to buffering by the magma. This effect is seen during the main phase of mineralisation at Boss Mountain and in the early mineralisation stages at Climax. Addition of a further meteoric component can produce considerable variability in $^{18}O/^{16}O$ ratios, such as at Butte, Casapalca and in late stage Climax mineralisation.

Origin of the water from which vein quartz crystallised

One of the contentious issues in the study of mineral deposit genesis is the origin of the ore forming fluid and, by inference, the metal(s) itself. For 'porphyry' deposits, models for ore genesis must account for the obvious spatial relationship between intermediate to felsic intrusions and zones of mineralisation. There are two schools of thought:

(1) meteoric water is circulated through the country rock, preferentially leaching and concentrating certain elements, in response to thermal instabilities caused by intrusion;

(2) magmatically derived water, containing concentrations of certain elements, is expelled from the magma chamber.

In both models, some other process(es) is(are) responsible for precipitation of the concentrated elements in veins, veinlets and breccia bodies.

In the early 1970's, oxygen and hydrogen isotopic data indicated that massive volumes of meteoric water had interacted with intrusions during cooling, intrusions commonly

associated with porphyry copper-style mineralisation (e.g. Taylor, 1971, 1974). At approximately the same time, Norton (1972) demonstrated how convecting meteoric hydrothermal fluids reacting with heated wallrocks are theoretically able to form the alteration assemblages commonly found in porphyry copper deposits. Cathles (1981) has shown that the mass of groundwater circulated by a cooling intrusion is 4 to 5 times greater than the possible mass of vented magmatic water. As a result of these developments in understanding, models of ore formation were developed that involved convecting meteoric water (e.g. Cathles, 1977). The thermal energy to initiate and sustain convection was proposed to be derived from a spatially associated intrusion. The model implicitly assumes that no water is derived from the magma and consequently that the metal(s) is(are) also of a non-magmatic source.

More recently, Cathles (1981) has expressed doubt as to the importance of meteoric water in the formation of porphyry copper deposits due to the difficulty in maintaining the critical thermal gradient at a constant elevation. Other isotopic studies, beginning with those of Sheppard et al. (1971), have demonstrated the preponderance of magmatic hydrothermal fluids during potassic alteration and copper deposition in most porphyry copper systems (Westra, 1979). Beane and Titley (1981) acknowledge this conclusion but add the caveat that the data do not prove a magmatic derivation for the metals, only for the water that deposited the gangue minerals in which the metals are found. The sulfur isotopic composition of sulfides indicates a deep crustal or mantle source of sulfur, irregardless of the age, nature or origin of the wall rocks (Ohmoto and Rye, 1979).

The problem of metal source was addressed by White et al. (1981) for Climax-type Mo deposits. Wallace et al. (1978) suggested that Mo and W in both the Climax and Henderson deposits came from the hostrocks. Strontium isotopic data for the intrusions related to mineralisation give initial ratios (0.705 - 0.71) closer to present 'mantle' material (0.704) than to average ratios for the hostrocks (0.8 to 1.0). White et al. (1981) query the postulate that the magmas responsible for mineralisation could have scavenged selectively Mo and W without considerable contamination of the initial strontium isotope ratios. Lead isotopic data suggest a lower crustal source for the lead: in detail, the data indicate that the source was a 'cratonised' lower crustal rock that lost uranium relative to thorium during granulite facies metamorphism (White et al., 1981, p.308). In addition to the spatial and temporal relationships described by Wallace et al. (1968, 1978), White et al. (1981) describe many compositional and textural features of the Climax-type Mo deposits that they ascribe to a magmatic-hydrothermal origin for these types of deposit and that the ore fluids exsolved directly from crystallising magmas.

To summarise, initial realisations that interaction between meteoric water and heated rocks are a direct corollary of magmatic intrusion, lead to models of porphyry genesis involving solely a convecting meteoric fluid. Subsequent detailed field mapping, thin section petrography, petrology and geochemistry, fluid inclusion microthermometry and isotope studies have modified these concepts somewhat: potassic alteration, associated with mineralisation is accepted to be of magmatic hydrothermal origin. Phyllic and propylitic alteration zones are dominated by the meteoric signature. All indications currently point toward a magmatic source for the metals (Westra, 1979; White et al., 1981; this study) which are commonly deposited at the magmatic/meteoric interface (Cathles, 1981).

Certain aspects of the mineralisation at Boss Mountain are pertinent to this problem:

- (1) The pressure of the ore-forming fluid has been interpreted to reflect lithostatic pressure as a minimum or vein fractures would close. Circulating meteoric water is derived from, and convects to the surface and is therefore at hydrostatic pressure. It is highly unlikely, therefore that the mineralising fluid was dominantly meteoric;

(2) The narrow range of $\delta^{18}\text{O}$ in the fluid suggests little mixing and is consistent with magmatic rather than meteoric $\delta^{18}\text{O}$. For the water to have been of meteoric origin, the measured $\delta^{18}\text{O}$ could only be obtained by complete equilibration with a magmatic oxygen supply at high temperatures;

(3) The high initial CO_2 content of the water suggests that the water is not meteoric, as does the $\delta^{13}\text{C}$;

(4) Where the "bottom" of ore zones can be investigated (the main breccia pipe) or inferred from drilling, they are observed to emanate from the Boss Mountain Stock.

Although no single line of evidence provides unequivocal proof of origin for the hydrothermal water, and by inference the elements carried within it, the results of detailed field mapping (Soregaroli, 1968; Macdonald, 1983) suggest an extremely intimate association between intrusion of the Boss Mountain Stock and the complex sequence of mineralisation. Indeed, the fluids apparently emanated from within the stock. This field observation does not preclude the suggestion, that could be made by opponents of the magmatic water theory, that meteoric water circulated through the stock after it crystallised (e.g. Cathles, 1981; Norton and Knight, 1977). Field evidence indicates, however, that the stock was not crystalline during the early mineralisation stages (Soregaroli, 1968) when minerals were precipitating in the breccia pipes and the sheeted veins (set v) from fluids derived from the stock. Consequently, if the fluids were initially of meteoric origin, they had somehow passed into the magma chamber before being expelled into the ore bearing structures, a process considered above to be highly unlikely. In any case, fluid volumes that could be expected to enter the magmatic environment by this process are approximately 10 orders of magnitude less (as indicated by a permeability study of the ore zones - Macdonald and Spooner, 1981b) than that which may have flowed out of the chamber into the mineral deposit.

Sulfur isotopes : Introduction

Twenty seven sulfur isotope analyses ($\delta^{34}\text{S}$) were obtained from pyrite (9) and molybdenite (18) samples from the sheeted vein complex. 18 of the samples, 9 molybdenite-pyrite pairs, either intergrown or in close physical contact, were analysed to determine the degree of fractionation of sulfur isotopes between the two minerals, which is temperature sensitive and may therefore be used as a geothermometer (Suvorova, 1974). Several samples of molybdenite were selected for isotopic analysis from the hanging and/or footwalls of veins, and from centres of the same veins, to determine whether $\delta^{34}\text{S}$ changed during vein deposition.

Analytical techniques

Sulfur isotopic compositions were determined in two laboratories. Twenty samples were analysed by Geochron Laboratories (Cambridge, Massachusetts) using the technique described by Thode et al. (1961) with mass spectrometric measurements made using a VG 6020. Replicate analyses indicated that reproducibility was $\pm 0.5\%$, which is in agreement with the laboratory's quoted overall precision and accuracy.

Eight samples and a standard were analysed by McMaster University, Ontario, using a similar technique, with mass spectrometric measurements as described by Hulston (1964), Thode and Rees (1971) and Beaver (1973). During the period of analysis (March, 1981), the McMaster laboratory reported a precision of ± 0.2 per mil, which was confirmed by submission of a sample of known sulphur isotopic composition. We conclude that the $\delta^{34}\text{S}$

error on each sample varies between a maximum of ± 0.5 and a minimum of ± 0.2 per mil.

Results

The Boss Mountain isotopic compositions (Figure 25, Table V) are compared with the sulphide sulphur isotopic values obtained from other porphyry and hydrothermal deposits (Figure 26). The bulk of the $\delta^{34}\text{S}$ values of the sulphides in these deposits, including Boss Mountain, fall between -3 and $+1$ per mil. The mean $\delta^{34}\text{S}$ for pyrite is $-2.3\% \pm 0.7$, and for molybdenite is $-1.5\% \pm 0.3$. Although the inferred temperature of formation of the sulphides at Boss Mountain is lower than the typical range for other porphyry deposits ($450^\circ - 650^\circ\text{C}$), these $\delta^{34}\text{S}$ values are consistent with igneous derived sulphur, either as magmatic fluids or by dissolution of igneous sulphides (Ohmoto and Rye, 1979, p.545). A more detailed consideration of the origin of the sulphur at Boss Mountain, taking into account the isotopic composition of the hydrothermal fluid, is presented below.

Sulphur isotopic fractionation between molybdenite and pyrite

The sulphur isotopic compositions and the $\Delta_{\text{PY-MO}}$ values for coexisting (intergrown) pyrite and molybdenite pairs are listed in Table V. The Δ values are calculated from:

$$\Delta_{\text{PY-MO}} = \delta^{34}\text{S}_{\text{PY}} - \delta^{34}\text{S}_{\text{MO}}$$

and range from -0.3% to $+1.4\%$. Table V indicates that the -0.3% value comes from a molybdenite-pyrite pair with anomalously heavy pyrite (-0.7% as opposed to lighter than -2% in all other samples) and is not considered further in the following discussion.

The mean $\Delta_{\text{PY-MO}}$ (from Table V) is $+1.0\%$ (with a range of $+0.3\%$ to $+1.4\%$) which correspond with a mean temperature (using the fractionation curve of Suvorova, 1974) of 250°C and the extreme $\Delta_{\text{PY-MO}}$ values give a range of 400° to 200°C . In addition to the 200°C range indicated by the sulphur isotopic fractionation factors, the 'errors' inherent in the isotopic analyses comprise an additional uncertainty and must be quantified. If two numbers, A ($\pm x$) and B ($\pm y$), are added or subtracted to give a value C ($\pm z$), then:

$$z = (x^2 + y^2)^{1/2}$$

i.e., in this case, where x and y are 0.5 per mil, z, or the error on the Δ value, can be calculated:

$$z = (0.25 + 0.25)^{1/2} = 0.7$$

i.e. the error on the calculated values of per mil fractionation factor is ± 0.7 . Therefore, considering the average $\Delta_{\text{PY-MO}}$, the value = $+1\% \pm 0.7$, or $+0.3\%$ to $+1.7\%$ which corresponds with a temperature range of 400° to 169°C , or a range of 231°C . The actual value of the temperature range will vary for each individual determination, as the curve is non-linear, but this example suffices to demonstrate that the uncertainties inherent in sulphur isotopic analyses do not permit precise determinations of formation temperatures. The relatively steep gradient of the fractionation curve also inhibits precise temperature determinations: a small change in $10^3 \ln \alpha$ can cause a large change in calculated temperature.

In conclusion, the calculated range of formation temperatures from the degree of sulphur isotopic fractionation between coexisting molybdenite and pyrite is between 400° and 200°C (omitting the errors in isotopic determinations) which is in good agreement with the range detected by microthermometric determinations on fluid inclusions in coexisting quartz (the bulk of the quartz forming from a hydrothermal fluid at temperatures between 250°C and 375°C). It is inferred, therefore, that the sulphur-bearing species precipitated from the

hydrothermal solution in equilibrium with coexisting vein quartz.

