GEOCHEMISTRY OF FLUID INCLUSIONS AND HYDROTHERMAL ALTERATION IN VEIN- AND FRACTURE-CONTROLLED MINERALIZATION, STOCKWORK MOLYBDENUM DEPOSITS

by

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Abstract

Molybdenum mineralization and coextensive alteration at Questa, Hudson Bay Mountain, and Endako occur in single/composite veinlets which exhibit distinctive alteration assemblages and paragenesis. Fluid inclusion populations from each veinlet type are compositionally distinct. Early fluorinerich, biotite-stable alteration is associated with hypersaline These inclusions homogenize most frequently by halite brines. dissolution at temperatures from 350°-600°+C. Molybdenum mineralization also coincides with guartz-sericite-pyrite alteration and inclusions having moderate to high salinity and lower (≤350°C) temperatures of entrapment. Ubiquitous low-salinity inclusions in addition to inclusion types which characterize each veinlet type suggest superposition of meteoric-dominated convective circulation. These data are evidence for magmatic fluids separate in both space and time from ingress of meteorichydrothermal solutions. Hypersaline brines were precursors to those solutions which precipitated distinctive alteration associations, and formed by boiling/condensation of fluids released by episodic fracturing and ensuing adiabatic decompression.

Highly variable and complex compositional zoning characterizes (K,Na)-feldspar, biotite, and muscovite solid solutions. Although zoning within individual grains is common, compositional trends in the averaged compositions can be correlated with both position in the emplacement sequence and textural characteristics of these alteration phases. Alkali feldspars coexisting in veinlets constitute sensitive geothermometers which pro-

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vide reliable depositional temperatures (≥ 350 °C). X(annite) is highest in magmatic biotite, intermediate in biotite which exhibits replacement textures, and significantly lower, in veinlet assemblages. X(fluorphlogopite) systematically increases from magmatic to veinlet biotite associations; f(H₂O/HF) ratios computed from these compositions predict log f(HF) of approximately -4.0. Departures from muscovite stoichiometry persist among different veinlet assemblages and textural associations, but were not sampled with enough regularity to define trends in spatial disposition.

Alteration geochemistry indicates that mineralization occurred from solutions equilibrated with veinlet assemblages. Fluid-mineral equilibria computations imply chemical characteristics of the ore-forming solutions similar to those measured in high-temperature geothermal fluids. Molybdenite solubility shows extreme dependence on temperature, pH, $f(O_2)$, and f(HF). Molybdenum concentrations up to 100ppm are predicted in oxidized solutions at 350°C. In near-neutral solutions significant amounts of molybdenum are transported as MoO_3F^- and $HMoO_4^-$, with lesser amounts as $H_2MOO_4^{\circ}$ and MoO_2^+ . Chloride and sulfide complex concentrations are not significant. MoO_3F^- becomes the primary transporter of molybdenum in acid solutions and high f(HF).

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I. CHEMISTRY OF INCLUSION FLUIDS: STOCKWORK MOLYBDENUM DEPOSITS FROM QUESTA, NEW MEXICO, AND HUDSON BAY MOUNTAIN AND ENDAKO,

BRITISH COLUMBIA

INTRODUCTION

The importance of superposition and interaction of successive hydrothermal events in modifying individual ore-related processes and obscuring the source(s) of ore-forming fluids in porphyry-type deposits is now commonly recognized. The association of molybdenum mineralization with composite rhyolite porphyries and porphyritic granites and the genetic relation to multiple intrusive events are firmly established (Wallace et al., 1968, 1978; Sharp, 1978, 1979). The close spatial and temporal affinity of these intrusions with molybdenum mineralization is prima facie evidence for a significant magmatic contribution to the ore-forming fluids.

Fluid inclusion studies of well-preserved alteration assemblages in porphyry-type deposits (Preece and Beane, 1979; Wilson et al., 1980) suggest that hydrothermal solutions may be of both direct magmatic and subsequent meteoric origin. Detailed studies of molybdenum-mineralized stockworks reveal a cross-cutting sequence of veinlets and associated alteration which recurs with such frequency as to imply similar fluids and processes common to the evolution of these porphyry-type deposits. They provide an excellent opportunity to obtain information on the hydrothermal solutions and to speculate on the processes which produced stockwork molybdenum orebodies.

The present work describes reconnaissance fluid inclusion studies of evolving fracture-controlled mineralization, alteration, and related fluids in the Questa, New Mexico (36° 42'N, 105° 29'W), Hudson Bay Mountain (54° 49'N, 125° 07'W) and Endako, British Columbia (54° 02'N, 125° 07'W) orebodies. Samples used in the study were collected from areas of the Questa and Endako deposits that were actively mined during 1976 (the 8480 and 3069 benches, respectively) and from drill holes collared on the 3500 exploration level at Hudson Bay Mountain.

GEOLOGY OF QUESTA, HUDSON BAY MOUNTAIN, AND ENDAKO

General characteristics of the Questa, Hudson Bay Mountain, and Endako deposits and their related intrusive rocks suggest that they are similar to stockwork molybdenum systems elsewhere in North America (Clark, 1972; Soregaroli and Sutherland Brown, 1976). Each differs in one or more respects from the configuration, emplacement, or paragenesis associated with well-preserved and documented molybdenum orebodies (Wallace et al., 1968, 1978). These differences as outlined below are reflected by the observed fluid inclusion populations and interpretations of the inclusion fluid chemistry.

Cogenetic Intrusive Rocks

The Questa and Hudson Bay Mountain deposits are associated with felsic, epizonal to hypabyssal intrusive complexes. At Questa, mid-Tertiary intrusions penetrate a column of andesite flow-breccias, crystal-lithic tuffs, and silicic ignimbrites. By contrast, a late-Oligocene plug at Hudson Bay Mountain sharply and discordantly intrudes a pre-molybdenite granodiorite sheet, itself intrusive into Jurassic pyroclastic and sedimentary rocks. The Endako mineralization is localized entirely within a zoned Jurassic batholith without apparent spatial relation to an intrusion of stock- or plug-like extent.

Intrusions associated with Questa and Hudson Bay Mountain are characterized by a variety of textural rock types including aplite, porphyries and crowded porphyries with variable phenocryst/ groundmass ratios, and equigranular to seriate biotite granites and quartz monzonites. The porphyries and crowded porphyries commonly contain quartz, K-feldspar, and minor biotite phenocrysts in aphanitic to aplitic groundmasses and in bulk compositions approximating the quartz-orthoclase-albite ternary minimum. Small systematic differences in bulk composition exist among the textural variations which imply a dynamic and strongly differentiating source intrusion (Ishihara, 1967; Hudson et al., 1979).

Clastic and fragmental textures are commonly observed where structurally high parts of intrusive complexes are preserved (e.g., Questa). Porphyries are dominant at intermediate depths and are truncated by deep-seated granitic rocks (e.g., Questa

and Hudson Bay Mountain). Intermineral dikes and breccias (Kirkham, 1971) are common features which clearly establish a close spacial and genetic relation between the intrusive event(s), mineralization, and alteration.

The Endako stockwork mineralization occurs wholly within an equigranular to weakly seriate quartz monzonitic phase (Endako Quartz Monzonite) of the late-Jurassic Topley Intrusions (Kimura et al., 1976). Hypabyssal aplite, granite porphyry and quartzfeldspar porphyry dikes, all of pre-molybdenite relative age and chemically as well as mineralogically similar to ore-related intrusions at Questa, Hudson Bay Mountain and other molybdenummineralized systems, intrude the Endako Quartz Monzonite. Dike intrusion is an immediate precursor to the ore-forming event(s). Mineralization and alteration, while possibly related to late stages of the same magmatic episode that produced the Toply Intrusions, are not conclusively cogenetic with the Endako Quartz Monzonite.

Alteration and Mineralization

1. Fracture Control

Questa, Hudson Bay Mountain, and Endako each show evidence for multiple fracturing events with consanguineous mineralization and alteration. Ingress of ore-forming solutions and geometry of individual orebodies was largely controlled by development of fractures, veinlets, and multiple vein systems. At Questa, well-developed vein systems parallel the contact between andesite and aplite porphyry in an easterly-trending, south-dip-

ping zone within the inferred source intrusion (Carpenter, Barren to weakly-mineralized stockworks have developed 1968). immediately adjacent to and separating the major veins. The Hudson Bay Mountain deposit contains stockworks immediately above, and gently-inclined vein systems within and largely parallel to the granodiorite sheet (Bright and Jonson, 1976). The rhyolite porphyry plug intrusive into the granodiorite is capped by a stockwork of pre-molybdenite veinlets. The Endako orebody, by comparison, is a complex array of mineralized fractures dominated by continuous, prominent vein systems without relation to lithologic boundaries. Major veins are surrounded by complex veinlet arrays which form stockworks complementing major vein trends (Kimura et al., 1976).

2. Crosscutting Relations

Fracture intensities in the orebodies were generally not sufficient to produce widespread coalescing of veinlets and alteration envelopes or to form pervasive zones of alteration. In each deposit, molybdenum mineralization and coextensive alteration occur as single and composite veinlets which exhibit an ordered sequence of emplacement. Among the samples studied, five main mineralization-alteration associations have been observed:

- (1) pre-molybdenite quartz;
- (2) quartz-biotite-K-feldspar-molybdenite;
- (3) quartz-molybdenite;
- (4) quartz-sericite-pyrite-molybdenite; and

(5) quartz-base metal sulfide veinlets.

The effects of individual hydrothermal events may be separated and identified with these specific veinlet assemblages.

A. Pre-molybdenite Quartz

Pre-molybdenite, barren quartz from veinlets and diffuse silicified envelopes has been observed from each deposit. In areas of high fracture density the veinlets increase in concentration, coalesce and form pervasive zones of silicification. Such a zone of silica replacement at Hudson Bay Mountain suggests that fluids were introduced through a stockwork localized at the apex of the rhyolite porphyry plug. The earliest recognized hydrothermal event at Questa is a similar stockwork of barren quartz veinlets, there localized in aplite porphyry immediately beneath the contact between the source intrusion and andesite. Pre-molybdenite quartz veinlets are present in the footwall of the Endako orebody, but unlike Questa and Hudson Bay Mountain they are associated with distinctive K-feldspar- and biotite-stable alteration envelopes.

B. Quartz-K-feldspar-Biotite

Quartz-K-feldspar-biotite "potassic" assemblages in the veinlet sequence mark the onset of molybdenum mineralization. K-feldspar occurs in thin selvages along fractures and irregular patches in veinlets, and in pervasive replacement of host rock separating veinlets. Concentrations of secondary minerals in hairline fractures, and wide-spread replacement of both ground-

mass and phenocryst feldspars by biotite, K-feldspar and magnetite, are recognized in each of the deposits.

Development of the potassic assemblage, although favored by the bulk rock compositions (Bloom and Brown, 1977), is not always associated with the earliest ore-forming event. For example, biotite-stable alteration preceded molybdenum mineralization at Questa and Hudson Bay Mountain. Composite veinlets with quartz-molybdenite interiors at Questa frequently exhibit barren, biotite-bearing selvages and envelopes. Veinlets which pre-date molybdenum mineralization at Hudson Bay Mountain also exhibit biotite selvages. By contrast, biotite-stable alteration is coextensive with mineralization at Endako.

C. Quartz-MoS₂ /Quartz-Sericite-Pyrite-MoS₂

One or more stages of quartz-molybdenite and quartzsericite-pyrite ± molybdenite mineralization are superimposed on the barren quartz and potassic veinlets, and are coeval with the bulk of the stockwork mineralization. The abundance and distribution of the "phyllic" alteration assemblage is controlled by fracture-related veins and stockworks. Prominent veins at Questa have developed wide phyllic envelopes surrounding the potassic assemblages, and coalescing alteration envelopes have produced locally pervasive quartz-sericite-pyrite zones. Molybdenite-bearing veinlets at Hudson Bay Mountain are of two types distinguished by textural and mineralogical features. The earlier veinlets contain fine-grained disseminated molybdenite in layers alternating with barren quartz ("ribbon veins").

Gangue minerals other than quartz are uncommon, and the veinlets rarely have appreciable alteration haloes. The later veinlets usually cut across and reopen earlier veinlets, but locally also exhibit contrary cross-cutting or gradational relations along a single veinlet. They contain coarse molybdenite flakes and rosettes associated with minor amounts of sericite, K-feldspar and scheelite irregularly distributed in coarse-grained, vuggy quartz. Quartz-sericite-pyrite alteration envelopes surround these veinlets.

Hydrothermal events related to Endako mineralization are also defined by a sequence of relative veinlet ages; molybdenum mineralization is associated with veinlets having both early potassic and crosscutting phyllic alteration envelopes.

FLUID INCLUSION PETROLOGY

Introduction

The major vein systems at Questa, Hudson Bay Mountain and Endako exhibit ribbon texture and local crustification. They appear to have formed by dilation and filling of pre-existing veinlets. Episodic reopening of the prominent veins permitted ingress of fluids throughout the evolution of the respective ore-forming systems, and resulted in complex overlapping of fluid inclusion populations. Fluid inclusions in stockwork quartz veinlets which are consistently related to molybdenite have been studied wherever possible. These veinlets formed by non-destructive dilation and filling, and presented more homogeneous inclusion populations.

It is very difficult to demonstrate a primary origin for specific inclusions (cf. Roedder, 1971). Primary inclusions were identified by their solitary location, presence along crystal growth zones, and absence of evidence for secondary origin. Because isolation as a criterion for the identification of primary inclusions is not sufficient (Wilkins and Bird, 1980), additional criteria were used to recognize inclusions formed at or near the time of mineralization and alteration. Quartz grains showing little evidence of recurrent fracturing were favored; those grains entirely contained within minerals having weak interlayer bond strengths (molybdenite, biotite, sericite) were frequently strain-free and without well-defined, multiple-stage inclusion populations. They often contained only large, solitary inclusions. This observation is evidence that such grains have been protected from repeated fracturing and the ensuing fluids. Another line of evidence favoring primary origin for "primary" inclusions is equivalent temperature estimates obtained by an independent technique. When two subsolidus alkali feldspar solid solutions coexist in a veinlet assemblage, a unique temperature can be obtained using the distribution of $KAlSi_3O_8$ component between the coexisting feldspars (Chapter 2). Temperatures so calculated are in good agreement with the fluid inclusion data, thus inferring primary origin for the inclusions. The method is not conspicuously pressure-dependent and is used subsequently in this communication to obtain first approximations to entrapment pressures.

Classification and Description of Fluid Inclusions

Inclusions from the three deposits, illustrated in Figure 1, were separated into five types:

- Type A: inclusions with 60 volume percent or less vapor and without halite or sylvite daughter minerals (L + V);
- Type B: inclusions with greater than 60 volume percent vapor and occasional halite daughter mineral (V);
- Type C: inclusions with less than 60 volume percent vapor and with a halite daughter mineral (L + V + H);
- Type D: inclusions with less than 60 volume percent vapor and with both halite and sylvite daughter minerals (L + V + H + S); and
- Type E: inclusions with 60 volume percent vapor and with a CO₂-rich liquid phase (L + V + CO₂).

The presence of halite and sylvite in types C and D inclusions has been inferred from optical examination. Other phases present in the inclusions are: (1) hematite, which occurs in some types A and B and many types C and D inclusions; (2) nearly opaque, hexagonal molybdenite, which is confined to types C and D inclusions and distinguished from frequently coexisting hematite by its distinctive color (Kamilli, 1978); and (3) small, opaque, non-magnetic phases which are present in some types C and D inclusions (tetragonal disphenoids observed in a few inclusions suggest that this opaque phase may be chalcopyrite). Some types C and D inclusions also contain unidentified anhedral grains with high birefringence and high refractive index, and unidentified rhombic prisms with symmetrical extinction and extreme birefringence. In view of the irregular distribution and the uncertain compositions of some solid phases, no further sub-







saline type B liquid (L)+vapor (V) ±hematite (Hm)±halite (H)

saline type C liquid (L)+vapor (V)+halite (H) ±hematite (Hm)



Hm V H

hypersaline type D liquid (L)+vapor (V)+halite (H) +sylvite (S)±hematite (Hm) ±molybdenite (M)±unknown (U)

CO₂-rich type E liquid (L)+vapor (V)+CO₂



Figure 1. Fluid inclusion types observed in fracture-controlled, molybdenum-mineralized veinlets and stockworks at Questa, New Mexico and Hudson Bay Mountain and Endako, British Columbia. The inclusions vary from 10 to 50 microns in their largest dimension. Abbreviations for the inclusion phases are as indicated. division of inclusion types C and D has been made.

Distribution of the Fluid Inclusions

The paragenetic relations among veinlets are so consistently observed that an ordered ingress of fluids is strongly suggested. This sequence may be used to relate stages of mineralization and alteration to distinct inclusion populations in the individual orebodies, and generally records the evolution from allied magmatic- to meteoric-hydrothermal events.

Within any single veinlet, it is virtually impossible to establish convincing age relations among the different inclusions. One or more types of inclusion commonly are superimposed to form a complex array of all inclusion types. Successive overprinting has caused pronounced changes in the type and abundance of <u>primary</u> inclusions preserved. It is possible, by a process of elimination similar to that applied by Chivas and Wilkins (1977) but using cross-cutting relations of veinlets together with the abundance and distribution of contained fluid inclusions, to deduce the ordered sequence of fluids which gave rise to the observed mineralization and alteration.

Inclusion types D and C are largely restricted to veinlets having relative ages and alteration assemblages considered premolybdenite (barren quartz, quartz-K-feldspar-biotite) or cogenetic with the ore-forming event(s) (quartz-K-feldspar ± molybdenite, quartz-molybdenite, quartz-sericite-pyrite ± molybdenite). The earliest events recorded at Questa and Hudson Bay Mountain are hypersaline brines (type D inclusions). The

presence of type D inclusions in pre-molybdenite veinlets is evidence that hypersaline precursors to the ore-forming solutions were present and are related to cogenetic intrusive rocks. The conspicuous absence of similar fluids at Endako may infer the absence of intrusions coeval with the molybdenum mineraliz-The relative abundance of type D inclusions at Questa ation. and Hudson Bay Mountain decreases markedly with the appearance and intensity of phyllic alteration. The fluid inclusion record from quartz-molybdenite and quartz-pyrite ± molybdenite veinlets having phyllic alteration envelopes indicates the dominance of more dilute, but still saline solutions. In each deposit, molybdenum mineralization is associated most commonly with liquid-rich type A followed in abundance by saline type C inclusions. As in other porphyry-type deposits (Chivas and Wilkins, 1977; Preece and Beane, 1979; Wilson et al., 1980), type D inclusions are found with potassic alteration assemblages and type C inclusions occur with phyllic alteration.

The position of vapor-rich type B inclusions in the paragenesis, and their relation to types D, C and A inclusions are variable and not firmly established. They occur in veinlets having both potassic and phyllic alteration envelopes. At Questa, type B and types C or D inclusions coexist in small isolated groups. Salinities inferred by the presence of halite daughter minerals in some type B inclusions cannot be readily explained without assuming entrapment of mixed liquid and vapor. Hypersaline brines and low-density fluids must have coexisted at least intermittently prior to and/or during molybdenite deposi-

tion. The presence of low-density fluids coexisting with the solutions which gave rise to type A inclusions is also indicated during the later stages of activity at Hudson Bay Mountain, when no hypersaline brines are observed in the fluid inclusion populations. Vapor-rich inclusions are not present in the fluid inclusion record at Endako. Clearly depths, confining pressures and fracture histories of the individual orebodies bear on the abundance and distribution of type B inclusions.

HOMOGENIZATION DATA

Introduction

A Chaixmeca heating/freezing stage was used for temperature measurement. Nine standards were used for calibration from - $100^{\circ}C$ to $+70^{\circ}C$, and ten were used in the $+70^{\circ}C$ to $+600^{\circ}C$ range. Repeated freezing and melting of single inclusions and standard compounds indicated that recorded melting points in the low range were accurate within $0.5^{\circ}C$ with a precision of $0.2^{\circ}C$ (2σ). For temperature measurements above approximately $70^{\circ}C$, deviation of observed temperature from actual melting point was statistically significant. Corrections to the readout temperature were calculated using the high temperature melting point measurements regressed and smoothly joined with the lower temperature data. Repeated observations on potassium dichromate indicate an accuracy of $4.2^{\circ}C$, reproducible within $2.0^{\circ}C$ at the 95% confidence level.

Sample chips were generally heated only once to avoid spurious measurements caused by stretching and/or rupture of

inclusion walls. In many liquid-rich (types A, C and D) inclusions, one or more daughter minerals persisted beyond the temperature of vapor disappearance. Homogenization by dissolution of halite after disappearance of the vapor phase was common in types C and D inclusions. Probable reasons for the persistence of halite above the temperature of vapor dissappeance are necking down, trapping of solid NaCl, and large pressure corrections (Ahmad and Rose, 1980) or entrapment under relatively unusual P-T conditions exceeding those of the solubility surface in the NaCl system (Wilson et al., 1980). Refractory daughter minerals (chalcopyrite, hematite, and/or molybdenite) remain present in some types A, C and D inclusions after both halite dissolution and vapor disappearance. Their persistence is ascribed to dissolution kinetics or post-entrapment oxidation of the inclusion fluids (Roedder, 1971). The highest temperature of reversible phase disappearance is accepted as the homogenization temperature.

Questa, New Mexico

The temperature of reversible phase changes and the homogenization behavior of 98 primary inclusions were recorded from 10 Questa samples (Figure 2). Liquid-rich inclusions that homogenized by vapor disappearance (types A, C and D) exhibit a skewed distribution of homogenization temperatures with a mode at about 390°C. Vapor-rich (type B) inclusions homogenized in the vapor phase by expansion of the vapor, and show a similar temperature distribution and mode which coincide with those of



Figure 2. Fluid inclusion homogenization (filling) temperatures (uncorrected for pressure) from Questa, Hudson Bay Mountain, and Endako. Separate histrograms are shown for inclusion types A, B,C, and D (Figure 1) as well as for inclusions which homogenize by halite dissolution (types C and D only) and by vapor disappearance (all types). Refer to text for discussion of this homogenization behavior.

the liquid-rich inclusions. A bimodal distribution of homogenization temperatures is suggested by a lower temperature mode at 300°C. Without specific relation to growth features and method of correlation among samples, errors in sampling distinct inclusions populations are implied.

Temperatures at which identifiable daughter minerals dissolved during the heating experiments were recorded for types C and D inclusions that homogenized both by vapor disappearance and by halite dissolution. The halite dissolution temperatures entirely overlap one another, with a mode at slightly higher temperature (400°C) than that of inclusions which homogenize by vapor disappearance. A bimodal distribution of halite-homogenizing type C inclusions is also present, with a lower-temperature mode at 330°C in agreement with vapor-homogenizing types A and C inclusions.

Hudson Bay Mountain, British Columbia

A total of 156 primary inclusions in 13 samples were heated and their homogenization characteristics observed (Figure 2). Liquid-rich inclusions without halite or sylvite and which homogenize by vapor disappearance (type A) were more abundant in the population of inclusions at Hudson Bay Mountain than at Questa. They occurred in a bimodal population with the higher temperature mode divisible into two subclasses at 350° C and 390° C, and the lower temperature mode at 150° C. Liquid-rich inclusions, some having a CO_2 -rich liquid phase (type E) decorate healed fractures and homogenize at temperatures overlapping these

modes; owing to their unmistakable secondary origin, they are not included in Figure 2. The mode of vapor-homogenizing (type B) inclusions (360°C) concurs with that of type A and is skewed toward higher temperature. Types C and D inclusions which homogenized by vapor disappearance did so from 140°C to 400°C and from 320°C to +600°C, respectively, but occurred so infrequently that definite modes were not established.

Types C and D inclusions which homogenized by halite dissolution form a bimodal temperature distribution with modes at 170°C and 390°C. The higher-temperature mode corresponds to early mineralization, whereas the lower-temperature mode is correlative with later molybdenite- and base metal sulfide-bearing veinlets. Note that the lower-temperature population shown by types A and C is shown by type D inclusions. Dissolution temperatures for identifiable daughter minerals were 150°C to 400°C for halite in type C and 330°C to +600°C for halite in type D inclusions, and 70°C to 120°C for sylvite in type D inclusions.

Endako, British Columbia

In contrast to observations of the Questa and Hudson Bay Mountain populations, 133 inclusions in 9 samples from Endako form a population dominated by liquid-rich type A inclusions which homogenized by vapor-disappearance (Figure 2). The single mode at 370°C is weakly skewed toward lower temperatures. Vapor-rich (type B) and liquid-rich type D inclusions seen at Questa and Hudson Bay Mountain are missing from the Endako population; only type C inclusions are present. Type C inclusions

which homogenize by halite dissolution occur at higher temperatures than do those which homogenize by vapor disappearance; liquid-homogenizing type C inclusions fill at temperatures which overlap those of type A inclusions.

INTERPRETATION OF THE FLUID INCLUSION DATA

Salinities of Inclusion Fluids

Salinities of the inclusion fluids are separable into distinct groups dominated by a single inclusion type, but the groups formed by inclusions from different deposits appreciably overlap (Figure 3). Type A inclusions contain no halite or sylvite daughter minerals at 25°C. The bulk composition in the system NaCl-KCl-H₂O must not exceed 21 and 11 weight percent NaCl and KCl, respectively. Direct salinity estimates were made on a number of type A inclusion fluids from each deposit by measurement of ice fusion temperatures and comparison with the data of Potter et al. (1978) for aqueous NaCl solutions. Type A inclusion fluids vary in salinity from about 2 to 15 percent NaCl equivalent (Figure 3). Complete heating data were not obtained for all type A inclusions on which freezing experiments were made owing to their size, extreme internal reflection, and difficulty in relocating specific inclusions.

Collins (1979) has shown that measurement of the depression of ice fusion temperatures by dissolved salts gives rise to inaccurate salinity estimates when clathration of carbon dioxide hydrate occurs. Cursory crushing tests performed on type A inclusions resulted in slight to moderate expansion of vapor at



Figure 3. Temperature-salinity determinations for types A,C, and D inclusion fluids from Questa, Hudson Bay Mountain, and Endako. Salinities given in equivalent weight percent NaCl (types A and C) and NaCl + KCl (type D) and determined from measured dissolution temperatures of halite and sylvite daughter phases. Clustering into low and high salinity populations and the array approximating the liquid-vapor-halite boundary discussed in text. Questa and Hudson Bay Mountain (but not Endako), indicating low partial pressures of gases other than H_2O in the inclusions. The presence of type E inclusions which have CO_2 -rich liquid phase imply that many type A inclusions may also contain sufficient CO_2 to produce clathration. It is suspected that ice and CO_2 gas hydrate may have frozen out simultaneously from some type A inclusions. Because the temperature of CO_2 hydrate decomposition was not observed, the salinity estimates for type A inclusions could be in error by as much as 50 percent (Collins, 1979). Nevertheless, separation of type A from types C and D inclusion fluids (Figure 3) remains as evidence that the type A are compositionally distinct from types C and D inclusion fluids.

For more concentrated solutions saturated with respect to halite but not sylvite (type C inclusions), salinity was approximated by observing the dissolution temperature of halite and converting to NaCl equivalents using regressed solubility data (Potter and Clynne, 1978; Linke, 1965; Keevil, 1942). The estimates for Questa, Hudson Bay Mountain and Endako are 31 to 58, 31 to 52 and 32 to 61 percent NaCl equivalent, respectively. Type C inclusions that homogenize by halite dissolution form an array that approximates the solubility curve in Figure 3. Vapor-homogenizing type C inclusions fall upon or near the hightemperature side of the boundary.

The salinities of hypersaline (type D) inclusion fluids were obtained directly from the halite and sylvite dissolution temperatures and the NaCl-KCl-H₂O diagram of Roedder (1971)

(Figure 4). Individual inclusions from Questa and Hudson Bay Mountain exhibit the following salinities for these inclusion fluids: Questa, minimum 33.5 and 10, and maximum 51 and 19 percent NaCl and KCl, respectively; Hudson Bay Mountain, minimum 19.5 and 13.5, and maximum 60.5 and 19 percent NaCl and KCl, respectively. The mean salinity (wt% NaCl + wt% KCl) is 52 percent at both Questa and Hudson Bay Mountain. Type D inclusions that homogenized by vapor disappearance do not form groups separate from those that homogenized by halite dissolution on Figure Saline and hypersaline (types C and D) inclusion fluids 3. occupy relatively small, compositionally distinct regions of the NaCl-KCl-H₂O system. Type D inclusion fluids also form linear arrays similar to those noted by Cloke and Kesler (1979) and designated halite trends (cf. Erwood et al., 1979; Wilson et al., 1980). The inclusion compositions from Questa and Hudson Bay Mountain produce individual trends that differ slightly in orientation, but project to similar points on the NaCl-KCl join. Inclusions that homogenized both by halite dissolution and by vapor disappearance fall along the halite trends in Figure 4.

Estimates of Pressure and Depth

No unequivocal determination of pressure can be obtained from the Questa, Hudson Bay Mountain or Endako fluid inclusion data, but estimates of vapor pressure from individual inclusion fluids limit the range of entrapment pressures (Figure 5). Close approximations to actual pressures are obtained from individual saline (type C) and hypersaline (type D) inclusions



Figure 4. Compositions of hypersaline type D inclusion fluids from Questa (squares) and Hudson Bay Mountain (triangles) in the NaCl-KCl-H₂O system (Roedder, 1967). Stippled area shows the range of compositions for saline type C inclusion fluids. Enlarged area shows the "halite trend" (Cloke and Kesler, 1979) defined by individual inclusions which homogenize by halite dissolution (solid symbols) and vapor disappearance (open symbols).



Figure 5. Vapor pressure estimates for inclusion fluids from Questa, Hudson Bay Mountain, and Endako. Shown are specific type C inclusions on the solubility surface or in the liquid field (Roedder and Bodnar, 1980), inclusion pairs showing evidence for boiling (or condensation), minimum vapor pressures required to prevent boiling, and K/Na feldspar geothermometry (temperatures for feldspar geothermometry and minimum vapor pressures undefined). Tie lines connect points to show the range of vapor pressure estimates obtained for saline (type C) inclusions. Shaded areas are estimates of lithostatic and hydrostatic load. trapped on the solubility surface, and from inclusion pairs which infer boiling. Those type C inclusions in which halite dissolution and vapor disappearance temperatures differ by 10°C or less are assumed to have been trapped along the solubility surface. The pressure maximum along this boundary decreases with addition of KCl approximating the halite trend exhibited by type D inclusions from Questa and Hudson Bay Mountain, but vapor pressure estimates from types C and D inclusions are comparable.

The presence of vapor-rich inclusions among populations dominated by liquid-rich types suggests that at least some fluids were trapped on a liquid-vapor boundary. Pairs of low density (type B) and saline or hypersaline (types C or D) inclusions at Questa homogenize by simultaneous disappearance of vapor and liquid in liquid- and vapor-rich inclusions, respectively. One or more vapor-rich inclusions may also contain a halite daughter mineral (Figures 1 and 6). High salinities inferred from these inclusions are not possible under boiling conditions in the range of observed temperatures, and suggest random proportions of vapor and high salinity liquid trapped in the inclusion. Samples from Hudson Bay Mountain also show evidence of coexisting liquid and vapor by virtue of coexisting liquid- (type A) and vapor-rich inclusions.

Alternate methods to estimate vapor pressures of individual inclusions provide only minimum estimates of entrapment pressure. Inclusion fluids which do not show evidence of boiling may also have been trapped at higher temperatures and pressures along appropriate isochores above the point of homogenization.


Figure 6. Fluid inclusion populations from Questa (B), Hudson Bay Mountain (A), and Endako (C). Abbreviations for daughter phases as in Figure 1. Note type A populations with both liquidand vapor-rich inclusions (boiling implied) at Hudson Bay Mountain and with coexisting hypersaline, liquid-rich (type D) and saline, vapor-rich (type B) inclusions which suggest boiling and/or condensation at Questa, but the uniformity of liquidvapor ratios in inclusions from Endako. The density of the homogeneous inclusion fluid together with the P-V-T-X measurements of Urusova (1975) was used to obtain the vapor pressure of saline (type C) inclusions that homogenize by halite dissolution (Roedder and Bodnar, 1980) and thus could not have been boiling. This method was used in preference to vapor pressures at temperatures of vapor disappearance on the solubility surface, which are the absolute minimum pressures required to prevent boiling. Minimum pressures of entrapment necessary to prevent coexisting liquid and vapor were also estimated for type C inclusions that homogenized by vapor disappearance using salinity data and the appropriate two-phase liquid-vapor curve (Sourarijan and Kennedy, 1962).

