Early Fracture-Controlled Disseminated Mineralization
at Butte, Montana

GEORGE H. BRIMHALL, JR.

Abstract

Solution transport through intensely fractured quartz monzonite wall rock resulted in the formation of a large-tonnage, low-grade mineralized zone in the Butte district before the formation of the much larger and more continuous high-grade vein structures that have been mined for almost a century. The early, pre-Main Stage, copper mineralization is directly related to the presence of small, alkali feldspar-stable, discontinuous veinlets and alteration halos which carry important amounts of disseminated chalcopyrite. Molybdenite occurs mainly in quartz or quartz and alkali feldspar veins. A general sequence of alteration assemblages, based on cross-cutting relationships, shows a systematic trend of decreasing mineralogic complexity toward the younger pre-Main Stage assemblages. Microscopic fabric studies show that alteration minerals around early veinlets are arranged in zones parallel to veinlet walls. The alteration mineralogy in the bands is very simple near veinlets and increases in mineralogic complexity away from the veins. Partial replacement textures in the alteration zones show that at least some of the discontinuities in mineral assemblages represent reaction fronts. Compositions of hydrothermal alkali feldspars and adjacent muscovites, determined with the electron microprobe, are generally constant within individual specimens, but vary considerably from sample to sample. A model is developed in this study of the partitioning of alkalies between muscovite and alkali feldspar at quartz saturation which implies temperatures in the range of 600° to 700° C for early alteration and mineralization. Phase equilibria applied to the early mineral assemblages in Butte are consistent with this temperature range and imply conditions near the triple point andalusite-alkali feldspar-muscovite in the presence of quartz. A genetic relationship between quartz porphyry intrusives and the earliest high temperature hydrothermal features seems reasonable, as these intrusives provide a possible solution source and fracture mechanism for mass transport of the important base metals into the densely fractured equigranular quartz monzonite country rock.

Introduction

The Butte mining district is located in the Rocky Mountains in southwest Montana. The regional setting lithology, mineralization, structure, stable isotopes, and alteration have been discussed in the literature (Weed, 1912; Sales, 1914; Hart et al., 1935; Sales and Meyer, 1948, 1951, 1956; Meyer, 1965; Garlick and Epstein, 1966; Sheppard and Taylor, 1974; Taylor, 1974). The existence of large-tonnage low-grade copper resources at Butte has long been recognized by Anaconda Company geologists, and as early as 1953 V. D. Perry recommended exploration of the low-grade copper potential. Two distinct ages of mineralization have been recognized and termed Main Stage and pre-Main Stage (Meyer, 1965) and are summarized by Meyer et al. (1968). The purpose of this paper is to describe the nature of pre-Main Stage alteration mineral assemblages of the Butte quartz monzonite (BQM) wall rock and to relate occurrence of the assemblages to a large-tonnage disseminated chalcopyrite-molybdenite zone in the Butte district.

General Geology

The Butte ore deposit is in the south end of the composite boulder batholith, in which the dominant rock type is the 70- to 72-m.y.-old Butte quartz monzonite (Smedes, 1973; Klepper, 1973; Tilling, 1973). Compositionally this rock type shows no obvious modal variation throughout the Butte district, nor is there significant cryptic zoning. The Butte quartz monzonite is a moderately coarse-grained hypidiomorphic equigranular rock with laths-shaped andesine plagioclase, interstitial anhedral quartz and alkali feldspar, subhedral biotite, hornblende, and accessories. Table 1 presents the modal mineralogy of fresh Butte quartz monzonite. Associated with the Butte quartz monzonite rock type are sporadic segregations of aplite pegmatite, and mixtures of the two phases. Rare rocks grading between Butte quartz monzonite and aplite-pegmatite are referred to as quartz monzonite porphyry or grano-aplite.

Large high-grade sulfide veins that control sericitic and argillic alteration envelopes in the Butte
GEORGE H. BRIMHALL, JR.

1. Fresh Butte Quartz Monzonite

Mode

- Andesine: 37 + 4
- Quartz: 23 + 5
- Orthoclase: 22
- Biotite: 8
- Hornblende: 4
- Magnetite: Minor
- Sphene: Minor
- Apatite: Minor
- Zircon: Minor

An = 44.3 ± 1.2, Ab = 53.0 ± 1.5, Or = 2.7 ± 0.7

SiO₂

Or = 91.0 ± 0.9, Ab = 8.4 ± 0.9, An = 0.6 ± 0.3

Fe/(Fe²⁺ + Mg) = 4.50 ± 0.5, TiO₂ = 3.5 ± 1 wt percent

(Na, K)₀Ca²⁺(Mg, Fe²⁺, Fe³⁺, Al)(Si₆₋₇Al₂₂O₅₂)(OH, F)₀.

Fe:O₄

Ca Ti (SiO₄)(O, OH, F)

Ca (PO₄) (OH, F, Cl)

ZrSiO₄

Andesine cores sometimes have oligoclase rims (An29, Ab68, Or3).

K-feldspars commonly are locally microperthitic.

Total Fe as FeO; oxides recalculated to mineral formula.

Quartz monzonite wall rock have been mined to great depths in the underground working at Butte. Mining of these veins in an area roughly three miles north-south, five miles east-west, and locally a mile deep has been largely restricted to throughgoing vein structures of immense size.

Sometimes these 57.4 m.y.-old veins (Meyer et al., 1968) are so far apart that the alteration halos do not overlap, and fresh or weakly argillized Butte quartz monzonite wall rock remains between them.

In these areas generally small discontinuous veinlets with narrow alteration envelopes of alkali feldspar, quartz, muscovite, anhydrite, andalusite, biotite, corundum, pyrite, chalcopyrite, and magnetite occur.

Several types of pre-Main Stage assemblages have been identified by different proportions of alteration minerals. One vein type recognized by Meyer (1963) is characterized by a potassium silicate assemblage termed "early dark micaceous" (EDM) which sometimes contains secondary biotite. This fine-grained biotite has been dated at 62.8 million years, five million years older than Main Stage activity (Meyer et al., 1968). Another significant time interval is an eight million year gap between the Butte quartz monzonite country rock and the alkali feldspar-stalinite pre-Main Stage events.

Figure 1 is a generalized map of the Butte district showing the area studied in this paper. Detailed mapping has shown that in general pre-Main Stage vein structures are present inside an elongate domical structure, shown in Figure 1 by mine level contours which close slightly above the 2,800 level. The dome represents the outer occurrence of abundant molybdenite veinlets (Meyer et al., 1968). Veinlets containing secondary alkali feldspar, pyrite, sphalerite, and magnetite do occur, however, above the copper-molybdenum dome on the northwest wall of the Berkeley pit. These are considered to be a propylitic fringe of pre-Main Stage activity, well above the main mineralized copper molybdenum zone.