Sulphur isotopes of molybdenite from different locations within veins

Table V shows $\delta^{34}\text{S}$ values for molybdenite from 3 veins, sampled from the hangingwall, centre and footwall (2 samples only). Within analytical error (estimated at $\pm 0.5\%$) the samples show no systematic variation from the vein walls into the centre. It can be inferred that the temperature difference during sulphide deposition at vein walls and vein centres was so slight as to be undetectable by variation in sulphur isotopic fractionation between the hydrothermal fluid and the sulphide. In addition, it is interpreted that the $\delta^{34}\text{S}$ (fluid) did not change appreciably either.

The chemical environment during mineralisation as indicated by sulfur isotopic composition

Ohmoto (1972), developing the concepts of Sakai (1968), has demonstrated that the sulfur isotopic composition of a species is a function of (a) the mean isotopic composition of sulfur, (b) the temperature, (c) the oxygen fugacity, (d) the pH and (e) the ionic strength of the hydrothermal solution from which the species precipitated. Knowledge, or inference, of a number of these parameters can place constraints upon the others. In the case of Boss Mountain, the temperature at which mineralisation commenced, and the sulfur isotopic compositions of pyrite and molybdenite are well constrained. The small range in $\delta^{34}\text{S}$ of the sulfides (-0.7% to -2.8%) indicates that the sulfides precipitated under one (or both) of two conditions:

- (a) little variability in T, $f\text{O}_2$ or pH;
- (b) the hydrothermal solutions were H_2S - dominated.

The temperature range during quartz precipitation may have been of the order of 100°C suggesting that the latter condition (H_2S - domination) prevailed. The equilibrium isotopic fractionation data compiled by Ohmoto and Rye (1979) indicate that when the fluids are dominated by H_2S , $\delta^{34}\text{S}_{\text{ss}} = \delta^{34}\text{S}(\text{H}_2\text{S})$. From the known isotopic fractionation factors between MOS_2 , FeS_2 and H_2S , it is possible to calculate an estimated range of values for the sulfur isotopic composition of the hydrothermal fluid. Ohmoto and Rye (1979, p.516) give what they believe to be the best fractionation factors for sulfides with respect to H_2S , governed by the general equation:-

$$1000\ln\alpha = \frac{A}{T^2} \times 10^6 + \frac{B}{T} \times 10^3 + C$$

where T is in K, α is the isotopic fractionation factor and A, B and C are constants specific to each sulfide. For pyrite and molybdenite, constant A is equal to 0.4 and 0.45 respectively (with an error of approximately 0.1) and constants B and C are 0. If T is taken to be 625 K, then:

$$1000\ln\alpha(\text{Py}-\text{H}_2\text{S}) = 1.0,$$

and,

$$1000\ln\alpha(\text{Mo}-\text{H}_2\text{S}) = 1.2.$$

i.e. the pyrite data (Table V) which range in isotopic composition from -2.8% to 0.7% suggest an H_2S sulfur isotopic composition from -3.8% to 1.7% . Similarly, the molybdenite data indicate an H_2S isotopic composition from -3.4% to -2.2% . i.e. the isotopic composition of the total sulfur in the system, or $\delta^{34}\text{S}_{\text{ss}}$ ranges from -3.8 to -1.7 per mil (i.e. an average of approximately -3%).

Origin of the Sulfur at Boss Mountain

The above discussion indicates that the calculated isotopic composition of the the total sulfur in solution at Boss Mountain ranges from approximately -4 to -2 per mil. Figure 2 summarises the $\delta^{34}\text{S}_{\text{S}_2}$ data for several hydrothermal ore deposits, calculated in the same way. There are three principal groups of isotopic populations:

- (1) slightly negative to slightly positive;
- (2) between 5 and 15 per mil;
- (3) greater than 20 per mil.

The first group includes deposits associated with felsic igneous rocks, with sulfur derived from igneous sources (including sulfur released from magmas and from leaching of sulfides in igneous rocks). Igneous sulfur is derived 'from the upper mantle or from the homogenization of large volumes of deeply buried or subducted crustal material' (Rye and Ohmoto, 1974, p.873). The second group includes deposits in which the sulfide was derived from seawater or evaporites. The third group of deposits contains sulfur from sedimentary and marine sources.

The Boss Mountain data fall within the first group, consistent with an igneous source for the derivation of the sulfur. Paragenetic relationships within the deposit suggest that the sulfur was introduced together with the Boss Mountain adamellite stock. Evidence from microthermometric studies indicates that H_2S was a component of the magmatic fluid and the probable sulfur source for the mineralisation.

Carbon isotopes - Introduction

Carbon isotopic ratios were obtained from 10 carbonate samples (from which oxygen isotopic values were also obtained) from the main stage (sheeted vein complex) of mineralisation. Each carbonate specimen selected was intergrown with either vein quartz or sulfide and showed no textural indications of being a late-stage phase (e.g. vug fill etc.). The carbon isotopic ratio ($\delta^{13}\text{C}$, standardised against PDB) of the fluid, from which the carbonate precipitated, may provide indications of the origin of the carbon within the hydrothermal fluid much in the same way as sulfur isotopic compositions were interpreted in the previous section. The carbonate samples were analysed in two laboratories, Hebrew University, Israel and the University of Waterloo. Carbon isotopes were analysed on the same CO_2 yield as oxygen isotopes. The data obtained for carbon isotopic compositions are in Table VI and in Figure 2B are compared with other deposits. The overall ranges obtained by the two laboratories are comparable (Hebrew University: -9.0% to -15.5%; University of Waterloo: -8.0% to -15.6%).

Carbon isotopic composition of the hydrothermal fluid

Although there are no fluid inclusion data on carbonates in the sheeted vein complex, intergrowth with both sulfides and quartz indicates precipitation over the same temperature range (approximately 375° to 250°C). As pyrite is the stable iron sulfide at Boss Mountain (as opposed to pyrrhotite) it is suggested that the dominant carbon species in the fluids was $\text{H}_2\text{CO}_3(\text{aq})$, (where $\text{H}_2\text{CO}_3(\text{aq})$ consists of CO_2 in solution as hydrated CO_2 molecules and as H_2CO_3). At temperatures in excess of 200°C, $\delta^{13}\text{C}(\text{CaCO}_3)$ is approximately equal to $\delta^{13}\text{C}(\text{H}_2\text{CO}_3(\text{aq}))$, which in turn, is approximately equal to $\delta^{13}\text{C}(\text{fluid})$ (Ohmoto and Rye, 1979, p.561): i.e. in the case of Boss Mountain, $\delta^{13}\text{C}_{\text{C}}$ ranges from approximately -8 to -15%. The same approximations hold for all the deposits studied (Rye and Ohmoto, 1974, p.879), where it is interpreted that the carbon in the early, or main stage, fluids in most of these deposits was probably derived from a deep-seated source. At Bluebell,

however, the $\delta^{13}\text{C}_{\text{C}}$ value of -7% has been interpreted as resulting from high-temperature exchange of the carbon in the hydrothermal fluids with graphite in the country rocks.

Origin of the carbon in the hydrothermal fluid

The carbon isotopic compositions of the hydrothermal fluid during main stage mineralisation at Boss Mountain (-8 to -15.6 per mil) are extremely light, compared to most other deposits, with the exception of Panasqueira (-8.4 to -14.2 per mil). Ohmoto and Rye (1979, p.553) have stated that $\delta^{13}\text{C}$ values of -5 ± 2 per mil are the values of carbon in magmas formed by partial melting of mantle rocks (based upon the work of Deines and Gold, 1973) and are approximately -5.5% for average sediments and metamorphic rocks. Hoefs and Touret (1975) and Hoefs (1978) have questioned the restriction of 'juvenile' carbon to approximately -5% , indicated by analysis of carbon from carbonatites and kimberlite carbonates (Deines and Gold, 1973). Hoefs and Touret (1975) analysed the carbon in CO_2 from inclusions in granulite facies rocks and found $\delta^{13}\text{C}$ around -15 per mil and as light as -20 per mil. Hoefs (1978) presents additional data:

- (1) trace amounts of reduced carbon in igneous rocks have $\delta^{13}\text{C}$ around -25 per mil;
- (2) some diamonds have $\delta^{13}\text{C}$ values ranging down to as light as -32% (Koval'skii and Cheskii, 1973);

and concludes that the mantle is not of homogenous carbon isotopic composition and that the commonly obtained values of approximately -5% might be due to simple mixing of carbonate-derived CO_2 and organically-derived CO_2 .

At Panasqueira, Kelly and Rye (1979) suggest that the light isotopic values indicate carbon derivation from, or exchange with, a graphitic or organic carbon source, although the host rocks at Panasqueira do not contain appreciable carbon. Hoefs and Touret (1975) showed that 'primary' carbon isotopic values present in granulite facies rocks have light $\delta^{13}\text{C}$ values around -15% , while inclusions that formed during retrograde metamorphism contain a heavier carbon, with values around -5 and -7 per mil. They suggest that it is these 'retromorphic' inclusions that have provided the values reported earlier for 'juvenile' carbon in carbonatites, kimberlites and diamonds. The process of heavy isotopic enrichment is poorly understood but may reflect the introduction of 'primary' CO_2 into the stability field of graphite, which can raise the $\delta^{13}\text{C}$ value of CO_2 with respect to the fluid (Ohmoto and Rye, 1979, p.553).

We suggest that the isotopically light C values for Boss Mountain carbonates are consistent with derivation from a granulitic source (possibly graphite bearing). A similar source rock, for the Boss Mountain Stock, has been suggested following separate lines of evidence (Macdonald et al., in prep.).

Conclusions

The light stable isotopic compositions of ore and gangue minerals associated with the principal stage of mineralisation at Boss Mountain indicate a dominantly magmatic origin for the hydrothermal fluid with at least some components (S,C) derived from an igneous source in the lower crust or upper mantle. The variability in δD values, contrasting with the small range in δO^{18} values, results from either addition of a small component of meteoric water or isotopic fractionation due to separation of hydrogen-bearing gas phases, such as H_2S , from the hydrothermal solution.

After being expelled from the magmatic environment, the hydrothermal fluid (molar composition 94% H₂O, 4% CO₂, 2% NaCl equivalent) entered the sheeted vein complex and breccia pipes, and intersected the H₂O-CO₂ solvus at approximately 350°C and 350 bars, inducing carbon dioxide effervescence. Within the mine, the phase separation is observed above the 4440ft (1353m) level, approximately 300m below the present surface. A fluid pressure of 350 bars, considered to be equivalent to or in excess of lithostatic pressure, corresponds to a maximum depth below surface of 1.3 km for the 4440ft level during the Cretaceous ore forming process.

Carbon dioxide effervescence was accompanied by precipitation of molybdenite within veins and breccia pipes. Unless the spatial association is coincidental, molybdenum solubility is suggested to be a function of the CO₂ (or CO₂²⁻) content of the hydrothermal solution, either because of complexing or pH control.

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Figures

1. Geology of the Boss Mountain area.
2. Geology of the Boss Mountain mine site.
3. Isometric perspective projection of the breccia pipes, sheeted vein complex and Boss Mountain stock.
4. Quartz-molybdenite vein; note euhedral molybdenite sheafs and growth planes in quartz.
5. Principal fluid inclusion types.
6. 2 phase aqueous inclusion, liquid rich. Scale bar 10 μ .
7. 3 phase H₂O-CO₂ inclusion, liquid rich. Scale bar 10 μ .
8. 3 phase H₂O-CO₂ inclusion, gas rich. Scale bar 10 μ .
9. Negative crystal. Scale bar 10 μ .
10. Irregular fluid inclusion. Scale bar 10 μ .
11. CO₂ fusion temperatures in fluid inclusions.
12. Calculated salinities from ice fusion temperatures in aqueous inclusions.
13. Calculated apparent salinities from ice fusion temperatures in H₂O-CO₂ inclusions.
14. Clathrate fusion temperatures.
15. Salinities (equivalent weight % NaCl) calculated from clathrate fusion temperatures.
16. CO₂ homogenisation temperatures.
17. Calculated CO₂ densities from CO₂ homogenisation temperatures.
18. Final homogenisation temperature, subdivided by composition.
19. Final Homogenisation temperature, subdivided by type of homogenisation (into liquid or vapour, or critically).
20. Calculated volume percentage CO₂ in fluid inclusions.
21. Spatial variability in fluid inclusion types: above 4440 level, CO₂ effervescence leads to wide variability in volume % CO₂ in

fluid inclusions.