First approximations of pressure were also obtained using the P-T-X dependence of subsolidus, hydrothermal minerals which exhibit solid solution. The distribution of orthoclase component between coexisting alkali feldspars which occur in veinlets of different relative ages from Questa and Hudson Bay Mountain is discussed in Chapter 2. Equations for the excess free energy of K- and Na-rich feldspar solid solutions were solved for unique temperatures of deposition. Temperatures so obtained are nearly pressure independent (-12°C/kbar correction required) and were thus used to estimate pressures of entrapment. The feldspar temperatures are equivalent to as much as 166°C greater than the homogenization temperatures of cogenetic fluid inclusions, suggesting that some but not all of the fluid inclusion data require a pressure correction.

Specific depths approximating any of the vapor pressure

estimates shown on Figure 5 are difficult to assign. Absolute minimums would be lithostatic conditions which give rise to these vapor pressures, but depths in accord with reasonable estimates of geologic cover require pressures that varied between the extremes of lithostatic and hydrostatic load. For example, reconstruction of late-Oligocene volcanic cover above the Questa deposit (Carpenter, 1968; Ishihara, 1967) suggests emplacement at depths of 1000 to 1600 meters. Maximum lithostatic loads of 275 to 400 bars, depending on the locus of mineralization, or hydrostatic pressures of 80 to 100 bars correspond to these Inclusion populations which show evidence of boiling depths. have vapor pressures which infer hydrostatic load, whereas minimum pressures required to prevent boiling of saline and hypersaline fluids and type C inclusions which homogenize by halite dissolution both infer vapor pressures in excess of reconstructed lithostatic load.

Although it is impossible to estimate the depth of ore formation by reconstructing the stratigraphy at Hudson Bay Mountain, Kirkham (1969) has estimated a minimum depth of 2000 meters from the present topography. Type C inclusions which homogenize on the solubility surface and minimum pressures necessary to prevent boiling approximate hydrostatic or greater pressures at this depth. Vapor pressures estimated from type C inclusions which homogenize by halite disappearance are in accord with two kilometers depth if lithostatic conditions are assumed.

At Endako, evidence is not available for an independent

estimate of geologic cover, but inferred vapor pressures may be utilized to reconstruct possible depths of mineralization. The most accurate estimate of vapor pressure is probably obtained from the single type C inclusion that homogenized at 385°C on the solubility surface. The estimate of 160 bars corresponds to depths of about 600 and 2000 meters under lithostatic and hydrostatic conditions, respectively. The minimum depths required to prevent boiling of saline type C inclusion fluids varies from 250 to 570 meters assuming lithostatic load, or 800 to 2000 meters if hydrostatic load is assumed. The hydrostatic depth of approximately two kilometers is consistent with high-level emplacement inferred from chilled, porphyritic margins and miarolytic cavities in the aplite, granite porphyry and quartz-feldspar porphyry dikes which were immediate predecessors of mineralization, whereas unreasonably shallow estimates of depths are generated if lithostatic load is assumed.

Several features are conspicuous on inspection of Figure 5. The range and overlap of vapor pressure estimates suggests that inclusion fluids were trapped under widely varying pressure conditions. The highest estimates of vapor pressure (800 bars) were obtained from inclusions in veinlets which exhibit earlystage cross-cutting relations and alteration. Lower estimates (100 to about 300 bars) were obtained from inclusions in veinlets having both early and late emplacement histories and alteration. Coexisting liquid and vapor appears to have been intermittent and to have occurred throughout a range of temperatures and pressures. Overpressures exceeding reasonable estimates of li-

thostatic load may from time to time have prevailed in the oreforming system(s). The range and overlap of fluid inclusion homogenization temperatures, inferred vapor pressures and alkali feldspar geothermometry are not consistent with a simple, monotonic decline in the temperature of solutions which flowed through the fractures. Processes more closely related to the composition and hence the source of the ore-forming solution(s) are envisioned to produce the observed sequence of veinlets and dominant alteration assemblages.

Temperature and Salinity Dispersion

The inclusion populations of Questa, Hudson Bay Mountain and Endako present a remarkable uniformity of modes although over a range of temperatures and salinities. A variety of processes can give rise to the range of temperatures (cf. Ahmad and Rose, 1980). Homogenization temperatures ≥ 500°C can be explained by trapping random mixtures of coexisting liquid and vapor (cf. Wilson et al., 1980); however, dilution of a single high salinity liquid with vapor in proportions which homogenize by vapor disappearance cannot produce the wide range of salinities observed.

Inclusions which homogenize by halite dissolution may give rise to estimates of entrapment temperatures more accurate than those provided by vapor-homogenizing inclusions. Cloke and Kesler (ibid.) have shown, however, that this behavior requires precipitation of halite from hydrothermal solutions before the fluid was trapped as inclusions. Although no evidence for this

phenomenon was observed (halite xenocrysts in the ore assemblage or host mineral), minute halite grains serving as loci for fluid inclusion formation cannot be rejected. Inclusions which so nucleated would give rise to anomalous salinities and homogenization temperatures which closely approximate the solubility curve in the NaCl-H₂O system; many type C inclusions (Figure 3) do in fact cluster near or on the solubility curve between 30 and 60 percent NaCl equivalent. The temperatures of halite dissolution presented here, however, are in excellent agreement with both NaCl-saturated (types C and D) and undersaturated (type A) inclusions which homogenize by vapor disappearance. The halite dissolution temperatures do not appear anomalous and nucleation of fluid inclusions on halite xenocrysts is not a major mechanism for dispersion of homogenization temperatures and salinity.

The most satisfactory explanation for the range of homogenization temperatures and salinities is that the inclusions are from an inhomogeneous population. Three compositionally distinct inclusion fluids and thus three recognizable hydrothermal solutions are present in the Questa and Hudson Bay Mountain deposits, as shown by the separation of fields representing types A, C and D inclusions on Figures 3 and 4. Fluids with two general ranges of salinity were present during the evolution of the ore-forming systems, one with 1 to 20 and another with 30 to 60 percent NaCl equivalent. More importantly, the high salinity solutions form two compositionally distinct groups distinguished by their K/Na atomic ratios, types C and D having ≤ 0.2 and \geq

0.2 K/Na, respectively. Although inclusions containing each solution type are found throughout the vertical extent of the orebodies, the abundance and distribution of inclusion types are related to veinlets having different relative ages and distinctive mineral assemblages and/or wallrock alteration. The observed cross-cutting relations of these veinlets suggest that the general order of appearance for the solutions is represented by type D (absent at Endako), type C and finally type A inclusion fluids. Extensive and recurrent fracturing must have permitted ingress of solution individually from time to time at any given location in the ore-forming systems. Some of the variation, however, might still reflect mixed-phase entrapment, modifications (necking down or opening of inclusions), and mixing of fluids, and the possibility of unrecognized secondary inclusions cannot be discounted.

Pressure Correction

The homogenization temperatures are uncorrected for the effects of pressure. The presence of vapor-rich inclusions and the equivalence of some feldspar temperatures suggest that at least some inclusions were trapped on the solubility surface and therefore that their homogenization temperatures do not require a pressure correction. Other inclusions give rise to vapor pressure estimates which infer entrapment pressures between hydrostatic and lithostatic load conditions, and still others infer pressures in excess of reasonable lithostatic load. These observations indicate that pressure varied during mineraliz-

ation, so that different pressure corrections are required for different inclusions. It is not possible, therefore, to obtain a universal pressure correction which can be applied to all data from a given deposit (except perhaps at Endako, where a hydrostatic load of approximately 160 bars has been inferred). Pressure variation at hydrostatic depths of about 2 kilometers gives pressure corrections on the order of 10°C or less for solutions of 5 to 25 percent NaCl equivalent (Potter, 1977). The effect of individual pressure corrections on temperatures of mineralization at Questa and Hudson Bay Mountain are difficult to assess, but there is no evidence to support excessive increases in modes or dispersion of the homogenization temperatures when pressure corrections are applied.

SOURCE AND EVOLUTION OF THE INCLUSION FLUIDS

Because the Questa and Hudson Bay Mountain deposits are spatially and temporally related to rhyolite porphyries, and mineralization at Endako is preceded by compositionally similar dikes intrusive into the Endako Quartz Monzonite, it is logical to appeal to the granitic intrusions as a source of hydrothermal solutions. The K/Na atomic ratios of the inclusion fluids together with observed homogenization data and temperatures inferred by K/Na feldspar compositions can be used to test this generalization. K/Na ratios of type D inclusion fluids yield average temperatures for water-rock equilibrium in the KAlSi₃O₈-NaAlSi₃O₈-NaCl-KCl-H₂O system of 645°C and 712°C for Questa and Hudson Bay Mountain, respectively (Lagache and Weisbrod, 1977).

Most equilibrium temperatures do not agree with the lower fluid inclusion temperatures, but the K/Na feldspar data predict temperatures remarkably close to the ternary minimum.

Ca contents (assuming type D inclusion fluids at Questa and Hudson Bay Mountain are in equilibrium with granitic rock at the appropriate K/Na feldspar and fluid inclusion homogenization temperatures) have been estimated using the K-Na-Ca geothermometer of Fournier and Truesdell (1973). The K/Na feldspar temperatures give rise to Ca molalities of 0.2 to 3.1 and 0.7 to 3.2 for Questa and Hudson Bay Mountain, respectively. If the observed fluid inclusion homogenization temperatures are used, Ca molalities range from 0.7 to 30.6 and 3.2 to 18.9 for the same deposits. The presence of fluorite in many quartz-molybdenite veins and the fluorine concentration of the ore-forming solutions calculated from H₂O-HF fugacity ratios derived from fluorine-rich biotite (Chapters 2 and 3) effectively limit Ca concentrations. K/Na feldspar temperatures predict Ca concentrations well within these limits; however, only the highest fluid inclusion homogenization temperatures could give rise to Ca concentrations indicative of water-rock equilibrium. Following the reasoning of Wilson et al. (1980), these observations indicate that type D inclusion fluids maintained equilibrium with granitic rocks only at temperatures of 500°C or more, and suggest that type D inclusion exsolved directly from a source intrusion of granitic composition.

Experimental data of Lagache and Weisbrod (1977) show that type C inclusion fluids equilibrate with granitic rocks at 500°C

Because this temperature is well below the ternary or less. minimum, type C inclusion fluids could not have exsolved directly from a granitic source intrusion. Alternative methods of producing type C inclusion fluids are: 1) re-equilibration of type D inclusion fluids with the source intrusion; 2) boiling of less saline solutions; and, 3) dilution of hypersaline brines. Processes such as isothermal or isenthalpic decompression, liquid-vapor phase separation (boiling), or dilution of hypersaline brines cause K/Na exchange between fluid and rock and corresponding adjustments of the K/Na ratio in the fluid to reach new equilibrium conditions. The molal K/Na ratios and alteration assemblages attending these water-rock interactions are consistent with re-equilibration of types D or A inclusion fluids and the rhyolite porphyries at Questa and Hudson Bay Mountain to form type C inclusion fluids, and supported by transitions from type D to type C inclusions in the veinlets with changes from potassic to phyllic alteration assemblages. Derivation of type C inclusion fluids by equilibration of meteoric solutions with the source intrusion(s) and attainment of their high salinities by boiling is also possible. An origin by boiling of a low salinity liquid, however, generates large volumes of vapor which are not evident in the fluid inclusion record as an abundance of vapor-rich inclusions. Type C inclusion fluids could also have originated from ingress of less saline solutions which remove NaCl precipitated along the halite trend by earlier hypersaline fluids (cf. Erwood et al., 1979). The agreement of type C inclusion homogenization temperatures

with those of types A, B and D, however, argues against random incorporation of halite xenocrysts in the inclusions.

The absence of salinities intermediate between about 15 and 30 percent NaCl equivalent is not unique to molybdenum-mineralized stockworks; in fact, it is commonly recognized in porphrytype deposits. The salinity hiatus in Figure 3 and discontinuity of the halite trend toward the H₂O apex in Figure 4 suggest that although the fluids were completely miscible, there was little or no mixing of types C or D inclusion fluids with meteoric solutions. The true source(s) of hypersaline (type D) and saline (type C) inclusion fluids is doubtless much more complex than the alternatives presented here, but magmatic derivation of these solutions under fluctuating hydrostatic to lithostatic load (with occasional overpressure) appears to best explain the observations.

Evolution of Inclusion Populations

No single path exists on a pressure-temperature projection of the NaCl-H₂O system (Figure 7) that will produce a mixed population which includes both liquid- and vapor-rich inclusions, exhibits a wide range of homogenization temperatures and contains types C and D inclusions homogenizing by halite dissolution as well as vapor disappearance (Cloke and Kesler, 1979). Saline and hypersaline (types C and D) inclusion fluids which homogenize by halite dissolution are trapped under temperaturepressure conditions exceeding the salinity surface (Wilson et al., 1980). Solutions under normal hydrostatic pressure flowing



TEMPERATURE (*centigrade*)

Figure 7. Solubility curve approximating the Questa and Hudson Bay Mountain halite trends in the NaCl-KCl-H₂O system (modified after Cloke and Kesler, 1979). Heavy and medium solid lines are boundaries for vapor + halite, liquid + vapor, liquid, and liquid + halite stable regions at 30 (stippled) and 50 percent NaCl equivalent (Sourarijan and Kennedy, 1962). Fine lines are paths by which types C and D inclusions could have formed. See text for discussion of points U to ZZ. out of an intrusion along U-V-W on Figure 7 decrease rapidly in temperature at nearly constant pressure. A solution with a total salinity of 50% at U will saturate with halite at V and precipitate halite along V-W as the solution becomes less saline. Such circulation loops involve increasingly smaller excursions in temperature as an intrusion cools (Cathles, 1977). Similar paths could thus exist at lower pressure entirely within the liquid field of less saline solutions to produce homogeneous inclusion populations which homogenize by vapor-disappearance (cf. Endako).

The fluid containing 50 percent NaCl equivalent at U could, with migration of the hydrothermal solution, drop in pressure and temperature to X on Figure 7. Further cooling will occur along the isochore X-Y if part of this solution is trapped as an inclusion at X. Cooling proceeds along a constant-volume path across the liquid + vapor region to VV, where halite begins to separate, and then along the solubility curve to ambient conditions. Small proportions of type C inclusions from Endako and types C and D inclusions from Questa and Hudson Bay Mountain homogenize by simultaneous disappearance of vapor and halite. This behavior requires entrapment of liquid without vapor along the solubility curve VV-Z. Further cooling at pressures exceeding the solubility curve along Z-ZZ produces inclusions which homogenize by halite dissolution. A decline in pressure can thus produce a series of inclusions on the halite trend which homogenize over a range of temperatures by vapor disappearance or halite dissolution.

Dynamic systems exhibiting sharp fluctuations in pressure and temperature account for mixed-phase entrapment in regions where vapor cannot stably coexist with liquid under conditions which produce inclusions homogenizing by halite dissolution. The pre-entrapment vapor necessary to produce coexisting hypersaline and vapor-rich (types D and B) inclusions at Questa and Hudson Bay Mountain could result from cooling along U-UU in Figure 7, in which boiling accompanies a rapid drop in pressure. Solutions trapped as fluid inclusions above the solubility curve and temperatures within the liquid (XX) or liquid + vapor (YY) fields can develop, simultaneously, vapor- and liquid-rich inclusions homogenizing by vapor disappearance. Further pressure reduction into the vapor + halite field (UU) prior to entrapment will cause boiling and precipitation of halite. Liquids on the halite trend are produced simultaneously with vapor, and cool to points such as VV or Z on the solubility curve. If the liquids at VV or Z were separated from coexisting vapor, cooling to WW or ZZ would produce more liquids on the halite trend which, when trapped as inclusions, homogenize by halite dissolution.

One mechanism capable of generating the observed inclusion populations is accumulation and episodic release of fluids exsolved directly from the source intrusion(s) (Ganster, 1977). The fluids so released would undergo irreversible, isenthalpic decompression (Barton and Toulmin, 1961). Initial fracture density need not be great and the resulting pressure drop could produce vapor pressures intermediate between lithostatic and hydrostatic load. The associated expansion of the fluids and

closure of the fractures by mineral deposition, however, would promote thorough and repeated fracture events consistent with the cross-cutting relations and multiple-stage introduction of solutions observed. Fracture propagation would eventually breach to hydrostatic pressures and convective circulation in a normal hydrostatic environment would ensue, as evidenced by light stable isotope data (Hall et al., 1974) indicative of extensive mixing of magmatic and meteoric solutions. The consequences of irreversible isenthalpic decompression with respect to cooling of the hydrothermal solutions can be visualized with the aid of Figure 8. A pressure decrease corresponding to the upper and lower limits of vapor pressures estimated from the fluid inclusion data will cause cooling of the fluid from solidus temperatures to about 400°C, in excellent agreement with the observed temperature modes for the ore-forming solutions. It should be noted that cooling by isenthalpic decompression as shown on Figure 8 is for pure H_2O only; little is known about the effect of dissolved solutes on the enthalpy of solution. Kasper et al. (1979) have directly measured the enthalpy of NaCl solutions at temperatures to 800°C and pressures to 1000 bars over a concentration range of 0 to 6 molal. Their data in the single-phase region of the NaCl-H₂O system shows that up to about 300°C and 500 bars the specific enthalpy of solutions 3 molal NaCl cannot be distinguished from that of pure H_2O , and the similarity extends to higher NaCl concentration at 1000 Thus, Figure 8 is a reasonable first approximation for bars. the cooling effects of isenthalpic decompression at low NaCl



Figure 8. Temperature-pressure diagram showing the effect of irreversible, isenthalpic cooling by decompression without conductive or convective heat exchange (modified after Barton and Toulmin, 1961). Solid arrow traces possible path of fluid undergoing decompression from pressures approximating lithostatic conditions to hydrostatic load as implied by the fluid inclusion vapor pressure estimates in Figure 5. concentrations. Significant deviations from Figure 8 can be expected for hypersaline brines, as evidenced by extremely negative partial molal volumes for NaCl derived by Urusova (1975), and the effect of decreasing NaCl concentration as a consequence of NaCl precipitation along the halite trend is unknown. Further work is necessary to verify irreversible isenthalpic decompression as a feasible mechanism for cooling precursors to the ore-forming solutions in stockwork molybdenum deposits.

CONCLUSIONS

The data and interpretations presented above permit the following tentative conclusions about the general evolution of ore-forming and related events in stockwork molybdenum deposits and the specific environments of deposition in the Questa, Hudson Bay Mountain and Endako orebodies. Early barren quartz and quartz-K-feldspar-biotite ± molybdenite veinlets at Questa and Hudson Bay Mountain formed from solutions with salinities of up to 70 percent NaCl + KCl and K/Na atomic ratios of 0.2 or These hypersaline fluids were in general precursors to more. the actual ore-forming solutions. They evolved directly from the source intrusions under lithostatic load or reasonable overpressures and at temperatures approximating the KAlSi₃O₈-NaAlSi₃O₈-SiO₂-H₂O ternary minimum down to about 500°C. These solutions are not evident in the fluid inclusion record at Endako, but the presence of pre-ore rhyolite porphyry dikes indicates that a similar intrusive event and similar inclusion populations could exist at depth.

Recurrent fracturing gave rise to multiple-stage mineralization and alteration. The bulk of the molybdenum mineralization at Questa, Hudson Bay Mountain and Endako is associated with quartz-sericite-pyrite alteration from fluids with salinities similar to the earlier hypersaline brines, but K/Na atomic ratios less than 0.2. Temperatures of homogenization from about 300° to 600°C with definite modes occurring at 390°C were observed. Equilibration with the source intrusion and/or scavenging of NaCl precipitated in the veinlet assemblage by earlier hypersaline fluids evolving along the halite trend could explain the similar salinities but different K/Na ratios. A significant increase in salinity by boiling, however, is not consistent with the fluid inclusion evidence for only localized, intermittent boiling.

The fluid inclusion record provides evidence for pressure fluctuations between the extremes of lithostatic and hydrostatic load and lends support to intermittent, perhaps cyclic overpressure. Fracture events with ensuing irreversible adiabatic decompression of escaping fluids is suggested as a possible mechanism of cooling the hydrothermal solutions from near-magmatic temperatures. Further fracturing of the hydrothermal systems permitted ingress of meteoric water which formed the ubiquitous low salinity inclusions. The ore-forming events at Endako may have occurred only during these late stages of evolution.

II. GEOCHEMISTRY OF HYDROTHERMAL ALTERATION

INTRODUCTION

Geochemists have in recent years had considerable success in reconstructing hydrothermal processes by experimentally or theoretically predicting phase relations among minerals and aqueous solutions from alteration assemblages deposited in particular ore-forming environments. For example, studies of mica geochemistry in stockwork molybdenum deposits (Gunow et al., 1980) have successfully shown the important role of fluorine in magmatic-hydrothermal fluids, and further understanding of oreforming processes in porphyry-type systems has been gained by calculating phase relations among silicates, copper-iron sulfides, and aqueous solutions at magmatic temperatures (McKenzie and Helgeson, 1980). Knowledge of the composition of mineral phases is a necessary prerequisite for computing chemical characteristics of the hydrothermal fluids coexisting with observed alteration assemblages and zonation.

Vein- and fracture-controlled mineralization in stockwork molybdenum deposits contains alteration assemblages in which crystalline solid solutions are common constituents. This paper reports electron microprobe analyses of alkali feldspar, scheelite, muscovite, and biotite solid solutions in samples from the Hudson Bay Mountain and Endako (British Columbia, Canada) and Questa (New Mexico, U.S.A.) stockwork molybdenum deposits. Activity-composition relations for representative analyses are

estimated in this communication, and the composition of aqueous solutions coexisting with the alteration assemblages as well as implications for the ore-forming process(es) are considered in Chapter 3.

ALTERATION PETROGRAPHY

A comprehensive review of the geology of Climax-type molybdenum deposits (White et al., 1981) has demonstrated close spatial and temporal relations of stockwork mineralization to specific intrusive phases, fracturing and hydrothermal events. Detailed studies of Questa, Hudson Bay Mountain, and Endako, have been presented by Carpenter (1968) and Dunlop et al. (1978); Bright and Johnson (1976); and Kimura et al. (1976), respectively. Important features of the veinlet and fracturecontrolled assemblages of these deposits are documented here in an abbreviated format to aid interpretation of the hydrothermal alteration and to application to computation of aqueous solution compositons.

Relative Age Relations

The configuration and localization of mineralization, alteration zoning, and vein paragenesis are strongly influenced by multiple events of intrusion and fracture. A generalized paragenesis of cross-cutting single and composite veinlets has been described for Questa, Hudson Bay Mountain, and Endako (Chapter 1 and Bloom, 1981) which indicates an ordered sequence of emplacement. The earliest-formed veinlets consist of barren

(molybdenite-free) quartz ± selvages of alkali feldspar and biotite. Beyond veinlet walls the original igneous textures are preserved and mesoscopic alteration envelopes are absent. The earliest molybdenum mineralization is associated with guartzalkali feldspar-biotite ± fluorite veinlets that exhibit alteration envelopes of similar mineralogy. One or more stages of quartz-molybdenite and quartz-sericite-pyrite molybdenite mineralization are superimposed on veinlets having the biotite-stable alteration assemblage. Early biotite-stable and later sericitestable assemblages may locally present contrary cross-cutting or gradational relations along a single veinlet; however, as a group the sericite-bearing veinlets invariably cut across and/or reopen earlier biotite-bearing veinlets which themselves may exhibit quartz-sericite-pyrite alteration envelopes. Alkali feldspar is common to both biotite- and sericite-stable veinlet assemblages, particularly at Hudson Bay Mountain. All three veinlet assemblages may contain topaz solid solution in addition to the minerals that characterize them. Still later base-metal sulfide (chalcopyrite-sphalerite-galena) veinlets with quartzpyrite ± carbonate ± fluorite gangue have selvages and/or envelopes of sericite ± alkali feldspar and cut across molybdenitebearing veinlets.

Textural Variations

Textural criteria as well as relative position in the paragenetic sequence may also be used to distinguish different origins for the alteration minerals biotite, white mica, and alkali feldspar. Textures of alteration minerals range from very fine-

grained aggregates to coarse, apparently unreacted grains. The criteria for identifying different origins for the alteration include: 1) textural evidence that the mineral was formed by subsolidus reaction of a magmatic phase with an aqueous fluid or by direct contact with the fluid phase and 2) the spatial disposition of alteration phases within single veinlets and composite veins.

Magmatic biotites from Questa and Hudsons Bay Mountain occur characteristically as coarse grained, subhedral to euhedral grains that are generally unaltered to other phases, free of cleavage, show uniform extinction, and have straight boundaries against adjacent minerals. Similar, apparently magmatic biotite from Endako appears on chemical grounds presented in this study to be completely recrystallized to grains enriched in fluorine and magnesium relative to their original igneous counterparts. Magmatic biotites may be partially to entirely replaced by sheath-like forms, radial fan-shaped arrays, and poorly-defined but optically continuous patches. Such replacements occur progressively inward from original grain boundaries, and the maximum individual grain size rarely exceeds 0.5mm. The replacement of magmatic grains is selective, because adjacent grains often remain unaltered. Fine grained biotite compositionally identical to the replacement biotite occurs scattered along grain boundaries of framework guartz and feldspar, or as patchy aggregates of grains replacing feldspar. Coarse grained hydrothermal biotite most commonly occurs as sheaves of randomly oriented, lenticular to tabular masses in selvages along veinlet

walls. Composite veins often exhibit a biotite selvage and one or more trains of biotite ± alkali feldspar ± molybdenite which are subparallel to the vein walls and separated by quartz-molybdenite or barren quartz. This feature is evidence for recurrent fracturing and reopening of the veins with ingress of aqueous fluids.

Sericite is rare in assemblages dominated by biotite-stable alteration, and where present is restricted to minute flakes wholly within slighty altered feldspar, or to rare scattered aggregates. Moderate development of white mica occurs peripherally to more intense fracture-controlled alteration. The sericite consists of aggregates of minute, unoriented, almost equant flakes less than 0.1mm in maximum dimension. Sericite within alteration envelopes occurs as felted masses which replace all constituents except quartz, and which occasionally show a vague preferred orientation. Fracture intensities were generally not sufficient to produce widespread coalescing of veinlets and alteration envelopes to form pervasive zones of alteration. Sericite within the veinlet occurs as selvages lining the veinlet walls, as well-developed solid-phase inclusion trails encased in guartz, and as encrustations upon or intimately intergrown with quartz-molybdenite + scheelite (at Hudson Bay Mountain only) + base metal sulfide assemblages in open space fillings.

Alkali feldspars occur as trains of euhedral crystals which may coalesce to form monomineralic fibres aligned either normal to or parallel with walls of composite veins, as irregularly

distributed solitary grains in single veinlets, and as metasomatic flooding adjacent to veinlets.

METHOD OF INVESTIGATION AND ANALYTICAL TECHNIQUES

Hand specimens were collected from each distinctive stage in the sequence of veinlet emplacement as well as from the diagnostic textural groups outlined herein. Sampling at regular intervals and over large portions of the known ore deposits to determine possible spatial and temporal trends accompanying mineralogic changes in alteration assemblages, however, was not Samples were taken from the 8480 and 3069 bench undertaken. levels at Questa and Endako, respectively, and from drill core at Questa and Hudson Bay Mountain. Petrographic examinations were undertaken on polished thin sections, and electron microprobe analyses were made on selected magmatic and hydrothermal minerals in the veinlets. Some minerals from alteration envelopes were analyzed, but emphasis was placed on those assemblages within veinlets in which position in the paragenesis relative to molybdenum mineralization could be established.

Mineral analyses were obtained using normal wavelength-dispersive (WDS) and energy-dispersive (EDS) methods on an automated Cameca MBX electron microprobe at the Los Alamos Scientific Laboratory, New Mexico. WDS analyses were made with a constant accelerating potential of 15 kV and a specimen current of 0.05 micro-amperes, measured on brass. Beam diameters were adjusted from 5 to 20 microns to maximize count rates with minimum alkali volatilization, and counts were accumulated to a constant, integrated beam current. All calibrations were carried out utilizing structurally similar synthetic and natural biotites, muscovite, and feldspars with Bence-Albee correction procedures.

A total of 550 individual microprobe analyses of biotite, white mica, alkali feldspar, and scheelite were made. Analyses reported in this communication represent a minimum of 10 spot analyses on each of several grains. Adjacent grains of each mineral in an assemblage were analyzed with repeated counts on several grains, and traverses across individual grains were made in an effort to determine compositional homogeneities within individual samples. Accuracy and precision were evaluated using replicate analyses of standard mineral grains (Table I). Mean compositions and sample variances were calculated from the multiple spot analyses. Mean analyses were combined to form the overall mean and standard error when separate grains from the same veinlet assemblage did not differ significantly in composi-When individual, optically continuous grains exhibited tion. compositional variation, only those analyses corresponding to the rims of those grains were employed here and used in the computations presented in Chapter 3.

Highly variable and complex compositional zoning is characteristic of biotite and to lesser extent white mica and alkali feldspar solid solutions from these assemblages. Although zoning within individual crystals is common, compositional trends in the averaged compositions can be correlated with position in the paragenetic sequence or coexisting mineral assem-

Solid Solution Standard # Anal in Mean	Feldspar OR-1' 16	Biotite FPHL7 51	Biotite B65F' 27	White Mica MU-1* 16
SiO2	64.18±0.72	42.74±0.36	34.39±0.29	45.40
TiOz				0.63
A1203	18.82±0.16	12.15±0.20	10.96±0.16	31.42
FeO			35.44±0.28	5.21
MnO			0.63±0.12	0.04
MgO		28.60±0.25	1.18±0.14	0.89
CaO	0.018±0.016	0.01±0.01	0.01±0.01	
BaO	0.884±0.080			
NazO	1.003±0.068		0.24±0.08	0.45
K20	14.65±0.19	11.08±0.24	8.35±0.23	10.23
F		8.95±0.27		
Subtotal		103.53	91.20	94.27
0 = F				•
Hi2O				
r - + - 1	00 0010 17			

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Table I. Average WDS Electron Microprobe Analyses of standard Solid Solution Phases.

'Amelia Albite 'Westrich and Navrotsky, 1981 'Pikes Peak Batholith 'Evans, 1965. blage. Compositional fluctuations within a single phase could be due either to true crystalline solid solution or to interlayering of a structurally similar second phase (Page and Wenk, 1979). Because the latter scale of heterogeneity cannot be resolved with the electron microprobe, local differences in composition were ascribed entirely to solid solution.

DATA PRESENTATION FOR MULTICOMPONENT SOLID SOLUTIONS

Introduction

Compilations of alteration phase compositions from stockwork molybdenum (Gunow et al., 1980), porphyry copper (Jacobs and Parry, 1979; Guilbert and Schafer, 1979), and active geothermal systems (McDowell and Elders, 1980) report data for crystalline solid solution phases as site occupancies or end member mole fractions derived from structural formulae. This paper departs from this convention because procedures for calculating the structural formulae of layer silicates assume that 1) the chemical analyses are both perfectly accurate and complete, and 2) either complete octahedral and/or tetrahedral site occupancy or a constant sum of positive cation charges per unit cell is achieved. The alternate methods each give rise to differing mole fractions of end members, particularly halogen site occupancies, in the solid solution which appear negligible but which can become significant when employing activity-composition relations to predict the composition of coexisting aqueous solutions. Regression methods for the calculation of end member mole fractions have been adopted which are not dependent on the

structural formulae and which consider analytical uncertainties in the compositional data. Electron microprobe analyses of secondary mineral in pre-molybdenite and molybdenum-mineralized veinlets and alteration envelopes are presented here as absolute oxide weight percentage and as mole fractions of component end members derived from the regression models; a more detailed presentation of analyses, including provisional structural formulae and individual analyses is given in the appendices.