Biotitic breccias and quartz porphyry intrusives

The earliest hydrothermal pre-Main Stage features yet recognized are dark-colored biotitic breccias. The first dike of this type was recognized in 1970 on the 4,200 level of the Steward mine by Meyer. Continued detailed mapping has revealed other dikes with a similar orientation, striking east-west and having steep dips. In both the Steward mine and in the Continental area (Fig. 1), an upthrown block to the east of the Butte district, these dikes and veinlets contain fragments of Butte quartz monzonite, aplite, pegmatite, and grano-aplite or Butte quartz monzonite porphyry in a groundmass of alkali feldspar, quartz, biotite, anhydrite, pyrite, and chalcopyrite. The biotitic breccias are commonly associated with the contacts of Butte quartz monzonite and quartz porphyry intrusives and occupy the same structural position along strike at the distal ends of the porphyries. The abundance of aplite fragments at elevations with sparse aplite occurrences implies a source deeper than the developed levels of the underground mines. A considerable vertical transport of these resistant fragments is therefore implied. The earliest introduction of significant copper, probably related to the crystallization of quartz porphyry intrusives, occurs in these biotitic breccias. The magmatic association and veinlike nature of these features imply a magmatic-hydrothermal origin.

East-west striking dikes of quartz porphyry, which have a high degree of lateral and vertical continuity (Fig. 1), are commonly associated with biotitic breccias (Brimhall, 1972, 1973). The porphyry contains phenocrysts of alkali feldspar, with generally rounded quartz "eyes," and relict phenocrysts of plagioclase surrounded by a groundmass of fine-grained alkali feldspar and quartz. Averaged electron microprobe data on the alkali feldspar phases are given in Table 2, showing that the phenocryst alkali feldspars contain a substantial celsian component and are less potassic than groundmass feldspar.
Pre-Main Stage veining and alteration

All of the intrusive rock types, i.e., Butte quartz monzonite, aplite, pegmatite, grano-aplite, early biotite breccias, and quartz porphyries, are cut and altered by pre-Main Stage veins. These veinlets are usually less than 3 cm wide and control alteration SiO halos 1 to 30 cm wide. They are characterized by the presence of fine-grained secondary alkali feldspar CaO Na2O and quartz without clay minerals. The veins may contain, in addition, anhydrite, molybdenite, calcite, BaO chalcopyrite, magnetite, muscovite, chlorite, and biotite. Often these veinlets are surrounded by alteration envelopes containing several or all of the following minerals: muscovite, andalusite, quartz, alkali feldspar, corundum, biotite, anhydrite, magnetite, calcite, pyrite, and chalcopyrite. Although

TABLE 2. Averaged Electron Microprobe Data

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<th>Weight percent</th>
<th>Phenocrysts</th>
<th>Groundmass</th>
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of the Steward, Kelley, and Mr. Con mines (Fig. 1). The mineralogical composition of the early veins is easily recognized in the field. Detailed mapping of early veins in the deep levels has revealed the discontinuous nature of the early veins. Occasionally the veins occur in parallel sets generally amounts to two to ten megascopically visible veins, striking about N. 80 ø W. and dipping moderately southwest. The number of veins is variable but from diamond drilling in the Continental area east of the dome and could possibly be upthrown 5,000 feet or more relative to the underground mine area.

The Continental fault also showed numerous early veins in two mineralogic respects: (1) the early veins do not control symmetric argillic alteration or sericitized Butte quartz monzonite, but the argillic halos. Early veins are often present in argillized zones, or have not altered the alkali feldspar in the Butte quartz monzonite with alkali feldspar envelopes, and (2) early ore veins may have added or secondary alkali feldspar alteration,

Pre-Main Stage veins do, in fact, present structural barriers or dams to Main Stage hydrothermal solutions, often producing sharp, asymmetric earlier veins that were not responsible for clay formation and alteration, pre-Main Stage alteration. Vein types 1, 2, and 3 imply a similar structural age for them; that is, they may all contain secondary biotite, alkali feldspar, and quartz but in greatly differing proportions, thus having a different appearance. There is a persistent offsetting relation of types 2 and 3 throughout the Butte district. Type 2 veins are generally exposed in the deepest zones containing disseminated chalcopyrite and magnetite and green biotite with alkali feldspar, quartz, anhydrite, calcite, and sericite. Types 2 and 3 are always cut and offset by Main Stage veins. Pre-Main Stage veins are always cut and offset by Main Stage veins. In order to present the mineralogic and temporal data of complex assemblages in a meaningful way, it made it possible to ascertain the distribution of mineralogic variations as a function of distance (ram) from the vein center. The point-counting data are presented in modal mineralogic proportions of the early veins, a general sequence of six pre-Main Stage vein types has been determined, based on mineralogy and cross-cutting features, that is valid on both sides of the Continental fault.

The six, listed from oldest to youngest, are:

1. Narrow brown biotite veinlets and biotitic alteration, green biotite with alkali feldspar envelopes,
2. Green mica veins composed of mixed brown mica and sericite minerals in the alteration halos,
3. "Early dark micaceous" veinlets (Meyer, 1965), green biotite with alkali feldspar, quartz, anhydrite, calcite, and sericite; of pre-Main Stage age but uncertain relative ages.
4. Quartz or quartz molybdenite veins with secondary and remnant primary Butte quartz monzonite minerals in the alteration halos.
5. Quartz or quartz molybdenite veins without alteration, or sericitic and green biotite with alkali feldspar envelopes,
6. Chalcopyrite-molybdenite and magnetite veinlets and alteration, or sericitic and green biotite with alkali feldspar envelopes.

Analytic Method

The lack of many vein intersections of types 2 and 3 throughout the Butte district was optically point-counted. This method made it possible to ascertain the distribution of mineralogic variations as a function of distance (ram) from the vein center. In order to present the mineralogic and temporal data of complex assemblages in a meaningful way, it made it possible to ascertain the distribution of mineralogic variations as a function of distance (ram) from the vein center. The point-count data are presented in modal mineralogic proportions of the early veins, a general sequence of six pre-Main Stage vein types has been determined, based on mineralogy and cross-cutting features, that is valid on both sides of the Continental fault.

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FR.4 C T URE- CONTR 022 ED DI,gSEMI:VA TED 3IIAERILIZ.4 TI O.ZV 41

When this graphical method is employed, mineral assemblages with a highly complex fabric and fine-grained mineralogy may be graphically described in relation to vein centers. Graphical integration of the mineral curves to the point of reference allows standardized quantitative representation of the average alteration mineral assemblage, including secondary and relict primary phases. Individual textural features may be related to overall zonal patterns within the alteration envelope, and systematic trends in mineral assemblages may be described.

Because each assemblage is standardized by using the edge of the megascopically visible halo to delimit the zone of strongest vein influence, it is possible to analyze trends in mineral assemblages with the equation

\[ N_{P_i,A_L} = 100.0 \]

where \( N \) is the total number of mineral phases in any one assemblage, and \( A \) represents the number of the assemblage sequence. \( P_i,x \) varies from one assemblage to the next.

Mineralogic Analysis of Typical Pre-Main Stage Structures

In order to illustrate the mineralogy of representative pre-Main Stage assemblages, the point-count data are shown in graphical form. Each of the major types of early structures is discussed separately and in order of decreasing relative age.