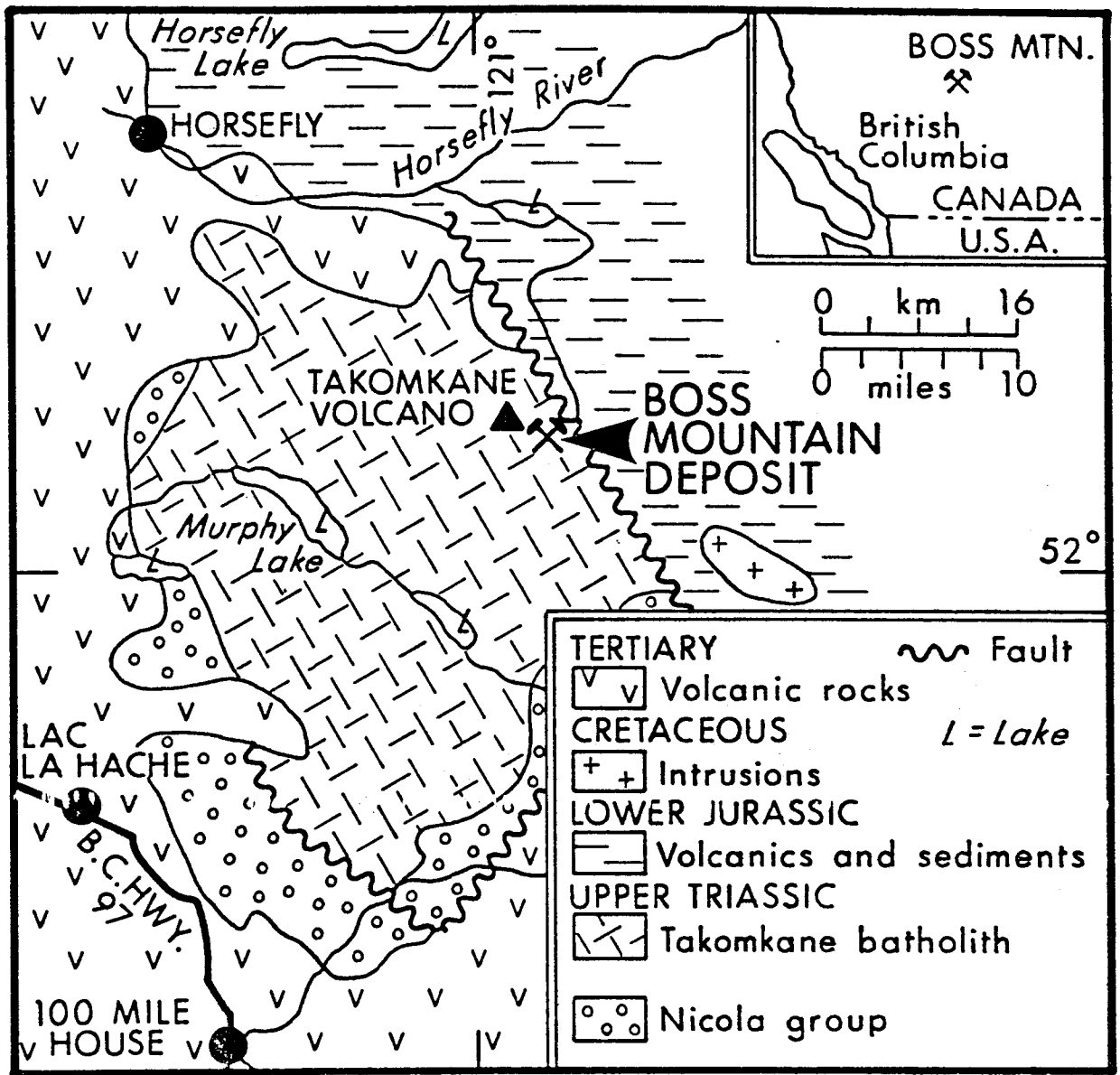
22. 2 phase region in the $\text{CO}_2\text{-H}_2\text{O-NaCl}$ hydrothermal system.
23. $\delta^{18}\text{O}$ and δD values for vein quartz (A' - B') and calculated values for hydrothermal fluid at 350°C (A-B).
24. $\delta^{18}\text{O}$ and δD values for hydrothermal fluids from several deposits.
25. $\delta^{34}\text{S}$ of vein pyrite and molybdenite.
26. $\delta^{34}\text{S}$ values from several hydrothermal ore deposits. (* : This study).
27. S isotopic composition of the hydrothermal solution for several hydrothermal ore deposits. (* : This study).
28. $\delta^{13}\text{C}$ of vein carbonate at Boss Mountain and other hydrothermal ore deposits. (* : This study)

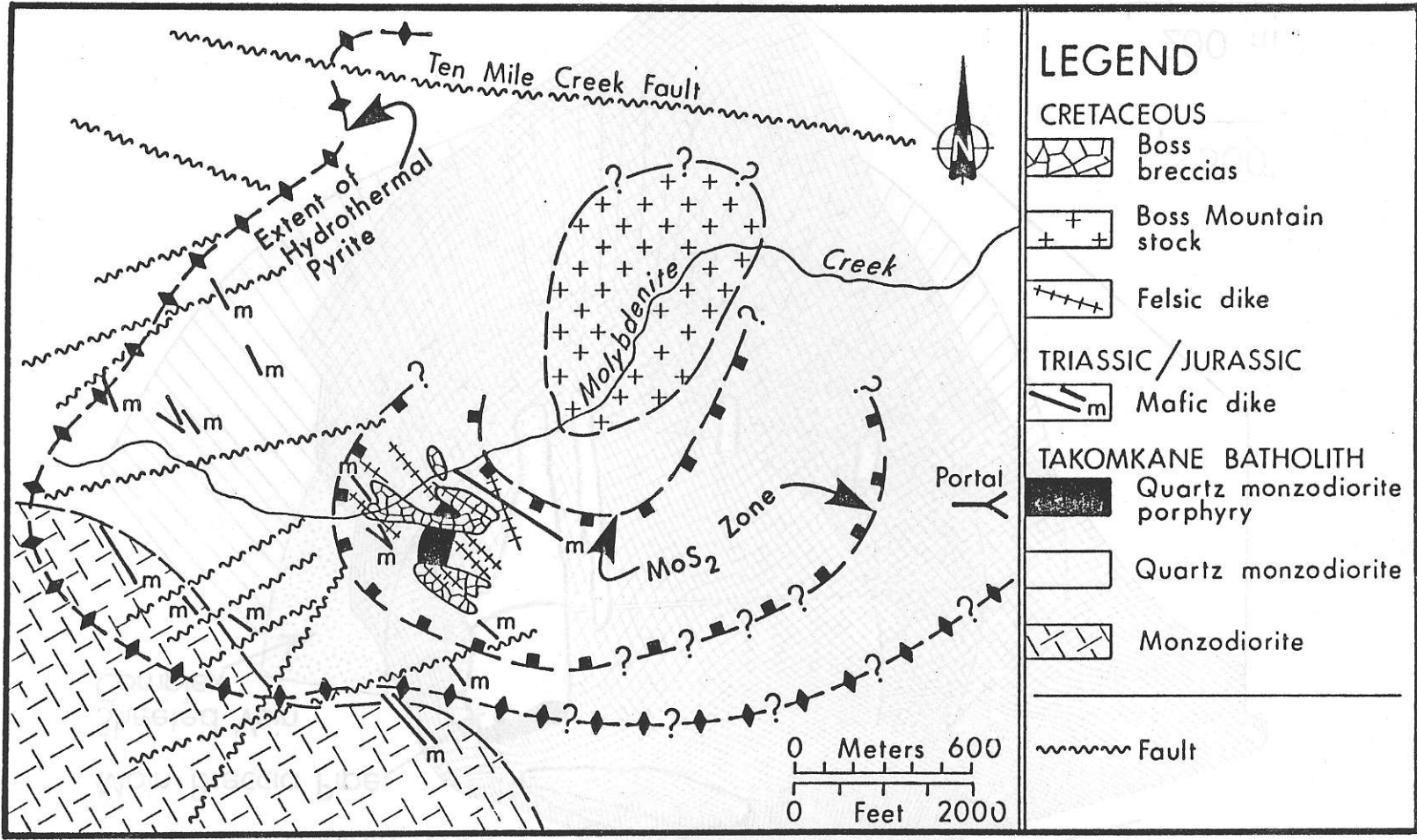
Appendix I : Fluid Inclusion Petrography and Microthermometric Data.

Appendix II : Calculation of mole percentage CO_2 .

TABLES

- Table I : Paragenesis of vein sets at Boss Mountain, from oldest (i) to youngest (ix). Based upon mapped cross-cutting relationships.
- Table II : Analysis of fluid inclusions in quartz from the main stage of mineralisation.
- Table III : Some physical and chemical properties of mineralising fluids in several Molybdenum deposits
- Table IV : Oxygen isotopic composition of quartz, calcite and potassium feldspar, and hydrogen isotopic composition of fluid inclusions in quartz, pyrite and molybdenite, main stage of mineralisation.
- Table V : Sulfur isotope values from the main stage of mineralisation; also given are the Δ values for coexisting pyrites and molybdenites
- Table VI : Carbon isotope values of calcite from the main stage of mineralisation.



