PHYSIOCHEMICAL CHARACTERISTICS DURING POTASSIC
ALTERATION OF THE PORPHYRY COPPER DEPOSIT AT
AJO, ARIZONA

by

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ABSTRACT

Potassium metasomatism is a widespread alteration type in porphyry copper deposits and is often spatially associated with hypogene sulfide ore formation. At Ajo, potassic alteration composes the dominant alteration type and is spatially, and to some extent temporally, associated with chalcopyrite and bornite mineralization. Physiochemical conditions prevailing during potassic alteration thus describe a significant portion of the hydrothermal ore-forming process. Studies of fractures, fluid inclusions in quartz, and structural and compositional characteristics of K-feldspar, all in the potassic alteration zone at Ajo, indicate that: fracturing was strongest during potassic alteration and sulfide deposition, pressures were at approximately 650 bars, temperatures started at a minimum of 580°C, continued through 470°C and possibly 280°C, log $a_{K^+}/a_{H^+}$ changed from 2.6 at 580°C to 3.2 at 470°C, log $a_{Na^+}/a_{H^+}$ changed from 2.7 at 580°C to 3.8 at 470°C, and the ratio $a_{K^+}/a_{Na^+}$ radically decreased from 0.8 to 0.3 in this temperature range.
CHAPTER 1
INTRODUCTION

Potassium metasomatism was first recognized as an important process in the early evolution of porphyry copper magma-hydrothermal systems by Gilluly (1942, 1946) in his extensive study of the Ajo mining district. Since then, it has been recognized and described in other porphyry copper deposits by Creasey (1959, 1966), Rose (1970), Lowell and Guilbert (1970), Hollister (1978), and Beane (1982). Potassic alteration is characterized by metasomatic potassium feldspar and biotite mineralization. These minerals differ in composition from their igneous counterparts (Beane, 1982): For example, hydrothermal K-feldspar is commonly more potassic than igneous K-feldspar, and hydrothermal biotite has a higher Mg and lower Ti content than igneous biotite. The compositional variations between hydrothermal and igneous biotite are more numerous and complex than are compositional variations from hydrothermal to igneous K-feldspar and are described in detail by Beane (1974) and Jacobs and Parry (1976). Quartz is also a common constituent of this assemblage, and sericitic micas may be present, usually coarser and closer to stoichiometric $\text{KA}_2(\text{AlSi}_3\text{O}_10)(\text{OH}_2)$ than the sericite formed during phyllic alteration (Meyer and Hemley, 1967). Other
minerals that commonly occur in this assemblage include chlorite, anhydrite, magnetite, pyrite, chalcopyrite, and bornite.

Potassic alteration is a fracture-controlled alteration in which K-feldspar and biotite occur as vein-filling minerals and as replacements of the host rock adjacent to the fractures. It is the earliest fracture-related stage of a porphyry copper hydrothermal system and is commonly centered on the intrusion that initiates the fluid circulation. In deposits associated with a quartz monzonite intrusion, K-feldspar dominates over biotite; where diorite is the intrusion composition, biotite is the dominant potassium silicate (Guilbert and Lowell, 1974; Hollister, 1978). Both these associations are present at Ajo, but quartz monzonite is the dominant rock type, and consequently, K-feldspar is far more common than biotite.

Hypogene sulfide mineralization is commonly associated spatially with potassic alteration, although temporally sulfide deposition often begins later than potassium metasomatism, which is the initial hydrothermal mineralizing event. This sequence is seen at Ajo, where the highest ore grades are found in potassic alteration zones (Gilluly, 1946; Dixon, 1966). Deposition of the sulfides, however, occurred after the introduction of secondary K-feldspar in these zones. These relations suggest an intimate connection in this porphyry copper deposit between potassic alteration and copper ore
deposition: The physiochemical conditions that here favor potassic alteration may be similar, or preparatory to, sulfide deposition.

The purpose of this study is to evaluate the intensive variables of pressure, temperature, and chemical potentials of solution components present during the potassic alteration stage at Ajo because they represent the early stages of an ore-forming hydrothermal system. Because potassic alteration is primarily fracture-controlled, the focus of this study is on the fractures in the deposit and on the mineralization deposited in those fractures. Hand sample and petrographic observations were made with specific attention to the veins, and all analytical data was gathered from vein-filling minerals. Information and data resulting from this study thus contribute to the growing body of knowledge on fracture-controlled ore-forming processes in porphyry copper systems.