Biotitic breccias and narrow biotitic veinlets

Both of these structure types are the earliest recognized pre-Main Stage features occurring in the Butte quartz monzonite. Biotitic breccias range in width from several centimeters to over three meters. Figure 2A shows the analytic mineralogy of a narrow biotitic breccia expressed as a function of the distance from the center of the structure. In the figure L is the edge of the small breccia contact with Butte quartz monzonite wall rock; the dike is 2 x 8 mm or 16 mm wide. In the mineralogic graphs only half of the structure is shown because the halos are symmetric about the geometric center. The graph...

![Graphical representation of mineralogic analysis](image)
within the biotitic breccia and that the breccia has more than twice as abundant in the biotitic breccia than a mineralogy quite different from fresh Butte quartz monzonite. Biotitic breccias are often closely related structurally to quartz porphyry dikes in the Butte district and are often assay up to 2.0 percent copper due to the chalcopyrite. The copper in the breccias is the earliest mineralization of significant copper values into the Butte quartz monzonite silicates are evident in Figure 2.

At distances greater than L: 8 mm, the Butte quartz monzonite contains 47 percent alkali feldspar, 21 percent quartz, 20 percent fine-grained biotite, 6 percent chlorite, 2 percent plagioclase, and 1 percent anhydrite. Fresh Butte quartz monzonite (see Table 1), by comparison, has 1Tluch opaques (pyrite and chalcopyrite), 3 percent plagioclase, and 1 percent anhydrite. There is, therefore, an absence of significant amounts of biotite and alkali feldspar and no sulfides but this changes in the biotitic structures are often associated with the quartz porphyries.

Biotite veinlets with alkali feldspar and anhydrite is similar to biotitic breccias, green mica veins, and "early dark micaceous" veins. Another early alteration assemblage, green mica veins occurs only in the deep exposures of the copper-molybdenum dome and may be a deep equivalent of the "early dark micaceous"-type vein. Figure 2C presents graphically the mineralogy and textural relations of the latter two assemblages.

Smaller mineralogic trends are evident when the green mica vein center. The vein is essentially all green pale green pleochroic biotite, 9 percent dark green pleochroic biotite surrounded by a quartz and brown feldspar-muscovite alteration halo.

Green mica veins almost always have quartz veins surrounded by feldspathic and micaceous halos, but green mica veins are more similar to biotite breccias because they have no quartz vein center line. Other early veins almost always have quartz veins surrounded by feldspar-muscovite alteration halos. Green mica veins show a closer mineralogic affinity to biotite breccias than "early dark micaceous" veins texturally because significant amounts of biotite and alkali feldspar streaming away from biotitic breccias associated with quartz porphyries.
values of fresh Butte quartz monzonite. Mcga-

pseudomorphs of hornblende around essentially all

alteration halo. Several general features evident in

texture of a typical "early dark micaceous" vein and

types of pre-Main Stage veins (Roberts, 1973).

Biotite and anhydrite are present even beyond L as

vein out to point L where plagioclase reaches modal

secondary biotite at an increasing distance from the

type. There is a gradual increase in the amount of

this figure apply to essentially all of the veins of this

alteration envelopes as well. Chalcopyrite is most

concentrated within the veins and alteration en-

velopes, but sometimes it occurs sporadically outside

Chalcopyrite, pyrite, magnetite, and molybdenite oc-

microscopic pre-Main Stage veinlets.

plagioclase, 7 percent andalusite, 5.5 percent nmsco-

areas and can be related to the presence of tiny,

2.5 percent anhydrite, 1 percent remnant biotite, and

vite, 4 percent dark secondary brown or green biotite,

the average mineralogy from vein center out to

and megascopically visible alteration halo is 53 per-

"fresh" rock. The average mineralogy of the vein

eralogy of the secondary mineral assemblage replac-

"early dark micaceous" vein is composed almost

muscovite is separated from quartz by very thin rims

called a "sericite island" texture in which sericite or

micaceous" envelopes described by Meyer (1965) is

The most common textural feature in the "early dark

features seen in thin section are obvious in :Figure 2C.

integration of the modal curves in Figure 2C gives

ary alkali feldspar in contact with quartz. These tex-
tural patterns are interpreted as being reaction rims
placement. For example, alkali feldspar is sometimes
acteristic form of muscovite with large fan-shaped
feldspar which retains the original outline of the mica
aggregates is often marginally replaced by alkali
found as a partial pseudomorph in bladed muscovite
quartz or andalusite-muscovite-alkali feldspar-quartz.

fan. This partial replacement relationship may also

halos. Figure 2D shows a modal variation diagram

percent dark secondary biotite, 3 percent anhydrite,

alkali feldspar, 4 percent remnant plagioclase, 3.5

age mineralogy as 74 percent quartz, 15 percent

differences between this type of vein and all earlier

earlier structures.

Molybdenite is the only common sulfide found in

veins controlling narrow alkali feldspar alteration

halos. Figure 2D shows a modal variation diagram

Quartz or quartz molybdenite veins with alkali el-

quartz or andalusite-muscovite-alkali feldspar-quartz.

contains almost no chalcopyrite but does often contain

of the earlier vein types.

Main Stage sulfides positioned along rebroken

ent in quartz veins without alteration but are usually

important systematic variations in the amounts of

Although there are several minerals that are ubi-

Mineralogic Trends
Figure 3. Integrated modal curves for representative pre-Main Stage alteration assemblages placed in general sequence from Butte quartz monzonite wall rock through quartz or quartz molybdenite veins without visible alteration halos. Limits to integration used are from the vein centers to the edge of the megascopically visible halo within which Butte quartz monzonite texture is modified. Broad mineralogic trends in time are evident in quartz, alkali feldspar, and biotite curves. Opaques include chalcopyrite, pyrite, and molybdenite. Chalcopyrite and pyrite are most prevalent in assemblages 1, 2, and 3, and molybdenite is most abundant in assemblages 4 and 5. Secondary magnetite is most abundant in assemblages 3 and 4.

Secondary minerals. Figure 3 shows the average integrated modal curve data, plotted in proper sequence, for each of the early assemblages described. In general, all of the early assemblages represent an alkali feldspar-stable environment, but the amount of total alkali feldspar decreases in the younger assemblages, as does total biotite. In contrast, quartz abundance increases in the younger assemblages. It is possible to characterize the major changes in pre-Main Stage alteration assemblages throughout the entire Butte district as alkali feldspar-stable events ranging from early biotite assemblages through aluminosilicate-muscovite assemblages, out to an essentially quartz anhydrite assemblage. The sulfides show a remarkably close parallelism to the changing silicate assemblages. Chalcopyrite occurs dominantly in the early pre-Main Stage assemblages together with abundant biotite, muscovite, and alkali feldspar. Molybdenite occurs in "early dark mica" veins in minor amounts but is more abundant in the younger pre-Main Stage assemblages. Little or no alteration is capable of destroying the original Butte quartz monzonite texture except vein silicification and weak K-feldspathization near veinlets.