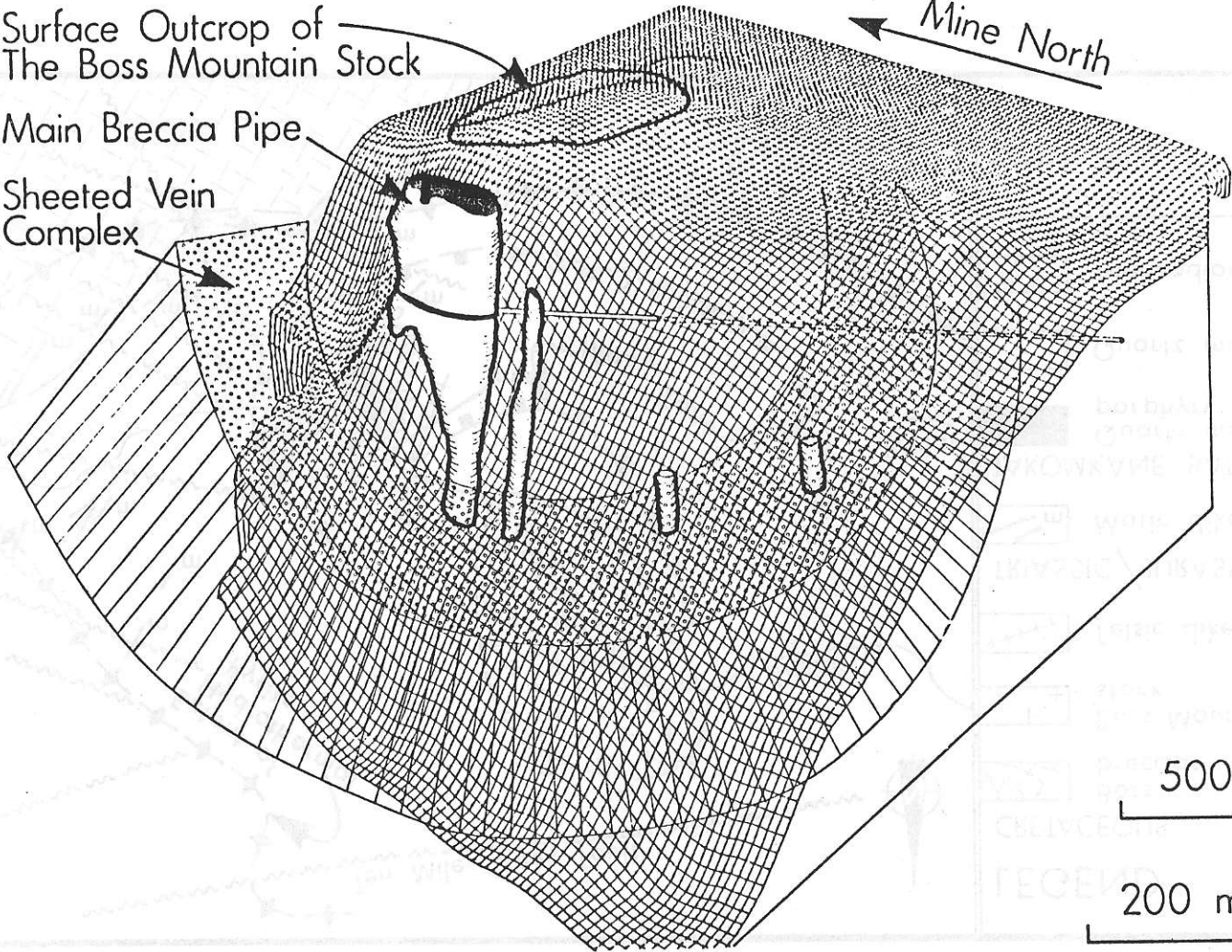


Surface Outcrop of
The Boss Mountain Stock

Main Breccia Pipe

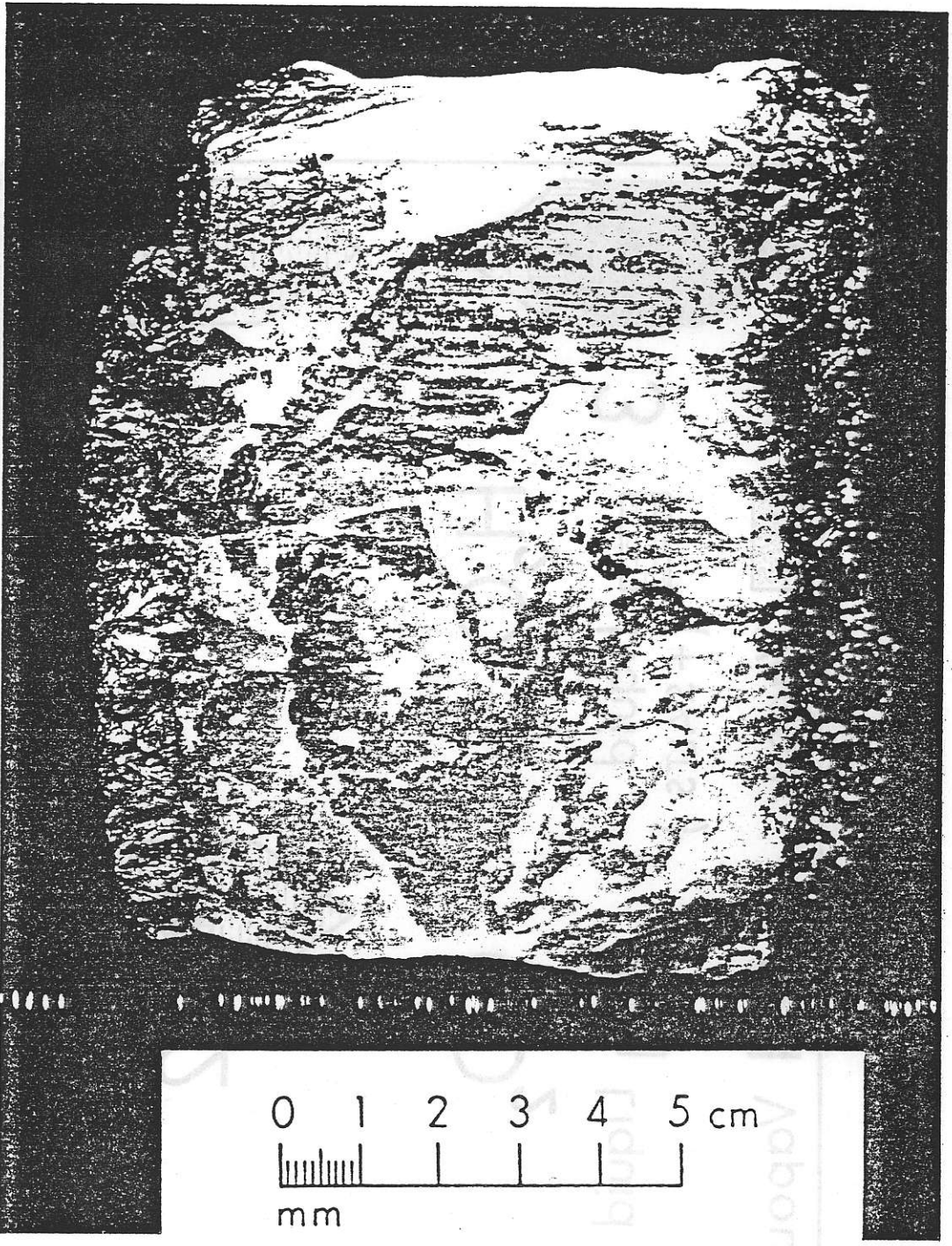
Sheeted Vein
Complex

Mine North

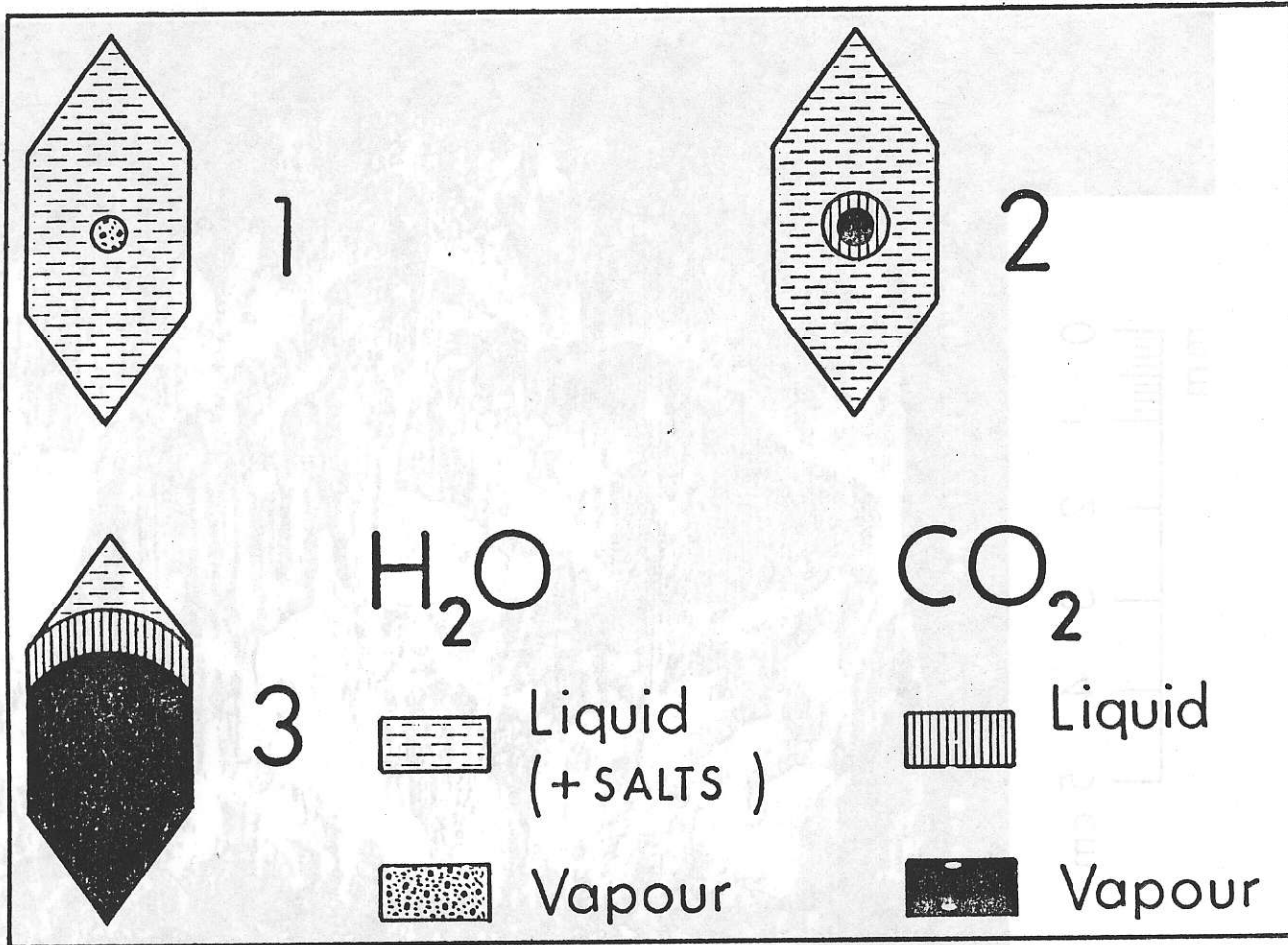


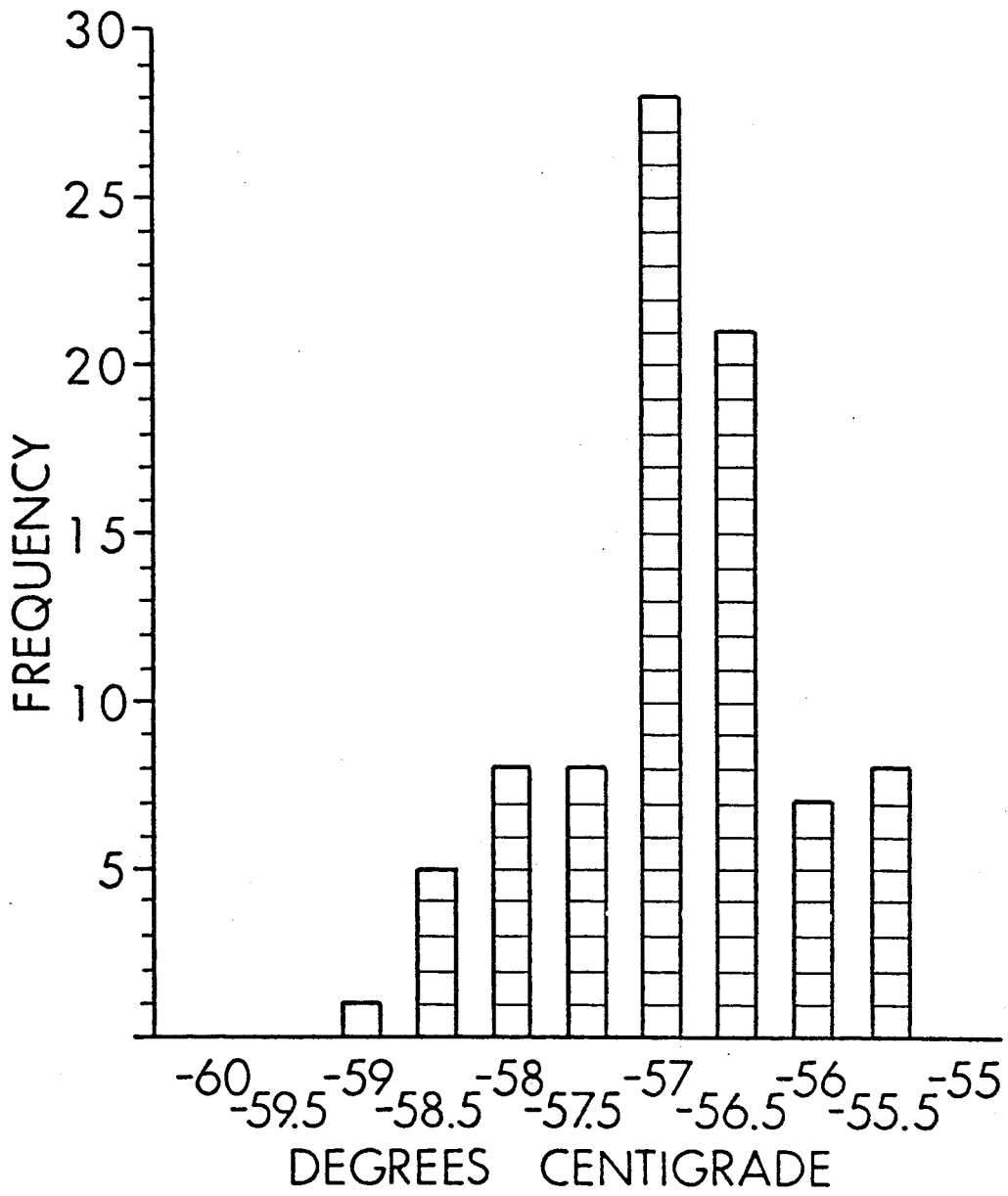
500'