Suitability of the Ajo Ore Deposit as a Study Area

The porphyry copper deposit at Ajo is particularly well-suited to this type of study because potassic alteration is the dominant alteration type, it occurs primarily in one rock composition, quartz monzonite, and it has not been significantly overprinted by succeeding alteration events. K-feldspar is the most common potassium silicate and occurs both as a vein-filling mineral and as pervasive alteration of the host rock, replacing all minerals nonselectively (nomenclature after Tittley, 1982).
The Ajo orebody originally contained a centrally located pegmatitic zone of introduced K-feldspar, quartz, chlorite, and biotite. Because this pegmatite was found to be the earliest phase of hydrothermal mineralization and contained high ore values (Gilluly, 1946), samples from it are the ideal subjects of this study. Although this zone is now mined out, a few remaining samples from it were available for study. In addition, some of the samples collected for this project contained very coarse K-feldspar and quartz and are probably offshoots of the original pegmatite. Destructive sericitization, or phyllic alteration, is poorly developed in the deposit, permitting the isolation of pristine, hypogene potassic alteration mineral assemblages. Vein-filling minerals are sericitized on only a local scale. In addition, supergene effects were also held to a minimum at Ajo. The enrichment zone is thin and easily distinguished, and the bulk of the deposit was not exposed to oxidizing processes.

These geologic characteristics simplified the sampling of the deposit and interpretation of the vein paragenesis, and the nearness of the mine to the University of Arizona and permission of the Phelps Dodge Corporation to enter and study it made it attractive for this research.
CHAPTER 2

GEOLOGICAL BACKGROUND OF THE
AJO ORE DEPOSIT

The New Cornelia open pit copper mine lies adjacent to the south side of the historic mining town of Ajo, Arizona. 136 miles west of Tucson, Arizona on Highway 86. Location and general geology are shown in Figure 1. Gilluly's comprehensive report on the Ajo mining district (1942, 1946) has served as the basis for all subsequent work and is summarized below.

Geologic Setting

Salient features of the geologic setting include the facts that two and possibly three levels of the pluton are exposed, the main body of the pluton is surrounded by gneiss whereas its apex is surrounded by predominantly rhyolitic volcanics, and the fracture patterns and alteration styles of each section are different.

The oldest unit present is the Cardigan Gneiss. It is of generally quartz dioritic composition and presumably of Precambrian age. Concentrator Volcanics, comprising rhyolitic and andesitic flows, flow breccias, and tuffs, were deposited upon the eroded surface of the gneiss. The Cornelia Pluton intruded both gneiss and volcanics and has been dated at 55 and 65 m.y. by Rose and Cook.
Figure 1. Generalized geological map of the New Cornelia Mine in its regional setting (modified after Dixon, 1966).
(1966) and at 63 ± 2 m.y. by Damon et al (1964). Deposition of the Locomotive Fanglomerate, interfingered with the andesitic Ajo Volcanics, followed erosion that exposed the mineralized tip of the intrusion.

Gilluly described three facies of the pluton: a narrow, irregular, quartz diorite border, equigranular quartz monzonite, and porphyritic quartz monzonite. A centrally located, north-northwest-trending pegmatitic zone occurs in the quartz monzonite, and aplite dikes are present. Wadsworth (1968) further distinguished a granodiorite portion of the border and a porphyritic micro-quartz monzonite facies of the main pluton.

During intrusion, a ridge-shaped cupola formed on the stock. Following solidification and mineralization, the cupola was faulted down and to the east on the steeply dipping Gibson Fault and then buried by the fanglomerate. Later rotation of the block containing the pluton on the Little Ajo Mountain Fault to the north resulted in the present steep dip of the fanglomerate to the south. Thus the surface shown on the map was originally a plane in the pluton that dipped approximately 50 degrees north or northeast before rotation. The long axis of the pit points southeastward to the tip of the cupola and northwestward to a "root zone" that was originally connected to the main body of the pluton. Subsequent imbricate and normal faulting in the pit were not recognized by Gilluly, probably because of insufficient depth of exposure. The Arkansas Mountain
Fault, shown in Figure 1 as passing completely through the stock, may have been approximately coeval with the Gibson Fault and served to further truncate and displace the cupola. Gilluly originally mapped it as a fault that merely offset the southwestern edge of the cupola. However, the block on the northwestern side of the Arkansas Mountain Fault bears fresh hornblende and is only weakly altered, whereas the block on the southeastern side, which contains the mine, has chloritized mafic minerals and is strongly altered (Dennis Cox, U.S.G.S., pers. comm., 1981).