Components and Compositional Space

A key to interpretation of the compositional space for any solid solution is the number of substitutions possible in a naturally-occurring mineral, each complete substitution defining an end member. Whenever possible, solid solution phases have been described in terms of binary solid solution models. Both the alkali feldspar (orthoclase-albite) and scheelite (scheelite-powellite) solid solutions are so described. There is, however, no generally accepted solid solution model for any mineral with greater than two solid solution end members, and in the case of layer silicates, there is insufficient data to make such models. As a first approximation, multi-component solid solutions for white mica and biotite assume ideal site substitution (Kerrick and Darken, 1975). The site occupancy of an analysed solid solution phase can be expressed independently of any assumptions made to calculate structural formulae, and can be related directly to mole fractions of end members using descriptors for the compositional space.

Solid solution descriptors relate the mole fractions of end members in binary substitution schemes to site occupancies in multi-component solid solutions as well as to expressions for structural formulae. To illustrate this concept, consider a solid solution phase in which isomorphic substitution occurs on two independent crystallographic sites, as in octahedral (Fe, Mg) and hydroxyl (OH, F) substitution in biotite. In this simple example one descriptor, say p, defines the mole fraction of octahedral magnesium end member (phlogopite), and another (q) defines the fluorine end member mole fraction (fluorphlogopite). Note that, since the mole fractions of end members in binary substitution schemes are linearly dependent, one descriptor is sufficient to describe each binary in terms of its end members. The mole fraction of each end member within this compositional space is proportional to the area of the rectangular cross section opposite the specified end member. For example, X(fluorphlogopite) in this model equals (1-p)(1-q). Thus, the composition of any phase within this subset of compositional space is uniquely defined by specifying a value for any two independent descriptors. If the compositional space is expanded to include substitution on one additional site (e.g., K-Na substitution on the interlayer site), then one additional descriptor is necessary to describe any analysis within the compositional space. A term must appear in each solid solution descriptor for each like substitution in the compositional space.

The solid solution descriptors used in this study have been determined by least-squares regression of the electron micro-

probe data for end member mole fractions in the compositional The framework oxides of Si and Al were corrected for space. minor-element substitution, so that imaginary end members such as Ti biotite were not considered. Stepwise linear regression of oxide weight percentages were subject to the constraint that the coefficient (mole fraction) of each end member in the model remain positive, i.e. the chemical analysis lies within the compositional space defined by the chosen set of end members. Α particular combination of end members is considered significant only if the residual between the observed compositions in terms of oxides and the modeled compositions in terms of end members is minimized relative to all other possible sets of end members which could describe the compositional space. The end members used in the regression analyses to describe the natural solid solutions together with equations relating measured mineral compositions to solid solution descriptors are given in Table II.

1. Dioctahedral Layer Silicates

Average compositions for white micas from Questa and Hudson Bay Mountain expressed both as oxide totals and as end member mole fractions are listed in Table III. Mole fractions of end members corresponding to stoichiometric $KAl_2(AlSi_3O_{10})(OH)_2$, $NaAl_2(AlSi_3O_{10})(OH)_2$, and $(K,Na)(Al,Fe,Mg)_2(Si_4O_{10})(OH)_2)$ (muscovite, paragonite, K-Na Fe-Mg-Al celadonite, respectively) were used as a first approximation to the compositional space representing white mica. This assumes that Fe and Mg are energetically equivalent when substituting for octahedral Al, because

fable	II.	Descriptors	and	Structural	Formulae	for	Natural	Solid	Solutions.
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Solid Solution	Descriptors
white mica	<pre>p = X(prgnt)/[X(mscvt)+X(prgnt)+X(cldnt)+X(F~cldnt)]</pre>
	q = X(cldnt) + X(F-cldnt)
	r = X(F-cldnt)
biotite	p = ΣX(Mg) ¹ /[X(Mg)+3X(annite)+3X(F-minnesotaite)]
	q = X(eastonite)
	r = X(F-phlogopite)+X(F-minnesotaite)
	s = X(F-minnesotaite)
scheelite	p = X(powellite)/[X(powellite)+X(scheelite)+X(stolzite)
	q = X(stolzite)

'IMg = 3X(phlogopite)+2.5X(eastonite)+3X(F-phlogopite)

Solid Solution	Structural Formulae
white mica	K(1-p)A1[Mg(s)Fe(q-s)A1(1-q)]A1(1-q)S1(3+q)O:o(OH)(2-2r)F(2r)
Diotite	K(1-s)Mg(3-q/2)pFe(3-q/2)(1-p)A1(q/2)A1(1+q/2-s)S1(3-q/2+s)O:o(2-2r)F(2r)
Scheelite	Ca(1-q)WO:(1-p)

Location Sample # anal	Questa QDH27-30 6	Questa QDH27-30 4	Questa QDH78-67	НВМ' H77-368.5	НВМ Н92-2 5	НВМ Н96-209.5	НВМ H72-2156
S10:	47.98	44.75	48.92	47.20	45.87	49.21	49,58
T101	0.193	0.282	0.400	0.078	0.476	0.164	0,118
A1201	30.79	34.54	30.99	30.03	29.34	28.68	33.14
Fe0	1.635	2.675	2.382	2.601	4,564	3.032	1.856
MnO	0.055	0.038	0.089	0.028	0.030	0.0	0.10
MaD	2.40	1.00	2.38	1.51	3.36	2.50	0.86
CaO	0.033	0.005	0.014	0.021	0.022	0.037	0.058
Ba0	0.118	0.048	NA	NA	0.058	NA	NA
Na 20	0.417	0.682	0.418	0.076	0.120	0.061	0.064
K20	10.72	10.20	10.76	10.97	10.43	10.88	10.76
F	NA	NA	0.777	0.268	NA	1.148	0.192
Subtotal	94.35	94.22	97.13	92.78	94.27	95.71	96.64
0 = F			0.327	0.113		0.483	0.081
H₂O			3.936	3.983		3.698	4.233
Total			100.74	96.65		98.93	100.79
		Molec	cular Percer	t End Members	<u>5</u>		
Muscovite	0.657	0.773	0.585	0.682	0.622	0.488	0.719
Paragonite K(Fe,Mg)	0.065	0.102	0.093	0.029	0.049	0.032	0.057
Celadonite	0.271	0.110	0.280	0.274	0.298	0.355	0.222
F Celadonite	0.005	0.013	0.083	0.029	0.028	0.120	0.008
Total	0.998	O.998	1.041	1.015	0.997	0.994	1.005

Table III. Mean WDS Electron Microprobe Analyses Of Hydrothermal White Mica Solid Solutions.

'Hudson Bay Mountain

ordering occurs in the two octahedral sites only with mole fractions of celadonite greater than 0.5 (Velde, 1978). Substitution schemes which entail tetrahedrally-coordinated Al and Si coupled to substitution of bivalent Fe or Mg for octahedral Al are not included here or in the activity-composition expressions. Significant amounts of fluorine in the analyses suggest that addition of fluorine-rich end members to the compositional space would more accurately describe the naturally-occurring phases. Addition of $Al_2Si_4O_{10}(OH)_2$ (pyrophyllite) to account for coupled interlayer-tetrahedral substitution did not result in any meaningful improvement of the regression models. Regression models of the white mica analyses in this compositional space are best described employing the three independent end members muscovite, fluormuscovite, and K-(Fe,Mg) celadonite.

2. Trioctahedral Layer Silicates

Average biotite analyses and mole fraction data tabulated according to relative age and alteration environment have been listed in Table IV. The range of substitution and hence the extent of solid solution in trioctahedral layer silicates (biotite) from ore-forming systems is largely unknown. Regression models using only isomorphic substitution in octahedral or hydroxyl site occupancies provided very poor fits to the oxide totals. Coupled substitutions between cations in octahedral and tetrahedral coordination combined with the isomorphic substitutions gave much-improved fits to the data. Tetrasilicic annite and phlogopite (Sabatier and Velde, 1970; Siefert and Schreyer,

Location	Questa	Questa	Questa	HBM H72-2148 5	HBM H72-2191	Endako E74170679	Endako FOM
Jampie ∦ anal	5	3	6	5	11	12	12
Textures	v	M-R	v	V	М	V	м
S 10 z	42.60	39.26	43.89	39.23	38.61	39.61	37.44
T102	1.623	2.516	0.904	2.637	3.596	1.888	2.953
A1202	11.46	13.10	10.29	13.85	13.84	13.86	15.59
Fe0	6.989	13.79	5.664	13.28	16.53	11.00	16.100
MnO	0.416	0.797	0.261	0.872	0.444	0.767	0.717
Mg0	22.28	15.46	22.70	16.20	13.78	18.56	15.19
CaO	0.032	0.042	0.013	0.014	0.065	0.049	0.064
BaO	NA	NA	NA	NA	NA	NA	NA
Na 20	0.337	0.226	0.290	0.149	0.094	0.152	0.160
K+0	9.939	9.857	10.24	9.910	9.399	10.36	9.575
F .	7.377	3.641	7.165	2.438	0.755	3.346	0.716
Subtotal	103.05	98.69	101.42	98.58	97.11	99.59	98.50
0 = F	3.106	1.533	3.017	1.027	0.318	1.409	0.301
HzO	0.691	2.180	0.803	2.752	3.468	2.384	3.530
Total	100.64	99.34	99.20	100.31	100.26	100.57	101.73
		Mol	lecular Percer	nt End Members			
Annite	0.038	0.209	0.014	0.197	0.236	0.183	0.257
Phlogopite	0.010	0.041	0.141	0.160	0.263	0.139	0.180
F-Phlogopite	0.706	0.308	0.680	0.170	0.059	0.316	0.000
Eastonite	0.111	0.306	0.026	0.346	0.395	0.282	0.465
F-minnesotaite	0.199	0.109	0.131	0.101	0.131	0.059	0.077
Total	0.984	0.973	0.992	0.974	1.016	0.979	0.979

Table IV. Mean WDS Electron Microprobe Analyses Of Hydrothermal Biotite Solid Solutions.

Hudson Bay Mountain

1965, 1971) which create octahedral deficiences as a means to balance charge inequalities were also considered, but addition of these end members to the regression model did not further improve the fit. In most cases, such models could not describe the chemical analyses within the chosen compositional space. Substitution schemes with negative valence deficiencies (e.g. tetrasilicic phlogopite; Forbes, 1972 and PD-oxyannite Beane, 1974) were not considered as the chemical analyses report only total iron concentration. Consistently low alkali oxide totals in the analyses of this study which cannot readily be explained by the analytical uncertainties reflect vacancies in the interlayer site. Fe and Mg end members derived from trioctahedral layer silicates by complete removal of all interlayer cations and filling tetrahedral occupancy with silica (minnesotaite and talc, respectively) were added to the compositional space to include provision for the interlayer deficiencies with the resulting regression models showing further improvement.

The compositional space which best represents biotites from this study includes six hydroxyl end members and six fluorinebearing counterparts. The set of end member components which uniquely defines analyses within this space correspond in stoichoimetry to $KFe_3(AlSi_3O_{10})(OH)_2$, $KMg_3(AlSi_3O_{10})(OH)_2$, $K(Mg_{2.5}Al_{0.5})(Al_{1.5}Si_{2.5}O_{10})(OH)_2$, $KMg_3(AlSi_3O_{10})(F)_2$, and $Fe_3(Si_4O_{10})(F)_2$ (annite, phlogopite, eastonite, fluorphlogopite, and fluorminnesotaite, respectively).

ACTIVITY-COMPOSITION RELATIONS

Any attempt to model the composition of a hydrothermal fluid in equilibrium with a given assemblage of crystalline solid solution phases must taken into account the activity of end member components. Equations relating measured mineral compositions to activities of end member components used to represent the natural solid solution are given in Table V. The activity-composition relations corresponding to observed solid solution phases are summarized in the discussions below.

Alkali Feldspars

Compositions of alkali feldspars from Questa, Hudson Bay Mountain and Endako which coexist with pre-molybdenite and molybdenum-mineralized veinlet assemblages are presented in Table VI. Because these subsolidus alkali feldspars generally have mole fractions less than .006 combined (Ca+Ba) end members, they are treated as a binary orthocalse(Or)-albite(Ab) solid solution. Individual feldspar grains are complexly zoned, with adjacent zones differing by as much as 0.10 X(orthoclase). Generally, however, X(orthoclase) lies between the extremes of 0.86 and 0.96, and X(albite) in coexisting Na-rich feldspars within the much narrower range from 0.92 to 0.99. Two alkali feldspars, one K-rich and one Na-rich solid solution phase, coexist in some veinlet assemblages from Hudson Bay Mountain. In such specific cases, a unique temperature of formation at a given pressure can be obtained. In the general case, however, only one alkali feldspar is present and temperature can only be
Solid Solution	Thermodynamic Component	Activity-Composition Relation				
White Mica	KA1:(A1S1:)0:0(OH): NaA1:(A1S1:)0:0(OH):	$a = (1-p)(1-q)[[2(1-r2)^{2}]]$ $a = p(1-q)[[2(1-r2)^{2}]]$				
Biotite	KFe;(A1S1;)0;0(OH); KMg;(A1S1;)0;0(OH); KMg;(A1S1;)0;0(F);	$a = (1-s)(1-p)^{3}(1-q)^{0-5}(1-r)^{2}$ $a = (1-s)(p)^{3}(1-q)^{0-5}(1-r)^{2}$ $a = (1-s)(p)^{3}(1-q)^{0-5}(r)^{2}$				
Alkali Feldspar	KA1S1:0. NaA1S1:0.	ln a = [X²(Ab)(W ₂i+2X(Or)(W i₂-W ₂i))]aRT + ln X ln a = [X²(Or)(W i₂+2X(Ab)(W ₂i-W i₂))]aRT + ln X				
Scheelite	CaWO₄ CaMoO₄	a = (1-p)(1-q) a = (p)(1-q)				

Table V. Activity-Composition Relations for Thermodynamic Components in Natural Solid Solutions.

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Location Sample # anal	Questa QDH27-30 6	Questa QDH31'32' 3	Questa Q57''66°° 2	HBM² H58-980 10	HBM H58-980 6	HBM H77-368.5 8	HBM H96-209.5 4
· · · ·	·		<u>, </u>		<u></u>	· · · · · · · · · · · · · · · · · · ·	
S10:	64.42±0.33	66.12±0.52	64.14±0.19	65.45±0.16	64.59±0.61	68.32±0.23	64.82±0.15
A1201	18.79±0.25	18.33±0.06	18.02±0.04	18.81±0.15	18.66±0.22	19.40±0.23	18.27±0.01
CaO	0.03±0.02	0.015±0.02	0.01±0.01	0.02±0.02	0.04±0.03	0.07±0.02	0.05±0.02
Na 2 O	0.43±0.11	1.86±0.18	0.54±0.03	1.18±0.20	0.47±0.17	11.70±0.13	2.18±0.30
K20	16.08±0.24	13.81±0.39	15.77±0.01	14.88±0.35	15.92±0.40	0.11±0.02	13.61±0.40
BaO	0.21±0.09	0.10±0.05	0.07±0.01	0.19±0.09	0.25±0.05	0.05±0.06	0.12±0.11
Total	99.96	100.24	99.55	100.53	99.93	99.65	99.06
		Mol	ecular Percent	End Members			
Orthoclase	0.958	0.827	0.949	0.889	0.951	0.002	0.799
Albite	0.040	0.168	0.050	0.107	0.043	0.994	0.195
Anorthite	0.002	0.000	0.000	0.001	0.002	0.003	0.003
Celsian	0.004	0.001	0.001	0.004	0.005	0.001	0.002
Total	1.004	0.995	1.000	1.001	1.001	1.000	0.999

Table VI. Mean WDS electron microprobe analyses! of hydrothermal alkali feldspar solid solutions.

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'analyst: M.S. Bloom

¹Hudson Bay Mountain

indirectly estimated from fluid inclusion studies (Chapter 1 and Bloom, 1981). Activities of end members in any solid solution can be written as

$$a = \gamma X \tag{1}$$

In this equation, a is the activity of the species and X is the mole fraction obtained from the regression model. For alkali feldspars, this statement is expressed as

and

$$aRTln\gamma(Or) = X^{2}(Ab)(W_{21} + 2X(Or)(W_{12} - W_{21})), \qquad (2)$$

$$aRTln\gamma(Ab) = X^{2}(Or)(W_{12} + 2X(Ab)(W_{21} - W_{12})).$$
(3)

In equations (2) and (3) a is the number of possible mixing sites, T is temperature in Kelvins, and R is the gas constant. W_{21} and W_{12} are Margule's excess free energy parameters (Thompson, 1967) for the first and second end members of the binary solid solution, respectively. Experimental determination of the solvus for disordered alkali feldspars has been critically reviewed by Parsons (1978), and revised values for the Margule's parameters are given in Brown and Parsons (1981). The expression for excess free energy of solution given by Thompson and Hovis (1979) has been used to generate these activities, but other expressions of the Margule's formulation could also be used. Values of a(orthoclase) so obtained are nearly identical to those calculated by using the Thompson and Hovis (1979) excess function for temperatures \geq 500°C, but increasingly negative deviations occur at lower temperatures (approximately one percent at 300°C).

Scheelite-Powellite

A multi-site solid solution of the type (Ca,Pb)(W,Mo)O4 has the four possible end members corresponding to the stoichiometry of scheelite (CaWO₄), powellite (CaMoO₄), stolzite (PbWO₄), and wulfenite (PbMoO₄). Binary oxide solid solutions with mixing on more that one site can be expected to show ideal behavior if the molar volumes of the two end members are nearly identical and if both are in the same crystallographic system (Kerrick and Darken, 1975). Each of the above end members satisfies the crystallographic criteria for ideal behavior in that all exhibit I4 /a space group symmetry. Molar volumes along the scheelite-powellite and stolzite-wulfenite binary joins generated by substitution in the tetrahedrally coordinated anion sites differ by 0.08 and 0.44 percent, respectively, and can thus be assumed to show ideal behavior. Molar volumes along the binary joins generated by cation substitution (scheelite-stolzite and powellite wulfenite), however, each differ by approximately 13 percent, and Hsu (1981) has experimentally demonstrated an asymmetric solvus along the scheelite-stolzite binary join. In view of the negligible stolzite-wulfenite component indicated by electron microprobe analyses of (Ca,Pb)(W,Mo)O₄ solid solution phases from Hudson Bay Mountain (Table VIII), compositions in this solid solution are assumed to lie along to the scheelitepowellite binary join.

Sample ∦ anal	H92-2 4	H92-2 2	H120-156.5 2	H12O-156.5 4	H120-156.5 3	H127-141 2	H127-141 3
Paragenesis	C 1	R'	С'	I ²	R	I	R'
MoO 3	19.745	5.175	20.005	10.592	0.117	7.73	0.140
PbO	0.02	0.0	0.0	0.025	0.010	0.017	0.0
CaO	19.710	18.37	19.965	16.422	17.870	18.693	17.705
WO 1	61.192	75.610	60.330	70.830	81.953	73.493	81.470
Total	100.667	99.155	100.300	97.869	99.950	99.276	99.315
			Molecular Perce	nt End Members	5		
Scheelite	0.649	0.896	0.649	0.760	0.988	0.864	0.987
Powellite	0.325 ,	0.089	0.334	0.153	0.000	0.125	0.0
Stolzite	0.013	0.007	0.009	0.044	0.010	0.006	0.011
Total	0.987	0.992	0.992	0.957	0.998	0.998	0.991

Table VII. Mean WDS electron microprobe analyses' of Hudson Bay Mountain scheelite solid solutions.

intermediate

' rim

4 analyst: M.S. Bloom

White Mica

Activity-composition relations for muscovite and paragonite end members in hydrothermal white micas are complicated by nonideality of the K-Na interaction at least along the muscoviteparagonite join and by the ubiquitous presence of celadonite and fluorine-bearing end members. Any activity model for white micas must consider at least these effects.

Excess functions in white mica compositional space have been experimentally determined only for Na-K interaction along the muscovite-paragonite binary join. Methods to calculate activities of end members require interaction (Margules) parameters to describe the excess behavior of natural white mica solid solutions. A mixing model could be constructed assuming that Margules parameters for K-Na interaction are identical for the muscovite-paragonite and K-Na celadonite binary joins, and that solid solution toward celadonite and fluorine-bearing end member is ideal. Such an approach does not seem warranted in the absence of nearly all the interaction parameters, and activitycomposition relations are employed assuming ideal site substitu-The expressions for muscovite and paragonite (the only tion. crystalline end members for which thermodynamic data are available) are given in Table V.

Trioctahedral Layer Silicates

The body of data which describes solid solution behavior of biotite is incomplete and inconclusive. Isomorphic substitution of octahedrally coordinated Fe and Mq occurs on energetically equivalent sites, as shown by crystal structure analysis (Hazen and Burnham, 1973) and nuclear magmatic resonance (NMR) studies (Sanz and Stone, 1977). The expected ideal solid solution behavior along this binary is further supported by the nearly linear volume composition relation shown over a large range of Fe-Mg substitution at fixed octahedral aluminum contect. Molar volume data along the phlogopite-fluorphlogopite binary join, when corrected for minor element substitution in the interlayer site, also describe a linear function of X(fluorphlogopite) and ideal behavior can be assumed (Bloom, 1976). Interaction of the two ideal isomorphous substitutions, however, produces possible ordering of F and OH in the phlogopite and annite structures and non-ideal behavior is predicted. NMR study of Fe, F, and OH distribution in the octahedral sheet of phlogopite (Sanz and Stone, 1979) shows that OH and F are highly differentiated with respect to cationic association, and that homogeneous F-rich domains (i.e., local ordering) occurs. Octahedral Al substitution at various fixed Mq/(Mq+Fe) ratios also give rise to a nonlinear volume-composition relation and thus non-ideal solid solution behavior (Newton and Wood, 1980).

In the absence of thermochemical evidence and interaction parameters for non-ideal behavior, natural F-bearing biotite solid solutions are treated in this study as ideal site mixing

models assuming no complications from Al-Si disorder. Activity expressions for end members are given in Table V.

DISCUSSION

Binary Solid Solutions

The compositional variation of alkali feldspars, scheelite, and the layer silicates have been summarized in Figures 9, 10, and 11 in the form of histograms for mole fractions of component end members. Unlike the multi-component layer silicate solid solutions which show regular compositional variation with relative position in the paragenetic sequence, histograms for the binary alkali feldspar and scheelite solid solutions each exhibit a distinctly bimodal distribution regardless of the relative The signature of late-stage hydrothermal activity and reage. mobilization of ore-forming components is shown by the presence of both scheelite-rich and relatively scheelite-poor populations in the solid solution from Hudson Bay Mountain (Figure 9a). The electron microprobe studies reveal that where early molybdenumrich scheelite grains are in contact with a subsequent alteration assemblage, thin irregular patches decorating healed fractures and along crystal faces become progressively depleted in the powellite component until the latest-observed scheelite solid solution (which occurs as euhedral crystals projecting into open vugs and as encrustations on intergrowths of quartzsericite-pyrite ± molybdenite) correspond with the powellitepoor population of Figure 9a. This is consistent with the general transport model for remobilization of molybdenum from W-Mo



Figure 9. Distribution of end members in binary solid solutions. a) Scheelite-powellite from Hudson Bay Mountain; skewed distribution toward lower scheelite mole fractions reflects solvation and redeposition of scheelite by post-magmatic solutions; b) Alkali feldspar solid solutions from Questa (solid bars) and Hudson Bay Mountain (hatchured bars); note K- and Narich compositions which provide an independant means to estimate temperatures of deposition. deposits by late meteoric fluids proposed by Wesolowski and Ohmoto (1981).

In the case of the orthoclase end member (Figure 9b), the presence of two coexisting alkali feldspars in equilibrium with the ore-forming solutions can be observed or inferred. Intergrowths of two compositionally distinct alkali feldspars in the same vein assemblage have been observed only from Hudson Bay Mountain, but vein associations do occur from Questa in which two feldspars are present. The failure to form discrete intergrowths which unambiguously define equilibrium is envisioned to be the result of discrete, randomly-distributed nucleation sites one the substrate vein walls. The averaged compositions of Krich alkali feldspar from Questa and Hudson Bay Mountain overlap one another and are similar to compositions reported from other vein and fracture-controlled styles of mineralization (Brimhall, 1977). The range of compositions observed at a single location and in individual grains, however, exhibits marked variation which is not resolved on Figure 9b. The mole fraction of the orthoclase end member shows small and locally oscillating, but overall regular increases with approach toward molybdenite or chalcopyrite grains. This behavior is consistent with decrease in temperature as inferred in Chapter 1 and Bloom, 1981 and attendant redistribution of alkali chlorides in the aqueous fluids (Lagache and Weisbrod, 1977; Pascal and Roux, 1981), and with the variation in activity ratios of aqueous species as a function of temperature computed by Bird and Norton, (1981).

MUSCOVITE/SERICITE SOLID SOLUTIONS

Histograms for the end members in alteration white micas show consistent values for alkalis in interlayer positions, a consistent range of departures from tetrahedral Si-Al stoichiometry (coupled with Fe and Mg substitution in octahedral coordination), and substantial substitution of fluorine for OH in the hydroxyl site. Figure 10 presents a remarkably uniform range of X(muscovite); both Questa and Hudson Bay Mountain have a near normal distribution with a standard deviation (1σ) of 0.14 about the mean of 0.65. The corresponding range of the Nabearing end member is confined to $0.0 \leq X(\text{paragonite}) \leq 0.1$ and $0.0 \leq X(\text{paragonite}) \leq 0.2$ at Hudson Bay Mountain and Questa, respectively (Figure 10). Departures from pure muscovite stoichiometry toward more trioctahedral celodonite-rich micas is suggested by the X(celadonite) component shown in Figure 10. The range of substitution is consistent and $0.0 \leq X(Fe, Mg cela$ donite) \leq 0.3 with Fe/Mg generally \leq 1.0. Although the potential for wide variation in fluorine content is produced by the evolving alteration process, the histogram of X(fluormuscovite) (Figure 11d) shows that the extent of fluorine substitution is limited at Questa and Hudson Bay Mountain to 0.14 ± 0.04 (1 σ) in accord with the experimental results of Munoz and Luddington (1977).

The wider range of paragonite mole fractions at Questa suggests an isothermal hydrothermal solution of higher Na/K ratio coexisting with the white mica alteration phase during one or more stages of the paragenesis, but is also in agreement with



Figure 10. Distribution of end members muscovite (a) and fluor-muscovite (b) in hydrothermal white mica solid solutions from Questa (solid bars) and Hudson Bay Mountain (hatchured bars). Note confluence of modes between deposits as well as from tex-tural types within individual deposits.

the observation by Capuano and Cole (1982) that solid solution in white mica is temperature-dependent and must be included in calculation of component activities for fluid-mineral equilibria. The dependence of compositional variation, both with the tetrahedral and octahedral sites, upon lateral and vertical position as observed by Guilbert and Schafer (1979) was not detected in this study; white micas were not sampled with enough regularity to define trends in their distribution or make unambiguous interpretations regarding their octahedral site occupancies or dependencies on possible physical gradients.

Compositions of white mica projected to the p:q, p:r, and (p+q):r descriptor faces of the compositional space are shown in Figure 12. White mica compositions from the Henderson stockwork molybdenum deposit (Gunow et al., 1980), from the Santa Rita porphyry copper deposit (Jacobs and Parry, 1979), and from the Salton Sea geothermal system (McDowell and Elders, 1980) are also shown for comparison. (The reader must exercise discretion with interpretations from the latter, as the models do not include analyses for fluorine; they are included here to demonstrate the possible problems arising from analytical data which do not include fluorine).

White micas from Henderson and Santa Rita occupy separate, distinct fields on the muscovite-paragonite-(K,Na)(Fe,Mg) celadonte (i.e., p:q face) with Henderson micas having the higher celadonite component. Dioctahedral layer silicates from Questa and Hudson Bay Mountain, however have compositions that are not restricted to either field. Both exhibit a narrow range of com-

position along the K-Na binary join and a wider range of celadonite component. A regular progression of layer silicate composition is shown by the Salton Sea sericites (McDowell and Elders, 1980), with regular compositional and textural changes as the alteration assemblage varies with temperature. There is a significant and regular approach toward pure muscovite stoichiometry until at the higher temperatures reported by McDowell and Elders (1980) and compatible with those inferred for white micas from this study, the compositions cannot be distinguished. There is an obvious separation of the micas from this study as well as from Santa Rita and those reported at Henderson when the analyses are projected to fluor-hydroxyl (p:r) compositional space. This indicates that the analysed white micas from Questa, Hudson Bay Mountain, and Santa Rita formed in a fluorine-poor environment relative to Henderson. Henderson sericites tend to be more fluorine-rich in character, as expressed by the compositions enriched in the fluormuscovite end member. Note, however, that the most fluorine-depleted white micas from Henderson overlap the most fluorine-rich compositions from this study, inferring similar chemical potentials of fluorine during the different ore-forming processes. Rotation of the compositional space and projection to the combined fluorhydroxyl-(K,Na) mica-(K,Na)(Fe,Mg) celadonite face ((p+q):r descriptor) also emphasizes the anamolously high fluorine in Henderson sericite when compared to samples collected from Questa, Hudson Bay Mountain, and Santa Rita. It is apparent that projections which do not consider fluorine-bearing com-

ponent end members do not adequately distinguish white micas from stockwork molybdenum and copper porphyry environments of deposition. It follows from the anomalously high fluorine values found in Henderson sericite, contrasted with the lower values found in similar molybdenum-mineralized deposits, that high fluorine although often diagnostic of molybdenum-bearing hydrothermal systems is not necessarily required for the mobilization, transport and deposition of molybdenum.

Biotite Solid Solution

Histograms presenting the distributions of end members for trioctahedral layer silicates at Questa, Hudson Bay Mountain and Endako are given in Figure 11. Wide, consistent ranges of phlogopite and eastonite component end member mole fractions are evident (Figures 11b and 11c) regardless of relative age, whereas the mole fractions of component annite, fluorphlogopite, and fluorminnesotaite (Figures 11a, 11d, and 11e) exhibit distributions in which the textural (paragenetic) variants can be deduced. Figures 11b and 11c show uniform ranges of $0.0 \leq$ $X(phlogopite) \le 0.3$ and $0.0 \le X(eastonite) \le 0.2$, respectively. No distinction among the various textural types is possible in any deposit, particularly for X(phlogopite). The apparent asymmetry of the populations (especially Questa) toward lower X(phlogopite) and higher X(eastonite) is probably an artifact of a sampling bias favoring vein biotites. Biotites from Endako maintain an eastonite component consistently lower than either Questa or Hudson Bay Mountain.



Figure 11. Distrubition of end members annite (a), phlogopite (b), eastonite (c), fluorphlogopite (d), and fluorminnesotaite (e) in hydrothermal biotite solid solutions from Questa (solid bars), Hudson Bay Mountain (hatchured bars), and Endako (open bars). Textural and/or genetic variations are discussed in text.





The distribution of the annite end member is presented in The range of annite contents shown is rather wide Figure 11a. $(0.0 \leq X(annite) \leq 0.4)$ but can be grouped according to relative position in the paragenesis. Vein biotite solid solutions from Ouesta exhibit compositions restricted to $0.0 \leq X(annite) \leq 0.1;$ the annite content increases in replacement biotite solid solution, until in magmatic phases X(annite) ranges between 0.3 and Note the faint suggestion of a bimodal population that can 0.4. again be ascribed to sampling bias. Biotite solid solutions from Hudson Bay Mountain span the compositional range for vein and replacement biotites shown by Questa. The similarity between biotite textures and compositions at Hudson Bay Mountian and Questa as well as resemblance of the fluid inclusion data can be used to imply isothermal conditions and/or constant chemical characteristics of the aqueous fluid. Note that biotite solid solutions from Endako are within the range $0.2 \leq X(annite)$ ≤ 0.4, in agreement with grains which show magmatic affinities from both Hudson Bay Mountain and Questa.

Significant departures from the hydroxyl subset of compositional space toward fluorine-rich end members is suggested by the X(fluorphlogopite) and X(fluorminnesotaite) histograms (Figures 11d and 11e, respectively). Questa shows the widest range of fluorphlogopite mole fractions, with $0.2 \leq$ X(fluorphlogopite) ≤ 0.8 for replacement and vein textures, but 0.0 to 0.1 for magmatic varieties. Hudson Bay Mountain and Endako both exhibit a narrower range at lower values, with $0.0 \leq$ X(fluorphlogopite) ≤ 0.4 . This is compelling evidence that the chemical potential of fluorine was considerably higher at Questa than at Hudson Bay Mountain or Endako.