Physical Nature of Pre-Main Stage Mineralization

The various types of small pre-Main Stage veinlets and alteration envelopes already described form complex low-grade chalcopyrite ore zones in which early copper molybdenum mineralization is sometimes inherited by a Main Stage copper contribution controlled by much larger, continuous vein structures. The pre-Main Stage chalcopyrite is generally controlled by sporadic and discontinuous veinlets and is present in vein structures, megascopically visible alteration halos, and in minor amounts in mine sites near visible alteration halos. The early sulfides are usually physically disseminated but are clearly controlled by and related to an early planar structure of pre-Main Stage age. Chalcopyrite occurring in mafic sites that are distant from well-defined alteration halos generally shows microscopic evidence of an early vein-related origin. Microscopic veinlets consisting sometimes of trails of fluid inclusions through quartz grains or tiny veinlets of quartz, alkali feldspar, anhydrite, and biotite often relate clumps of chalcopyrite and pyrite in mafic sites to larger pre-Main Stage veinlets. The disseminated nature of early sulfides in the Butte quartz monzonite is in no way evidence that these sulfides are related to the magmatic crystallization of the Butte quartz monzonite country rock. On the contrary, the early sulfides are clearly related to pre-Main Stage planar structures and alteration halos. Pervasive pre-Main Stage alteration between these structures correlates with the density of early veinlets.

Economic Significance of Pre-Main Stage Mineralization

Detailed mapping of vein types and wall-rock alteration has made it possible to estimate the contribution of the two ages of mineralization to the total copper and molybdenum in the country rock at Butte. Development crosscuts and diamond drill core have provided the most useful information for this study. Correlation of mapping and assay data shows that...
FRACTION CONTROLLED DISSOLUTION MINERALIZATION

Large zones of fresh Butte quartz monzonite contain significant copper, present as disseminated, veinlet-controlled pre-Main Stage chalcopyrite in which individual early veinlets and alteration halos assay up to 2 percent copper (Brimhall, 1973). Molybdenite is almost exclusively associated with quartz veins, with or without early alteration, and is of pre-Main Stage origin. Sometimes Main Stage veins contain quartz molybdenite vein fragments or show evidence of having rebroken earlier structures. Main Stage sulfides may parallel molybdenite bands but often cut across the molybdenite bands in detail.

Relatively large continuous Main Stage veins are frequently present in Butte quartz monzonite that has been previously mineralized during pre-Main Stage events. The superposition of these two mineralization events imparts copper grades in the range of 0.3 to 0.9 percent total copper, with 0.02 to 0.06 percent molybdenum. All of the molybdenum and a large part of the copper were introduced before the formation of large throughgoing Main Stage structures. The possibility of Main Stage remobilization of earlier copper exists and presents an interesting genetic problem as to the ultimate source of the base metals at Butte. Much of the copper may have been introduced during pre-Main Stage events and then remobilized and concentrated by solutions that formed the large Main Stage veins. Sometimes in the sericitic zone adjacent to large Main Stage veins the copper grade is significantly lower than that in surrounding Butte quartz monzonite. Therefore there is local evidence that Main Stage activity partially removed and concentrated early copper in Main Stage structures. The distribution of sphalerite in the pre-Main Stage environment, as small propylitic veinlets over and around the more intensely altered pre-Main Stage zone, parallels the geometry of Main Stage sphalerite with respect to copper sulfide.

COMPOSITIONS OF SECONDARY MINERALS IN EARLY ALTERATION ASSEMBLAGES

Secondary minerals in pre-Main Stage veins and alteration halos are often very fine grained and complexly intergrown in replacement textures involving numerous phases. The electron microprobe provides a means of determining the mineral compositions of these very small grains and thereby contributes detailed mineralogic information to the description of early phenomena in the Butte geologic history.

Alkali feldspar, muscovite, and biotite compositions in early alteration assemblages were determined using natural mineral standards analyzed by Professor I. S. E. Carmichael (see Appendix 1 for a description of analytic techniques of compositional determination). Compositional data were obtained on the mineral phases to determine the scale of compositional homogeneity within individual specimens and possible spatial and temporal trends accompanying mineralogic changes in alteration assemblages.

Composition of muscovite and alkali feldspar from deep Continental diamond drilling

An area in the Butte district that is relatively free of Main Stage alteration is the Continental block, which provides an opportunity to observe deep pre-Main Stage assemblages that are essentially unaffected by Main Stage veins. Type 3 veinlets contain secondary alkali feldspars with K-feldspar ranging from 0.905 to 0.940, with the feldspars treated as a K-Na binary because these hydrothermal alkali feldspars generally have less than 0.003 XCa_feldspar. The X_m, of adjacent muscovites in the "sericite-island" varies from 0.89 to 0.96 when treated as a muscovite-paragonite binary solid solution. The thirteen muscovite and alkali feldspar analyses from the Continental area show a compositional range remarkably similar to that of analyses from the deep underground mines, three miles away. An average of all the early muscovites and alkali feldspars is given in Table 3. The formula of the average early muscovite is:

$$ \text{(K}_{1.2} + \text{Na}_{0.12} + \text{Ba}_{0.01}) \times (\text{Al}_{1.41} + \text{Ti}_{0.02}, \text{Fe}_{0.2a}, \text{Mg}_{0.20}) \times (\text{Al}_{1.80}, \text{Ti}_{0.11}, 0.8i_{0.10} \text{O}_{20}) \times (\text{Si}_{4.10}) $$

From this formula it is possible to calculate the tetrahedral Si/A1 ratio as 3.23 for the average muscovite from the early wall-rock alteration assemblages at Butte. Ideally the tetrahedral (Si/A1) ratio is 3.00 for an ideal (K-Na)-mica with no octahedral substitution of Fe+2, Fe+3, Mg+2, or Ti+4 for Al+3. This ratio reflects the degree of substitution of the other cations for aluminum and approaches the ratio of the ideal formula of a dioctahedral alkali mica. The sum of the cations in the X-position of the average TABLE 3. Averaged Electron Microprobe Data of Minerals from Early Veins at Butte

<table>
<thead>
<tr>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali feldspars</td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>FeO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na2O</td>
</tr>
<tr>
<td>KO</td>
</tr>
<tr>
<td>BaO</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

* Total iron as FeO.
Figure 4 shows a plot of the alkali feldspar and muscovite compositions for various veins from two drill holes in the Continental area. In order to determine any different compositional trends the specimens from GRL 8884 were collected by going down a deep drill hole out into the periphery of the low-grade copper molybdenum orebody in the Continental area.

Muscovite and alkali feldspar compositions from the deep level Steward mine area

The compositions of adjacent alkali feldspar muscovite pairs from specimens from the deep level Steward mine are shown in Figure 5 for comparison with the Continental area early alteration feldspars and muscovites.

Biotite compositions

Biotite compositions determined with the electron microprobe show consistent variations in TiO₂ and Fe/Mg in Butte quartz monzonite, quartz porphyry, biotitic breccia, and early vein assemblages. Remnant Butte quartz monzonite biotites inside the copper molybdenum dome show a range of 2.8 to 3.4 weight percent TiO₂. The TiO₂ content of quartz porphyry intrusives is somewhat less, with 2.0 weight percent which is very similar to the value for biotitic breccias associated with the dikes containing 1.9 to 2.3 weight percent TiO₂ in the biotites. All early hydrothermal or vein-related biotites contained from 0.6 to 2.5 percent TiO₂. These secondary biotites are generally brown or green in thin section except for reddish-brown, high TiO₂ biotites found in vein centers with quartz and a carbonate of unknown composition. Lower TiO₂ brown biotites are normally found in alteration halos and not as coarse blades in vein centers. Hydrothermal biotites gen-
Generally are more magnesian than igneous biotites (Roberts, 1973).