200 m



0 1 2 3 4 5 cm
mm



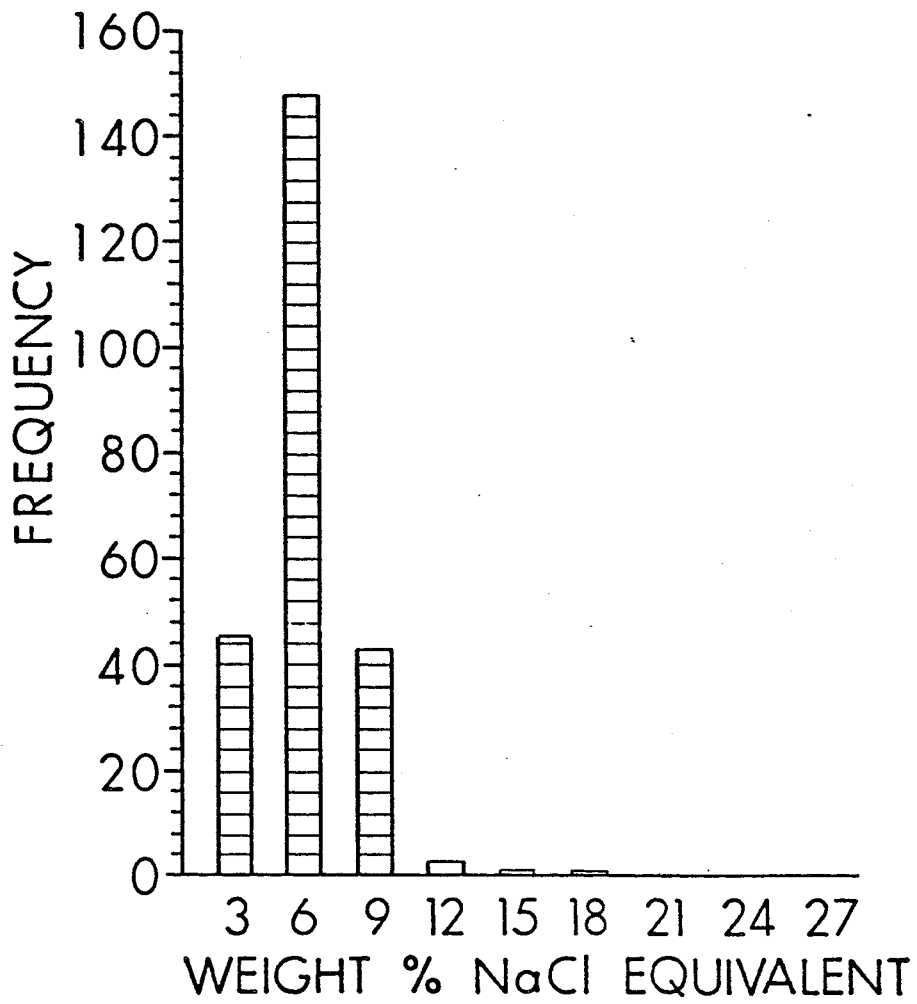


ii

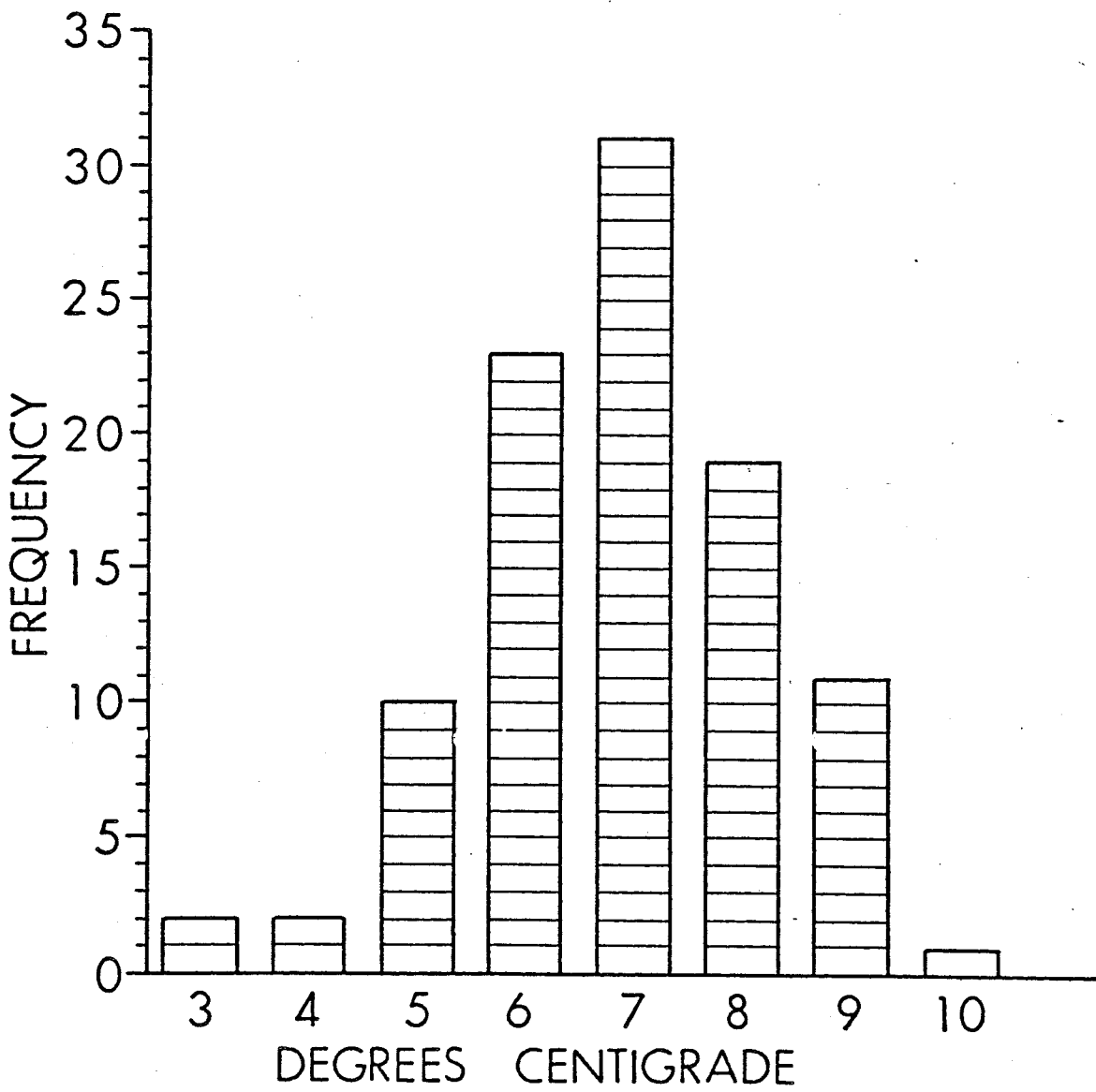
mean = 6.0

s. d. = 2.0

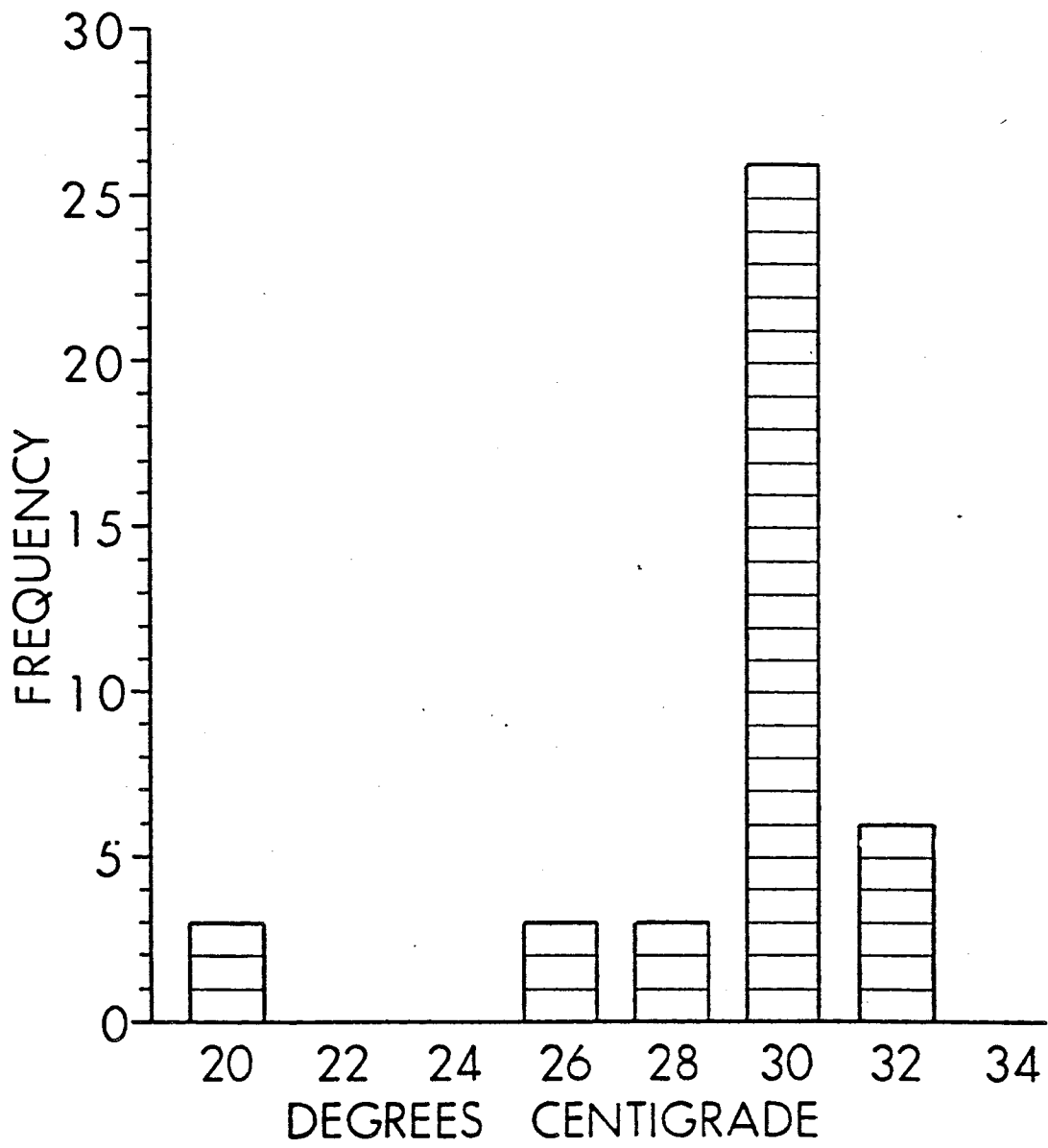
n = 242



12

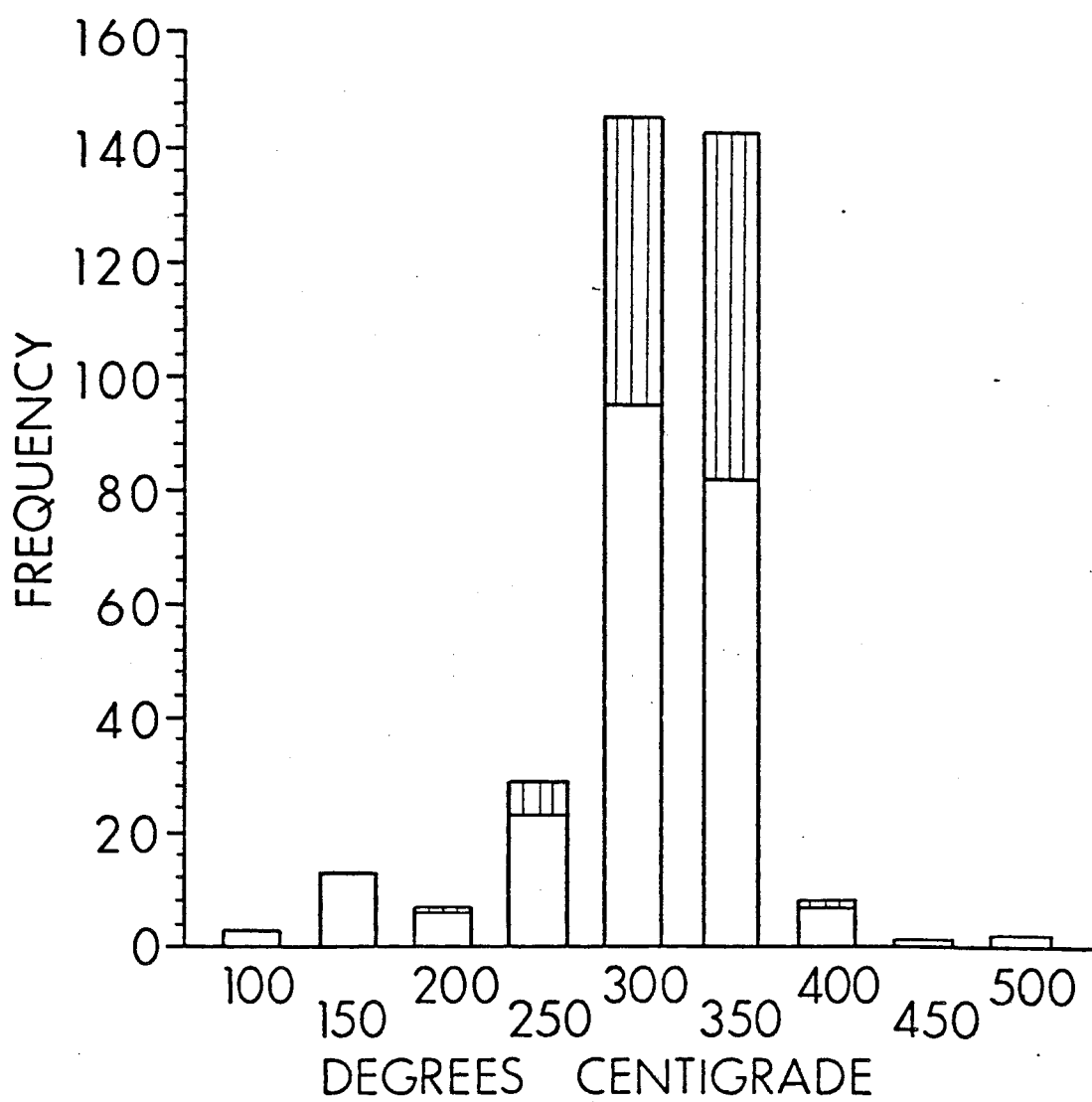
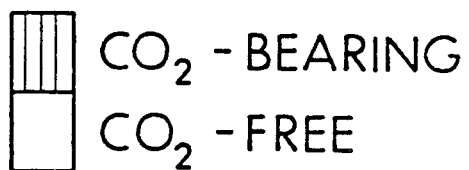