A similar although less pronounced separation is evident (Figure 11e) for the component end member fluorminnesotaite. The population of solid solutions from Questa suggests a bimodal distribution, with vein associations showing less $(0.0 \leq X(fluorminnesotaite) \leq 0.2)$ and replacement plus magmatic associations greater $(0.0 \leq X(fluorminnesotaite) \leq 0.5)$ mole fractions of this end member. The distribution from Hudson Bay Mountain shows the same range and is consistent with this observation (vein biotites show fewer interlayer vacancies than those having intermediate replacement textures or magmatic affinities). Analyses from Endako give rise to a more restricted range $(0.2 \leq X(fluorminnesotaite) \leq 0.5)$ which reinforces the compositional variation shown in magmatic and replacement biotites from Questa and Hudson Bay Mountian.

Biotite compositions projected to the p:q, p:r and (p+q:r) descriptor faces for that portion of the compositional space which includes the end members annite, phlogopite, siderophyllite, eastonite, and their fluorine counterparts are shown in Figure 12b. Biotite compositions from Henderson (Gunow et al., 1980), Santa Rita (Jacobs and Parry, 1979), and the Salton Sea geothermal system (McDowell and Elders, 1980) are again shown for comparison. Regular compositiona changes occur as a function of textural variant or of relevant position in the paragenetic sequence.

The overall pattern is particularly well-developed on the



Figure 12. Compositional spaces for hydrothermal mica solid solutions. End members of solid solution hypervolumes from regression analyses of electron microprobe data; composition points projected from hypervolume to faces of cube. a) White micas from Questa (open circles) and Hudson Bay Mountain (triangles). Analyses from Henderson (solid triangles), Santa Rita (pluses), and Salton Sea (solid diamonds) also shown for comparison. b) Biotites from Questa, Hudson Bay Mountain, and Endako (symbols as for white micas). Also shown for comparison are Henderson, Santa Rita, and Salton Sea biotites.



hydroxyl (p:q) face of the compositional space is one of a gradual approach of the naturally-occurring biotite from aluminous (eastonite-siderophyllite) compositions toward the most Mg-enriched end member phlogopite. The linear trend proceeds from compositions near the siderophyllite-eastonite join (Henderson biotite from phyllic alteration) to those on the annite-phlogopite join (hydrothermal vein biotites from Questa). Analyzed biotites from Questa, Hudson Bay Mountain, and Endako as well as Henderson, Santa Rita, and the Salton Sea fall along this trend without any apparent means for distinction. Note particularly that magmatic biotite cannot be distinguished from hydrothermal biotite. This trend might suggest control of biotite compositions by the chemistry of an aqueous solution or by temperature, pressure, etc. - characteristics common to numerous ore-forming processes (despite the differing and unique geological environment of the individual deposits), but could also be a consequence of the free energy surface for biotite.

Compositional trends between the various textural variants, and especially between the same variant associated with different deposits, are shown by projecting to the p:r face. The biotite from Questa, Hudson Bay Mountain, and Endako is similar in phlogopite content to hydrothermal biotite associated with porphyry copper deposits and active geothermal systems, while the fluorine contents are higher from the molybdenum-mineralized systems. Biotite compositions from Hudson Bay Mountain and Endako occupy a position intermediate between the extremes of fluorine content shown by "Climax-type" stockwork molybdenum and

porphyry copper deposits or active geothermal systems. Note that magmatic biotites from Henderson are distinctly separate from all other textural and/or paragenetic variants, containing among the lowest fluorine end member and the highest annite end member of the biotites associated with molybdenum mineralization.

It would appear from this separation and from a similar separation on the projection to the (p+q):r face, that the total content of fluorine-bearing end members does provide a chemical distinction between biotites of definite magmatic origin and those of certain hydrothermal origin. Another interesting feature is the much wider scatter of compositions. The variation of these end members is similar to that noted by McDowell and Elders (1980) for biotite compositions in the Salton Sea geothermal system. On increasing temperature, there is a significant and regular trend away from the phlogopite-fluorphlogopite join on this diagram. Biotites from this study as well as from Henderson follow this same trend, with hydrothermal vein biotites for Questa occurring nearest the join. The Endako biotite compositions, and to some extent those from Hudson Bay Mountain, infer a relatively higher magmatic component for these phases. Clearly, additional research is required to establish the relative magmatic and hydrothermal contribution to the biotite composition, and the dependence on temperature.

CONCLUSIONS

Highly variable and complex compositional zoning is characteristic of solid solutions phases (alkali feldspar, scheelite, white mica, and biotite) from vein assemblages in molybdenummineralized ore-forming systems at Questa, New Mexico and Hudson Bay Mountain and Endako, British Columbia. Although zoning within individual grains is common, compositional trends in the averaged compositions of these solid solution phases can be correlated with relative position of a vein assemblage in the paragenetic sequence and/or textural characteristics of the phases.

The key to interpretation of compositional space for any of these solid solutions is the number of substitutions possible in the naturally-occurring mineral. Whenever possible, activitycomposition relations for solid solution phases have been described in terms of binary solid solution models; however, ideal site substitution has been employed as a first approximation when multi-component solid solutions must be described using more than two end members. The site occupancies of the analysed solid solution phases have been expressed independently of any assumptions made to calculate structural formulae, and using regression techniques have been related directly to mole fractions of end members used as descriptors for the compositional space.

Histograms of the end members for the binary alkali feldspar and scheelite solid solutions each exhibit distinctly bimodal frequency distributions. The two coexisting alkali feldspars, one K-rich and the other Na-rich, are assumed to have grown from the same aqueous fluid. Combined with Margule's parameters used to describe excess free energy functions of this solid solution, the analytical data constitutes a sensitive and reliable geothermometer which can provide a unique temperature of deposition (or a minimum estimate if only one alkali feldspar is present). The two populations shown by scheelite solid solution are considered the product of ingress of meteoric hydrothermal solutions which gave rise to the redistribution of oreforming components.

Departures from pure white mica and biotite end member stoichiometries are persistent among different vein assemblages and textural associations. Analysed white micas contain nontrivial values of fluorine, and significant substitution on octahedral sites which suggest that addition of celadonite and fluorine-rich end members to the compositional space more accurately describes the naturally-occurring phases than a ternary model. White micas were not sampled with enough regularity, however, to define trends in spatial disposition, or to make unambiguous interpretations regarding their octahedral site occupancies. Systematic compositional variation is common to three of the five end members chosen to describe biotite solid solutions. Mole fractions of the annite component end member are highest in magmatic biotite solid solutions, intermediate in those which exhibit replacement textures, and significantly lower in biotite solid solutions from vein assemblages. The distribution of component fluorine-bearing end member (fluorphlogopite and fluorminnesotaite) mole fractions also show sys-

tematic change with paragenesis. There is a regular decrease in the mole fraction of fluorminnesotaite, and thus progressively fewer interlayer vacancies, from magmatic to vein biotite solid solution associations. The fluorphlogopite end member mole fraction is greater by a factor of approximately 5 in vein biotite solid solution than is its magmatic counterpart.

An important implication from the data of mole fractions describing white mica and biotite solid solutions involves the influence of temperature on the distribution of components. A number of authors (Capuano and Cole, 1982; Bird and Norton, 1981; McDowell and Elders, 1980) have noted that both biotite and white mica solid solutions are temperature dependent. Although fluid inclusion data (Chapter 1 and Bloom, 1981) indicate similar depositional temperatures for the assemblages examined in this study, no attempt has been made to separate the effects of evolving isothermal fluid composition from temperature-dependence. Additional research is required to establish the relative contributions of coexisting aqueous fluids and the dependence of temperature on layer silicate solid solutions.

III. THEORETICAL PREDICTION OF FLUID-MINERAL EQUILIBRIA

INTRODUCTION

The origin and evolution of certain hydrothermal solutions can be understood in terms of the equilibration of an aqueous phase with its mineralogical environment. Probably the best known work of this general nature is on active geothermal systems (Bird and Norton, 1981; Capuano and Cole, 1982), which provide a unique glimpse at the chemical and physical processes that occur during hydrothermal alteration. Other works which have discussed the influence that temperature, pressure, and fluid composition have on the formation of coexisting mineral phases include Merino (1975), Knight(1977), and McKenzie and Helgeson (1979).

Our perception of hydrothermal environments, however, and particularly those which have resulted in precipitation of ore components, is impaired by our inability to sample hydrothermal solutions in an active ore-forming system. Detailed petrographic and geochemical investigations of hydrothermal alteration phases have led to the use of alteration mineralogy and compositional variation therein to discriminate among alteration assemblages of different origin, and to assess possible origins of the ore-forming solution(s). The known chemistry of these mineral assemblages places limits upon the temperature, pressure, and fluid composition under which the assemblage can form and allows reasonable estimation of the composition of such ore-for-

ming solutions.

Alteration mineralogy characteristic of molybdenum mineralized granite-molybdenum systems is used in this paper to evaluate quantitatively fluid-mineral equilibria. The calculations employ mineral compositions and associations reported in Chapter 2. The purpose of this chapter is twofold. First, it is to characterize, with the aid of logarithmic activity and fugacity diagrams, phase relations among minerals and aqueous solutions in the system $K_2O-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-MoO_2-H_2S-HF-HCl-H_2O$. Secondly, the dependence of the coexisting fluid chemistry upon compositional variation among phases of the alteration assemblage most closely associated with molybdenum mineralization is assessed.

THEORETICAL CONSIDERATION OF THE THERMODYNAMIC MODEL

Thermochemical Data and Conventions

Evaluation of chemical equilibria between minerals and aqueous solutions in hydrothermal systems has been accomplished using equilibrium constants for dissociation reactions of dependent aqueous species and the hydrolysis reactions of solid mineral phases. The source of thermochemical data for aqueous species considered in these calculations is Helgeson (1969), supplemented by data from CODATA (1976,1977), and Smith (pers. comm.). Thermochemical equilibrium constants for minerals and gases are calculated using data reported by Helgeson et al. (1978), unless otherwise specified. Explanation of the sources and data treatment for those solid phases and gases not considered by Helgeson et al. (1978) is given in Table XI. Although these data may not be entirely consistent with the Helgeson et al. (1978) data base, they at least provide a reasonable approximation of the actual equilibrium conditions.

In the calculations which follow, the standard state for H₂O and the intercrystalline standard state for solids is unit activity of the pure component at any temperature and pressure. The intracrystalline standard state for solid solution minerals requires that all activity coefficients of atoms on the lattice sites approach unity as the mole fractions of the atoms on the sites approach those of the stoichiometric end member species chosen as thermodynamic components at any pressure and tempera-The standard state for aqueous species other than H_2O is ture. one of unit activity in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. For gases the standard state is one of unit activity of the hypothetical ideal gas at one bar and any temperature. The specific expressions for calculating activities of the components, listed in Chapter 2, are derived from the general equation relating site occupancy in the given mineral to the activity of the thermodynamic component as reported in Chapter 2. These expressions are consistent with those presented in Helgeson et al. (1978) and Helgeson and Aagaard (1981), except that preferential site occupancies and order-disorder in tetrahedral coordination have not been considered.

The distribution of element concentrations among aqueous species is calculated using program PATH (Helgeson et al., 1970)

		5°291	Ср с	S	
Phase	∆H°zs∎		a	bx103	cx10-*
Fluortopazi	-3084.45	105.40	225.20	-1.46	-78.31
Fluorphlogopite	-6268.05	317.57	414.26	80.04	-0.84
Molybdenum	0.0	28.61	20.41	8.20	0.0
Molybdenum dioxide	-587.85	50.0	50.95	30.08	0.0
Molybdenum trioxide	-745.17	77.76	65.11	43.92	0.0
Molybdenite	-275.31	62.59	73.30	5.89	- 10.87
Powellite	-1546.07	122.59	88.62	72.56	18.04

Table VIII. Thermochemical data for molybdenum and fluorine minerals.

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¹Barton et al., (1982) ²Westrich and Navrotsky, (1981)

rewritten by T.H. Brown and E.H. Perkins (Perkins, 1981). The activity diagrams presented heren were calculated using program NEWDIAG (Brown, pers. com.) and error propogations using program ERRPROP (Bloom, 1982). All software was written for an IBM 370H and subsequently modified by the author to compile and execute on a VAX 11/780. Diagrams depicting equilibrium phase relations were prepared by computer program DIAGPLT (Bloom, 1982).

Computation of Fluid Chemistry

Numerous methods for computing homogeneous chemical equilibria in aqueous solution (the distribution of aqueous species) have been presented in the geochemical literature and are comprehensively reviewed by Nordstrom et al. (1979) and Wolery (1979). Few of the existing numerical algorithms have been adapted for computing heterogeneous equilibria in geochemical systems. Wolery (1979) and Reed (1982) have described methods for calculating the characteristics of heterogeneous chemical equilibria for specified bulk compositions, temperature, and pressure. The approach employed here for solving the heterogeneous equilibrium problem is essentially the monotone sequences technique (Wolery and Walters, 1975), modified for a heterogeneous chemical system consisting of an aqueous phase with dissolved ions and complexes and one or more solid and gas phases. Unlike other methods described in the literature, the algorithm does not require that an initial fluid/rock ratio be specified, although it should be stated that other techniques may be better. suited for alternative applications of chemical equilibria com-

putations.

In any system at equilibrium, there is one mass balance equation for each component and one independent mass action equation for each non-component phase or species in the system. The mass balance and mass action equations constitute a set of non-linear equations in the concentration of the species present and must be solved simultaneously using iterative techniques. Ionic and uncharged complexes are generally used to describe components in the aqueous phase. The only thermodynamic constraint upon the nature and number of components, however, is that the components must form an independent basis vector for the compositional space of all possible phases and species. Within these broad limits there is no unique choice of components and any independent basis will suffice to describe the In this study, mineral phases in equilibrium with the system. coexisting aqueous solution have been chosen as part of the com-The monotone sequences technique for computing ponent basis. equilibrium distributions of aqueous speicies has thus been modified to provide for changing of the component basis to include solid phases in equilibrium with the aqueous solution. Other modifications include provision for aqueous species or gases whose activities or fugacities are known and/or fixed, and for constraints on the activity of water (Perkins, 1981).

Limitations of the Model

Recent advances in theoretical geochemistry allow quantitative description of the chemical characteristics of supercritical hydrothermal solutions from detailed observations of alteration mineralogy. These advances permit calculation of the thermodynamic properties of aqueous solutions, gases, and minerals from the equations presented by Helgeson and Kirkham (1974a,b; 1976) and Helgeson et al. (1981). A consideration of supercritical fluid-mineral equilibria (cf. McKenzie and Helgeson, 1979; McKenzie, 1981), however, is beyond the scope of this study. Bird and Norton (1981) have shown that although reaction-dependent, the dramatic effects of the thermochemical properties of aqueous species near the critical point are negligible for liquid-vapor equilibrium below approximately 300° to 350°C. The computation of fluid-mineral equilibria in the present communication are thus an acceptable first approximation to the chemical characteristics of the aqueous solutions, but the numerical results will be further improved by consideration of these effects.

ASSERTIONS AND PHYSICAL DESCRIPTION OF THE MODEL

The assumption made here in computing chemical characteristics of the ore-forming fluids is equilibrium among stoichiometric minerals, solid solution phases, and solutes in the aqueous solution. Although overall equilibrium is rarely attained in natural processes, the recurrence of specific alteration assemblages associated both in space and time with molybdenum miner-

alization (Chapter 2) attests to the widespread occurrence of local equilibrium conditions.

Critical to the results of such calculations is selection of a specific temperature, salinity, and hydrogen ion concentration (pH) at which the calculations are performed. The calculations may also be sensitive to the standard state thermodynamic data, the chemical analyses of alteration minerals here presumed to coexist in an equilibrium state with the aqueous solution, and approximations of the activity-composition relations of solid solution phases. Whenever possible, these variables have been fixed at values which are expected to be representative of the equilibrium conditions which precipitated the documented alteration assemblages. The effects of those variables which could not be fixed directly were examined and the results of these tests are described later in this communication.

Temperature-Pressure

The temperature at which the calculations are performed can be chosen from several independent lines of evidence. It may correspond with direct measurements of temperature in active hydrothermal environments having alteration assemblages similar to those described for molybdenum-mineralized systems (Chapter 2), or it may represent fluid-mineral equilibria defined by independent geothermometry. The extensive data base on the Salton Sea geothermal system (Helgeson, 1968) provides measured temperatures which range from 300° to 350°C for aqueous solutions in equilibrium with stoichiometric quartz and solid solutions of

biotite, white mica, and alkali feldspar. Homogenization temperatures of primary fluid inclusions observed in alteration assemblages which typify the onset of molybdenum mineralization (Chapter 1 and Bloom, 1981) exhibit a range of temperatures from approximately 320° to 400°+C. The distribution of orthoclase component between coexisting alkali feldspars in the alteration assemblages (Chapter 2) also indicates depositional temperatures in the range 320° to 400°+C. A single temperature (350°C) consistent with these observed temperatures has been chosen to model the fluid-mineral equilibria.

Salinity, Ionic Strength, and $a(H_2 O)$

The salinity at which the computations are performed, while not affecting the activity ratios for aqueous species, will have a significant effect on the total molalities of solutes and the predominant dissolved species. Salinity is here assumed to be controlled by equilibrium between halite and the fluid (Cloke, The aqueous phase coexisting with halite and the sili-1979). cate alteration assemblage contains large concentrations of NaCl and KCl with stoichiometric ionic strength less than ten. Hypersaline brines are commonly reported in porphyry-type deposits. Both direct evolution from a crystallizing magma and partitioning of dissolved constituents into an aqueous solution attending condensation of a supercritical magmatic fluid (Henley and McNabb, 1978; Eastoe, 1981) are possible contributors to the hypersaline solutions. The high concentrations of electrolytes associated with molybdenum mineralization and documented in
Chapter 1, Bloom(1981), and White et al. (1981) are here regarded as products of processes that operated on fluids that were progenitors of those considered in this study. The hypersaline fluids present a multitude of geochemical problems, and here it is intended to examine only the fluid-mineral equilibria associated with the primary deposition of molybdenum at 350° C. High concentrations of electrolytes notwithstanding, the activity of H₂O relative to the liquid standard state is commonly close to unity (Helgeson, 1981). The phase relations among minerals and aqueous solutions presented below were generated for $a(H_2O) = 1.0$ in the activity and fugacity diagrams, and for $a(H_2O) = X(H_2O)$ in the fluid for distribution of aqueous species.

THERMODYNAMIC COMPONENTS AS CONSTRAINTS FOR SOLUTE SPECIES

Equilibria among any alteration mineral, or any specified solid phase in the presence of an aqueous fluid, and ionic or complexed aqueous species can be written (Bird and Norton, 1981)

$$0 = \Sigma \eta(\mathbf{i}, \mathbf{r}) \psi(\mathbf{i}) + \Sigma \eta(\mathbf{l}, \mathbf{r}) \phi(\mathbf{l})$$
(4)

where the subscripts i and l respectively denote the mineral (ψ) and the species (ϕ) in the coexisting fluid. In this equation η is the stoichiometric reaction coefficient for the rth reaction which is positive for products and negative for reactants. The logarithm of the law of mass action for equation (4) allows the thermodynamic activities of aqueous species to be written

 $\Sigma\eta(1,r)\log[a\phi(1)/a(H^{+})] = \log K(P,T,r) - \Sigma\eta(i,r)\log a\psi(i)$ (5)

K(P,T,r) in equation (5) is the equilibrium constant for the statement of reaction (4) at a specified pressure and temperature; a is the activity of the subscripted reaction component, and z is the charge of the ith aqueous species. Simultaneous evaluation of specific statements of equation (5) for equilibria between a mineral phase and an aqueous solution, computed implicitly with the modified monotone sequences algorithm, are used in this study to calculate the chemical characteristics of an ore-forming fluid compatible with the observed mineral assemblages from molybdenum mineralized systems. Minerals included as constraints to the fluid-mineral equilibria are those described as alteration phases in F-rich, biotite-stable assemblages reported in Chapter 2. The choice of mineral phases used in the model to constrain solutes in the aqueous phase and implications for the computed fluid-mineral equilibria are considered in the following discussion. Typical reactions used to evaluate thermodynamic activities and fugacities of solute species in the aqueous solution are summarized in Table IX.

The definition of components states that, for any geochemical system involving oxidation-reduction equilibrium, the minimum number of thermodynamic components necessary to completely describe the system is the number of elements plus one. Inspection of Table IX reveals a total of 13 elements. Any combination of 14 stoichiometric solids, solid solution end members, gases, and aqueous species will then quantify the chemical

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Table IX.	Dissociational	Equilibria for	Thermodynamic	Components a	nd Expressions	tor	Solute	ACTIVITIES

Element	Dissolution/Hydrolysis reaction	Species	Solute Activity
н	$H_2O = 2H^+ + 1/2O_2 + 2\Theta^-$	[H+]	([K+][A1'+]'[H+SiO+]'/[KA1'S1'0'*(OH)']K)-'"
0		f(0:)	externally fixed
F	$CaF_2 = Ca^{2+} + 2F^{-}$	[F ⁻]	(K[CaFz]/[Ca ^{z+}]) ⁻ ^z
Na	NaAlSi;0: + 4H* + 4H:0 = Na* + Al³* + 3H:Si0: NaCl = Na* + Cl ⁻	[Na+]	K[NaA1S1;0;][Hz0]*[H*]*/[A1;+][H*S10;] K[NaC1]/[C1-]
Mg	KMg;AlS1;0;oF2+8H*+2H20 = K*+3Mg2++Al3++3H4S104+2F-	[Mg²+]	(K[KMg;A1S1;0;oF2][H20]2[H+]*/[K+][A13+][H4S104]2[F
A 1	AlzSiO4Fz + 4H* = 2Al'* + H4SiO4 + 2F ⁻ KAljSijO40(0H)z+10H* = K* + 3Al'* + 3H4SiO4O4	[A1'+]	(K[A12S104F2][H+]4/[H4S104][F-]2)-2 (K[KA12S12040(OH)2][H+]20/[K+][H4S104]2)-3
Si	$S10_2 + 2H_20 = H_4S10_4$	[H4S104]	K/[S10:][H:0]
s		f(S2)	externally fixed
C 1	NaC1 = Na ⁺ + C1 ⁻	[01-]	K[NaC1]/[Na+]
к	$KA151_{2}O_{1} + 4H^{+} + 4H_{2}O_{2} = K^{+} + A1^{2}^{+} + 3H_{4}S1O_{4}$ $KA1_{2}S1_{2}O_{10}(OH)_{2} + 1OH^{+} = K^{+} + 3A1^{2}^{+} + 3H_{4}S1O_{4}$	[K+]	K[KA15130+][H20]4[H+]4/[A13+][H45104]3 K[KA135130+](OH)2][H+]10/[A13+][H45104]3
Ca	$CaSO_4 + 2H^+ = Ca^{2+} + 1/2S_2 + 3/2O_2 + H_2O_3$	[Ca'+]	K[CaSO4][H+] ² /[S2] ³ ² (H2O]
Fe	Fe:D; + 6H ⁺ = 2Fe ^{;+} + 3H:D KFe;AlS1;D:o(OH): + 10H ⁺ = K ⁺ + 3Fe ^{;+} + Al ^{;+} + 3H ₄ S1O ₄	[Fe ¹⁺] [Fe ¹⁺]	K[FezO3][H+]*/[H2O]' (K[KFe3A1S13O1*(OH)2][H+]'*/[K+][A13+][H*S1O4]')-'
Мо	$MOS_2 + H_2O + 32O_2 = MOO_4^{} + S_2 + 2H^+$	[MoO ₄]	K[H:0][0:]''[S:][H+]'

characteristics of the aqueous solution, provided that the entire component basis is linearly independent.

It has been shown (Chapter 2) that alteration assemblages and fluid inclusions most closely associated with the onset of molybdenum mineralization at Questa, Hudson Bay Mountain, and Endako contain the solid solution phases alkali feldspar, biotite, and white mica as well as stoichiometric anhydrite, fluorite, halite, hematite, molybdenite, and quartz. In addition, the $f(O_2)$, $f(S_2)$, f(HF), and pH are independently calculated or measured. This set of components (including the end members of solid solutions) overdetermines the geochemical system, and in so doing violates the phase rule. This is not to say that the mineral assemblage under consideration here is not in equilibrium, although in some instances this may certainly be the case. Indeed, the superposition and interaction of hydrothermal events and assemblages is commonly recognized. Rather, it indicates that each thermodynamic component can be used to constrain only one non-component species, giving some flexibility to the selection of stoichiometric solid phases or solid solution end members to be specified as components in the model assemblage. The ultimate and most reliable check of equilibrium conditions and the selection of constraining components lies in comparing the observed alteration assemblages with solubilities of minerals found in the altered rock and the computed concentration of dissolved species. In the paragraphs which follow, it is convenient to identify specific components as constraints for individual solutes. It is important to note, however, that

the computational algorithm does not make such distinctions, but simultaneously evaluates the set of all mass action expressions.

A select group of phases can place limits on only one independent species. Molybdenite is the only molybdenum phase found in sufficient abundance to be considered the primary ore mineral. It is used throughout this study to constrain the molybdenum concentration in the aqueous phase. Fluorphlogopite, halite, and quartz are likewise used exclusively to constrain the respective concentrations of Mg²⁺, Na⁺, and H₄SiO₄.

Constraints for aqueous Al³⁺ and K⁺ can be from among the orthoclase component of alkali feldspar, the muscovite component of white mica, and fluortopaz. These phases do not contain divalent cations and thus cannot serve as constraints for Ca²⁺, Mg²⁺, or Fe²⁺. Different permutations of these phases each give rise to differing activities of K⁺; Al³⁺ remains essentially constant regardless of the phase eliminated from the model assemblage. Computations assuming the muscovite component as the K⁺ constraint result in unrealistic Na⁺/K⁺ ratios in the fluid which are not in agreement with the ratios inferred from saline fluid inclusions. Because white mica is the predominant phase in lower temperature alteration assemblages (Chapter 1 and Bloom, 1981), it is here regarded as the possible product of overprinting and omitted as part of the model assemblage. It will be reintroduced subsequently to test hydrogen ion activities. Fluortopaz also contains fluorine, and along with fluorite and fluorphlogopite can serve as the constraint for dissolved fluorine. Fluorphlogopite places limits on Mg²⁺,

which precludes this end member as a constraint for other constituents. Together with fluortopaz and fluorphlogopite as parts of the model assemblage, fluorite places reasonable limits on $F^$ concentrations. The log H₂O/HF values so predicted by the model are consistent with those reported by Gunow et al. (1980) and calculated in this study.

Fluorite is common to another group of phases capable of placing limits upon the concentration of aqueous Ca²⁺. Stepwise addition of anhydrite, anorthite, and clinozoisite to the model assemblage containing fluorite conclusively demonstrates that anhydrite sets the upper limit for dissolved Ca²⁺. Clinozoisite and anorthite both result in an aqueous phase supersaturated with respect to fluorite, even when vanishingly small activities of the end members are employed. Moreover, clinozoisite has not been observed in the alteration assemblages and anorthite is clearly a reactant phase and is not in equilibrium with the aqueous solution.

The constraint on Fe^{2+} may be from among the stoichiometric phases hematite and magnetite, and the end member annite (for which an activity has been calculated). Hematite is the most plausible constraint. The occurrence of both hematite and, to a lesser extent, magnetite in the alteration assemblage suggests that $f(O_2)$ cannot be far removed from the hematite-magnetite boundary. This is in agreement with direct measurement of fluid inclusion gas fugacities (Smith and Norman, 1981) which place $f(O_2)$ within the hematite stability field, and with hematite observed as a daughter product in fluid inclusions (Chapter 1

and Bloom, 1981).

Finally, three to four independent variables $(f(O_2) \text{ and } f(S_2)$, pH, and Cl) have been fixed for each computation. The gas fugacities are consistent with the fluid inclusion gas analyses reported by Smith and Norman (1981) and the pH with the assumption of a hydrothermal solution approximately one pH unit below neutrality. Gas fugacities could also be constrained by solid-solid gas buffers which employ end member species of solid solutions not yet used as thermodynamic components. The annite component of biotite solid solution could constrain $f(O_2)$ by the reaction

 $2KFe_{3}AlSi_{3}O_{10}(OH)_{2} + 3/2 O_{2} = 2KAlSi_{3}O_{8} + 3Fe_{2}O_{3} + 2H_{2}O$ (6)

By replacing $f(O_2)$ with activities of the annite component ranging from 0.001 to 0.1 (Chapter 2), $f(O_2)$ in the narrow range from -24 to -27 is obtained, in excellent agreement with the measured value. Chloride ion is fixed as an independent component because one ionic species must be present in the component basis for balancing electrical neutrality in the aqueous fluid.

DISCUSSION OF FLUID-MINERAL EQUILIBRIA

Activity Ratios of Solute Species

Evaluation of chemical equilibria between minerals and solutions in molybdenum-mineralized hydrothermal systems requires determination of the solubilities of ore and gangue minerals known to occur in the altered rocks as well as aqueous molybdenum speciation. In the first instance, fluid-mineral equilibrium is represented as activity and fugacity ratios in the oreforming fluids without consideration of molybdenum in the aqueous phase; the molybdenum speciation and concentration will be addressed subsequently. The stability field boundaries in Figures 13 through 19 depicting phase relations among alteration minerals, gases, and the aqueous solution were generated for 350°C using thermochemical data cited previously.

1. Volatile Species

Phase relations among minerals in the system Mo-Fe-O-H-F-S are depicted in Figure 13 as a function of log $f(O_2)$ and $f(S_2)$ in the fluid phase. The bold curves and labels delimit stability fields for minerals in the subsystem Mo-O-H-S in the presence of an aqueous solution. The light curves and labels represent phase relations for minerals in the subsystem Fe-O-H-S in the presence of an aqueous phase and either iron oxide, magnetite, hematite, pyrrhotite, or pyrite. The $f(O_2)$ and $f(S_2)$ at which hematite and molybdenite are compatible is quite limited if these phases are in equilibrium. These limits are between -22 and -28 for log $f(O_2)$ and -3 to -9 for log $f(S_2)$. A much



Figure 13. Phase relations in the system MoS_2 -FeS-FeS $_2$ -H $_2O$ in the presence of an aqueous solution at 350°C and steam saturation. Bold and fine phase boundaries for the molybdenum and iron subsystems, respectively. Sources of thermochemical data for phase diagrams in Figures 13 through 19 discussed in text.

larger range of $f(O_2)$ and $f(S_2)$ is attainable in molybdenitepyrite veinlets for which $f(O_2)$ is not constrained by the presence of hematite or magnetite. Although reasonable to allow $f(S_2)$ and $f(O_2)$ to be wholly dependent on coexisting phases, fluid inclusion gas analyses calculated by Smith and Norman (1981) place values for these fugacities within the hematite stability boundaries. In the computations which follow, the respective log $f(O_2)$ and log $f(S_2)$ are -26 and -9 unless otherwise specified.

2. $[a(K^+)/a(H^+)]$ and $[a(Fe^{2+})/a(H^+)^2]$

The consequences of variable f(HF) in the fluid phase on mineral compositions, compatibilities and $[a(K^+)/a(H^+)]$ are shown in Figure 14. It can be seen that at quartz saturation the stability field for stoichiometric muscovite is located at larger log $[a(K^+)/a(H^+)]$ values than is the andalusite stability field. At even greater log $[a(K^+)/a(H^+)]$ orthoclase is stable. Stoichiometric K-feldspar and muscovite are here depicted by the bold phase boundaries. The superimposed boundaries shown in lighter lines are for a(K-feldspar) and a(muscovite) equals 0.96 and 0.66, respectively (Chapter 2). It can be seen that these solid solutions may coexist with stoichiometric fluortopaz only a log f(HF) near -2.75, remarkably close to the f(HF) calculated from F-biotite compositions, and at $[a(K^+)/a(H^+)]$ of approximately 4.7. The effect of compositional variation in fluortopaz solid solution on the respective $[a(K^+)/a(H^+)]$ and f(HF) in aqueous solution is to shift the fluortopaz phase boundary to more negative values of log f(HF). The range of a(fluortopaz)



Figure 14. Phase relations in the system $K_2O-Al_2O_3-SiO_2-H_2O-HF$ as a function of log $[a(K^+)/a(H^+)]$ and log f(HF). Computed for presence of an aqueous solution at 350°C saturated with respect to steam and quartz. Stoichiometric compositions (bold boundaries) and those adjusted for the activities of orthoclase and muscovite in alkali feldspar and white mica solid solutions (fine boundaries) considered as well as flourtopaz activity (equals 1.0 for bold and 0.1 for fine boundaries).

shown here is 0.1 to 1.0; topaz analyses from molybdenum-mineralized systems, however, indicate compositions very near stoichiometric fluortopaz. The corresponding activities calculated from the activity-composition relations for topaz reported in Barton et al. (1982) are consistent with log f(HF) between -2.7 and -2.8. Phase relations in the subsequent activity and fugacity diagrams depict equilibria for K-feldspar and muscovite solid solutions and stoichiometric fluortopaz.