Chemical Considerations

In order to better understand the physical environment during early mineralization, the mineral assemblages, fabrics, and mineral compositions in terms of phase equilibria and solid solution models have been considered. As outlined earlier, the pre-Main Stage alteration mineral assemblages are characterized by the presence of alkali feldspar and quartz usually with muscovite, biotite, and sometimes andalusite. Three distinct assemblages occur in close proximity to one another containing muscovite or andalusite "island" textures with alkali feldspar separating them from quartz. The most common assemblage is quartz-alkali feldspar-muscovite with partial pseudomorphic replacement of muscovite by alkali feldspar along the mica cleavage. The second assemblage is quartz-alkali feldspar-andalusite with alkali feldspar separating quartz and andalusite. The third assemblage is quartz-alkali feldspar-muscovite-andalusite with definite partial pseudomorphic replacement of muscovite by alkali feldspar. Andalusite in this assemblage is sometimes partially replaced by retrograde muscovite without a replacement by alkali feldspar. In terms of phase equilibria these assemblages imply a condition of muscovite dehydration in the presence of quartz. Because dehydration of muscovite is dependent upon pressure, especially low pressure, it is difficult to determine the pressure or temperature strictly from the mineral phases present. However, as a guide, a $P\cdot T$ value of 1 kilobar would correspond to a muscovite stability limit in the region of 600øC.

Chemical Thermodynamics of Simultaneous Exchange Reactions Involving Solid Solutions

In order to assess the thermal regime of early mineralization, chemical equilibria were studied that had only a small volume of reaction, thereby rainfall—
order to interpret the electron microprobe data of
albite and mica from the Early Stages. Knowledge of $K_4(p, T)$ as a function of tem-
perature allows calculation of coexisting alkali feld-
spar and mica compositions. Two methods to
determine this compositional dependence as a func-
tion of pressure and tem-
perature were worked out in this study in
which the activities of the potassium and sodium mineral
localities. Equation (3) represents the chemical
composition of temperature.

It is possible to consider equation (3) as relating
the activities of the end member alkali components
to the activities of the Na-mica (paragonite) - t- K +
feldspar and mica components are not all independent.

Because the dependence of the equilibrium constant
volumes (2.09 cm$^3$) of reaction
for Na-feldspar (albite), O for K-feldspar (ortho-
clinose), P for paragonite, and M for muscovite. $X_x$
and $X_y$ are the mole fraction of Na-feldspar in the alkali feld-
spar solid solution; $X_p$ is the mole fraction of pargonite in the alkali micas;
and $X$ is the mole fraction of muscovite in the alkali
micas.

The equilibrium constants for equations (5) and
(6) have been determined experimentally (Hemley,
molality ratio. Calculation of the
free energy of a binary alkali feldspar solid solution
has little compositional variation within individual
specimens but substantial variation between different
multi bombs. Direct comparison of these isolated ex-
periments is the simplest method of deter-
mining $K_4(p, T)$. For a given exchange isotherm
change experiments is the simplest method of deter-
ing $K_4(p, T)$.

In the calculations the subscripts used will be: A
May be expressed as:

\[ G_{\text{total}} = G_{\text{ideal mixing}} + \Delta G_{\text{excess}} \]

Term 1 is the free energy at 1 bar and temperature of interest of pure albite in the solid solution. This number can be obtained from Robie and Waldbaum (1968). The free energy is multiplied by the mole fraction of albite in the solid solution. For example, the alkali feldspar is 7.0 percent albite, so \( X_A = 0.07 \). Term 2 is for pure \( \text{KA}_2\text{Si}_2\text{O}_5 \). \( X_0 \) is the mole fraction of \( \text{KA}_2\text{Si}_2\text{O}_5 \), where \( X_0 = 0.93 \) for this example. Terms 1 and 2 give the free energy of a mechanical mixture of pure albite and pure microcline, disregarding any surface energy effects. Term 3 is the ideal mixing term which arises from the entropy of mixing when the enthalpy change is equal to zero for no atomic interaction:

\[ G_{\text{ideal mixing}} = RT(X_A \ln X_A + X_0 \ln X_0) \]

Term 4 is the excess free energy or the free energy that cannot be accounted for by this model. Terms 3 and 4 add on to the value of free energy for the mechanical mixture giving:

\[ G_{\text{excess}} = G_{\text{total}} - G_{\text{ideal mixing}} - \Delta G_{\text{excess}} \]

Thompson and Waldbaum (1967, 1968, 1969 a, b) made it possible to calculate the thermodynamic properties of these minerals over a wide range of temperatures and pressures. From equation (7) it can be seen that in order to calculate the free energy of a binary solid solution, as a function of composition, it is necessary only to describe the excess free energy. \( G_0 \), or the free energy, can be expressed in terms of \( X_A \) and \( X_0 \) for the alkali feldspars, by using

Figure 6. Theoretical exchange isotherms for the system K-Na feldspar, K-Na mica, and aqueous fluid, derived from the method described in the text, using the alkali exchange data of Iiyama (1964, 1965) on alkali feldspars and micas at 1 kilobar total pressure. This diagram is used in conjunction with adjacent alkali feldspars and muscovites to estimate the possible temperatures of equilibration for early alteration assemblages. Dehydration of muscovite and muscovite plus quartz are plotted in approximate positions (Evans, 1965; Chatterjee, 1972), according to temperature.
Fro. 7. Theoretical exchange isopleths of K/(K + Na) in aqueous solution in equilibrium with coexisting alkali feldspars and muscovite, using the exchange data of Iiyama (1964, 1965).

Two coefficients, 5G and 5VG, called Margule's parameters, which are themselves functions of pressure and temperature. These parameters are a fit to experimental data over a range of pressure and temperature. The general case is more complicated, but for the alkali feldspars this approach is satisfactory.

For alkali feldspars equation (10) expresses the regressed parameters.

\[
\text{Ge,}_{(p, T)} = (6326.7, [0.0925 p - 4.6321 T])X,^2 + (7671.8, [0.1121 p - 3.8565 T])X_0^2 \quad (10)
\]

where \( X, \) is the mole fraction of NaAlSiO\(_3\) in the solid solution and \( X_0 \) is the mole fraction of NaAlSiO\(_3\), \( T \) is in degrees Kelvin, and \( p \) is in bars (Thompson and Waldbaum, 1967, 1968, 1969a, b).