14

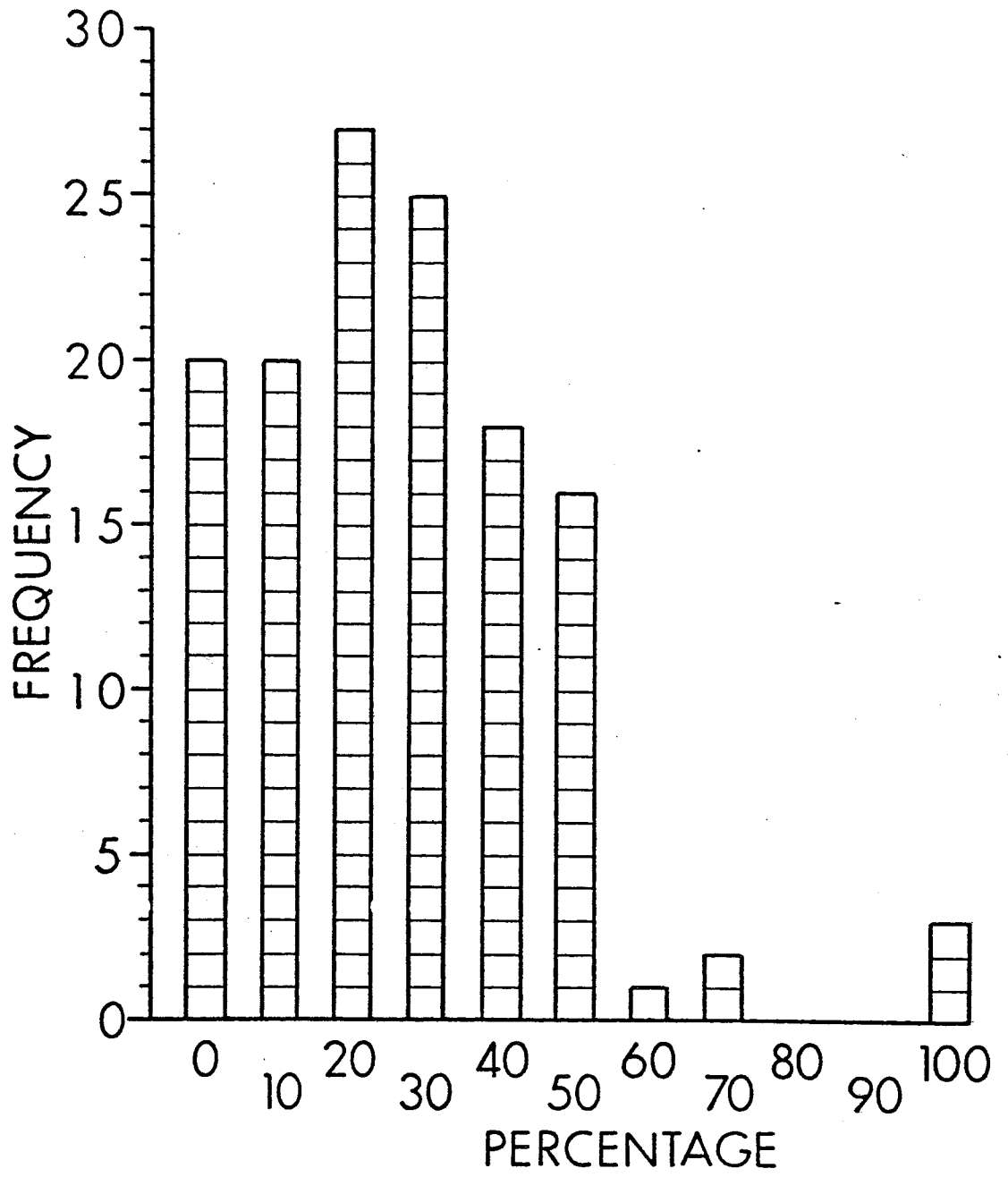


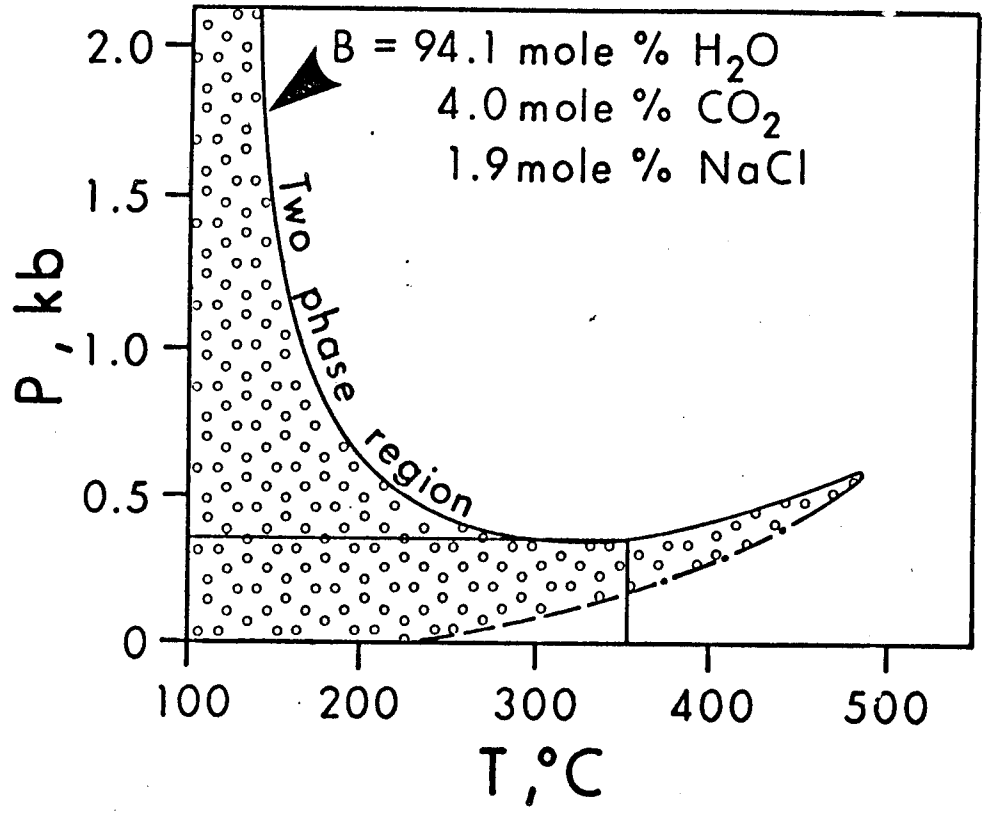
16

COMPOSITION

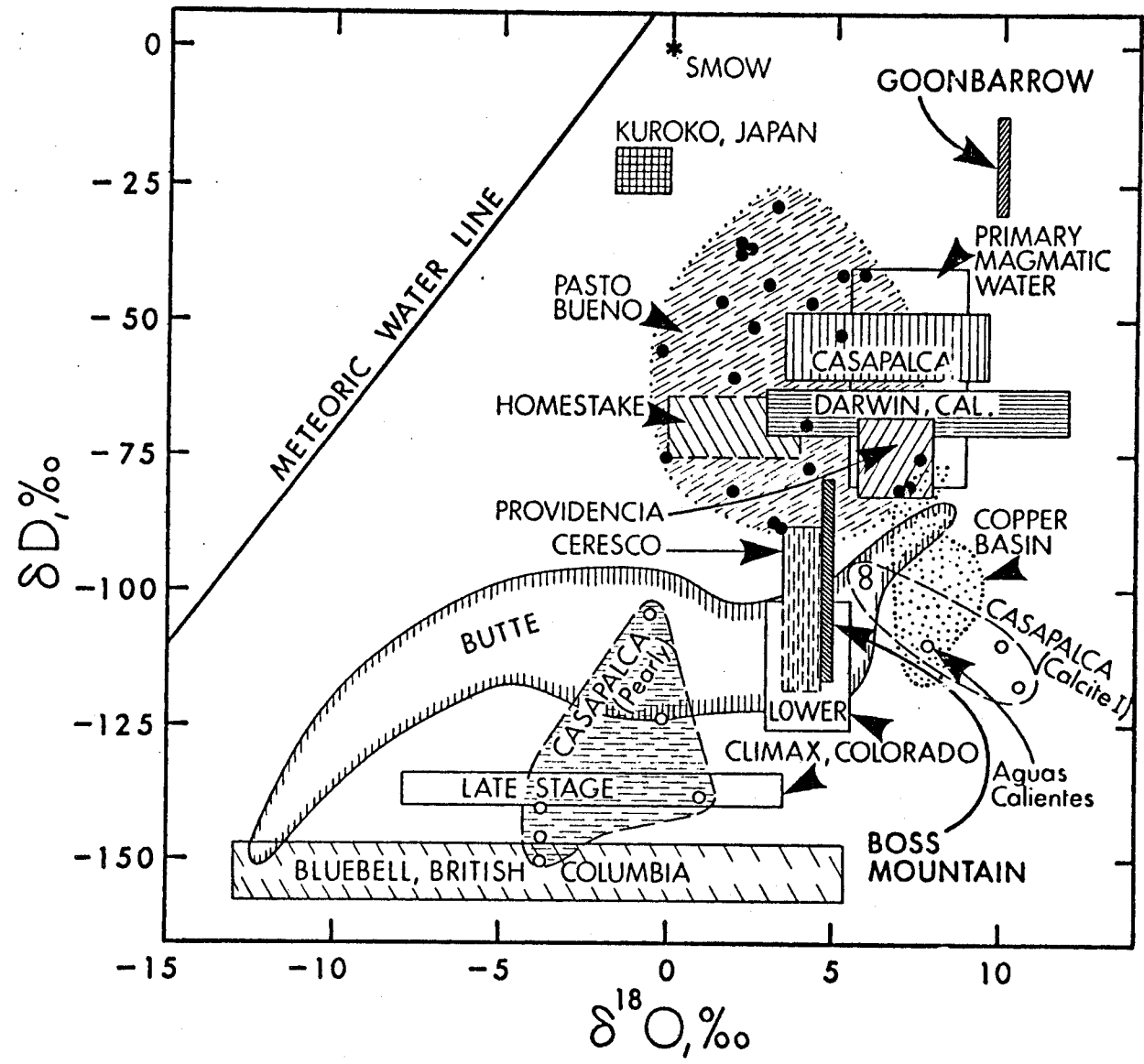


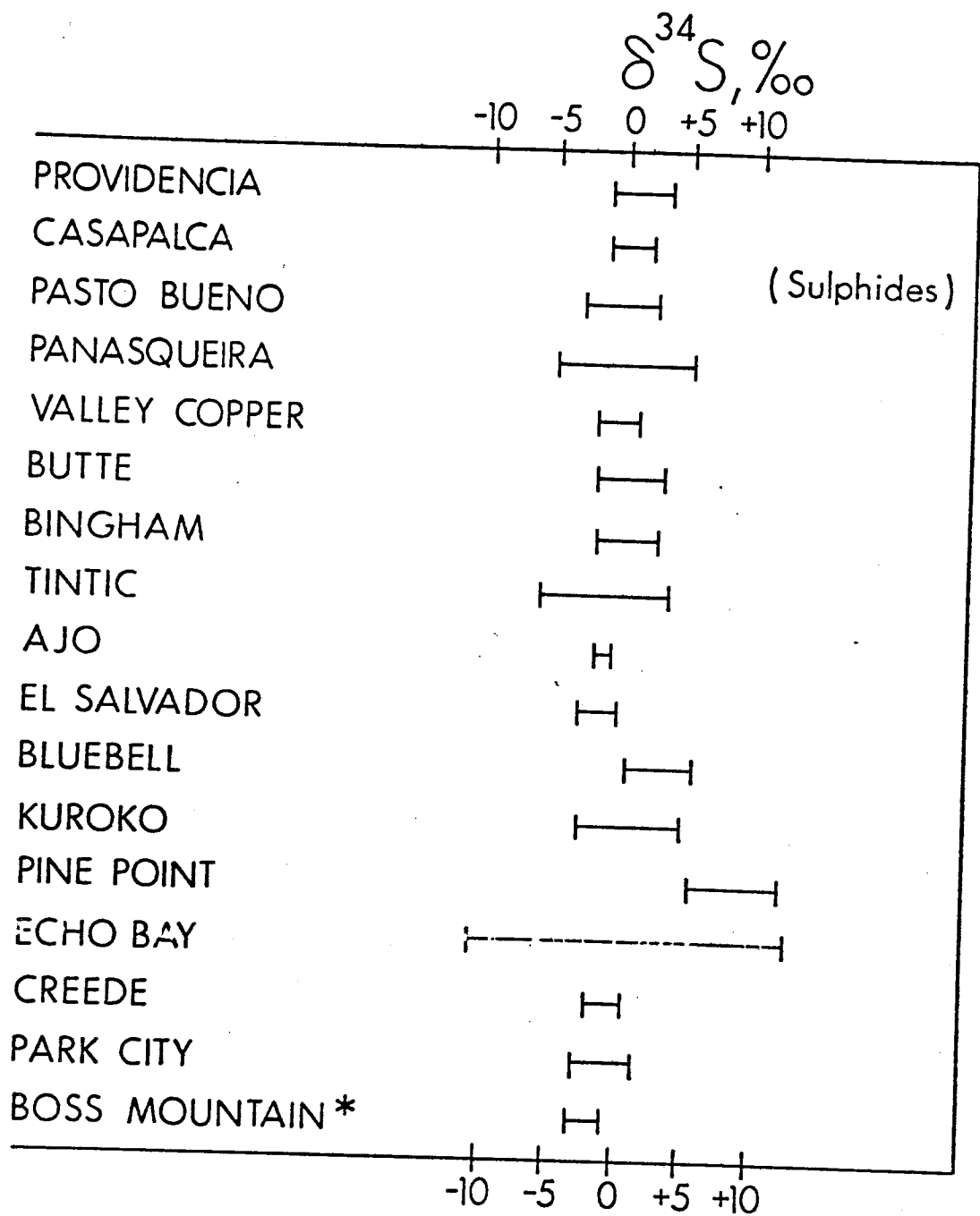
18

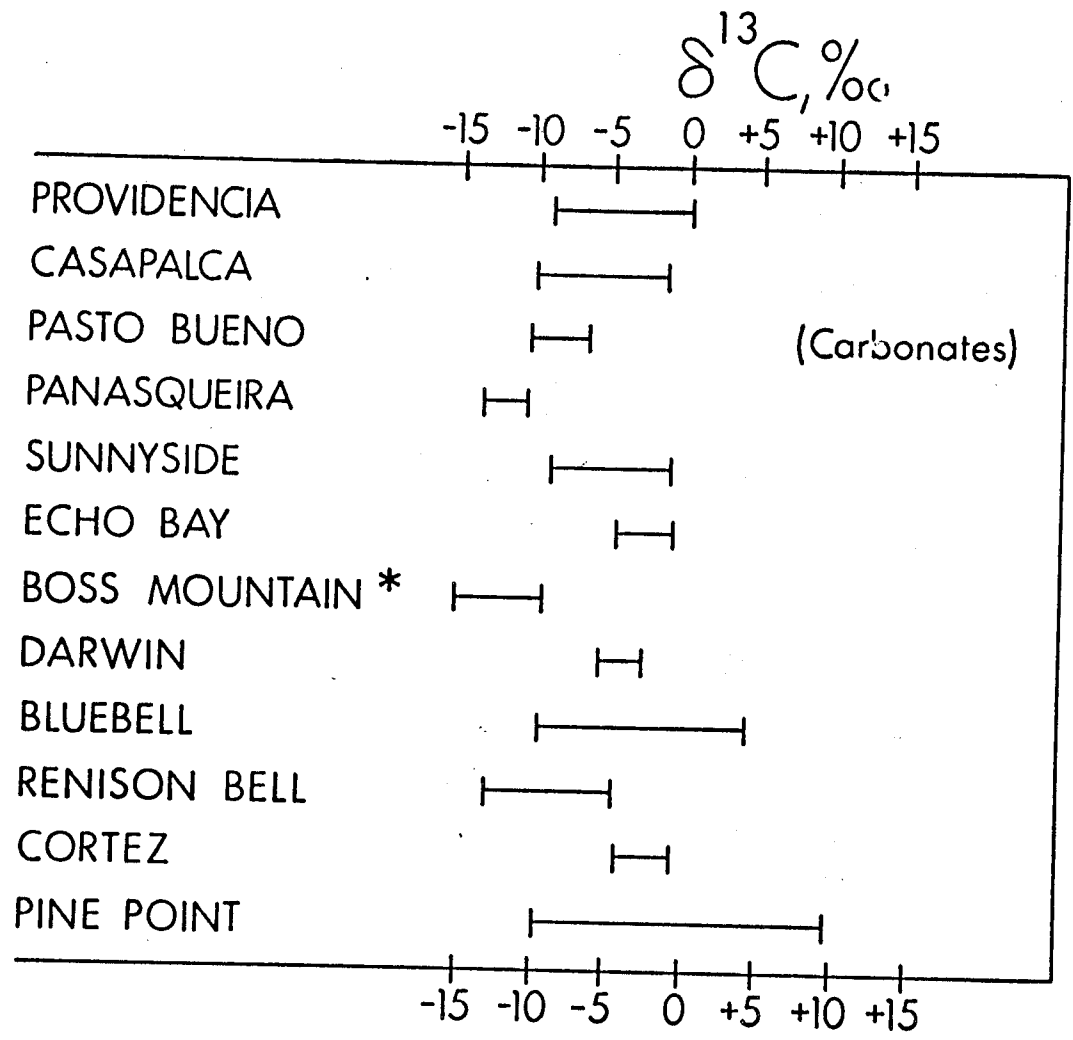




22







25

| | | | | | | | | | | |
|-----|-------|------|------|------|-----|----|---|---|---|------|
| 70 | | -2.8 | | | 338 | | L | H | S | |
| 70 | -56.4 | -4.0 | +7.3 | | 369 | 10 | L | C | S | |
| 70 | -56.3 | -4.9 | +7.4 | | 324 | 20 | L | C | S | |
| 70 | | -2.8 | | | 374 | | L | H | S | |
| 70 | | -2.1 | | | 280 | | L | H | S | |
| 70 | | -2.5 | | | 319 | | L | H | S | |
| 70 | | -3.1 | | | 336 | | L | H | S | |
| 70 | | -3.0 | | | 339 | | L | H | S | |
| 70 | | -3.4 | | | 315 | | L | H | S | |
| 70 | | -3.4 | | | 378 | | L | H | S | |
| 70 | | -2.8 | | | 310 | | L | H | S | |
| 70 | -56.3 | -5.0 | +9.0 | | 349 | 20 | L | C | S | |
| 70 | | -2.8 | | | 373 | | L | C | S | |
| 633 | | -2.7 | | | | | L | H | S | 5670 |
| 633 | | -3.0 | | | | | L | H | S | |
| 633 | | -4.2 | | | | | L | H | S | |
| 633 | | -2.8 | | | | | L | H | S | |
| 633 | | -2.5 | | | | | L | H | S | |
| 633 | | -4.0 | | | | | L | H | S | |
| 633 | | -3.1 | | | | | L | H | S | |
| 633 | | -4.9 | | | | | L | H | S | |
| 633 | | -3.6 | | | | | L | H | S | |
| 633 | | -5.1 | | | | | L | H | S | |
| 496 | -56.1 | -5.2 | | 30.5 | 300 | 20 | L | C | S | 4440 |
| 496 | | -4.9 | | | 140 | | L | C | S | |
| 496 | | -5.3 | | | 133 | | L | H | S | |
| 496 | | -4.8 | | | 352 | | L | H | S | |
| 496 | | -4.9 | | | 338 | | L | H | S | |
| 496 | | | +6.1 | | 298 | | L | C | S | |
| 496 | | -0.4 | | | 326 | | L | C | S | |
| 496 | -56.1 | | +5.8 | | 328 | 30 | L | C | S | |
| 496 | | | | | 332 | | L | C | S | |
| 496 | | | | | 317 | | L | H | S | |
| 496 | | | | | 325 | | L | H | S | |
| 496 | | | | | 332 | | L | H | S | |
| 496 | | | | | 344 | | L | H | S | |
| 488 | | | +6.0 | | 296 | 20 | L | C | S | 4636 |
| 488 | | | | | 308 | | L | C | S | |
| 488 | | -3.0 | +5.5 | | 293 | 1 | L | C | S | |
| 488 | | -3.0 | +5.5 | | 333 | 30 | L | C | S | |
| 488 | | -3.4 | | 25.4 | 293 | 20 | L | C | S | |
| 488 | -56.5 | -3.5 | +6.0 | 30.0 | 353 | 20 | L | C | S | |
| 488 | | -2.3 | | | 330 | | L | C | S | |
| 488 | | -4.5 | +5.0 | 30.0 | 257 | 10 | L | C | S | |
| 488 | -56.5 | | +7.1 | 30.2 | 313 | 20 | L | C | S | |
| 488 | -56.9 | -3.0 | +6.3 | 27.1 | 293 | 30 | L | C | S | |
| 488 | | -3.5 | +7.2 | | 273 | 10 | L | C | S | |
| 488 | | -3.3 | +7.0 | | 270 | 15 | L | C | S | |
| 488 | | -3.8 | | | 100 | | L | C | S | |
| 488 | | -2.9 | | | 190 | | L | H | S | |