Equilibria among stoichiometric kaolinite and the muscovite, K-feldspar, and biotite solid solutions in the presence of an aqueous fluid are depicted in Figure 15 as a function of log $[a(Fe^{2+})/a(H^{+})^{2}]$ and log $[a(K^{+})/a(H^{+})]$. It can be seen in thisfigure that K-feldspar and muscovite solid solutions may coexist with biotite solid solution having log a(annite) between -1.0 and -3.0 over a wide range of $[a(Fe^{2+})/a(H^{+})^{2}]$. The range of $[a(Fe^{2+})/a(H^{+})^{2}]$ consistent with biotite solid solution in which a(annite) is similar to that reported in Chapter 2 is restricted to log $[a(Fe^{2+})/a(H^{+})^{2}]$ between 0.0 and 0.5 and is independent of $[a(K^{+})/a(H^{+})]$ if it is to coexist with the K-feldspar solid solution.

3. $[a(Mg^{2+})/a(H^{+})^{2}]$ and $[a(Ca^{2+})/a(H^{+})^{2}]$

The relative stabilities of stoichiometric kaolinite and fluortopaz and the K-feldspar and fluorphlogopite solid solutions are shown in Figure 16 as a function of log $[a(Mg^{2+})/a(H^{+})^{2}]$ and log $[a(K^{+})/a(H^{+})]$. The a(fluorphlogopite) in this diagram equals 0.8 (Chapter 2). As f(HF) in the fluid phase increases, lower magnesium ratios are required to stabi-



Figure 15. Phase relations in the system $K_2O-Al_2O_3-SiO_2-FeO-H_2O$ as a function of log $[a(K^{+})/a(H^{+})]$ and log $[a(Fe^{2+})/a(H^{+})^2]$. Computed for steam-saturated water at 350°C in the presence of quartz. Muscovite and alkali feldspar phase boundaries calculated for activities of respective end members in corresponding solid solution. Annite activity varied from 0.1 (bold boundaries) to 0.001 (fine boundaries).



Figure 16. Phase relations in the system $K_2O-Al_2O_3-SiO_2-MgO-H_2O-HF$ as a function of log $[a(K^+)/a(H^+)]$ and log $[a(Mg^{2+})/a(H^+)^2]$. Computed for steam-saturated water in the presence of quartz. Muscovite and K-feldsar phase boundaries calculated as in Figure 15. Log f(HF) varies from -4.0 (bold boundaries) to -2.0 (fine boundaries); note that fluortopaz is increasingly stable with respect to muscovite + K-feldspar such that the assemblage fluorphlogopite + fluortopaz + muscovite + K-feldspar defines a unique log f(HF). lize fluorphlogopite at a given potassium ratio. Note that at log f(HF) greater than approximately -3.0 kaolinite disappears and is replaced by fluortopaz as the stable phase. The stability boundary of fluortopaz shifts to larger $[a(K^+)/a(H^+)]$ values with increasing f(HF), and muscovite is similarly replaced as the stable phase at log f(HF) \geq -2.3. It can be deduced from Figure 16 that equilibrium among the fluorphlogopite, and Kfeldspar solid solutions, stoichiometric fluortopaz and quartz and an aqueous phase with log f(HF) from -2.5 to -3.0 requires log $[a(Mg^{2+})/a(H^+)^2]$ in the limited range from 8.0 to 8.5.

Compositional constraints imposed for calcium in the aqueous phase are shown as a function of log $[a(Ca^{2+})/a(H^{+})^{2}]$ and log $[a(K^+)/a(H^+)]$ in Figure 17. Calcium-bearing silicates which have not been observed in the alteration assemblage (clinozoisite and grossular) are depicted on this diagram at vanishingly small activities (log activity equals -3.0). The absence of clinozoisite solid solution establishes the upper limit for log $[a(Ca^{2+})/a(H^{+})^{2}]$ at a value dependent upon log f(HF) in the fluid. At log f(HF) less than approximately -3.0, stoichiometric fluortopaz does not occur as a stable solid phase. An increase in f(HF) progressively replaces first kaolinite followed by muscovite with fluortopaz, until at log f(HF) = -2.75 only fluortopaz and K-feldspar can stably coexist. Contours of fluorite saturation as a function of log f(HF) establish log $[a(Ca^{2+})/a(H^{+})^{2}]$ consistent with the absense of clinozoisite and the assemblage fluorite-K-feldspar-(muscovite)quartz at -6.0.



Figure 17. Phase relations in the system $K_2O-Al_2O_3-SiO_2-CaO-H_2O-HF$ as a function of log $[a(K^*)/a(H^*)]$ and log $[a(Ca^{2*})/a(H^*)^2]$. Computed for the presence of an aqueous solution at 350°C saturated with respect to steam, quartz, and fluorite at log f(HF) equals -4.0 (fine boundaries) and -2.0 (bold boundaries). Absence of clinozoisite in the alteration assemblage places upper limit on relative Ca^{2} -+ concentration. Increasing log f(HF) progressively stabilizes fluortopaz at the expense of muscovite and K-feldspar as in Figure 16.

4. $[a(Al^{3+})/a(H^{+})^{3}]$ and $a(H_{4} SiO_{4})$

Phase relations among stoichiometric quartz, kaolinite, and fluortopaz and the K-feldspar and white mica solid solutions are shown as a function of log $[a(K^*)/a(H^*)]$ and log $[a(Al^{3+})/a(H^{+})^{3}]$ in Figure 18. Increase in log f(HF) from -4.0 to -2.0 results in a shift of the fluortopaz phase boundary to smaller values of log $[a(Al^{3+})/a(H^{+})^{3}]$. Simultaneously, the muscovite-fluortopaz boundary moves to higher values of log $[a(K^{+})/a(H^{+})]$ for a given log $[a(Al^{3+})/a(H^{+})^{3}]$. Increasing HF thus favors fluortopaz relative to other silicate minerals considered in this study. Kaolinite is no longer a stable phase when log f(HF) exceeds approximately -3.5, but equilibria among quartz, K-feldspar, and fluortopaz cannot be achieved until log f(HF) equals approximately -2.75 owing to the presence of the muscovite solid solution. At greater HF fugacities the Kfeldspar-fluortopaz assemblage progressively stabilizes at the expense of the muscovite solid solution stability field. It can be deduced from Figure 18 that stoichiometric quartz and fluortopaz are stable in the presence of the K-feldspar and muscovite solid solutions and an aqueous phase at log $[a(Al^{3+})/a(H^{+})^{3}]$ equal to approximately -1.9.

Finally, the dependence of the equilibrium composition for an aqueous phase coexisting with stoichiometric quartz and fluortopaz and the K-feldspar and muscovite solid solutions on log f(HF) can be assessed with the aid of Figure 19, shown as a function of log $[a(Al^{3+})/a(H^{+})^{3}]$ and log $a(H_{4}SiO_{4})$. The accessible aqueous field is limited by the saturation boundaries of



Figure 18. Phase relations in the system $K_2O-Al_2O_3-SiO_2-H_2O-HF$ as a function of log $[a(K^+)/a(H^+)]$ and log $[a(Al^{3+})/a(H^+)^3]$. Computed for the presence of steam-saturated water at 350°C with log f(HF) from -2.0 (bold boundaries) to -4.0 (fine boundaries). Increasing log f(HF) progressively stabilizes fluortopaz at lower values of log $[a(Al^{3+})/a(H^+)^3]$.



Figure 19. Phase relations in the system $K_2O-Al_2O_3-SiO_2-H_2O-HF$ as a function of log $[a(Al^{3+})/a(H^+)^3]$ and log $a(H_4SiO_4)$. Computed for steam-saturated water at 350°C with log f(HF) from -2.0 (bold boundaries) to -4.0 (fine boundaries). Presence of the assemblage quartz + K-feldspar + muscovite + fluortopaz with activities of solid solution phases as in Figure 15 uniquely defines log f(HF). stoichiometric gibbsite, andalusite, fluortopaz, and quartz. At quartz saturation, the value of log $a(H_4SiO_4)$ equals -2.05. The accessible values of log $[a(Al^{3+})/a(H^+)^3]$ are established by f(HF) in the fluid phase. Fluortopaz saturation approaches that of andalusite at a log f(HF) value of approximately -3.0. It is clear from this diagram that andalusite is precluded from the alteration assemblage by the presence of fluortopaz at log f(HF) consistent with the inferred values.

Aqueous Molybdenum Speciation

Complexed ions of molybdenum in oxidation states from (III) to (VI) are known to exist in low-temperature aqueous solutions. Hexavalent molybdenum is present in oxidized solutions over a wide pH range as an oxy-cation or an oxy-acid anion. The existance and properties of the MoO_2^{2+} ion in extremely acid solutions (Nazarenko and Shelikhina, 1971) and of the MoO_4^- ion in alkaline solutions (Zhidikova et al., 1973) are well known. In solutions of intermediate concentration and pH, molybdic acid $(H_2MoO_4^{\circ})$ dissociates to bimolybdate $(HMoO_4^-)$ ion. Hydrolysis and polymerization are known to occur in dilute solutions (Kinslinskaya et al., 1977). The speciation and properties of monomeric and dimeric hydroxo-complexes have been reported by Shpak et al. (1977).

Table V lists the thermochemical data for aqueous molybdenum species at 25°C. Dissociation constants for the complexes have been measured only at room temperature, and entropies of very few of these molybdenum complexes are known (Deillen et al., 1976). Third law entropies were thus estimated from entro-

py correlation plots (Cobble, 1964a, 1964b). Properties for twelve molybdenum species have been considered. These include hydroxo-, chloro-, fluor-, and sulfo-complexes of hexavalent molybdenum, as well as the molybdyl ion and a chloride complex of pentavalent molybdenum.

Much less is known about the speciation and stability of molybdenum species in lower oxidation states and in reduced aqueous solutions. Kudrin et al. (1980) have suggested that in acid and near-neutral solutions at 450° C buffered by Ni-NiO, reduced molybdenum (V, IV, and III) predominates and have presented free energy data for the neutral complex $MoO_2(OH)^{\circ}$. Mit'kina et al. (1978) have investigated complex formation of molybdenum (III) with hydroxide ions at 20° C in reduced solutions of unknown $f(O_2)$. Westrich (1974) studied the solubility of molybdenite in pH-buffered KCl-HCl fluids coexisting with the pyrite-pyrrhotite-magnetite $f(O_2) - f(S_2)$ buffer. Solubilities of up to several hundred ppm were found to be dependent on temperature and chloride concentration. These data suggest molybdenum complexing with chloride at $f(O_2)$ less than those at which the molybdenum (VI) aqueous species are stable.

Only oxidized molybdenum species have been considered in this study. Reduced aqueous complexes and the alkali metal and silica complexes implied by Zhidikova et al. (1973) and Westra and Keith (1982) might conceivably enhance the solubility of molybdenite. It should also be noted that natural analogs for the reduced conditions studied experimentally (Westrich, 1974) exist (e.g. Trout Lake, British Columbia), suggesting that re-

			Cp coefficients					
Species	ΔH° 2 9 8	S° 2 9 8	a	bx10'	cx10-5			
Mo0 4	-997047	38.07	-481.16					
HMoO 🖬 -	-980740	172.80	12.73					
H₂MoO₄⁰	-970328	246.02	145.19					
MoO:(OH)+	-718378	82.38	307.36					
MoD 2 2 +	-461933	-77.49	430.48					
MoOıF-	-1056005	159.16	43.88					
Mo0 2 S 2	-553975	116.69	-219.68					
MoO₂Cl+	-619917	3.93	212.76					
MoOzClzº	-780138	74.06	-53.60 ⁻					
Mo02C11-	-932427	144.18	320.07					
Mo0 z +	-530996	-5.90	366.80					
MoOCl3º	-701903	252.17	2.708					
HF º	-321691	93.51	-297.022					
NaC1º	-417868	62.76	183.259					
Clg	0.0	222.97	34.642	2.677				
HClg	-92312	186.80	25.724	5.676	-1.7499			
HFg	-272546	173.67	26.148	3.886	-2.2282			

Table X. Thermochemical Data For Gases And Aqueous Molybdenum Species.

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duced molybdenum species may contribute significantly to the ore-forming process in some if not many molybdenum-mineralized deposits. The numerical values of molybdenite solubility presented here may thus change as estimates of the thermochemical properties for reduced aqueous molybdenum species become available.

Using the thermochemical properties of oxidized molybdenum species reported at 25°C, the high-temperature properties of the complexes have been estimated. The temperature dependence of equilibrium constants involving the dissociation of aqueous complexes to MoO_4^{--} and bare anions is expressed in terms of Helgeson's (1967) equation of state describing aqueous dissociation reactions. The average heat capacity of the molybdate ion was computed using the correspondence principle (Criss and Cobble, 1964a, 1964b). Average heat capacity values for aqueous complexes were computed from Δ Cp(reaction) values (Smith, pers. com.) using corresponding properties of the other reactants and products from Table XII and Helgeson et al. (1978).

The thermochemical data for dissolved molybdenum species and molybdenum minerals, when combined with the thermodynamic properties for other aqueous species and solid phases in the system can be used to compute aqueous molybdenum speciation. To properly evaluate the relative importance of the various complexes, however, it is necessary to compare their equilibrium distributions in hydrothermal solutions that contain concentrations of the complexing ligands typical for the alteration assemblage. Figure 20 shows the effect of important intensive

variables on the aqueous molybdenum speciation at 350°C.

The relative importance of molybdenum complexes for typical concentrations of fluoride, chloride, and sulfide ligands is presented in Figure 20a as a function of log $f(O_2)$ and pH. Fluorine and sulfur have been varied and values separating equal abundances of the complexes are shown as bold and medium lines for log f(HF) equals -2.0 and -4.0 at log $f(S_2)$ of -9.0, and for log $f(S_2)$ of -6.0 at log f(HF) equals -2.0 by light lines, respectively. This diagram indicates that in near-neutral solutions and log $f(O_2)$'s between -25.0 and -30.0, two complexes (HMoO₄ $^-$ and MoO₃F⁻) with lesser amounts of H₂MoO₄ $^{\rm o}$ and MoO₂ $^+$ contribute to the transport of molybdenum. Chloride complexes, although considered in the calculations, do not occupy separate regions of predominance; similarly, sulfide complexes do not predominate at any geologically reasonable pH or $f(O_2)$. Chloride and sulfide complexes are therefore unimportant to the transport of molybdenum under oxidizing conditions.

The central stability field in Figure 20a is indicated as a region of predominance for both $HMoO_4^-$ and MoO_3F^- . At any log f(HF) less than approximately -2.2 $HMoO_4^-$ is in greater abundance than MoO_3F^- . Increasing log f(HF) above -2.2 in the fluid leads to an enlarged region for the fluoride complex at the expense of $H_2MOO_4^{0}$ at acid pH values and of MoO_4^{2-} in alkaline solution. Simultaneously, the MOO_2^+/MOO_3F^- and $MOO_2S_2^{2-}/MOO_3F^-$ boundaries shift to more negative values of log $f(O_2)$ at a given pH. With increasing log $f(S_2)$ the region for $MOO_2S_2^{2-}$ every-where shifts to greater log $f(O_2)$ values at a given pH.



Figure 20. Activity-activity diagrams depicting the predominant oxidized aqueous molybdenum species in steam-saturated water at 350° C. All boudaries drawn at equal abundances of the complexes. Thermochemical data from Table X. Relations shown as functions of a) log $f(O_2)$ and pH at log $f(S_2)$ equals -9.0 and log f(HF) from -4.0 (bold boundaries) to -2.0 (fine boundaries); note large central stability field in which MoO₃F⁻ predominates over HMoO₄⁻ at log $f(S_2)$ to -6.0 (dashed boundary); b) log f(HF) and pH where log $f(S_2)$ to -6.0 (dashed boundaries); c) log $f(O_2)$ and log f(HF) and pH where log $f(S_2)$ equals -9.0 and log $f(S_2)$ varies from -26.0 (bold boundaries) to -24.0 (fine boundaries); c) log $f(O_2)$ and log f(F) and log f(HF) at pH equals 5.0 and log $f(S_2)$ varies from -9.0 (bold boundaries) to -6.0 (fine boundaries); d) log $f(O_2)$ and log $f(S_2)$ at pH equals 5.0; note phase boundaries for the system $MOS_2-H_2S-H_2O-HF$ as in Figure 13 indicates speciation predominated by MOO_3F^- and/or $HMOO_4^-$ depending on log f(HF).





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The apparent reversal in the predominance of HMoO₄ and MoO_3F^- can be better understood by inspection of Figure 20b, which shows aqueous molybdenum speciation as functions of log f(HF) and pH in the fluid at constant log $f(O_2)$ (-26.0) and log f(S₂) (-9.0). For the conditions specified in the construction of this diagram, the $MoO_{3}F^{-}$ and $HMoO_{4}^{-}$ are in equal abundance at approximately log f(HF) of -2.2. Above this value, MoO₃F⁻ predominates and becomes increasingly important whereas at log f(HF) less than -2.2 it is replaced by $HMoO_{q}^{-}$. It can also be seen that a narrow region of $H_2MoO_4^{\circ}$ predominance separates the MoO_2^+ and $HMoO_4^-$ fields. This region enlarges at the expense of MoO_2^+ with increasing log $f(O_2)$, but vanishes entirely when log $f(O_2)$ drops below -26.0. This further emphasises the importance of molybdenum (VI) species in oxidized solutions. At constant f(HF) and increasing $f(O_2)$, the MoO_3F^- region enlarges by a shift toward lower pH values. This infers that with a decrease in pH at constant $f(O_2)$ and f(HF), the fluorine complex becomes increasingly important as a transporter of molybdenum.

The effect of log $f(S_2)$ on aqueous molybdenum speciation can be examined with the aid of Figure 20c, which shows the predominant complexes as functions of log $f(O_2)$ and log f(HF) at a pH of 5. The large region for $MoO_2S_2{}^{2-}$ progressively encroaches upon first the $MoO_2{}^+$ and $MoO_3F{}^-$ followed by the $HMoO_4{}^-$ and $MoO_3F{}^-$ regions toward higher values of log $f(O_2)$ with an increase in log $f(S_2)$. The magnitude of this shift is such that the sulfide complex cannot contribute significantly to the transport of molybdenum are near-neutral pH until the log $f(S_2)$ exceeds approximately -3.0 if log $f(O_2)$ between -25.0 and -30.0 are still in effect. In extremely alkaline solutions, much lower $f(S_2)$ are required to enter the predominant region for $MoO_2S_2^{2-}$. Gas analyses of inclusion fluids from Questa (Smith and Norman, 1981) indicate log $f(S_2)$ as high as -3.0 during the final stages of mineralization. Sulfide complexes may thus have become important in late H_2S -rich fluids; however, $MoO_2S_2^{2-}$ is unimportant to molybdenum transport in early stages of alteration/mineralization where the observed mineral assemblages infer log $f(S_2)$ several orders of magnitude lower.

Having established which aqueous molybdenum species are plausible contributors to molybdenum transport, it is now possible to examine the relevant speciation under the $f(O_2) - f(S_2)$ conditions imposed by fluid-mineral equilibrium in the subsystem Mo-Fe-O-H-S-F (Figure 20d) and consistent with the observed silicate alteration assemblage. In near-neutral but still acid solutions the regions for MOO_3F^- and $HMOO_4^-$ coincide with the molybdenite-hematite-(pyrite) association. Values of pH one or more units below neutrality increase the $H_2MOO_4^\circ$ and MOO_2^+ concentration, whereas values on the alkaline side of neutrality progressively favor $MOO_2S_2^{2-}$.

Absolute Solute Concentrations

The equilibrium relationship between the alteration assemblage, ore mineralogy, and the coexisting hydrothermal solution is quantitatively calculated at 350°C and the results of these calculations are discussed below.

Table VIII shows the computed fluid-mineral equilibrium for

Species	log molality	log grams/kgm H₂O	concentration(ppm)
A1''+	- 14 . 40	- 12.97	0.00
A1(OH)4-	-6.05	-4.08	0.04
K+	0.39	1.98	46391.
Na†	0.91	2.27	90447.
C1-	1.01	2.56	177824.
NaCl º	0.82	2.59	189436.
Cał+	-3.76	-2.15	3.41
Mg²+	-4.65	-3.27	0.26
MgSO + °	-3.25	-1.17	32.85
Fe ²⁺	-7.39	-5.65	0.00
Fe't	-19.08	-17.34	0.00
F-	-3.04	-1.76	8.35
H4S104	-2.49	-0.51	151.10
51-	-11.81	-10.31	0.00
SO 4 2 -	-1.36	0.63	2065.
H₂Sº	-4.70	-3.17	0.33
HMoO 🖌 [–]	-4.27	-2.06	4.22
H₂MoO₄º	-6.16	-3.95	0.06
MoO 3 F -	-4.11	-1.90	6.10
MoO 2 +	-5.09	-2.98	0.51

Table XI. Fluid/Mineral Equilibria: Computed¹ Concentration of Aqueous Species Coexisting with Alteration Phases² at 350°C.

¹pH=5, log $f(S_2)$ =-9.0, and log $f(O_2)$ =-26.0 ²Molybdenite-biotite solid solution-quartzfluortopaz-fluorite-halite-hematite-anhydrite •

the mineral association outlined below. Only the distribution of bare ions and the predominant aqueous species is given in the table, along with the predominant molybdenum species.

1. Hydrogen Ion Concentration

Fluid inclusion analyses and thermochemical calculations indicate that hydrothermal solutions are near-neutral to acidic, chloride solutions (McKenzie, 1981). The pH used in the computations presented here (5) is for a hydrothermal solution approximately one pH unit below neutrality. The pH value fixed for these computed fluid-mineral equilibria can be explicitly cross-checked using alteration mineral compatibility. Replacing the fixed hydrogen ion activity with a specific activity of end member muscovite component permits calculation of pH values consistent with a(muscovite). The pH so computed varies between 4 and 6 for a range of muscovite activities from 0.6 to 0.7, in remarkable agreement with those calculated from the white mica analyses.

2. Error Propogation

The chemical-thermodynamic model of fluid-mineral equilibria presented in this communication involves the use of mineral analyses and activity-composition relations which are themselves associated with numerical uncertainties and are subject to errors which are poorly known at best. The form of these uncertainties or error distributions of the input activities are also largely unknown. It is therefore of considerable interest to estimate how sensitive the chemical characteristics computed

from the model are to possible errors in the mineral activities used to constrain thermodynamic components. The Monte Carlo method of error propagation (Anderson, 1976) has been implemented to study the effects of these errors and uncertainties, and consisted of repeated computations of heterogeneous equilibrium constrained by the presence of a given mineral or mineral assemblage, each time varying the input activity of one or more constraining solid solution phases randomly within the observed limits using a 'rectangular' or 'uniform' error probability distribution. The calculated aqueous speciation then shows the effect of the imprecision of the constraining activities. Imprecision and systematic error in the electron microprobe analyses are implicitly accounted for, and explicit treatment of errors introduced in the activity-composition relations or by the failure to unambiguously identify the equilibrium alteration assemblage is possible. Results of error propagation calculations are summarized for various solute species and activity ratios respectively in Table IX. These results indicate that, although absolute uncertainties in both compositions and thermochemical data can be significant, the effects are not apparent in the final computations.

3. Molybdenum Concentration and Precipitation Mechanisms

Fluid-mineral equilibrium calculations at 350° C show that molybdenite is soluble to the extent of only a few ppm for any geologically reasonable range of pH, $f(O_2)$, and $f(S_2)$ where fluorine is present only in trivial concentrations. Signifi-

	mean	1	enecias	log molality		log grams/kgm H₂O mean 1∢		concentration(ppm) mean 1a	
	Mean				····				
fluorphlogopite	0.214	0.09	Ma²+	-4.67	-5.45	-3.29	-4.06	0.25	0.04
· · · · · · · · · · · · · · · · · · ·			MaSO . º	-3.26	-4.04	-1.18	-1.95	32.30	5.44
			ĸŤ	0.32	-5.64	1.92	-4.05	40480.	0.18
fluortopaz	0.900	0.10	A1'+	-14.35	-15.52	-12.92	-14.09	0.00	0.00
			A1(0H)4-	-5.99	-7.05	-4.01	-5.10	0.05	0.004
			K+	0.33	-0.77	1.92	0.82	40755.	3086.
K-feldspar	0.55	0.05	К+	0.90	0.01	2.49	1.61	133160.	14433.
	••••		Na+	0.82	-0.61	2.18	0.75	65317.	3957.
			C1-	1.15	-0.12	2.70	1.43	215488.	6597.
			NaC1º	0.73	-0.66	2.49	1.10	134852.	8593.
			Ca ²⁺	-3.71	-5.63	-2.10	-4.02	3.41	0.04
			Ma²+	-4.79	-6.26	-3.41	-4.88	0.17	0.01
			MaSO 4 º	-3.52	-4.61	-1.44	-2.53	15.63	1.64
			H45104	-2.53	-10.93	-0.54	0.00	124.0	2.85
K-feldspar	0.06	0.04	к+	-1.30	-1.43	0.29	0.17	1001.	747.0
			Na+	0.95	-1.85	2.31	-0.49	104666.	234.0
			C1-	0.95	-1.66	2.50	-0.11	159876.	292.0
			NaC1º	0.87	-1.91	2.64	-0.14	220365.	510.0
			Ca ²⁺	-3.79	-6.68	-2.19	-5.08	3.29	0.00
			Ma²+	-4.06	-4.50	-2.68	-3.12	1.08	0.39
			MaSO 4 º	-2.59	-5.37	-0.47	-3.39	159.0	57.91
			H4S104	-2.45	-5.37	-0.47	-3.39	172.0	0.32
all phases?	0.30	0.25	К+	0.33	0.20 -	1.92	1.79	39872.	27887.
			Na⁺	0.92	-0.29	2.28	1.07	92580.	8482.
			C1 -	1.00	0.001	2.56	1.55	175403.	11474.
			NaC1 ^o	0.83	-0.35	2.60	1.41	194085.	18421.
•			Ca ² +	-3.76	-5.06	-2.16	-3.46	3.39	0.06
			Ma² +	-4.59	-4.99	-3.21	-3.60	0.31	0.13
			MaSO .	-3.17	-3.40	-1.09	-1.39	40.46	21.10
			HASIDA	-2.48	-3.78	-0.50	-1.80	154.0	12.38

Table XII. Monte Carlo Simulation of Error Propogation in Computed Distribution of Aqueous Species.

¹bare ions and predominate complexes which vary by more than 0.1 log unit 2 K-feldspar activity equals 0.30 ± 0.25, other solid solution phases as above

cantly higher molybdenum levels in solution are predicted in the presence of fluoride complexing, although the importance of fluoride complexing decreases markedly in a model where the aqueous solution is undersaturated with respect to fluorite. The solubility computations presented here differ in detail from those reported by Smith et al. (1980). Although these differences may considerably affect the quantitative results of aqueous molybdenum speciation, the trends and precipitation mechanisms presented in this study are probably much as shown.

The example of computed molybdenite solubility (Table XIV) shows that approximately 12 ppm molybdenum can be transported in a slightly acid solution at 350° C. The H₂O/HF ratios resulting from the calculations are in the range for Questa presented here and for the Henderson deposit reported by Gunow et al., (1980), and are consistent with dissolved fluorine constrained by fluidfluorite equilibrium. At the level of molybdenum concentration predicted by fluid-molybdenite equilibria, approximately 10⁵ kilograms of solvent H₂O is required to deposit one kilogram molybdenum as molybdenite, and 4x10¹³ kilograms water are necessary to account for the 4.14x10⁵ metric tons molybdenite present in a typical stockwork deposit. This resulting 'geologic solubility' of molybdenite is plausible in light of the fluid flux calculated by numerical models of meteoric-hydrothermal convective circulation (Cathles, 1977) if 100 percent efficiency in extracting molybdenum from the aqueous solution is assumed. Such low concentrations are not in agreement, however, with the magmatic-hydrothermal model in which molybdenum-bearing fluids

are exsolved directly from a silicate melt (Ganster, 1978) and deposited directly from the rising column or plume of magmatic The 'geologic solubility' thus infers that precursors to fluid. the solutions which gave rise to the F-biotite-K-feldsparquartz-fluorite ± molybdenite alteration assemblage were significantly enriched in molybdenum relative to the computed fluidmineral equilibria at 350°C. Precipitation of molybdenite from such progenitor solutions could have been controlled primarily by physical temperature gradients as inferred from fluid inclusion data (Chapter 1 and Bloom, 1981) and suggested by Carten et Indeed, the extreme temperature dependence of mo-(1981).al. lybdenite solubility reported by Smith et al. (1980) predicts that rising ore-forming solution(s) would deposit molybdenite in a narrow, confined zone as temperature decreased.

Fluid-mineral equilibria, however, do infer that controls on molybdenite deposition by reactions which involve fluorinebearing phases and/or K-feldspar can also be extremely effective under isothermal conditions. One such reaction (Carten et al., 1981) is

$3KAlSi_3O_8 + MOF_4^{\circ} + 2H_2S^{\circ} =$

 $KAl_{3}Si_{3}O_{10}(F)_{2}+6SiO_{2}+MoS_{2}+H_{2}O+2KF^{0}$ (8).

(9)

This reaction assumes the presence of Mo(IV) in solution. Similar reactions using oxidized fluormolybdenum complexing may be written as

> $3KAlSi_{3}O_{8} + 4MOO_{3}F^{-} + 8H_{2}S^{0} + 4H^{+} =$ $KAl_{3}Si_{3}O_{10}(F)_{2} + 2KF^{0} + 6SiO_{2} + 4MOS_{2} + 10H_{2}O + 2O_{2}$

and
$$KAlSi_{3}O_{8} + MOO_{3}F^{-} + 3MgF_{2}^{0} + 2H_{2}S^{0} + H^{+} = KMg_{3}AlSi_{3}O_{10}(F)_{2} + MOS_{2} + 5HF^{0} + 1/2O_{2}$$
(10).

The widespread occurrence of the assemblage K-feldsparfluorphlogopite-quartz-white mica-molybdenite which coincides with the bulk of the molybdenum mineralization is thus explained in terms of reaction of the ore-forming fluid with the K-feldspar component of the wall rock. Partitioning of fluoride ion from the aqueous phase into a solid phase such as fluorite, fluorphlogopite, or fluortopaz can also reduce Mo(VI) mobility in hydrothermal solutions and lead to precipitation of molybdenite by a reaction such as

$$MoS_2 + 1/2CaF_2 + 10H^+ + 5/2O_2 = MoO_3F^- + 2S^- + 1/2Ca^{2+} + 5H_2O$$
 (11).

Note that any such reaction which involves reduction of Mo(VI) to Mo(IV) evolves oxygen and thus progressively oxidizes the coexisting fluid. Roedder and Bodnar (1980) have suggested that the occurrence of hematite as a daughter product in fluid inclusions may be the product of post-entrapment oxidation induced by hydrogen diffusion through the quartz lattice. Precipitation of molybdenite or cooling of trapped inclusion fluid containing dissolved molybdenum could, however, effect post-entrapment oxidation without hydrogen diffusion. Temperature decrease redistributes aqueous molybdenum species from fluormolydate to bimolydate complexes, and in so doing decreases the solubility of molybdenite. Reduction of Mo (VI) to Mo(IV) aqueous species is thus an 'auto-oxidation' process which could give rise to concurrent precipitation of hematite from solution given the proper mass balance of dissolved iron.