These relations are valid for asymmetric binary solutions such as alkali feldspars. The quantities in parentheses in equation (10) are \( W \) and \( W_G \), respectively, with

\[
W = a + b p + c T \quad (10a)
\]

\[
W_G = a + b + c T \quad (10b)
\]

The constants in equations (10a and b), \( a, b, \) and \( c \), are determined experimentally from data over a temperature range of 500 ø to 700øC and 2 to 10 kilobars. For alkali feldspars, \( a = 6326.7, b = 0.0925, c = 4.6321, \) \( = 7671.8, \) \(  = 0.1121, \) and \(  = 3.8565. \)

The Gibbs free energy of a solid solution, may be written as'

\[
\Delta G_{T, 0} = XAG - XoGo + X^RT \ln X^ + W, X_a X_0 + W, X_o X^ + XoRT \ln Xo \quad \text{binary solution} \quad (11)
\]

The chemical potential of the ith mole fraction is expressed as'

\[
\mu_i = C_{21-ii} (1 - X_i) \quad (12)
\]

The chemical potential is also related to the activity of the ith component , by'

\[
\mu = \mu_i + RT \ln a_i = \mu_i + RT \ln X_i - RT \ln X^ \quad (13)
\]
Data Points formulated using activity coefficients of alkali micas at quartz saturation and Henley data formulated assuming ideality (G: X) and Henley data formulated using octivity coefficients of alkali micas and Iiyama (1964) data.

Temperature $^\circ$C

Fro. 8. Plot of log $K(p = \text{kb}, T)$ as a function of temperature $^\circ$C for exchange reactions of alkali feldspars (Curve 1) and alkali micas (Curve 2). Tables 4 and 5 show the method of calculation of data points using solvus pairs at each temperature. Values of mole ratio $K/Na$ aqueous are from Hemley (pers. commun.). Equilibrium constants for exchange reactions are calculated using activity coefficient data (Thompson, 1967; Thompson and Waldbaum, 1968; 1969a, b; Eugster et al., 1972.) The equilibrium constants of the micas are also calculated assuming ideality in solid phases for comparison with nonideal cases. Curve 2 is calculated from thermodynamic data (see Appendix 2). Brackets are the range of Iiyama's (1964) data formulated using activity coefficients.

### Table 4. Alkali Feldspar Exchange Data Along Solvus

<table>
<thead>
<tr>
<th>$T^\circ$C</th>
<th>$X_0$</th>
<th>$X_A$</th>
<th>$K/Na$</th>
<th>$a_0/Na$</th>
<th>$a_A/Na$</th>
<th>$K_s(p, T)$</th>
<th>$\log K_s(p, T)$</th>
<th>$\log K_s(p, T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.80</td>
<td>0.96</td>
<td>0.235</td>
<td>0.8352</td>
<td>0.967</td>
<td>0.2720</td>
<td>--9.566</td>
<td>--0.535</td>
</tr>
<tr>
<td>600</td>
<td>0.65</td>
<td>0.09</td>
<td>0.308</td>
<td>0.7365</td>
<td>0.932</td>
<td>0.3891</td>
<td>--0.410</td>
<td>0.4258</td>
</tr>
<tr>
<td>650</td>
<td>0.53</td>
<td>0.83</td>
<td>0.325</td>
<td>0.6768</td>
<td>0.907</td>
<td>0.4356</td>
<td>--0.360</td>
<td>0.509</td>
</tr>
</tbody>
</table>

Mole fraction compositions from solvus data of Orville (1963), activity coefficients from Thompson and Waldbaum (1969) and mole ratios (aqueous) from Hemley (pers. commun.). Assume activity ratio is equal to mole ratio $K/Na$. 

---

*Note: Figure 8 and Table 4 are not included in the image.*
TABLE 5. Alkali Mica Exchange Data

\[ \text{X}_p - \text{p} \cdot a : + \]

Nonideal Nonideal Ideal

\begin{tabular}{|c|c|c|c|c|c|}
\hline
T & \text{X}_m & \text{X}_p & \text{K}/\text{Na} & a & a_0 \\
\hline
300 & 0.935 & 0.985 & 0.054 & 0.99 & 0.943 \\
400 & 0.890 & 0.98 & 0.0925 & 0.982 & 0.909 \\
500 & 0.82 & 0.94 & 0.145 & 0.953 & 0.864 \\
600 & 0.70 & 0.90 & 0.208 & 0.930 & 0.809 \\
650 & 0.73 & 0.88 & 0.245 & 0.920 & 0.813 \\
\hline
\end{tabular}

Solvus compositions and activity coefficients are from Eugster et al. (1972) and mole ratios (aqueous) are from Hemley. Assume activity ratio is equal to mole ratio K/Na.

Using these relations gives the following equations that are necessary in calculating the activity coefficients:

\[ \log \frac{3}{\text{Na}_2\text{Si}_2\text{O}_5} \]
\[ = 2.3RT (\text{X}_m - \text{X}_p) \]

The equilibrium constants for equation (5) involving the micas may be rewritten in terms of logarithms:

\[ \log K(p, T) = \log a_X - \log a_+ + \log a_+ / a_+ \]

Separating the activities into mole fractions and activity coefficients gives:

\[ \log K_{\text{Na}_2\text{Si}_2\text{O}_5}(p, T) = \log X_3 - \log 3 + \log a_+ / a_+ \]

Similarly the feldspar equilibrium constant may be written as:

\[ \log K(p, T) = \log X_3 + \log a - \log X_0 - \log a_+ / a_+ \]

Substituting equation (17) in (20) and equation (18) in (21) allows the calculation of the equilibrium constants for the feldspar and mica exchange experiments. Figure 8 shows plots of these equilibrium constants calculated from experimental data (Hemley, pets. commun.; Orville, 1963; Iiyama, 1964, 1965) with theoretically derived activity coefficients (Appendix 2).

Table 4 shows the reduction of two-phase data on the alkali feldspar solvus to the equilibrium constant \( K_{\text{Na}_2\text{Si}_2\text{O}_5}(p, z) \) using exchange data of Hemley at quartz saturation and the above equations to establish activities in the solids. Also shown is the comparison with calculated values using thermodynamics (Orville, 1963; Robie and Waldbaum, 1968; Hemley, pets. commun., ideal column). Table 5 shows similar calculations for the alkali mica equilibrium from Hemley’s data (pets. commun.), also using an activity coefficient calculation for the solid phases. Using the data from Tables 4 and 5 on \( K_{\text{Na}_2\text{Si}_2\text{O}_5}(p, z) \) and \( K_{\text{Na}_2\text{Si}_2\text{O}_5}(p, T) \), it is possible to calculate the \( K_{\text{Na}_2\text{Si}_2\text{O}_5}(p, z) \) in Table 6 shows
FRAC TRATE-CONTROLLED DISSEMINATED MINERALIZATION.

From Figure 8 it is apparent that both near end member micas and feldspars may be treated as ideal solution solutions. Assuming ideality in the potassic solid phases, for both the major and minor components ($X_0 > 0.8$), the theoretical dependence of muscovite compositions on alkali feldspar compositions has been calculated. Figure 9 shows this theoretical behavior.