| 75 | -56.7 | | +7.3 | 30.0 | 303 | 50 | V | C | S | 5790 |
| 75 | -56.6 | -5.6 | +8.4 | | 293 | 50 | V | C | S | |
| 75 | -56.6 | -4.2 | +8.0 | | 279 | 40 | V | C | S | |
| 75 | -56.5 | | +5.9 | | 287 | 30 | V | C | S | |
| 75 | | -3.4 | +5.8 | 32.4 | 302 | 30 | L | C | S | |
| 75 | -56.6 | | +7.4 | | 320 | 30 | V | C | S | |
| 75 | | -3.8 | | | 290 | | L | H | S | |
| 75 | | -1.4 | | | | | L | H | S | |
| 75 | -56.6 | -0.5 | +7.1 | | 298 | 40 | V | C | S | |
| 75 | | | | | 299 | | V | C | S | |
| 75 | | -3.1 | | | 335 | | L | H | S | |
| 75 | -56.7 | -2.0 | | | | 2 | L | C | S | |
| 75 | | | | | 243 | | L | H | S | |
| 75 | | -3.2 | | | | | L | H | S | |
| 75 | | -8.0 | +6.0 | 29.5 | 320 | 30 | L | C | S | |
| 75 | | -5.2 | | | 360 | | L | H | S | |
| 75 | | -3.8 | | | 300 | | L | H | S | |
| 193 | | -2.5 | | | 169 | | L | H | S | 5193 |
| 193 | | -3.8 | | | 343 | | L | H | S | |
| 193 | | -3.9 | | | 342 | | L | H | S | |
| 193 | | -4.0 | | | 303 | | V | H | S | |

| | | | | | | | | | |
|-----|-------|-------|------|-----|-----|---|---|---|------|
| 370 | -5.9 | | | | | L | H | B | |
| 370 | -3.9 | +9.0 | | 283 | 30 | L | C | B | |
| 370 | -2.3 | | | | | L | H | B | |
| 370 | -3.5 | | | 319 | | L | H | B | |
| 370 | -3.6 | | | 318 | | L | H | B | |
| 370 | -3.4 | +5.0 | | 311 | 40 | L | H | B | |
| 370 | -3.5 | | | | | L | H | B | |
| 370 | -3.3 | | | 301 | | L | H | B | |
| 370 | -55.7 | | | 304 | 30 | L | C | B | |
| 370 | | | | | | L | H | B | |
| 370 | -56.3 | | | 332 | 50 | V | C | B | |
| 370 | | | | 345 | | L | H | B | |
| 370 | -3.8 | | | 365 | | L | H | B | |
| 370 | -4.7 | | | 349 | | L | H | B | |
| 370 | -4.1 | | | 369 | | L | H | B | |
| 370 | -5.2 | | | 368 | 30 | V | C | B | |
| 370 | -56.4 | -10.6 | +7.0 | 353 | | L | H | B | |
| 370 | | -4.5 | | 337 | | L | H | B | |
| 370 | | -3.3 | | 313 | 50 | V | C | B | |
| 370 | -56.4 | | +7.7 | 346 | 45 | L | C | B | |
| 486 | -57.4 | -5.1 | | 350 | 15 | L | C | B | 4636 |
| 486 | -57.1 | | +6.6 | 338 | 25 | L | C | B | |
| 486 | | | +8.0 | 306 | 30 | L | C | B | |
| 486 | | | 31.0 | 346 | 30 | L | C | B | |
| 486 | | | +6.5 | 323 | 20 | L | C | B | |
| 486 | | | +6.5 | 233 | | L | H | B | |
| 486 | | | +5.6 | 326 | 50 | L | C | B | 4846 |
| 486 | | | +6.5 | 319 | | L | H | B | |
| 482 | | | +7.7 | 296 | 40 | V | C | B | |
| 482 | | | +7.7 | 324 | 40 | V | C | B | |
| 482 | | | +6.5 | | 100 | L | C | B | |
| 482 | -58.6 | | +6.5 | | 100 | L | C | B | |
| 482 | -58.5 | | +6.5 | | 100 | L | C | B | |
| 482 | -58.5 | | | | 100 | L | C | B | |
| 482 | -58.4 | | | | 100 | L | C | B | |