CONCLUSIONS

Studies of alteration geochemistry in molybdenum-mineralized hydrothermal systems (Chapter 2) indicate that mineralization occurred from solutions that were in equilibrium with vein mineral assemblages. The compositions of alteration minerals from these assemblages and activity-composition relations for the solid solution phases reported in Chapter 2 have been used as constraints in a chemical-thermodynamic model to deduce the composition of the coexisting aqueous solutions. The composition of the ore-forming fluid at 350°C is similar in composition to fluids found in high-temperature geothermal systems. The activity of mineral components and the approximation that dissolved silica activity equal $a(H_4SiO_4)$ at quartz saturation and $a(H_2O) = X(H_2O)$ are used to calculate $[a(K^+)/a(H^+)]$, $[a(Fe^{2+})/a(H^{+})^{2}], [a(Mq^{2+})/a(H^{+})^{2}], [a(Ca^{2+})/a(H^{+})^{2}], and$ $[a(Al^{3+})/a(H^{+})^{3}]$ in the fluid phase for specific statements of the mass action equations.

The model also permits computation of minimum molybdenite solubilities in the coexisting aqueous solution using thermochemical properties of oxidized molybdenum aqueous species. Molybdenite is soluble to the extent of tens to several hundred ppm in oxidized ore-forming solutions at 350°C. Significant amounts of molybdenum are transported as fluormolybdate and bimolybdate species; chloride and sulfide complexes are not significant under the conditions inferred from fluid inclusion data (Chapter 1 and Bloom, 1981) and the phase relations discussed here. MoO_3F^- and $HMoO_4^-$ are present in subequal proportions at the near-neutral values of pH inferred from observed mineral compatibilities and calculated H_2O/HF ratios, but MoO_3F^- becomes increasingly important in more acid solutions and at higher f(HF).

The occurrence of fluorine-bearing minerals in a molybdenum-mineralized intrusion is not <u>a priori</u> evidence for molybdenum transport as fluoride complexes. Computations of fluid-mineral equilibria presented in this study, however, indicate that under constraints imposed by fluorite saturation at 350°C, the fluormolybdate complexing is often the primary transporter of molybdenum. Sufficient molybdenum can be transported when only oxidized complexes are considered without invoking complex models of aqueous transport which require reduced molybdenum speciation.

LITERATURE CITED

- 1. Ahmad, S.N., and Rose, A.W., 1980. Fluid inclusions in porphyry and skarn ore at Santa Rita, New Mexico. Economic Geology, v.75, p.229-250.
- Anderson, G.M., 1976. Error propagation by the Monte Carlo method in geochemical calculations. Geochemica et Cosmochemica Acta, v. 40, p. 1533-1538.
- 3. Barton, M., Haselton, H.T. Jr., Hemingway, B.S., Kleppa, O.J., and Robie, R.A., 1982. The thermodynamic properties of fluortopaz. American Mineralogist, v. 67, p. 350-355.
- 4. Barton, P.B. and Toulmin, P., 1961. Some mechanisms for cooling hydrothermal fluids. USGS Prof. Paper 424-D, p.D348-D352.
- 5. Beane, R.E., 1974. Biotite stability in the porphyry copper environment: Economic Geology, v.69, p.241-256.
- Bird, D.K. and Norton, D., 1981. Theoretical prediction of phase relations among aqueous solutions and minerals in the Salton Sea geothermal system. Geochemica et Cosmochemica Acta, v. 45, p. 1479-1493.
- Bloom, M.S. and Brown, T.H., 1977. Mass constraint on iron: the role of biotite in generation of potassic zone ores. Geol. Assoc. Canada, 1977, Annual Meeting, Vancouver, Program with Abstracts, v.2, p.8.
- Bloom, M.S., 1976. Solid solution behaviour and free energy surface of annite-fluorannite-phlogopite-fluorphlogopite: unpublished report, the University of British Columbia, 27p.
- Bloom, M.S., 1981. Chemistry of inclusion fluids: stockwork molybdenum deposits from Questa, New Mexico, Hudson Bay Mountain and Endako, British Columbia. Economic Geology, v. 76, p. 1906-1920.
- 10. Bright, M.J. and Jonson, D.C., 1976. Yorke-Hardy in Sutherland Brown, J., ed., Porphyry deposits of the Canadian cordillera: CIM Special Volume 15, p.455-461.
- 11. Bright, M.J. and Jonson, D.C., 1976. Yorke-Hardy in Sutherland Brown, J., ed., Porphyry deposits of the Canadian cordillera. CIM Special Volume 15, p.455-461.
- Brimhall, G.H., Jr., 1977. Early fracture-controlled disseminated mineralization at Butte, Montana. Economic Geology, v. 72, p. 37-59.

- Brown, T.H., 1970. Theoretical predictions of equilibria and mass transfer in the system CaO-MgO-SiO₂-H₂O-CO₂-NaCl-HCl. Unpublished Ph.D. Thesis, Northwestern University.
- Brown, W.L. and Parsons, I., 1981. Towards a more practical two-feldspar geothermometer: Contribitutions to Mineralogy and Petrology, v. 76, p.369-377.
- 15. Candella, P.A. and Holland, H.D., 1981. The effect of fluorine on the partitioning of molybdenum between a magma and a hydrothermal fluid. Geological Society of America, Abstracts with Programs, v. 13, p. 422.
- 16. Capuano, R.M. and Cole, D.R., 1982. Fluid-mineral equilibria in a hydrothermal system, Roosevelt Hot Springs, Utah. Geochemica et Cosmochemica Acta, v. 46, p. 1353-1364.
- 17. Carpenter, R.H., 1968. Geology and ore deposits of the Questa molybdenum mine area, Taos County, New Mexico, in Ridge, J.D., ed., Ore deposits of the United States, 1933-1967: New York, Am. Inst. Mining Metall. Petroleum Engineers, p.1328-1350.
- 18. Carpenter, R.H., 1968. Geology and ore deposits of the Questa molybdenum mine area, Taos County, New Mexico in Ridge, J.D., ed., Ore deposits of the United States, 1933-1967. New York, Am. Inst. Mining Metall. Petroleum Engineers, p.1328-1350.
- 19. Carten, R.B., Shannon, J.R., Ward, A.D., and Geraghty, E.P., 1981. Controls on molybdenite deposition at Henderson Mine, Empire, Colorado (Abst.). Geological Society of America, Abstract with Programs, v. 13, p. 423.
- 20. Cathles, L.M., 1977. An analysis of the cooling of intrusives by groundwater convection which includes boiling. Economic Geology, v.72, p.804-826.
 - 21. Chivas, A.R., and Wilkins, R.W.T., 1977. Fluid inclusion studies in relation to hydrothermal alteration and mineralization at the Koloula porphyry copper prospect, Guadalcanal. Economic Geology, v.72, p.153-169.
 - Clark, K.F., 1972. Stockwork molybdenum deposits in the western cordillera of North America. Economic Geology, v.67, p.731-758.
 - Cloke, P.L., and Kesler, S.E., 1979. The halite trend in hydrothermal solutions. Economic Geology, v.74, p.1823-1831.
 - 24. Collins, P.L.F., 1979. Gas hydrates in CO₂-bearing fluid

inclusions and the use of freezing data for the estimation of salinity. Economic Geology, v.74, p.1435-1444.

- 25. Criss, C.M. and Cobble, J.W., 1964a. The thermochemical properties of high temperature aqueous solutions IV. Entropies of the ions to 200° and the correspondance principle. American Chemical Society Journal, v. 86, p. 5385-5390.
- 26. Criss, C.M. and Cobble, J.W., 1964b. The thermochemical properties of high temperature aqueous solutions. V. The calculation of ionic heat capacities up to 200°C: Entropies and heat capacities above 200°. American Chemical Society Journal, v. 86, p. 5390-5393.
- 27. CODATA Task Group on Key Values for Thermodynamics, 1976. Recommended key values for thermodynamics, 1975. Journal Chemical Thermodynamics, v. 8, p. 603-605.
- 28. Dunlop, G., Lorinczi, G.I., and Starquist, V.L., 1978. Some geologic aspects of the stockwork molybdenum deposits at Questa, New Mexico: Unpublished report, Molybdenum Corporation of America, 10p.
- 29. Eastoe, C.J., 1981. Physics and chemistry of the hydrothermal system at the Parguna porphyry copper deposit, Bougainville, Papua New Guinea. Economic Geology, v. 77, p. 127-153.
- 30. Erwood, R.J., Kesler, S.E., and Cloke, P.L., 1979. Compositionally distinct saline hydrothermal solutions, Naica, Chihuahua, Mexico. Economic Geology, v.74, p.95-108.
- 31. Evans, B.W., 1965. Application of a reaction rate method to the breakdown equilibria of muscovite and muscovite plus quartz. American Journal of Science, v. 263, p. 647-667.
- 32. Forbes, W.C., 1972. An interpretation of the hydroxyl contents of biotites and muscovites: Mineralogical Magazine, v.38, p.712-72.
- 33. Fournier, R.O., and Truesdell, A.H., 1973. An empirical Na-K-Ca geothermometer for natural waters. Geochemica et Cosmochemica Acta, v.37, p.1255-1275.
- 34. Ganster, M.W., 1976. Evidence for the localized accumulation of hydrothermal fluids at the Henderson molybdenum deposit, Empire, Colorado. Geol. Soc. America Abstracts with Programs, v.8, no. 6, p.880.
- 35. Greenwood, H.J., 1975. Thermodynamically valid projections of extensive phase relationships. American

Mineralogist, v. 60, p. 1-8.

- 36. Guilbert, J.M. and Schafer, R.W., 1978. Preliminary geochemical characterization of muscovites in porphyry basemetal alteration assemblages. Fifth IAGOD Quadrennial Symposium, Snow Bird, Utah, p.57-68.
- 37. Gunow, A.J., Ludington, S. and Munoz, J.L., 1980. Fluorine in micas from the Henderson molybdenite deposit, Colorado: Economic Geology, v. 75, p.1127-1137.
- 38. Hall, W.E., Friedman, I., and Nash, J.T., 1974. Fluid inclusion and light stable isotope study of the Climax molybdenum deposit, Colorado. Economic Geology, v.69, p.884-901.
- 39. Hazen, R.M. and Burnham, C.W., 1973. The crystal structure of one-layer phlogopite and annite. American Mineralogist, v.58, p.889-900.
- 40. Helgeson, H.C. and Aagaard, P., 1981. Activity/composition relations among silicates and aqueous solutions. I. Thermodynamics of intra-site mixing and substitutional order/disorder in minerals. American Journal of Science, in press.
- 41. Helgeson, H.C. and Kirkham, D.H., 1974a. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. I. Summary of the thermodynamic/electrostatic properties of the solvent. American Journal of Science, v. 274, p. 1089-1198.
- 42. Helgeson, H.C. and Kirkham, D.H., 1974b. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. II. Debye-Huckel parameters for activity coefficients and relative partial molal properties. American Journal of Science, v. 274, p. 1199-1261.
- 43. Helgeson, H.C. and Kirkham, D.H., 1976. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes of high pressures and temperatures. III. Equation of state for aqueous species at infinite dilution. American Journal of Science, v. 276, p. 97-240.
- 44. Helgeson, H.C., Brown, T.H., Nigrini, A., and Jones, T.A., 1970. Calculation of mass transfer in geochemical processes involving aqueous solutions. Geochemica et Cosmochemica Acta, v. 34, p. 569-592.
- 45. Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K., 1978. Summary and critique of the thermodynamic

properties of rock-forming minerals. American Journal of Science, v. 278-A, 229 p.

- 46. Helgeson, H.C., Kirkham, D.H., and Flowers, G.C., 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 5 kb and 600°C. American Journal of Science, v. 281, p. 1249-1516.
- 47. Helgeson, H.C., 1968. Geologic and thermodynamic characteristics of the Salton Sea geothermal system. American Journal of Science, v. 266, p. 129-166.
- 48. Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. American Journal of Science, v. 267, p. 729-804.
- 49. Helgeson, H.C., 1981. Prediction of the thermodynamic properties of electrolytes at high pressures and temperatures, <u>in</u> Wickman, F. and Rickard, D., eds., Chemistry and Geochemistry of Solutions at High Temperatures and Pressures. Royal Swedish Academy of Science, Stockholm, in press.
- 50. Henley, R.W. and McNabb, A., 1978. Magmatic vapor plumes and groundwater interaction in porphyry copper emplacement. Economic Geology, v. 73, p. 1-20.
- 51. Hsu, L.C., 1981. Phase relations of some tungstate minerals under hydrothermal conditions. American Mineralogist, v.66, p.298-308.
- 52. Hudson, T., Smith, J.G., and Elliott, R.L., 1979. Petrology, composition and age of intrusive rocks associated with the Quartz Hill molybdenite deposit, southeastern Alaska. Canadian Journal of Earth Sciences, v.16, p.1805-1822.
- 53. Ishihara, S., 1967. Molybdenum mineralization in Questa mine, New Mexico, U.S.A. Japan Geol. Survey Report 218, 64 p.
- 54. Jacobs, D.C. and Parry, W.T., 1979. Geochemistry of biotite in the Santa Rita porphyry copper deposit, New Mexico: Economic Geology, v.74, p.860-887.
- 55. Kamilli, R.J., 1978. The genesis of stockwork molybdenite deposits -implications from fluid inclusion studies at the Henderson mine. Economic Geology, v.73, p.1392.
- 56. Kasper, R.B., Holloway, J.R. and Navrotsky, A., 1979. Direct calorimetric measurement of enthalpies of aqueous

sodium chloride solutions at high temperatures and pressures. J. Chem. Thermo-dynamics, v.11, p.13-24.

- 57. Keevil, N.B., 1942. Vapor pressures of aqueous solutions at high temperatures. Jour. Am. Chem. Soc., v.64, p.841-850.
- 58. Kerrick, D.M. and Darken, L.S., 1975. Statistical thermodynamic models for ideal oxide and silicate solid solutions, with application to plagioclase. Geochimica et Cosmochimica Acta, v.39, p.1431-1442.
- 59. Kimura, E.T., Bysouth, G.D. and Drummond, A.D., 1976. Endako, <u>in</u> Sutherland Brown, J., ed., Porphyry deposits of the Canadian Cordillera. CIM Special Volume 15, p.444-454.
- 60. Kirkham, R.V., 1969. A mineralogical and geochemical study of the zonal distribution of ores in the Hudson Bay Range, British Columbia. Unpublished Ph.D. Thesis, Univ. Wisconson, 152 p.
- 61. Kirkham, R.V., 1971. Intermineral intrusions and their bearing on the origin of porphyry copper and molybdenum deposits. Economic Geology, v.66, p.1244-1249.
- 62. Kislinskaya, G.E., Ermolenko, V.I., and Seklka, I.A., 1977. Polymerization of molybdenum (VI) in dilute aqueous solutions: Russian Journal Inorganic Chemistry, v. 22, p. 1292-1295.
- 63. Knight, J.E., 1977. A thermochemical study of alunite, enargite, luzonite, and tennantite deposits. Economic Geology, v. 72, p. 1321-1336.
- 64. Kudrin, A.V., Rekharsky, V.I., and Khodakovsky, I.L., 1980. Experimental study of solubility of tugarinovite MoO₂ in water solutions at 250 and 450°C (in Russian). Geokimya, v. 5, no. 12, p. 1825-1834.
- 65. Lagache, M., and Weisbrod, A., 1977. The system: two alkali feldspars KCl-NaCl-H₂O at moderate to high temperatures and pressures. Contrib. Mineral. Petrol., v.62, p.77-101.
- 66. Linke, W.F., 1965. Seidell's solubilities of inorganic and metal-organic compounds, 4th edition. Am. Chem. Soc., Washington, D.C.
- 67. McDowell, S.D. and Elders, W.A., 1980. Authigenic layer silicate minerals in borehole Elmore 1, Salton Sea geothermal field, California, U.S.A. Contributions to Mineralogy and Petrology, v. 74, p. 293-310.

- 68. McKenzie, W.F. and Helgeson, H.C., 1980. Calculated phase relations among silicates, copper iron sulfides, and aqueous solutions at magmatic temperatures (abs.). Geological Society of America, Abstracts with Programs, v. 12, p. 481.
- 69. McKenzie, W.F., 1981. Theoretical calculation of equilibrium constraints in geochemical processes to 900°C. Unpublished Ph.D. Thesis, University of California, Berkeley, 105 p.
- 70. Merino, E., 1975. Diagenesis in Tertiary sandstones from Kettleman North Dome, California. II. Interstitial solutions: distribution of species at 100°C and chemical relation to the diagenetic mineralogy. Geochemica et Cosmochemcia Acta, v. 39, p. 1629-1646.
- 71. Mit'kina, L.I., Mol'chakova, N.V., and Peshkova, V.M., 1978. Complex formation by Mo(III) with hydroxide ions: Russian Journal Inorganic Chemistry, v. 23, p. 693-695.
- 72. Munoz, J.L. and Ludington, S.D., 1977. Fluorine-hydroxyl exchange in synthetic muscovite and its application to muscovite-biotite assemblages: Am. Mineralogist, v.62, p.304-308.
- 73. Nazarenko, V.A., and Shilikhira, E.I., 1971. Spectrophotometric determination of the formation constants of mononuclear hydroxo-complexes of molybdenum (VI): Russian Journal Inorganic Chemistry, v. 16, p. 88-90.
- 74. Newton, R.C. and Wood, B.J., 1980. Volume behaviour of silicate solid solutions. American Mineralogist, v.65, p.733-645.
- 75. Nordstrom, D.K., Plummer, L.N., Wigley, T.M.S., Wolery, T.J., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.M., Fritz, B., Hoffman, M., Holdren, G.R., Jr., Lafon, G.M., Mattigod, S.V., McDuff, R.E., Morel, F., Reddy, M.M., Sposito, G., and Thrailkill, J., 1979. A comparison of computerized chemical models for equilibrium calculations in aqueous systems, <u>in</u> Jenne, E.A., ed., Chemical Modelling in Aqueous Systems. ACS Symposium Series 93, American Chemical Society.
- 76. Page, R. and Wenk, H.R., 1979. Phyllosilicate alteration of plagioclase studied by transmission electron microscopy. Geology, v.7, p.393-397.
- 77. Pascal, Marie-Lola and Roux, Jacques, 1982. Proprietes thermodynamique des solutions (Na,K)Cl-H₂O entre 400° et 800°C, 1-2 Kb: une revue des equilibres d'echange avec les silicates sodi-potassiques. Geochemica et Cosmochemica Acta, v.46, p.331-338.

- 78. Perkins, E.H., 1980. A reinvestigation of the theoretical basis for the calculation of isothermal-isobaric mass transfer in geochemical systems involving an aqueous phase. Unpublished M.Sc. Thesis, The University of British Columbia, 149 p.
- 79. Potter, R.W., and Clynne, M.A., 1978. Solubility of highly soluble salts in aqueous media-Part I., NaCl, KCl, CaCl₂, Na₂SO₄, K₂SO₄, solubilities to 100°C. Journal Research U.S. Geological Survey, v.6, p.701-705.
- 80. Potter, R.W., Clynne, M.A., and Brown, D.L., 1978. Freezing point depression of aqueous sodium chloride solutions. Economic Geology, v.73, p.284-285.
- 81. Potter, R.W., 1977. Pressure correction for fluid inclusion homo-genization temperatures based on the volumetric properties of the system NaCl-H₂O. Jour. Research, USGS, v.5, p.603-607.
- 82. Preece, R.K., and Beane, R.E., 1979. Studies of mineralization and alteration at the Sierrita porphyry copper deposits, Arizona: I. Paragenetic relations and associated fluid characteristics (abs.). AIME mtg., 108th, New Orleans, Abstracts with Programs, p.76
- 83. Reed, M.G., 1982. Calculation of multicomponent chemical equilibria and reaction processes in systems involving minerals, gases, and an aqueous phase. Geochemica et Cosmochemica Acta, v. 46, p. 513-528.
- 84. Roedder, E., and Bodnar, R.J., 1980. Geologic pressure determinations from fluid inclusion studies. Ann. Rev. Earth Planet. Sci., v.8, p. 263-301.
- 85. Roedder, E., 1971. Fluid inclusion studies on porphyrytype deposits at Bingham, Utah, Butte, Montana and Climax, Colorado. Economic Geology, v.66, p.98-120.
- 86. Sabatier, H. and Velde, B., 1970. Trioctahedral micas in the system K₂O-FeO-Fe₂O-SiO₂-H₂O. Prog. Ann. Meet. Geol. Soc. Amer., Milwaukee, p.671.
- 87. Sanz, J. and Stone, W.E.E., 1979. NMR study of micas, II. Distribution of Fe, F, and OH in the octahedral sheet of phlogopites. American Mineralogist, v.64, p.119-126.
- 88. Seifert, F. and Schreyer, W., 1971. Synthesis and stability of micas in the system K₂O-MgO-SiO₂₂₂-H₂O and their relations to phlogopite. Contrib. Mineral. and Petrol., v.30, p.196-215.

89. Sharp, J.E., 1978. A molybdenum mineralized breccia pipe

complex, Redwell Basin, Colorado. Economic Geology, v.73, p.369-382.

- 90. Sharp, J.E., 1979. Cave Peak, a molybdenum-mineralized breccia pipe complex in Culberson County, Texas. Economic Geology, v.74, p.57-65
- 91. Shpak, T.P., Kolosov, I.V., and Senyavin, M.M., 1976. An ion-exchange study of hydroxo-complexes of molybdenum (VI) in aqueous solutions: Russian Journal Inorganic Chemistry, v. 21, p. 1823-1826.
- 92. Smith, R.W. and Norman, D.I., 1981. Gas analyses of fluid inclusions from Questa, N.M. Molybdenite deposits. Geological Society of America, Abstracts with Programs, v. 13, p. 557.
- 93. Smith, R.W., Norman, D.I., and Popp, C.J., 1980. Calculated solubility of molybdenite in hydrothermal solutions. Geological Society of America, Abstracts with Programs, v. 12, p.
- 94. Soregaroli, A.E., and Sutherland Brown, A., 1976. Characteristics of Canadian Cordilleran molybdenum deposits: in Sutherland Brown, A., ed., Porphyry deposits of the Canadian Cordillera, CIM Special Volume 15, p.417-431.
- 95. Sourarijan, S., and Kennedy, G.C., 1962. The system H₂O-NaCl at elevated temperatures and pressures. American Journal of Science, v.260, p.115-141.
- 96. Thompson, J.B., and Hovis, G., 1979. Entropy of mixing in sanidine. American Mineralogist, v.64, p.57-65.
- 97. Thompson, J.B., Jr., 1967. Thermodynamic properties of simple solutions, in Abelson, P.H., ed., <u>Researches in</u> Geochemistry v. 2, p. 340-361. Wiley, New York.
- 98. Urusova, M.A., 1975. Phase equilibria and thermodynamic characteristics of solutions in the system NaCl-H₂O and NaOH-H₂O at 350-550°C. Geochemistry International, no. 11, p.944-950.
- 99. Velde, B., 1978. Infrared spectra of synthetic micas in the series muscovite-MgAl celadonite. American Mineralogist, v.63, p.343-349.
- 100. Wallace, S.R., MacKenzie, W.B., Blair, R.G., and Muncaster, N.K., 1978. Geology of the Urad and Henderson molybdenite deposits, Clear Creek County, Colorado, with a section on a comparison of these deposits with those at Climax, Colorado. Economic Geology, v.73, p.325-368.
- 101. Wallace, S.R., Muncaster, N.K., Jonson, D.C., MacKenzie,

W.B., Brookstrom, A.A. and Surface, V.E., 1968. Multiple intrusion and mineralization at Climax, Colorado, in Ridge, J.D., ed., Ore Deposits of the United States, 1933-1968. Am. Inst. Mining and Metall. Petroleum Engineers, New York, p.603-640.

- 102. Wesolowski, D. and Ohmoto, H., 1981. Remobilization of molybdenum from W-Mo skarns by late meteoric fluids at King Island, Tasmania. Geological Society of America, Abstracts with Programs, v. 13, p. 578.
- 103. Westra, G. and Keith, 1981. Classification and genesis of stockwork molybdenum deposits. Economic Geology, v. 76, p. 844-873.
- 104. Westrich, H., 1974. The solubility of molybdenite in pHbuffered KCl-HCl fluids (Abst.). EOS Transaction, American Geophysical Union, v. 55, p. 1200.
- 105. Westrich, H.R. and Navrotsky, A., 1981. Some thermodynamic properties of fluorapatite, fluorpargasite, and fluorphlogopite. American Journal of Science, v. 281, p. 1091-1103.
- 106. White, W.H., Bookstrom, A.A., Kamilli, R.J., Ganster, M.W., Smith, R.P., Ranta, D.E. and Steininger, R.C., 1982. Character and origin of the Climax-type molybdenum deposits. Economic Geology, 75th Anniversary Volume, p. 270-316.
- 107. Wilkins, R.W.T., and Bird, J.R., 1980. Characterization of healed fracture surface in fluorite by etching and proton irradiation. Lithos, v.13, p.11-18.
- 108. Wilson, J.W.J., Kesler, S.E., Cloke, P.L., and Kelly, W.C., 1980. Fluid inclusion geochemistry of the Granisle and Bell porphyry copper deposits, British Columbia. Economic Geology, v.75, p.45-61.
- 109. Wolery, T.J. and Walters, L.J., 1975. Calculation of equilibrium distributions of chemical species in aqueous solutions by means of monotone sequences. Journal International Society of Mathematical Geology, v. 7, p. 99-115.
- 110. Wolery, T.J., 1979. Calculation of chemical equilibrium between aqueous solution and minerals; the EQ 3/6 software package. UCRL-52658, Lawrence Livermore Laboratory.

APPENDIX A - MEAN ELECTRON MICROPROBE ANALYSES OF HYDROTHERMAL ALKALI FELDSPARS

Sample	0DH31*32*	0DH31*32*	0DH31*32*	QDH31*32?	0DH27-30	QDH27-30	QDH27-30	H92-2
Analyses	3	2	1	1	6	2	1	3
	4 969		0.700	4 640	0.408	0 975	1 570	1 720
Nazu	1.860	1.170	. 0.730	4.610	0.428	0.8/5	1.570	18 790
		18.180	18.580		64 420	62 920	65 370	65 210
5102	12 910	45.360	14 700	19 140 .	16 080	15 450	14 480	14 170
	13.810	15.040	0.010	0.040	0.030	0.020	0.0	0.083
BaO	0.100	NA '	NA NA	NA NA	0.210	0.145	0.140	0.180
Total	100.235	99.770	100.060	109.120	99.958	99.360	100.480	100.153
	·	Struct	ural Formulae	e on the Basis	of 32 (0)			
Sf+4	11.942	11.962	11.965	11.899	11.938	11.913	11.959	11.955
A1+3	3.992	3.992	3.992	3.977	4.076	4 . 102	4.052	4.057
Tetrahedral Cation	s 15.934	15.954	15.957	15.876	16.014	16.015	16.011	16.012
Ca+'	0.003	0.004	0.002	0.008	0.032	0.046	0.566	0.029
Na ⁺¹	0.670	0.422	0.294	1.663	0.144	0.278	3.387	0.623
K+ '	3.305	3.563	3.693	2.298	3.788	3.627	0.050	3.326
Ba+ '	0.006	0.0	0.0	0.0	0.041	0.053	0.0	0.025
EAlkali Cations	3.984	3.989	3.989	3.969	4.005	4.004	4.003	4.003
			Component	Mole Fraction	S			
Orthoclase	0.826	0.891	0.923	0.574	0.947	0.907	0.847	0.832
Albite	0.168	0.105	0.073	0.416	0.036	0.070	0.142	0.156
Anorthite	0.001	0.001	0.001	0.002	0.008	0.011	0.0	0.007
Celsian	0.001	0.0	0.0	0.0	0.010	0.013	0.012	0.006
Total	0.996	0.997	0.997	0.994	1.001	1.001	1.001	1.001

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'No Analysis 'Analyst: M.S. Bloom

Sample	H92-2	H92-2	H92-2	H92-2	H70-536	H70-536	H70-536	H70-536
Analyses	.6	1	1	1	6	2	1	1
Nato	1 380	2.110	1.090	0.640	1.500	2.040	0.210	1.160
	18 830	18 670	18,960	18,590	18.760	18,940	18.670	18.860
510,	65.420	65.110	64.830	64.750	65.110	65.210	64.750	64.220
K+0	14.690	13.620	14.730	15.550	14.360	13.680	16.150	14.890
CaD	0.037	0.040	0.020	0.0	0.045	0.070	0.040	0.020
BaO .	0.228	0.210	0.250	0.320	0.312	0.290	0.200	0.300
Ţotal	100.585	99.760	99.880	99.850	100.087	100.230	100.020	99.450
		Struct	ural Formulae	on the Basis	of 32 (0)			
S1+4	11.960	11.967	11.933	11.966	11.955	11.940	11.957	11.924
A1+1 .	4.057	4.042	4.104	4.050	4.063	4.076	4.068	4.093
ETetrahedral Cations	16.017	16.009	16.037	16.016	16.018	16.016	16.025	16.017
Ca+ '	0.022	0.016	0.040	0.259	0.023	0.032	0.027	0.035
Na ⁺¹	0.507	0.760	0.421	3.698	0.557	0.731	0.106	0.405
K+1	3.445	3.202	3.493	0.046	3.388	3.201	3.839	3.511
Ba ⁺ ²	0.031	0.024	0.055	0.0	0.036	0.040	0.034	0.053
∑Alkali Cations	4.005	4.002	4.009	4.003	4.004	4.004	4.006	4.004
			Component I	Mole Fraction	5			
Orthoclase	0.861	0.800	0.873	0.925	O.847	0.800	0.960	0.878
Albite	0.127	0.190	0.105	0.065	0.139	0.183	0.027	C.101
Anorthite	0.005	0.004	0.010	0.0	0.006	0.008	0.007	0.009
Celsian	0.008	0.006	0.014	0.011	0.009	0.010	0.009	0.013
Total	1.001	1.000	1.002	1.001	1.001	1.001	1.003	1.001

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'Analyst: M.S. Bloom

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Sample	H83-601	H83-601	H83-601	H83-601	H79-402	H79-402	H79-402	H77-368.5
Analyses	4	2	1	1	2	3	2	8
Natu	1 420	1 130	1 910	2 530	1 560	0 800	1, 120	. 11.700
	18,900	18,720	19.890	19.060	18.210	18,100	18,210	19.400
S10:	65.200	65.130	65.480	65.800	64.690	64.940	64.550	68.320
K ₂ O	14.550	14.720	13.710	13,180	14.620	15,600	15.120	0.105
CaO	0.040	0.030	0.050	0.050	0.045	0.043	0.035	0.071
BaO	0.220	0.240	0.200	0.260	0.150	0.387	0.260	0.049
Total	100.330	99.970	101.240	100.880	99.275	99.870	99.295	99.645
		Structu	ıral Formulae	on the Basis	of 32 (0)			
Si+4	11.948	11.962	11.866	11.947	11.965	11.920	11.957	11.986
A1+3	4.074	4.067	4.187	4.064	4.012	4.018	4.018	4.009
Tetrahedral Cations	16.022	16.029	16.053	16.011	15.977	15.938	15.975	15.995
Ca+ ^z	0.030	0.024	0.085	0.026	0.009	0.008	0.007	0.010
Na†'	0.520	0.448	0.673	0.890	0.556	0.285	0.401	3.972
K+1	3.417	3.499	3.167	3.051	3.420	3.666	3.568	0.016
Ba+'	0.038	0.036	0.089	0.035	0.010	0.026	0.018	C.O
EAlkali Cations	4.005	4.007	4.014	4.002	3.995	3.985	3,994	3.998
			Component M	ole Fractions				
Orthoclase	0.854	0.875	0.792	0.763	0.855	0.917	Q.892	0.004
Albite	0.130	0.112	0.168	0.223	0.139	0.071	0.100	0.993
Anorthite	0.008	0.006	0.021	0.007	0.002	0.002	0.002	0.003
Celsian	0.010	0.009	0.022	0.009	0.002	0.006	0.004	0.0
Total	1.002	1.002	1.003	1.002	0.998	0.996	0.998	1.000
Total	1.002	1.002	1.003	1.002	0.998	0.996	0.998	1.000