Thermodynamics imposes several important constraints on the derivation of a phase diagram such as Figure 9. If equation (4) represents the coexistence of a mica solid solution with an alkali feldspar solid solution, the equilibrium constant for this reaction may be rewritten, assuming ideality of the solid solution at high temperatures, where $a$ approaches $X_t$.

$$X = \frac{1}{1 + \frac{K_2}{K_1} X_t}$$  \hspace{1cm} (22)

Solving for $X$ gives:

$$X = \frac{1}{1 + \frac{K_2}{K_1}}$$  \hspace{1cm} (23)

This relation was used for the calculations shown in Figure 9. At the potassium end of Figure 9 the first derivation of $X$ with respect to $X_0$, in the limit of $X_0$ equal to 1, gives:

$$\frac{\partial X}{\partial X_0} = \frac{K_2}{K_1}$$  \hspace{1cm} (24)

Therefore, the slope of the exchange isotherms in Figure 9 at the potassium end of the diagram should be equal to the equilibrium constant of the four solid-phase equation (4). Table 6 shows a comparison of this limit with 

A comparison of Figure 9 with Figure 6 shows considerable difference in the exact form of the exchange isotherms.
change isotherms, largely due to the source of data used for each derivation. Figure 9 is constructed from thermodynamic calculations of activities of solid solutions and aqueous ions using the experimental data of Hemley (pers. commun.). Thermodynamic constraints such as equation (24) imply that Figure 9 is preferred over Figure 6. The natural alkali feldspar and muscovite compositions from Main Stage assemblages imply an average temperature and range of 650°C ± 100°C for possible equilibration of both solid solutions and early hydrothermal fluids. The natural muscovites analyzed in this study contain Mg e+, Fe e+, Fe 3', and Ti 4' substituting for octahedral AP, making direct comparison of phase diagrams such as Figure 9 and electron microprobe data less certain. However, implied temperatures of 650°C derived using this method are consistent with temperatures estimated for the experimental thermal stability limit of natural muscovite in the presence of quartz at pressures of several kilobars.

Temperature estimates made using alkali partitioning between alkali micas and feldspars show a definite position correlation of the TiO2 content in hydrothermal biotites with an increasing temperature for assemblages containing another titanium-bearing phase such as rutile. The variation in biotite TiO2 content is quite high with about 1.4 weight percent TiO2 at 600°C and 2.5 weight percent at 700°C. TiO2 contents of coexisting muscovites do not show any similar variation of TiO2 content with possible equilibration temperatures determined by alkali substitution.
**Representative Electron Microprobe Sericite Analyses**

<table>
<thead>
<tr>
<th></th>
<th>906</th>
<th>55</th>
<th>125</th>
<th>33</th>
<th>46</th>
<th>68</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.33</td>
<td>45.88</td>
<td>45.96</td>
<td>46.47</td>
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<tr>
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<tr>
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<tr>
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<td>4.21</td>
<td>2.26</td>
<td>2.01</td>
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<tr>
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<tr>
<td>CaO</td>
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<tr>
<td>Na$_2$O</td>
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<td>0.72</td>
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<td>K$_2$O</td>
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<td>10.20</td>
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<tr>
<td>BaO</td>
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<td>0.06</td>
<td>0.01</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
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<td>95.39</td>
<td>95.38</td>
<td>95.35</td>
<td>95.18</td>
<td></td>
</tr>
</tbody>
</table>

Number of ions on the basis of 24E0, OH$^-$:

| 6.126 | 6.147 | 6.096 | 6.153 | 5.980 |

Octahedral Al:

| 3.087 | 3.281 | 3.616 | 3.604 | 3.517 |

Tetrahedral Al:

| 1.874 | 1.853 | 1.904 | 1.847 | 2.020 |

Ti*:

| 0.039 | 0.041 | 0.003 | 0.007 | 0.009 |

Fe:

| 0.489 | 0.424 | 0.225 | 0.200 | 0.299 |

Mg:

| 0.540 | 0.263 | 0.196 | 0.225 | 0.202 |

Ca:

| 0.004 | 0.001 | 0.016 |       |       |

Na:

| 0.113 | 0.148 | 0.185 | 0.131 | 0.201 |

K:

| 1.839 | 1.756 | 1.700 | 1.722 | 1.579 |

Ba:

| 0.008 | 0.010 | 0.003 | 0.001 | 0.025 |

H:

| 3.938 | 4.118 | 4.086 | 4.105 | 4.270 |

Tetrahedral Si/Al:

| 3.269 | 3.317 | 3.203 | 3.330 | 2.960 |

Si + Al$_{tetra}$ = Z:

| 8.000 | 8.000 | 8.000 | 8.000 | 8.000 |

Al$_{octa}$ + Ti + Fe + Mg = Y:

| 4.154 | 4.010 | 4.040 | 4.036 | 4.027 |

K + Na + Ca + Ba = X:

| 1.964 | 1.916 | 1.888 | 1.853 | 1.821 |

K/X:

| 0.936 | 0.917 | 0.900 | 0.929 | 0.867 |

Ca/X:

| 0.002 | 0.001 | 0.000 | 0.000 | 0.009 |

Ba/X:

| 0.004 | 0.005 | 0.002 | 0.000 | 0.014 |

K/Na + Ca:

| 0.942 | 0.922 | 0.902 | 0.902 | 0.887 |

Na/Al + Ca:

| 0.058 | 0.078 | 0.098 | 0.071 | 0.113 |

**Mole percent assuming stoichiometry**:

| 90.22 | 86.92 | 84.98 | 86.25 | 78.81 |

| 5.30  | 7.02  | 8.87  | 6.28  | 9.61  |

| 0.40  | 0.13  | 0.00  | 0.00  | 1.48  |

| 0.83  | 1.06  | 0.33  | 0.05  | 2.73  |

| 96.77 | 95.15 | 94.19 | 92.59 | 92.65 |

**Binary calculations**:

| 0.944 | 0.925 | 0.905 | 0.932 | 0.891 |

| 0.056 | 0.075 | 0.095 | 0.068 | 0.109 |

Both methods of calculation of the binary mole fraction give very close results. Compare K/[K + Na] and Xsim; Xs was used for phase diagrams.

**On the Nature of Alteration Processes**

High temperature alteration reactions have occurred around pre-Main Stage fractures developed in the Butte quartz monzonite wall rock. The implied temperature of 650 ø ---+ 100øC is only slightly below the magmatic temperature for a quartz monzonite.