| 482 | -58.6 | | | | 100 | L | C | B | |
| 238 | | | +7.6 | 283 | 5 | L | C | B | 5690 |
| 238 | | | | 290 | | L | H | B | |
| 238 | | | +6.2 | 282 | 2 | L | C | B | |
| 238 | | | +7.0 | 277 | 5 | L | C | B | |
| 238 | -57.0 | | +6.2 | 343 | 50 | V | C | B | |
| 238 | -57.0 | | +6.9 | 342 | 40 | V | C | B | |
| 238 | | | +6.7 | 349 | 5 | L | C | B | |
| 238 | | | | 220 | | L | H | B | |
| 238 | | | -4.9 | 368 | 25 | L | C | B | |
| 238 | | | +6.1 | 315 | | L | H | B | |
| 238 | | | | | | L | H | B | |
| 238 | | | -5.4 | | | L | H | B | |

Abbreviations:

Tf(CO₂) : Fusion Temperature of CO₂
Tf(ice) : Fusion Temperature of Ice
Tf(Cl) : Fusion Temperature of Clathrate
Th(CO₂) : Homogenisation Temperature of CO₂
Th : Final Homogenisation Temperature
V(CO₂) : Volume of CO₂ (%)
Type : Homogenisation Type (L:Liquid,
V:Vapour, C:Critical)
Comp : Composition (H:Aqueous, C:Hydrocarbonic)
Ore : Type of Ore (S:Sheeted Vein Complex,
B:Breccia, R:Ribbon Veins)

TABLE I

| VEIN SET | ATTITUDE Strike; Dip | TEXTURE | ESSENTIAL MINERALOGY |
|----------|-------------------------|---------|-----------------------------|
| (i) | N40-60°E; Vert | F.G. | Sugary Qz (+ Mo, Py) |
| (ii) | N70-130°E; <30° | F.G. | Sugary Qz (+ Py) |
| (iii) | N40-60°E; Vert | F.G. | Sugary Qz (+ Mo, Py) |
| (iv) | N65°E; 60° | F.G. | Ribbon Qz-Mo-Py |
| (v) | (a) Shallow; variable | C.G. | Qz-Or-Py-Mo + accessories * |
| | (b) ditto, see text | C.G. | Qz-Or-Py + Oxides, Sulfides |
| | (c) N35°W; Vert | C.G. | Qz-Or |
| (vi) | Horizontal | C.G. | Qz-Cc-Or |
| (vii) | Variable (see text) | F.G. | Ribbon Qz-Mo-Py * |
| (viii) | N80°E; Vert | F.G. | Chlorite seams |
| (ix) | Variable | F.G. | Cc +/- Qz, Zeolites |

Abbreviations :

Vert : vertical

F.G, C.G : Fine grained, Coarse grained

* : Economically Significant

Qz : Quartz Or : K-Feldspar

Mo : Molybdenite Cc : Calcite

Py : Pyrite

| DEPOSIT | T (°C) | P (bars) | Sal (% NaCl) | CO ₂ | Reference |
|-----------------|---------|----------|--------------|-----------------|-----------|
| Hudson Bay Mtn. | 300-400 | 215-270 | 0 - 12 | yes | 1 |
| Questa | 350-450 | 275-450 | 5 - 12 | yes | 1 |
| Endako | 350-400 | ? | 5 - 14 | no | 1 |
| Copper Basin | 300-400 | <300 | 4 - 12 | yes | 2 |
| Climax | 395-415 | <500 | 0.7 - 12 | yes | 3 |
| Henderson | 500-650 | 350-585 | 0 - 5 | no | 4 |
| Trout Lake | 375-450 | ? | ? | yes | 5 |
| Boss Mtn. | 250-370 | 350 | 2 - 8 | yes | 6 |

- References : (1) Bloom (1981)
(2) Blake et al. (1979)
(3) Hall et al. (1974)
(4) White et al. (1974)
(5) Linnen (oral communication, 1983)
(6) This study.