'Analyst: M.S. Bloom

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Sample	H96-209.5	H96-209.5	H96-209.5	H72-2148.5	H72-2148.5	H72-2148.5	H58-980 6	H58-980 10
	<u>۲</u>							
Nato	2.040	2.180	1.500	1,740	1.670	1.750	0.465	1.180
A1,0,	18.40	18.270	18.220	18.120	18.130	18.360	18.660	18.81
510,	64.46	64.820	64,480	65.240	64.800	64.880	64.590	65.45
K,0	13.74	13.610	14.510	14.320	14.560	14.180	15.920	14.88
CaO	0.070	0.052	0.046	0.045	0.043	0.035	0.043	0.023
BaO	0.235	0.125	0.343	0.080	0.243	0.165	0.250	0.186
Total	98.945	99.057	99.099	99.545	99.446	99.370	99.928	100.53
·		Structu	iral Formulae	on the Basis	of 32 (0)			
\$ { + 4	11.971	11,966	11.947	11.948	11.947	11.991	11.952	11.965
A1+ ?	4.024	4.013	4.026	3.999	4.013	4.009	4.063	4.059
<pre> [Tetrahedral Cations] [Continue] [Cont</pre>	15.995	15.979	15.973	15.947	15.960	16.000	16.015	16.024
Ca+ '	0.011	0.010	0.009	0.008	0.008	0.002	0.025	0.022
Na ⁺¹	0.727	0.780	0.538	0.620	0.591	0.637	0.177	0.449
K+ 1	3.246	3.196	3.422	3.354	3.376	3.354	3,768	3.504
Ba+²	0.014	0.008	0.024	0.004	0.015	0.007	0.034	0.031
EAlkali Cations	3.998	3.994	3.993	3.986	3.990	4.000	4.004	4.006
			Component	Mole Fraction	s			
Orthoclase	0.812	0.799	0.856	0.839	0.844	O.839	0.942	0.876
Albite	0.182	0.195	0.135	0.155	0.148	0.159	0.044	0.112
Anorthite	0.003	0.003	0.002	0.002	0.002	0.001	0.006	0.005
Celsian	0.004	0.002	0.006	0.001	0.004	0.002	0.009	0.008
7-4-1	4 004	0.000	0.000	0.007	0.000	1 001	1 001	1 001

'Analyst: M.S. Bloom

Sample	053 ** 68 * 4	Q53 • • 68 ° •	Q57''66°°	Q57'166°°	Q59**67**	Q58 * '65 * *
Analyses	4	1	2	2	5	5
		0.005	0.544	0.784	0.944	0.559
Na 20	1.010	0.395	0.541	0.781	19 100	19 220
A1203	18.210	18.120	18.020	18.140	65 020	64 910
S 10 2	64.980	63.990	64.140	65.040	65.020 15.050	4.910
K 2 O	15.300	16.150	15.770	15.520	15.050	19.370
CaO	0.016	0.030	0.008	0.024	0.018	0.022
BaO	0.021	0.109	0.069	NA '	0.023	0.113
Total	99.537	98.794	98.548	99.505	99.155	99.203
	Struct	ural Formulae	on the Basis	of 32 (0)		
C 1 + 4	11 976	11 992	11 976	11.964	11.958	11.957
S1 A1+3	3 997	4 003	4 000	3,994	3,991	4.002
	3.337	4.005	4.000	0.001		
ETetrahedral Cations	15.973	15,995	15.976	15.958	15.949	15.959
Catt	0.003	0.001	0.001	0.004	0.003	0.004
Na ⁺¹	0.364	0.139	0,199	0.285	0.349	0.217
	3 625	3 856	3,789	3.700	3.634	3.760
Ba+ ²	0.001	0.003	0.004	0.0	0.001	0.008
EAlkali Cations	3.993	3.999	3.993	3.989	3.987	3.989
		Component	Mole Fraction	IS		
Orthoclase	0.906	0.964	0.947	0.925	0.909	0.940
Albite	0.091	0.035	0.050	0.071	0.087	0.054
Anorthite	0.001	0.0	0.0	0.001	0.001	0.001
Celsian	0.0	0.001	0.001	0.0	0.0	0.002
Total	O.998	1.000	O.998	0.997	0.997	0.997

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¹No Analysis ²Analyst: M.S. Bloom

Analyses	QDH27-30 5	Q39°°57°° 6	Q39 ⁵ °57 ⁵ ° 4	Q43 ¹ °O4 ¹ ° 3	Q53**68*5 10	Q53++68*+	Q53**68**	Q53**68**
			·					
S102	42.60	41.66	42.67	39.26	41,98	41.54	43.32	41.90
TiOz	1.623	1,576 3	1.651	2.516	1.769	2.021	1.326	2.119
A1201	11.46	14.95	11.45	13,10	11.51	11.46	11.33	11 37
e0'	6.989	7 8 1 8	7 644	13 790	8 567	9 2 1 2	6 511	9 422
1n0	0.416	0 496	0 395	0 797	0 342	0 270	0.311	0.704
laO	22 28	18 13	22 02	15 46	21 20	20.270	0.237	0.234
la0	0 032	0.026	22.02	15.46	21.28	20.32	22.11	20.81
200	0.032	0.026	0.020	0.042	0.029	0.028	0.031	0.015
		0.024		NA	NA	NA	NA	NA
Na 10	0.337	0.288	0.309	0.226	0.309	0.303	0.261	0.371
120	9.939	10.21	9.865	9.857	10.03	9.876	10.02	9.873
-	7.377	NA	7.049	3.641	5.732	6.162	7.336	5.900
Subtotal	103.05	95.18	103.07	98.69	101.55	101.19	102.50	102.07
)=F	3.106	0.0	2.968	1.533	2.413	2.595	3.089	2.484
120	0.691	3.933	0.829	2.180	1.383	1.174	0.724	1,301
otal	100.64	99.11	100.93	99.34	100.52	99.77	100.14	100.89
			Structural For	mulae on the Ba	sis of 22 (0,0H	I,F)		
24+4	6 089 6 165	5 996 6 175	6 000 6 161	E 069 E 094	C 045 C 140	C 017 C 105		C 000 C 107
1+4	4 044 4 005	5.998 6.175	6.090 6.161	5.868 5.984	6.045 6.119	6.047 6.135	6.193 6.298	6.033 6.107
Totpshodpsl	1.911 1.035	2.004 1.825	1.910 1.839	2.132 2.016	1.963 1.881	1.953 1.865	1.807 1.702	1.939 1.893
retraneurai	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.008 8.000	8.000 8.000	8.000 8.000	7,972 8.000
1+=	0.030 0.120	0.545 0.787	0.026 0.110	0.187 0.338	0.0 0.096	0.023 0.130	0.112 0.240	0.0 0.061
1 * *	0.174 0.177	0.171 0.176	0.177 0.179	0.283 0.288	0.192 0.194	0.221 0.224	0.143 0.145	0.229 0.232
e**	0.835 0.846	0.941 0.969	0.912 0.923	1.724 1.758	1.032 1.044	1.121 1.138	0.778 0.792	1.135 1.149
In+*	0.050 0.051	0.060 0.062	0.048 0.048	0.101 0.103	0.042 0.042	0.033 0.034	0.031 0.032	0.036 0.036
g+'	4.748 4.807	3.890 4.006	4.685 4.740	3.445 3.513	4.568 4.624	4.410 4.474	4.712 4.792	4.467 4.522
Octahedral	5.838 6.000	5.608 6.000	5.849 6.000	5.739 6.000	5.833 6.000	5.809 6.000	5.776 6.000	5.867 6.000
a+*	0.005 0.005	0.004 0.004	0.003 0.003	0.007 0.007	0.004 0.005	0.004 0.004	0.005 0.005	0 002 0 002
a+2	0.0 0.0	0.001 0.001	0.0 0.0	0.0 0.0	0 0 0 0	0 0 0 0	0 0 0 0	0 0 0 0 0
la+'	0.063 0.064	0.054.0.056	0.058.0.058	0 044 0 045	0.058.0.059	0.058 0.058	0.049 0.050	0.0 0.0
+ 1 .	1.812 1.835	1 875 1 931	1 796 1 817	1 879 1 917	1 842 1 865	1 834 1 861	1 827 1 858	1 912 1 926
Interlayer	1.880 1.904	1.934 1.992	1.857 1.878	1.930 1.968	1.905 1.928	1.896 1.924	1.881 1.913	1.885 1.909
- 1	3.303 3.376	0.0 0.0	3 164 3 219	1 698 1 755	2 593 2 642	2 793 2 878	3 269 3 373	2 677 2 720
H- I	0.697 0.624	4.000 4.000.	0.836 0.781	2.302 2.245	1.407 1.358	1.207 1.122	0.731 0.627	1.323 1.280
				•••				
			Com	ponent Mole Fra	ctions			
nnite	0.038		0.045	0.209	0.089	0.097	0.016	0.098
hlogopite	0.010		0.039	0.041	0.146	0.061	0.029	0.119
-Phlogopite	0.706		0.663	0.308	0.544	0.590	0.682	0,555
astonite	0.111		0.113	0.306	0.104	0.124	0.120	0.102
-Minnesotalte	e 0.199	•	0.123	0.109	0.099	0.109	0.140	0.106
0+a1	0.984		0 983	0 973	0 982	0 981	0 987	0 990

APPENDIX B - MEAN ELECTRON MICROPROBE ANALYSES OF HYDROTHERMAL TRIOCTAHEDRAL MICAS

Sample	054 7819	054 1 78 1 9 1	054178101	055146711	0551 6711	0055146710	056796894	0567 9
Analyses	3	4	3	6	4	5	5	5
							<u></u>	un-un-uu · — — —
S10:	42.91	43.07	43.61	43.65	43.91	43.34	43.43	43.65
•T10:	1.154	1.198	1.007	1.291	1.215	1.374	1.353	1.461
A1:01	10.87	10.87	10.60	10.55	10.44	10.30	10.67	10.29
FeO ⁺	8.535	8.496	7.809	8.202	7.510	7.048	7.903	7.760
MnO	0.325	0.341	0.348	0.352	0.319	0.289	0.336	0.302
MgÚ	21.56	21.78	21.96	21.74	22.06	22.12	22.16	21.85
CaO	0.037	0.021	0.057	0.016	0.021	0.021	0.020	0.015
Ba0	NA Z	NA	NA	NA	NA	NA	NA	NA
Na 20	0.215	0.224	0.250	0.320	0.328	0.326	0.278	0.308
K:0	10.07	10.13	9.659	9.627	9.678	9.966	9.671	10.04
F	6.001	6.036	6.865	7.055	7.214	7.832	7.099	6.437
Subtotal	101.68	102.17	102.16	102.80	102.69	102.62	102.92	102.11
0=F	2.527	2.541	2.891	2.971	3.037	3.298	2.989	2.710
H±0	1.271	1.262	0.914	0.828	0.770	0.491	0.811	1.097
Total	100.42	100.89	100.19	100.66	100.43	99.81	100.74	100.50
			Structural For	mulae on the Ba	asis of 22 (0,0)	ł.F)		
C : + 4	C 170 C 040	C 467 C 000	C 053 C 030	C 040 C 005	C 07E C 0CC	C 040 C 045	C 000 C 074	C 054 C 050
31**	6.1/3 6.248	6.167 6.239	6,253 6.332	6.243 6.325	6.2/5 6.366	6.246 6.345	6.202 6.2/1	6.251 6.353
Al ¹	1.82/ 1./52	1.833 1.761	1.747 1.668	1./5/ 1.6/5	1.725 1.634	1.758 1.655	1,805 1.729	1.745 1.647
Lietraneurai	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.004 8.000	8.007 8.000	7.996 8.000
Al+6	0.025 0.114	0.010 0.095	0.054 0.146	0.030 0.126	0.042 0.150	0.0 0.122	0.0 0.087	0.0 0.118
Ti**	0.125 0.126	0.129 0.131	0.109 0.110	0.139 0.141	0.131 0.132	0.149 0.151	0.145 0.147	0.157 0.160
Fe+7	1.027 1.039	1.017 1.029	0.936 0.948	0.981 0.994	0.898 0.911	0.849 0.863	0.944 0.954	0.929 0.944
Mn+ł	0.040 0.040	0.041 0.042	0.042 0.043	0.043 0.043	0.039 0.039	0.035 0.036	0.041 0.041	0.037 0.037
Mg+1	4.624 4.680	4.649 4.703	4.694 4.753	4.635 4.696	4.700 4.768	4.752 4.828	4.718 4.770	4.665 4.741
[Octahedral	5.840 6.000	5.847 6.000	5.836 6.000	5.828 6.000	5.808 6.000	5.786 6.000	5.847 6.000	5.788 6.000
Ca+2	0.006 0.006	0.003 0.003	0.009 0.009	0.002 0.002	0.003 0.003	0.003 0.003	0.003 0.003	0.002 0.002
Ba+ '	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
Na+I	0.040 0.041	0.042 0.042	0.047 0.047	0.060 0.061	0.061 0.062	0.061 0.062	0.052 0.052	0.058 0.059
K+1	1.848 1.871	1.850 1.872	1.767 1.789	1.756 1.779	1.764 1.790	1.832 1.861	1.762 1.781	1.834 1.864
[Interlayer	1.894 1.917	1.895 1.918	1.822 1.845	1.819 1.842	1.829 1.855	1.897 1.927	1.817 1.837	1.894 1.925
F-1	2.708 2.764	2.724 2.765	3.073 3.152	3,163 3,233	3.223 3.308	3.500 3.626	3.181 3.242	2.890 2.963
0H- I	1.292 1.236	1.276 1.235	0.927 0.848	0,837 0.767	0.777 0.692	0.500 0.374	0.819 0.758	1.110 1.037
			Com	ponent Mole Fra	ictions			
Annite	0.079	0.080	0.021	0.026	0.011	0.35	0.029	0.049
Phlogopite	0.179	0.184	0.125	0,100	0,105	0.035	0.098	0.190
F-Phlogopite	0.565	0.570	0.618	0.633	0.647	0.754	0,650	0,590
Eastonite	0.054	0.046	0.071	0.070	0.064	0.031	0.065	0.026
F-Minnesotaite	9 0.111	0.107	0.155	0.157	0.161	0.130	0.144	0.131
Total	O.988	0.987	0.990	0.986	0.988	0.985	0.986	0.986
17-4-1								

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¹Total Iron as FeO ²No Analysis ³Analyst: M.S. Bloom

Sample	Q57316600	Q57 ' 166 ° °	057376781	Q57'°65'*	0 58076955	058076955	058976051	05942650
Analyses	6	4	5	10	8	2	458- 69- C	02802@ 5
			······					
\$10:	43.89	44.23	43.13	41.70	41 85	42 58	13 17	42 22
TiOz	0.904	1.159	1.860	1.978	1 907	1 758	1 225	43.22
A1201	10.29	10.78	10.45	11.84	11 68	11 16	11.200	1.307
FeO'	5.664	6.694	8,733	8 448	9 249	9 254	7 172	10.99
MnO	0.261	0.244	0 287	0 277	0 363	0.334	7.173	8.205
Mg0	22:70	22 33	21 36	21.02	0.303	0.320	0.323	0.281
CaO	0.013	0.036	21,30	21.02	20.76	21.18	22.39	21.64
3a0	NA Z	0.000	0.023	0.039	0.030	0.020	0.053	0.032
Na , D	0,290	0 293		NA	NA	NA	NA	NA
() ()	10 24	0.203	0.204	0.221	0.229	0.248	0.262	0.240
F	7 165	10.18	9.815	10.25	9.795	9.829	9.810	9.550
	7.105	6.744	5.740	4.550	5.273	5.880	7.101	7.146
Subtotal	101.42	102.68	101.60	100.32	101.13	101.33	102.82	102 69
J=F	3.017	2.840	2.417	1.916	2.220	2.476	2 990	3 009
420	0.803	0.990	1.392	1.904	1.581	1 328	0,822	0.700
lotal	99.20	100.83	100.58	100.31	100,50	100.18	100.65	100.47
			Structural For	mulae on the Ba	sis of 22 (0,0H	I,F)		
51+4	6 317 6 434	6 275 C 200	C 400 C 074	0.000.0.007				
1 3 + 4	1 692 1 566	0.275 0.390	6.188 6.274	6.009 6.095	6.032 6.101	6.130 6.217	6.195 6.273	6.190 6.265
Tetrahednal	P 000 P 000	1.725 1.610	1.776 1.726	1.991 1.905	1.968 1.899	1.870 1.783	1.805 1.727	1.810 1.735
, retraneurar	8.000 8.000	8,000 8,000	7.964 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8,000 8,000	8.000 8.000
1 * *	0.071 0.212	0.086 0.226	0.0 0.066	0.030 0.135	0.026 0.107	0.033 0.137	0.051 0.144	0.055 0 143
1**	0.098 0.100	0.124 0.126	0.201 0.204	0.214 0.217	0.207 0.209	0.190 0.193	0.132 0.134	0 149 0 151
e+ 2	0.682 0.694	0.794 0.809	1.048 1.062	1.018 1.033	1.115 1.127	1 006 1 020	0 855 0 866	0.140 0.101
In+2	0.032 0.032	0.029 0.030	0.035 0.035	0.034 0.034	0 044 0 045	0.039.0.040	0.039 0.000	0.303 0.335
1g+2	4.870 4.961	4.723 4.810	4.569 4.632	4.516 4 580	4 461 4 511	4 546 4 610	4 757 4 947	0.034 0.035
Octahedral	5.752 6.000	5.756 6.000	5.852 6.000	5.812 6.000	5.853 6.000	5.814 6.000	5.834 6.000	5.842 6.000
a+ 2	0.002 0.002	0.005.0.006	0 004 0 004	0.005.0.005	0.005 0.005	0.000.0.000		
a+1	0.0 0.0		0.004 0.004	0.008 0.008	0.005 0.005	0.003 0.003	0.008 0.008	0.005 0.005
la + 1	0.055 0.056	0.052.0.053	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
+ 1	1 880 1 915	1 942 1 976		0.042 0.042	0.043 0.044	0.047 0.047	0.049 0.049	0.045 0.045
Interlaver	1 936 1 973	1 900 1 925	1.790 1.021	1.884 1.911	1.801 1.321	1.805 1.831	1.783 1.806	1.745 1.766
and a rayer	1.550 1.575	1.500 1.535	1.838 1.864	1.932 1.960	1.849 1.870	1.855 1.881	1.840 1.863	1.795 1.816
-1	3.184 3.322	3.008 3.082	2.589 2.641	2.062 2.103	2.390 2.431	2.649 2.715	3,173 3,241	3,203 3 276
H- 1	0.816 0.678	0.992 0.918	1.411 1.359	1.938 1.897	1,610 1.569	1.351 1.285	0.827 0.759	0.797 0.724
			Com	ponent Mole Fra	ctions			
nnite	0.014	0.019	0.000	0.400				• •
hlogopite	0.144	0.019	0.062	0.103	0.085	0.058	0.019	0.025
-Phlogonite	0.141	0.151	0.234	0.248	0.169	0.159	0.086	0.052
astonita	0.000	0.608	0.510	0.423	0.476	0.530	0.651	0.645
-Minnogate (*	0.026	0.068	0.044	0.122	0.136	0.105	0.089	0.107
-minnesotait	e 0.131	0.142	0.132	0.086	0.115	0.130	0.142	0.156
otal	0.992	O.988	0.982	0.982	0.981	0 982	0 987	0 985

'Analyst: M.S. Bloom

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Sample	Q58 * * 65 * *	Q594*68*°	Q59**68*°	Q59**68**	Q60°'65°'	Q62 ° ° 64 * *	Q62°°64°°	Q68, 68,
Analyses	10	6	4	4	10	3	7	6
Si0.	42.80	41.69	42.50	42.58	42.74	39.89	40.76	39.73
T10z	1.414	1.738	1,652	1.538	1.426	2.374	2.310	2.161
A1:03	10.81	11.76	10.72	10.96	10.90	13.47	12.74	13.84
FeO'	7.538	9.696	8.101	7.584	7.479	10.170	8.458	7.464
MnO	0.287	0.474	0.343	0.350	0.251	0.229	0.292	0.152
MgO	22:32	20.40	21.29	21.38	22.51	19.60	21.20	20.73
Ca0	0.044	0.032	0.020	0.029	0.051	0.038	0.020	0.029
Ba0	NA ^z	. NA	NA	NA	NA	NA	NA	NA
Na:0	0.220	0.279	0.282	0.259	0.246	0.240	0.221	0.238
K20	10.00	10.04	10.26	10.32	9.935	9.892	9.876	10.17
F	6.778	6.592	6.020	6.868	7.135	4.435	4.338	5.078
Subtota1	102.21	110.70	101.19	101.87	102.67	100.34	100.21	99.59
0=F .	2.854	2.776	2.535	2.892	3.004	1.867	1.827	2.138
H20	0.943	0.963	1.253	0.890	0.790	1.925	2.002	1.660
Total	100.30	100.89	99.91	99.87	100.46	100.40	100.39	99.11
			Structural For	mulae on the Ba	isis of 22 (0,0⊦	1,F)		
51+4	6.145 6.214	5.700 6.094	6.152 6.251	6.157 6.264	6.127 6.189	5.789 5.850	5.864 5.917	5.784 5.859
A1+4	1.838 1.786	1,905 1,906	1.838 1.749	1.843 1.736	1.851 1.811	2,211 2.150	2.136 2.083	2.216 2.141
<pre>ETetrahedra1</pre>	7.983 8.000	7.605 8.000	7.990 8.000	8.000 8.000	7.977 8.000	8.000 8.000	8.000 8.000	8.000 8.000
A] + 6	0.0 0.064	0.0 0.120	0.0 0.110	0.034 0.164	0.0 0.049	0.105 0.178	0.036 0.097	0.170 0.264
Ti+•	0.153 0.154	0.179 0.191	0.180 0.183	0.167 0.170	0.154 0.155	0.259 0.262	0.250 0.252	0.237 0.240
Fe+'	0.905 0.915	1.109 1.185	0.981 0.997	0.917 0.933	0.897 0.906	1,234 1.247	1.018 1.027	0.909 0.920
Mn+*	0.035 0.035	0.055 0.059	0.042 0.043	0.043 0.044	0.030 0.031	0.028 0.028	0.036 0.036	0.019 0.019
Mg+z	4.777 4.831	4.158 4.445	4.594 4.668	4.609 4.689	4.810 4.859	4.241 4.285	4.547 4.588	4.499 4.557
2Octahedral	5.870 6.000	5.501 6.000	5.797 6.000	5.770 6.000	5.891 6.000	5.867 6.000	5.886 6.000	5.833 6.000
Ca+i	0.007 0.007	1.177 1.258	0.003 0.003	0.004 0.005	0.008 0.008	0.006 0.006	0.003 0.003	0.005 0.005
Ba+*	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
Na + 1	0.041 0.042	0.050 0.053	0.053 0.054	0.049 0.050	0.046 0.047	0.046 0.046	0.042 0.042	0.045 0.046
K+1	1.832 1.852	1.751 1.872	1.894 1.925	1.904 1.937	1.817 1.835	1.831 1.850	1.813 1.829	1.889 1.913
EInterlayer	1.880 1.901	2.978 3.183	1.951 1.982	1.957 1.991	1.871 1.890	1.883 1.902	1.857 1.874	1.938 1.963
F - 1	3.043 3.112	3.070 3.047	2.718 2.800	3.090 3.195	3.200 3.268	2.026 2.057	1.965 1.992	2.293 2.368
JH₋ •	0.957 0.888	0.930 0.953	1.282 1.200	0.910 0.805	0.800 0.732	1.974 1.943	2.035 2.008	1.707 1.632
			Com	ponent Mole Fra	ctions			
Annite	0.058	0.109	0.091	0.079	0.054	0.133	O.089	0.096
Phlogopite	0.120	0.019	0.172	0.066	0.079	0.080	0.207	0.021
F-Phlogopite	0.654	O.586	0.584	0.677	0.692	0.414	0.393	0.503
Eastonite	0.046	0.128	0.040	0.063	0.052	0.267	0.200	0.289
F-Minnesotait	e 0.108	0.094	0.097	0.101	0.109	0.083	0.089	0.071
[ota]	0.986	O.936	0.984	0.986	O.986	0.977	0.979	0.980

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'No Analysis 'Analyst: M.S. Bloom

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Sample Analyses	Q74°°00°°	QDH78-67	QDH78-67	QDH78-67	H58-980	H72-2148.5	H72-2191	H77-781.5
Analyses	8	5		6	5	5	11	2
StÒz	40.00	41.18	41 93	40 59	20 70	20.02	22 <i>4</i>	
T102-	2.254	1.565	1 336	40.53	38.72	39.23	38.61	39.89
A1201	13.39	13 68	14 79	14 04	1.371	2.637	3.596	2.862
FeO'	13.470	12 860	10,600	14.24	13.62	13.85	13.84	13.12
Mn0	0.406	0 584	0 334	0 525	14.320	13.280	16.530	13.690
MgO	14.68	17 16	17 70	16 70	0.80.	0.872	0.444	0.244
CaO	0.042	0.022	0.005	10.79	15.54	16.20	13.78	16.57 '
3a0	NA 7	NA	D.095	0.018	0.062	0.014	0.065	0.023
Na 20	0 196	0 194	0 100		NA	NA	NA	NA
G0	9 563	0.154	0.199	0.200	0.080	0.149	0.094	0.112
F	4 025	5.655	9.916	9.916	9.763	9.910	9.399	9.756
	4.025	5.457	5,272	4.631	2.223	2.438	0.755	1.167
Subtotal	98.03	102.56	102.17	101.57	97.50°	98.58	97.11	97.43
J-r	1.695	2.298	2.220	1.950	0.936	1.027	0.318	0.491
120	2.020	1.457	1.593	1.818	2.816	2.752	3.468	3.335
otar	98.35	101.72	101.55	101.44	99,38	100.31	100.26	100.28
			Structural Fo	rmulae on the Ba	asis of 22 (0,0)	1,F)		
51+4	5.993 6.156	5.954 6.049	5 986 6 121	5 888 5 984	5 914 6 003	E 730 E 830	E 244 E 856	.
11+4	2.007 1.844	2.046 1.951	2 014 1 879	2 112 2 016	2 096 1 003	5.779 5.872	5.741 5.852	5.852 5.950
Tetrahedral	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	2.259 2.148 8.000 8.000	2.148 2.050 8.000 8.000
7 + 0	0.370 0.585	0.296 0.417	0.487 0.666	0.334 0.458	0 316 0 430	0 196 0 315	0 178 0 224	0 100 0 050
- i + o	0.254 0.261	0.170 0.173	0.143 0.147	0.181 0 184	0 154 0 156	0.190 0.313	0.178 0.324	0.132 0.256
e+*	1.688 1.734	1.555 1.580	1.266 1.294	1 576 1 601	1 783 1 810	1 636 1 662	0.402 0.410	0.316 0.321
In+2	0.052 0.053	0.072 0.073	0.040 0.041	0.066.0.067	0 101 0 103	0 109 0 111	2.055 2.095	1.680 1.708
fg+2	3.279 3.368	3,699 3,758	3,767 3 852	3 631 3 690	3 450 3 503		0.056 0.057	0.030 0.031
Octahedral	5.642 6.000	5.791 6.000	5.703 6.000	5.787 6.000	5.804 6.000	5.791 6.000	5.746 6.000	3.624 3.684 5.782 6.000
a+ 1	0.007 0.007	0.003 0.003	0.015 0.015	0 003 0 003	0.010.0.010	0.002.0.002	0.010.0.011	
a + 2	0.0 0.0	0.0 0.0		0.000 0.000		0.002 0.002	0.010 0.011	0.004 0.004
la+'	0.038 0.039	0.037 0.037	0.037.0.038	0.028 0.028		0.0 0.0	0.0 0.0	0.0 0.0
+ 1	1.828 1.877	1 818 1 847	1 806 1 847	1 935 1 965		0.029 0.029	0.018 0.019	0.021 0.022
Interlayer	1.873 1.924	1.858 1.888	1.857 1.899	1 875 1 906	1.854 1.882	1.862 1.892	1.783 1.817	1.826 1.856
				1.075 1.000	1.000 1.908	1.893 1.924	1.811 1.846	1.851 1.882
	1.861 1.959	2.511 2.535	2.393 2.434	2.136 2.159	1.037 1.063	1.135 1.154	0.356 0.362	0.543 0 551
H-1	2.139 2.041	1.489 1.465	1.607 1.566	1.864 1.841	2,963 2.937	2.865 2.846	3.644 3.638	3.457 3.449
			Com	ponent Mole Fra	ctions			
nnite	0.152	0.145	0.069	0 159	0.000	0 107		
hlogopite	-0.035	-0.112	-0.122	-0.076	0.200	0.197	0.236	0.190
-Phlogopite	0.294	0.475	0 410	0.070	0.102	0.160	0.263	0.376
astonite	0.396	0.335	0 450	0.331	0.129	0.1/0	0.059	0.011
-Minnesotait	e 0.172	0.140	0.179	0.131	0.349	0.346 0.101	0.395 0.131	O.285 O.111
otal	0.979	0.983	0.988	0.983	0.985	0.974	1.016	0.973
Total Iron a	s FeO							
No Analysis	Bloom							
maryat, M.J						1		

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Sample	H79-295	H83-601	H92-2	H92-728 5		H112-500	LI112-1100	
Analyses	3	5	3	102 120.0	n106-475		H113-1139	H132-314
			-					
S102	39.65	39.66	37.72	40.40	39.34	38.94	41.01	39.92
TIO	1.872	2.260	1.853	0.794	1.642	1.757	1.245	1.541
'A1203	13.68	13.33	14.72	12.86	13.22	14.74	13.87	14.18
FeD'	14.230	9.558	16.580	13.440	16.210	13.430	9.112	12.370
MnO	0.788	O.386	0.933	1.015	0.677	0.457	O.355	0.297
MgO	15.68	19.91	15.46	17.96	15.06	15.87	19.40	17.04
Ca0	0.025	0.020	0.123	0.016	0.037	0.023	0.017	0.042
BaO	NA 2	0.114	0.140	NA	NA	NA	NA	NA
Na 10	0.116	0.172	0.067	0.112	0.116	0.143	O.164	0.116
K 20	9.778	9.876	8.400	9.334	9.527	9.801	10.03	9.874
F	2.378	NA .	NA	2.466	2.727	3.146	3.748	2.242
Subtotal	98 20	95 29	96.00	98 40	00 50	00.04	00.05	07.00
0=F	1 001	0.0	0.00	1 028	90.00	98.31	98.95	97.62
H ₂ O	2 763	3 879	3 707	2 750	1, 140	1.325	1.5/8	0.944
Total	99,96	99 17	99 79	100 11	2.070	2.422	2.246	2.855
		55.17	33.75	100.11	33.30	99.40	99.62	99,53
			Stougtups] For	mulao am tha D				
			Structural For	mutae on the Ba	1515 OF 22 (U,UF	1, F)		
S1+4	5.871 5.961	5.787 5.840	5,624 5,608	5,939 5,952	5.876 5.939	5 779 5 868	5 944 6 035	5 869 5 959
A1+4	2.129 2.039	2.213 2.160	2.376 2.392	2.061 2.048	2,124 2,061	2.221 2.132	2 056 1 965	2 131 2 041
<pre>£Tetrahedral</pre>	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000
A1+*	0.270 0.385	0.091 0.154	0 224 0 187	0 179 0 185	0 215 0 291	0 371 0 495	0 226 0 444	0 000 0 450
T1+*	0.208 0.212	0.248 0.250	0 208 0 207	0.088.0.088	0.213 0.231	0.371 0.485	0.326 0.441	0.338 0.453
Fe+1	1.762 1.789	1.166 1.177	2.068 2.061	1 652 1 656	2 025 2 047	1 667 1 692	1 105 1 101	1 504 4 544
Mn''	0.099 0.100	0.048 0.048	0 118 0 117	0 126 0 127	0.086.0.087	0.057.0.059	0.044.0.044	1.521 1.544
Ma+ 2	3.461 3.514	4 331 4 371	3 437 3 427	3 936 3 945	3 353 3 389	2 511 2 565	4 102 4 250	0.037 0.038
[Octahedral	5.800 6.000	5.885 6.000	6.054 6.000	5.981 6.000	5.863 6.000	5.803 6.000	5.802 6.000	5.801 6.000
Ca+1	0 004 0 004	0 002 0 002	0 000 0 000	0 000 0 000	A A A A A A A A A A			
Ra+7		0.003 0.003	0.020 0.020	0.004 0.003	0.006 0.006	0.004 0.004	0.003 0.003	0.007 0.007
Nati	0.0 0.0	0.007 0.007	0.008 0.008	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
K+1	4 847 4 975			0.022 0.022	0.023 0.023	0.028 0.028	0.031 0.032	0.022 0.023
Fintenlayon	1.04/ 1.0/0	1.838 1.835	1.598 1.593	1.750 1.754	1.815 1.835	1.856 1.884	1.855 1.883	1.852 1.880
Linterlayer	1.873 1.902	1.881 1.898	1.639 1.634	1.774 1.778	1.844 1.864	1.887 1.916	1.888 1.917	1.881 1.909
F ~ 1	1.109 1.131	0.0 0.0	0.0 0.0	1.144 1.149	1.282 1.302	1.460 1.499	1.700 1.744	1.034 1.058
0H- I	2.891 2.869	4.000 4.000	4.000 4.000	2.856 2.851	2.718 2.698	2.540 2.501	2.300 2.256	2.966 2.942
			Com	ponent Mole Fra	ctions			
Annite	0.200			0.155	C.239	0.189	0.086	Ö. 159
Phlogopite	0.164			0.293	0.122	0.001	0,147	0.200
F-Phlogopite	0.148			0.154	0.198	0.247	0.300	0.135
Eastonite	O.348			0.259	C. 308	0.433	0.332	0.374
F-Minnesotait	e 0.120			0.127	0.115	0.113	0.124	0.118
Total	0.980			O.988	0.982	0.983	0.989	0.986
ITotal Iron a	s FeO						· · · · · · · · · · · · · · · · · · ·	