Alteration assemblages produced from the Butte destruction around early veins, implying conditions of chemical attack on wall-rock minerals by hydrothermal fluids. In detail, the alteration process involved the introduction of high temperature fluids into fractures in the Butte quartz monzonite, producing alteration envelopes which represent reaction zones of early fluids and surrounding igneous rock. Within these zones, igneous Butte quartz monzonite minerals such as plagioclase, biotite, and alkali feldspar have been partially or completely replaced by secondary mineral assemblages which represent a closer approximation to equilibrium of high temperature fluid and wall rock. For some minerals, such as plagioclase, a relatively high degree of disequilibrium with respect to hydrothermal fluids is indicated.
quartz alkali feldspar or quartz molybdenite asseral in the Butte quartz monzonite texture are minute veinlets controlling the alteration halos which destroy the Butte quartz monzonite country rock and aqueous fluids. The multiplicity of secondary assemblages is indicative of an overall near-equilibrium between phases produced in the high temperature environment. The different solid solution phases in the Butte wall rock. Quartz molybdenite mineralization may be epigenetically related to the Butte quartz monzonite. Impressed events of sulfide deposition, both probably imposed events of sulfide deposition, both probably have been very different for these two mineralization events. The early fracture-controlled disseminated mineralization of pre-Main Stage time is represented in Figures 2 and 3. It is possible that these mineralization must have been accomplished by aqueous fluids apparently has caused very intense hydrothermal stability of muscovite is the exchange of Ca-o+ with a similar formation of anhydrite. Both of these reactions involving muscovite, alkali feldspar, andalusite or muscovite could produce increasing aK+/aH + ratios moving the solution compositions toward the alkali feldspar stability component to either andalusite or muscovite could be accomplished isothermally by the increased activity of K+/H + oxving to the alteration of Butte quartz monzonite plagioclase to these minerals and to the site, and quartz (Shade, 1974) are considered, then extraction from the aqueous fluid. If the hydrolysis consumption of 14+ ions at a rate faster than the K+ reaction often has formed anhydrite within the original plagioclase site. At somewhat lower temperatures and pressures, butte quartz monzonite alkali feldspar is unaltered. In direct contrast to this high temperature alkali feldspar assemblage are the much lower temperature alkali feldslar-destructive assemblages of the Main Stage drothermal fluids. The multiplicity of secondary quartz monzonite alkali feldspar is unaltered. In direct contrast to the apparent disequilibrium of andesite, the overall tendency toward equilibration between states between igneous wall-rock mineral assemblages might have produced modifications of the reaction rims of secondary alkali feldspar between andalusite and muscovite. One reaction that has apparently occurred at temperatures above the thermal stability of muscovite is the exchange of Ca-o+ and complex alteration reactions. One reaction that could have been very different for these two mineralization episodes. The highly fractured discontinuous disseminated mineralization of pre-Main Stage time supports the secondary activity around vein structures. Calcium released in this reaction often has formed anhydrite within the original plagioclase site. At somewhat lower temperatures and pressures, both stages of mineralization effected through a much larger, more continuous network of tiny irregular discontinuous fractures at high temperature and complex alteration reactions. One reaction that could have been very different for these two mineralization episodes. The highly fractured discontinuous disseminated mineralization of pre-Main Stage time supports the secondary activity around vein structures.
for the formation of the multistage Butte ore deposit.

gest the quartz porphyries as a possible source for at porphyry dikes and mineralized biotitic breccias sug-
age, structural distribution, and association of quartz drothermal events to Main Stage activity.

represent a transitiou from the early lnagmatic-hy-
least some of the early hydrothermal solutions. How-
remains a matter of speculation. The apparent early
the Butte district.

requires an extremely large heat source at depth in
ever, the immense size of the early thermal anomaly
fully acknowledged. Vincent D. Perry recognized
the chemical aspects of this investigation are grate-
pany has been very rewarding. Dr. Mitchell Rey-
novels provided invalnable criticism of textural fea-
Zeihen, and Rick Ramseier of the Anaconda Com-
geologic data collected. Material support from an
mements with the formulation of the thermodynamic
Charles Meyer with the field problems as well as with

is sincerely appreciated.

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FR,4 C T URE- CON TROLLED DISSEMINA TED MINER.LIZA TION 5 7
Thompson, J. B., and Waldbaum, D. R., 1968, Mixing properties of simple alkali feldspar components are 8.462, 4.962, and 2.448.

The second method assumes stoichiometry in the micas. In order to express conveniently the composition of alkali feldspars and muscovites, the factors that convert Na\textsubscript{2}O, CaO, and BaO into mole fractions usually are within 0.003 mole fraction, calculated from methods 1 and 2 given above. These factors may be too small by 4R\left[\frac{1}{4} + \frac{3}{4} \ln \frac{3}{4}\right] (XValder and Waldbaum, 1968) may be in the literature (Robie and Waldbaum, 1968) may be incorrect.

The iron and magnesium contents of the muscovites, in any one specimen, varied significantly more than the activity of the potassium component. The alkali feldspar composition has been treated as a binary solid solution of \([K, Na]\) micas.

The entropy at 298 \(\degree\) for paragonite may be too small by 4R\left[\frac{1}{4} + \frac{3}{4} \ln \frac{3}{4}\right] (Valder and Waldbaum, pers. commun.). The entropy at 298 \(\degree\) for paragonite could be 73.47 cal/deg-mole. A good estimation of the third law entropy of paragonite could be 73.47 cal/deg-mole. A good estimation of the third law entropy of paragonite could be 73.47 cal/deg-mole.

The iron and magnesium contents of the muscovites, in any one specimen, varied significantly more than the activity of the potassium component. The alkali feldspar composition has been treated as a binary solid solution of \([K, Na]\) micas.

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The entropy of reaction can be assumed to be zero for the following reaction:

\[
\text{Muscovite} + \text{Na}^+ = \text{Paragonite} + \text{K}^+
\]

At 298 K, the third law entropy of paragonite is 71.22 cal/deg-mole. Using the standard andalusite heat from Ulbrich and Merino (1974), which is consistent with kaolinite and microcline experimental data, the heat of formation of muscovite may be calculated using the experimental curves of Althaus. This gives an average of 1422.818 kcal for the experimental data points. A similar reduction of Chatterjee's (1972) paragonite + quartz using sanidine breakdown gives a heat of formation of paragonite as --1411.257 kcal. This information was used to calculate the alkali exchange reaction for the alkali micas. A summary of the data used is given in Table 9.

Adjusting the standard enthalpy of muscovite within the limits of error to --1421.0 kcal gives the curve shown in Table 9.

### Table 9: Optimized Thermodynamic Data

<table>
<thead>
<tr>
<th>Component</th>
<th>Coefficient</th>
<th>Enthalpy [kcal/mol]</th>
<th>Entropy [cal/deg-mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Muscovite</td>
<td>1.000</td>
<td>--1421.000</td>
<td>73.47</td>
</tr>
<tr>
<td>2. Na⁺</td>
<td>1.000</td>
<td>--57279.0</td>
<td>14.40</td>
</tr>
<tr>
<td>3. Paragonite</td>
<td>1.000</td>
<td>--1411.257</td>
<td>71.22</td>
</tr>
<tr>
<td>4. K⁺</td>
<td>1.000</td>
<td>--60040.0</td>
<td>24.50</td>
</tr>
</tbody>
</table>

### Coefficients of CP Expansion for the Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>A [kJ/mol K], B [1/K], C [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Al₂Si₂O₅(OH)₄</td>
<td>97.559, 0.2638E-01, -0.2544E-07</td>
</tr>
<tr>
<td>2. Na⁺</td>
<td>9.799, 0.0, 0.0</td>
</tr>
<tr>
<td>3. K⁺</td>
<td>96.139, 0.2908E-01, -0.2544E-07</td>
</tr>
<tr>
<td>4. SiO₂</td>
<td>3.400, 0.0, 0.0</td>
</tr>
</tbody>
</table>