'No Analysis 'Analyst: M.S. Bloom

Sample	E64 ' º 08 * '	E66' *08 * *	F69º +08 * º	F69010820	E74110010	F74110010		
Analyses	6	6	4	10	2	E/4//06/0	E77º •07º • 10	EQM ¹
<u></u>								
5102	37.42	38.32	37.94	38.09	39.61	38.60	38 24	37 44
1102	2.071	2.312	2.080	2.059	1.888	2 040	2 056	37.44
A1203	14.24	14.29	14.36	. 14.11	13.86	14 12	14 78	2.900
FeU	15.750	15.140	15.310	14.800	11.000	13 770	14 120	15.59
MnO	0.709	0.632	0.639	0.525	0.767	0.391	0 585	16.100
MgO	14.93	15.71	15.29	15.71	18.56	16 74	15 25	0.717
CaO	0.021	0.027	0.022	0.029	0 049	0.023	13.25	15.19
BaO	NA ^z	NA	NA	NA	NA	NA	0.038	0.064
Nato	0.137	O.138	O.135	0.137	0 152	0 150		NA
K 2 O	10.35	10.31	10.44	10.50	10 36	10, 28	0.116	0.160
F	3.263	2.988	2.867	3.242	3,346	2 988	10.33	9.575
Subtotal	00 00					2.000	2.001	0.716
	90.09	99.87	99.08	99.20	99.59	99.20	98.40	98.50
0-F	1.374	1.258	1.207	1.365	1.409	1.258	1.213	0 301
Total	2.304	2.481	2.508	2.344	2.384	2.492	2.514	3 530
Total	99.82	101.09	100.38	100.18	100.57	100.44	99.70	101.73
					•			
			Structural Fo	rmulae on the Ba	asis of 22 (0,0)	1,F)		
Si++	5.644 5.707	5.670 5.737	5,666 5,738	5 690 5 764	5 777 5 844	5 709 E 77E	F 700 F 501	
A1+4	2.356 2.293	2.330 2.263	2.334 2.262	2,310,2,236	2 222 2 156	2 202 2 225	5.706 5.804	5.496 5.532
[Tetrahedra]	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	2.294 2.196	2.504 2.468
A1+*	0.187 0 267	0 174 0 258	0.207.0.200	0 400 0 004				0.000 0.000
Ti⁺♥	0 235 0 238	0.257 0.258	0.207 0.298	0.186 0.281	0.171 0.255	0.181 0.265	0.318 0.447	0.206 0.247
Fe+2	1 987 2 009	1 973 1 905	0.234 0.237	0.231 0.234	0.207 0.210	0.227 0.230	0.231 0.235	0.326 0.328
Mn+1	0.091.0.092	0.070 0.000	1.912 1.936	1.849 1.873	1.342 1.357	1.703 1.723	1.762 1.792	1.976 1.989
Ma+2	3 357 3 305	2.465 2.500	0.081 0.082	0.066 0.067	0.095 0.096	0.049 0.050	0.074 0.075	0.089 0.090
SOctabedral	5 856 6 000	5.465 3.506	3.404 3.447	3.498 3.544	4.036 4.083	3.690 3.734	3.392 3.450	3.324 3.346
-	5.856 8.000	5.849 6.000	5.838 6.000	5.831 6.000	5.851 6.000	5.850 6.000	5.777 6.000	5.922 6.000
Ca+ *	0.003 0.003	0.004 0.004	0.004 0.004	0.005 0.005	0.008 0.008	0.004.0.004	0.000.0.000	0 040 0 040
Ba**	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0		0.004 0.004	0.008 0.006	0.010 0.010
Na * '	0.027 0.027	0.027 0.027	0.026 0.027	0.027 0.027	0 029 0 029	0.028 0.028	0.0 0.0	0.0 0.0
K + 1	1.991 2.014	1.946 1.969	1.989 2.014	2.001 2.027	1 928 1 950	1 058 1 024	0.023 0.023	0.031 0.031
∑Interlayer	2.022 2.044	1.977 2.000	2.019 2.044	2.032 2.059	1.964 1.987	1.991 2.014	1.966 2.000	1.793 1.805
F-1	1 545 1 574	1 407 4 445		•			1.000 2.029	1.034 1.846
ึกษา	0 455 0 400	1.407 1.415	1.353 1.371	1.526 1.552	1.543 1.551	1.397 1.414	1.349 1.383	0.338 0.335
0.1	2.433 2.420	2.593 2.585	2.647 2.629	2.474 2.448	2.457 2.439	2.603 2.586	2.651 2.617	3.662 3.665
		,	Com	ponent Mole Fra	ctions			
Annite	0 337	0.000	0.000					•
Phlogonite	-0.049	0.288	0.309	0.303	0.183	0.262	0.258	0.257
F-Phloponite	0.046	0.288	0.015	0.005	0.139	0.080	-0.006	0.180
Fastonita	0.35/	0.029	0.299	0.348	0.316	0.302	0.267	-0.009
E-Minnonat-it	0.321	0.322	0.326	0.299	0.282	0.299	0.398	0.465
- minnesotait	e 0.021	0.041	0.029	0.024	0.059	0.038	0.062	0.077

0.978

0.979

0.981

0.979

0.988

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Total

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'Total Iron as FeO 'No Analysis 'Endako Quartz Monzonite 'Analyst: M.S. Bloom

0.978

0.977

0.978

Sample	QDH27-30	QDH27-30	QDH78-67	H70-959	H70-2011	H72-2156	H72-2156	H77-368.5
Analyses	· 6	4	9					
S102	47.98	44.75	48 92	48 06	17 00	40.37	40 50	10.10
T10:	0.193	0.282	0 400	0 258	47.50	49.33	49.58	46.40
A1203	30.79	34 54	30 99	20 27	0.322	0.196	0.118	0.410
FeO1	1 635	2 675	2 282	4 600	29.01	30.99	33.14	27.96
MnO	0.055	0.038	2.382	4.000	3.908	3.131	1.856	3.738
ΜαΟ	2 40	1.00	0.009	0.052	0.067	0.013	0.010	0.010
CaO	0.033	0.005	2.30	1.68	2.45	1.46	0.86	3.37
BaO	0.118	0.005	0.014	0.056	0.027	0.059	0.058	0.015
Na + O	0 417	0.048	NA 0 448		NA	NA	NA	NA
K+0	10 72	10,002	10,76	0.090	0.116	0.071	0.064	0.122
F	NA 7	NA	0.76	10.58	10.85	11.04	10.76	10.92
		NA	0.777	0.241	0.427	0.215	0.192	0.406
Subtotal	94.35	94.22	97.13	94.95	95.96	96.51	96.64	93 35
Q=F	0.0	0.0	0.327	0.101	0.180	0.091	0.081	0 171
H20	4.191	4.161	3.936	4.057	4.015	4,171	4 233	3 898
Total	98.54	98.38	100.74	98.90	99.79	100.59	100.79	97.07
			. · ·					
			Structural Form	nulae on the Bas	ais of 22 (0,0H,	,F)		
S1+4	6.481 6.439	6.087 6.004	6,483 6,425	6.540 6.463	6 470 6 374	6 550 6 519	6 502 6 407	C 450 C 044
A1++	1.519 1.561	1.913 1.996	1.517 1.575	1 460 1 537	1 530 1 626	1 450 1 481	1 407 1 502	0.458 6.341
[Tetrahedral	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000
A1+#	3 407 3 340	3 653 3 467	2 240 2 200	0.075 0.410				
~ · T i + 0	0.000 0.040	3.653 3.467	3.348 3.223	3.275 3.119	3.231 3.041	3.423 3.345	3.651 3.616	3.068 2.844
Fotz	0.020 0.019	0.029 0.028	0.040 0.040	0.026 0.026	0.033 0.032	0.020 0.019	0.012 0.012	0.043 0.042
re ··	0.185 0.184	0.304 0.300	0.264 0.262	0.519 0.513	0.441 0.434	0.348 0.346	0.204 0.203	0.435 0.427
	0.006 0.006	0.004 0.004	0.010 0.010	0.006 0.006	0.008 0.008	0.001 0.001	0.001 0.001	0.001 0.001
My ···	0.484 0.481	0.203 0.200	0.471 0.466	0.340 0.336	0.492 0.485	0.289 0.288	0.168 0.168	0.698 0.686
Loctaneorat	4.102 4.000	4.194 4.000	4.133 4.000	4.167 4.000	4.205 4.000	4.081 4.000	4.036 4.000	4.246 4.000
Ca+*	0.005 0.005	0.0 0.0	0.002 0.002	0.008 0.008	0.004 0.004	0.008 0.008	0.008 0.008	0 002 0 002
3a+ '	0.006 0.006	0.003 0.003	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0 0 0 0
Na+1	0.074 0.073	0.121 0.120	0.072 0.072	0.016 0.016	0.020 0.020	0.012 0.012	0.011 0.011	0.022 0.022
(+ 1	1.847 1.835	1.770 1.746	1.819 1.803	1.837 1.815	1.865 1.839	1.870 1 861	1 800 1 799	1 939 1 904
EInterlayer	1.932 1.919	1.895 1.869	1.893 1.877	1.861 1.839	1.891 1.863	1.891 1.882	1.819 1.818	1.963 1.928
F - 1			0 314 0 323	0 099 0 103	0 174 0 170	0 007 0 000	0.077.0.000	
DH- 1	4.000 4.000	4.000 4.000,	3.686 3.677	3.901 3.897	3.826 3.821	3.913 3.910	3.923 3.920	0.166 0.175
			Comp	onent Mole Frac	tions			
Muscovite	0.657	0.773	0.585	0.610	0.608	0.661	0.719	0.583
Paragonite	0.065	0.102	0.093	0.052	0.052	0.041	0.057	0.036
<-Fe Cldnt*	0.063	0.087	0.130	0.219	0.168	0.168	0,124	0 136
(-Mg Cldnt	0.208	0.023	0.150	0.098	0.138	0.118	0.098	0.203
K-Mg Cldnt	0.005	0.013	0.083	0.031	0.056	0.020	0.008	0.065
[oto]	0 998	0 999	1.041					

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APPENDIX C - MEAN ELECTRON MICROPROBE ANALYSES OF HYDROTHERMAL DIOCTAHEDRAL MICAS

'No Analysis 'Analyst: M.S. Bloom 'Celadonite

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\$ample	H77-368.5	H79-402	H79-402	H79-512	H83-180.5	H83-437	H83-601	1102-004
Analyses	- 1	2	4	6	6	2	3	4
6.40					······································	······	······································	<u> </u>
5101	47.20	46.40	47.66	48.51	49.17	46.79	47.90	48 14
1101	0.078	0.029	0.199	0.190	0.061	0.089	0.287	0 220
A1201	30.03	35.47	28.54	29.32	29.63	34 36	30.80	31 20
Fe0'	2.601	0.727	3.481	3 476	3 146	2 642	3 202	32.20
Mn0	0.028	0.029	0.034	0.034	0.024	2.042	3.303	2.795
MgO	1.51	0.08	.2 20	1 74	4 92	0.038	0.017	0.010
CaO	0.021	0.022	0.000	1.74	1.82	0.71	1.57	1.54 ,
BaO	NA 2	0.022 NA	0.023	0.057	0.051	0.118	0.015	0.040
Natio	0.076		NA	NA	NA	NA	0.073	0.055
K.O	0.078	0.171	0.116	0.072	0.050	0.241	0.063	0.075
	10.97	11.01	10.90	10.84	10.74	10.27	10.72	10.66
r	0.268	0.146	0.242	0.210	0.493	0.058	NA	NA
Subtotal	92.78	94.08	93.40	94.45	95 19	95 32	94 75	05 74
()≃F	0.113	0.061	0.102	0 088	0 209	0.024	94.73	95.74
H20	3.983	4,144	3.999	4 072	2 003	0.024	0.0	0.0
Total	96.65	98 16	97 29	9.072	3.365	4.211	4.187	4.248
		00.10	57.25	50.43	98.97	99.51	98.94	99.99
			Structural Form	nulae on the Bas	sis of 22 (0,0H,	F)		
S i + +	6.526 6.503	6.245 6.258	6.580 6.524	6 600 6 560	6 632 6 502	6 354 6 402	6 476 6 400	
A1++	1.474 1.497	1.755 1.742	1 420 1 476	1 400 1 440	1 269 1 409	0.254 0.193	6.476 6.420	6.415 6.35
Tetrahedral	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	1.524 1.580	1.585 1.64
1+•	3.444 3.380	3,900 3,896	3 247 3 128	3 335 3 333	2 205 2 074	0.004.0.554		
ſ}+¢	0.008.0.008	0.003.0.003	0.001 0.000	3.325 3.233	3.365 3.274	3.694 3.554	3.408 3.285	3.497 3.36
	0.301 0.300	0.003 0.003	0.021 0.020	0.019 0.019	0.006 0.006	0.009 0.009	0.029 0.029	0.022 0.02
un+1	0.007 0.000	0.082 0.082	0.402 0.398	0.396 0.393	0.355 0.353	0.295 0.292	0.373 0.370	0.311 0.30
···· 1 Ara + 2	0.003 0.003	0.003 0.003	0.004 0.004	0.004 0.004	0.003 0.003	0.004 0.004	0.002 0.002	0.001 0.00
ny . Cotobolas I	0.310 0.309	0.015 0.015	0.453 0.449	0.353 0.351	0.366 0.364	0.142 0.141	0.316 0.314	0.306 0.30
octanedral	4.066 4.000	4.003 4.000	4.127 4.000	4.098 4.000	4.095 4.000	4.144 4.000	4.129 4.000	4.138 4.000
a+1	0.003 0.003	0.003 0.003	0.003 0.003	0.008.0.008	0.007.0.007	0.017.0.017		
3a+z	0.0 0.0			0.008 0.008	0.007 0.007	0.017 0.017	0.002 0.002	0.006 0.00
la+1	0 014 0 014	0.030 0.030	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.004 0.004	0.003 0.003
(+)	1 075 1 020	0.030 0.030	0.021 0.021	0.013 0.013	0.009 0.009	0.042 0.042	0.011 0.011	0.013 0.013
Intonlayon	1.935 1.928	1.890 1.894	1.920 1.903	1.881 1.870	1.848 1.837	1.751 1.734	1.849 1.833	1.812 1.795
mentayer	1.952 1.945	1.924 1.928	1.944 1.927	1.903 1.891	1.864 1.853	1.810 1.792	1.866 1.850	1.834 1.817
· - 1	0.109 0.117	0.059 0.062	0.099 0.105	0.085 0.090	0.200 0.209	0.023 0.024	0.0 0.0	0.0 0.0
- m	3.891 3.883	3.941 3.938	3.901 3.895	3.915 3.910	3.800 3.791	3.977 3.976	4.000 4.000	4.000 4.000
			Comp	onent Mole Frac	tions		,	
luscovite	0.682	0.849	0.612	0 626	0 600	0.700	0.004	0.740
aragonite	0.029	0.041	0.034	0.020		0.768	0.681	0.710
-Fe Cldnt4	0.149	0.065	0.004	0.040	0.054	0.077	0.040	0.050
-Ma Cldnt	0 125	0.003	0.170	0.182	0.182	0:115	0.151	0.119
K-Mg Cldnt	0.029	0.017	0.103	0.138	0.139	0.032	0.119	0.115
		0.002	0.033	0.023	0.048	0.006	0.003	0.002
στά Ι	1.015	1.004	1.013	1.009	1.026	`0.999	0.994	0.995
Total Iron a No Analysis	s FeO	······································		······································			*/************************************	

*Celadonite

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Sample	H85-563	H92-2	H92-234	H96-209.5	H112-304	H118-178	- H110-E00	
Analyses	6	5	5	1	11112 004	11113-170	0110-283	H124-629.5
S10,	47.62	45 87	49 10	40.24	48 40	10 11		
+ T 102	0.255	0 476	43.10	49.21	40.12	49.14	48.25	48.40
A1201	29.23	29 34	20.15	0.104	0.314	0.198	0.077	0.312
FeO	3 803	4 564	30.19	20.00	29.39	28.92	30.80	28.88
MnO	0.035	4.004	3.610	3.032	3.802	2.970	3.062	3.732
Man	0.035	0.030	0.051	0.0	0.032	0.031	0.018	0.038
mg0 Ca0	2.47	3.36	1.69	2.50	2.12	2.38	1.34	3.33
Ra0	0.072	0.022	0.027	0.037	0.351	0.033	0.055	0.060
	NA	0.058	NA	NA	NA	NA	NA	NA
	0.083	0.120	0.096	0.061	0.099	0.080	0.097	0,109
K 2 U	10.79	10.43	11.00	10.88	10.98	11.07	10,62	11.01
٢	0.321	NA	0.187	1.148	0.330	0.586	0.303	0.553
Subtotal	94.67	94.27	96.09	95.71	95.59	95 41	94 62	00 40
0=F	0.135	0.0	0.079	0.483	0 160	0 247	0 129	90.42
HzO	4.012	4.116	4.151	3 698	4 019	2 042	0.128	0.233
Total	98.55	98.39	100.17	98.93	99 45	99 11	4.034	3.972
	•			00.00	00.40	55.11	98.00	100.16
			Structural Form	ulae on the Bas	is of 22 (0,0H,	F)		
Si+4	6.499 6.410	6.309 6.139	6.568 6.521	6.65% 6.606	6.515 6.462	6 636 6 593	6 531 6 492	6 509 6 307
A1**	1.501 1.590	1.691 1.861	1.432 1.479	1,344 1,394	1,485 1,538	1 364 1 407	1 469 1 508	
[[[][][][][][][][][][][][][][][][][][]	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000	8.000 8.000
A1+•	3.224 3.047	3.089 2.767	3.345 3.241	3.251 3.143	3.229 8 113	3 262 3 167	3 469 3 376	2 100 0 800
T' 1 * °	0.026 0.026	0.049 0.048	0.019 0.018	0.017 0.017	0 032 0 032	0.020.0.020		3.109 2.896
Fe+1	0.434 0.428	0.525 0.511	0.404 0.401	0.343 0.340	0 431 0 427	0.335 0.323	0.008 0.008	0.032 0.031
Mn+*	0.004 0.004	0.003 0.063	0.000 0.006		0.004 ().004	0.001 0.001	0.347 0.345	0.420 0.413
Mati	0.502 0.495	0.689 0 670	0 337 0 334	0.504 0.500	0.409 ().404	0.004 0.004	0.002 0.002	0.004 0.004
EOctahedral	4.190 4.000	4.355 4.000	4.110 4.000	4.115 4.000	4.123 4.000	4.100 4.000	4.096 4.000	0.668 0.656
Ca+ '	0.011 0.010	0.003 0.003	0.004.0.004	0.005.0.005	0.051.0.051	0.005 0.005		
Ba+'	0.0 0.0	0.003.0.003	0.004 0.004	0.003 0.003	0.051 0.051	0.005 0.005	0.008 0.008	0.009 0.008
Na+1	0.015 0.015	0 022 0 021	0.017 0.017	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0	0.0 0.0
K+1	1.879 1.853	1.830 1.781	1 877 1 864	3 977 4 963		0.014 0.014	0.017 0.017	0.019 0.019
EInterlayer	1 904 1 878	1 858 1 808	1 000 1 004	1.077 1.083	1.896 1.881	1.907 1.895	1.834 1.823	1.889 1.856
Linter rayer	1.00, 1.070	1.636 1.608	1.090 1.084	1.893 1.879	1.965 1.949	1.926 1.914	1.859 1.848	1.916 1.884
F-1	0.131 0.137	0.0 0.0	0.076 0.079	0.465 Ũ.487	0,155 0,161	0 238 0 249	0 122 0 129	0 226 0 224
OH- 1	3.869 3.863	4.000 4.000	3.924 3.921	3.535 3.513	3.845 3.839	3.762 3.751	3.877 3.871	3.774 3.769
			Comp	onent Mole Frac	tions			
Muscovite	0.611	0 622	0 637	0.499	0.640	A == -		• .
Paragonite	0.044	0 049	0.037	0.488	0.612	0.581	0.659	0.562
K-Fe Cldnt4	0 164	0.070	0.041	0.032	0.041	0.045	0.055	0.050
K-Ma Cldnt	0 153	0.122	0.102	0.137	0.183	0.167	0.169	0.147
F K-Ma Clast	0.133	0.170	0.127	0.218	0.134	0.176	0.102	0.197
	0.040	0.028	0.021	0.120	0.047	0.063	0.029	0.074
Total	1.017	0.997	1.008	0.994	1.018	1.032	1.014	1.031

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⁴No Analysis ³Analyst: M.S. Bloom ⁴Celadonite

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APPENDIX D - MEAN ELECTRON MICROPROBE ANALYSES OF HYDROTHERMAL AMPHIBOLES FROM HUDSON BAY MOUNTAIN

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Sample	H58-980-1	H58-980-2	H58-980-3	458-080-A
Analyses	10	5	8	2
\$102	50.44	49.71	50.41	50.97
T t O z	0.253	0.270	0.199	0.265
A1203	3.90	3.64	3.89	3 95
Fe0'	12.97	12.89	12.81	12 97
MnO	1.361	1.322	1 349	1 443
MgO	15.09	15.00	15 22	1.440
CaO	11.71	11.57	11 30	11 72
Na 20	1.027	0 817	1,006	0 975
K10	0.478	0 484	0.420	0.875
F	0.877	0.886	0.698	0.463
Subtotal	88.10			
O=F	98.10	90.09	97.30	98.39
H-0	0.369	0.373	0.294	0.257
Total	3.310	3.255	3.374	3.450
	101.04	99.47	100.38	101.59
	Structu	ral Formulae on the Basis of 48	8 (0,0H,F)	
S1+4	15.50 14.80	15 52 14 79	15 55 14 90	
A1++	0 497 1 203	0 492 4 244	15.55 14.86	15.55 14.85
[Tetrahedra]	16 00 16 00	0.482 1.214	0.446 1.144	0.453 1.155
	18:00 18:00	16.00 16.00	16.00 16.00	16.00 16.00
A1+*	0.922 0.144	0.864 0.062	0.975 0.207	0.974 0 201
Τί+ *	0.058 0.056	0.063 0.060	0.046 0.044	0.061.0.058
Fe+ '	3.33 3.18	3.37 3.21	3 31 3 16	3 31 3 16
Mg + *	6.914 6.599	6.981 6.651	7 001 6 687	6 975 6 565
Mn+2	0.211 0.019	0 219 0 020	0.088.0.0	0.075 0.585
M2 Cations	11.44 10.00	11.49 10.00	11.42 10.10	11.42 10.00
Ca+1	3.856 3.681	3 870 3 687	3 736 3 569	0 004 0 004
Mn+*	0.144 0.319	0 130 0 313	0.264.0.337	3.834 3.661
M4 Cations	4.000 4.000	4.000 4.000	4.000 3.905	4.000 4.000
Na ⁺¹	0.412 0.394	0 333 0 317	0 106 0 387	0.040.0.000
K+1	0 187 0 179	0.193.0.194	0.406 0.387	0.349 0.333
A Cations	0 600 0 572	0.133 0.184	0.165 0.158	0.180 0.172
	0.000 0.372	0.526 0.501	0.571 0.545	0.529 0.505
F - 1	0.812 0.814	0.820 0.833	0.644 0.651	0 564 0 562
OH- 1	3.188 3.186	3.180 3.167	3.356 3.349	3.436 3.438
		Component Mole Fractions		
Tremolite	0.295	0.324	0.300	0.305
(Na,K) Edenite	0.370	0.343	0.373	0.362
Ferroedenite	0.338	0.336	O.335	0.341
Total	1.003	1.003	1.008	1 008

'Total Iron as FeO 'Analyst: M.S. Bloom

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APPENDIX E - MEAN ELECTRON MICROPROBE ANALYSES FOR SCHEELITE-POWELLITE FROM HUDSON BAY MOUNTAIN

Sample	H92-21	H92-2'	H127-141*	H127-141'	H126-127.5+	H126-127.5*	H126-127.5'	H120-156.5 ² 4	
	••	<u>د</u>		.				<u></u>	
MoOs	19 745	5 175	7.073	0.140	7.076	2.514	0.483	10.592	
PhO	0 020	0.0	0.017	0.0	0.010	0.058	0.020	0.025	
CaO	19.710	18.370	18,693	17.705	18.678	18.216	17.366	16.422	
WO 1	61, 192	75.610	73.493	81,470	74.412	78.992	81.677	70.830	
Total	100.667	99.155	99.276	99.315	100.176	99.780	99.546	97.869	
		S	tructural Form	lae on the B	asis of 16 (0)			
Ca+1	0.974	0 985	0 989	0.979	0.983	0.985	0.965	0.912	
04 Ph+1	0.013	0.007	0.006	0.000	0.008	0.008	0.000	0.044	
r 55 W + 4	0 662	0.903	0.870	0.997	0.870	0.953	0.991	0.804	
т Мо† [€]	0.325	0.089	0.125	0.011	0.121	0.040	0.018	0.153	
			Compone	ent Mole Frac	tions				
				0.007		0.045	0.073	0 760	
Scheelite	0.649	0.896	0.864	0.987	0.862	0.945	0.973	0.153	
Powellite	0.325	0.089	0.125	0.000	0.121	0.040	0.000	0.044	
Stolzite	0.013	0.007	0.006	0.011	0.008	0.008	0.016	0.044	
Total	0.987	0.992	O.995	O.998	0.991	0.993	0.991	0.957	
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fanalyst: M.S. @Bloom

1.273 D.057 17.843 80.790 99.963	0.117 0.010 17.870 81.953 99.950	20.005 0.0 19.965 60.330 100.300	0.315 0.015 17.820 81.305 99.455	5.760 0.010 18.165 75.590 99.525	6.080 0.025 18.375 74.835 99.315	25.360 0.100 20.720 53.680 99.860	
1.273 0.057 17.843 80.790 99.963	0.117 0.010 17.870 81.953 99.950	20.005 0.0 19.965 60.330 100.300	0.315 0.015 17.820 81.305 99.455	5.760 0.010 18.165 75.590 99.525	6.080 0.025 18.375 74.835 99.315	25.360 0.100 20.720 53.680 99.860	
0.057 17.843 30.790 99.963	0.010 17.870 81.953 99.950	0.0 19.965 60.330 100.300	0.015 17.820 81.305 99.455	0.010 18.165 75.590 99.525	0.025 18.375 74.835 99.315	0.100 20.720 53.680 99.860	
9.037 17.843 30.790 99.963	17.870 81.953 99.950	19.965 60.330 100.300	17.820 81.305 99.455	18.165 75.590 99.525	18.375 74.835 99.315	20.720 53.680 99.860	
30.790 99.963	81.953 99.950	60.330 100.300	81.305 99.455	75.590 99.525	74.835 99.315	53.680 99.860	
99,963	99.950	100.300	99.455	99.525	99.315	99.860	
39.963	99.950	100.300	55.455	00.020			
	St	ructural Form	ulae on the B	asis of 16 (0))		
		0.000	0.001	0 975	0.982	0.992	
0.976	0.981	0.983	0.981	0.373	0.002	0.005	
0.013	0.000	0.009	0.000	0.013	0.000	0.576	
0.976	0.998	0.658	0.994	0.893	0.007	0.421	
0.012	0.010	0.334	0.010	0.094	0.104	0.421	
		Compon	ent Mole Frac	tions			
0 963	0 988	0.649	0.984	0.880	0.878	0.571	
0.000	0.000	0.334	0.000	0.094	0.104	0.421	
0.012	0.000	0.009	0.010	0.013	0.009	0.005	
0.013	0.010	0.000					
0.988	0.998	0.992	0.994	0.987	0.991	0.997	
).976).013).976).012).963).012).013).988	St 0.976 0.981 0.013 0.000 0.976 0.998 0.012 0.010 0.963 0.988 0.012 0.000 0.013 0.010 0.988 0.998	Structural Form 0.976 0.981 0.983 0.013 0.000 0.009 0.976 0.998 0.658 0.012 0.010 0.334 Compon 0.963 0.988 0.649 0.013 0.010 0.334 0.988 0.649 0.029 0.988 0.998 0.992	Structural Formulae on the B 0.976 0.981 0.983 0.981 0.013 0.000 0.009 0.000 0.976 0.998 0.658 0.994 0.012 0.010 0.334 0.010 Component Mole Fract 0.963 0.988 0.649 0.984 0.012 0.000 0.334 0.000 0.013 0.010 0.009 0.010 0.988 0.992 0.994	Structural Formulae on the Basis of 16 (0 0.976 0.981 0.983 0.981 0.975 0.013 0.000 0.009 0.000 0.013 0.976 0.998 0.658 0.994 0.893 0.012 0.010 0.334 0.010 0.094 Component Mole Fractions 0.963 0.988 0.649 0.984 0.880 0.012 0.000 0.334 0.000 0.094 0.963 0.988 0.649 0.984 0.880 0.012 0.000 0.334 0.000 0.094 0.013 0.010 0.009 0.010 0.094 0.988 0.992 0.994 0.987	Structural Formulae on the Basis of 16 (0) 0.976 0.981 0.983 0.981 0.975 0.982 0.013 0.000 0.009 0.000 0.013 0.009 0.976 0.998 0.658 0.994 0.893 0.887 0.012 0.010 0.334 0.010 0.094 0.104 Component Mole Fractions 0.963 0.988 0.649 0.984 0.880 0.878 0.012 0.000 0.334 0.000 0.094 0.104 Component Mole Fractions 0.963 0.988 0.649 0.984 0.880 0.878 0.012 0.000 0.334 0.000 0.094 0.104 0.013 0.010 0.009 0.010 0.009 0.013 0.009 0.988 0.998 0.992 0.994 0.987 0.991	Structural Formulae on the Basis of 16 (0) 0.976 0.981 0.983 0.981 0.975 0.982 0.992 0.013 0.000 0.009 0.000 0.013 0.009 0.005 0.976 0.998 0.658 0.994 0.893 0.887 0.576 0.012 0.010 0.334 0.010 0.094 0.104 0.421 Component Mole Fractions 0.963 0.988 0.649 0.984 0.880 0.878 0.571 0.012 0.000 0.334 0.000 0.094 0.104 0.421 Component Mole Fractions 0.963 0.988 0.649 0.984 0.880 0.878 0.571 0.012 0.000 0.334 0.000 0.094 0.104 0.421 0.013 0.010 0.009 0.013 0.009 0.005 0.988 0.998 0.992 0.994 0.987 0.991 0.997

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¹core ¹intermediate

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