Alteration exposed in the deep interior portion of the pluton west of the Gibson Fault is also different from that of the cupola. Compared to the intimate fracturing and intense alteration that characterizes the orebody, there is only weak development of epidote, hematite, and clay (Dennis Cox, U.S.G.S., pers. comm., 1981), and the fractures are spaced further apart.

**Rock Types**

Rock types exposed in the pit comprise quartz monzonite of the Cornelia intrusion, its quartz diorite border facies, the host Concentrator Volcanics, and the fanglomerate that postdates formation of the orebody (Fig. 2). Aside from some clasts eroded from the orebody, the fanglomerate is not mineralized. The bulk of the mineralization occurs in the quartz monzonite, and ore values are also present in the quartz diorite and the host volcanics. The bodies of quartz diorite and volcanic rocks present in the center of
GENERALIZED GEOLOGY OF THE MINE

Figure 2. Recent geologic map of the New Cornelia mine.

Tlf = Locomotive Fanglomerate; Kcv = Concentrator Volcanics; Tcm = Cornelia Quartz Monzonite; Tcd = Cornelia Quartz Diorite. Modified from maps made public by the Phelps Dodge Corporation.
the pit may be outcrops of the underside of the tilted cupola, or alternatively, xenoliths that were stope and entrained during emplacement.

In the mineralized quartz monzonite, the facies most common in the mine area is porphyritic micro-quartz monzonite (Gilluly, 1946; Wadsworth, 1968). The phenocrysts of K-feldspar, plagioclase, biotite, and occasionally quartz are often of similar size but can also be seriate. All of these minerals are also found in the groundmass, but the groundmass is most commonly microapllitic in texture and composition (Figures 3a and 3b). Within this facies, rounded blebs of quartz occur that are interstitial to and poikilitically enclosed by K-feldspar. Where these quartz blebs are present, Gilluly designated this texture as "corroded" and attributed it to later magmatic resorption of K-feldspar by quartz. Although this texture is best developed in the mine area, Gilluly found no strong correlation between the presence of "corroded" texture and extent of mineralization. Porphyritic quartz monzonite in which both phenocrysts and matrix are coarser is also present, as is a more equigranular facies. Aplitic dikes and a strongly mineralized pegmatitic zone also formed part of the original orebody. The pegmatite, striking along the long axis of the intrusion and concentrated in the southeast of what was originally the tip of the intrusion, was at the center of the potassic alteration zone. Secondary K-feldspar was introduced along fractures, replacing the
Figure 3a. Representative sample of quartz monzonite showing micro-quartz monzonitic texture and open-space filling.

Figure 3b. Close-up view of above textures.
quartz monzonite. Silicification and very coarse quartz veins were also found in the pegmatitic zone together with leafy biotite and chlorite. Gilluly established this zone as the site of earliest hydrothermal activity, commencing with the introduction of the K-feldspar.

The quartz dioritic samples collected for this study vary from the samples described by Wadsworth (1968) in that they are composed primarily of even- and fine-grained quartz, biotite, and plagioclase, in that order of abundance (Fig. 4) and contain no pyroxene. In many samples, the biotite and plagioclase are altered to chlorite and sericite. Perhaps the quartz and biotite result from an earlier potassic alteration phase because in the collected samples biotite becomes extremely abundant adjacent to quartz-K-feldspar-anhydrite veins. The quartz diorite was emplaced before the quartz monzonite and is present now only as a narrow border facies on the quartz monzonite.

General Features of Alteration

The most prominent characteristics of hypogene alteration at Ajo are: intense potassium metasomatism; strong chloritization occurring as primary mineralization, alteration of ferromagnesian minerals, and saussuritization of plagioclase; and the absence of clay mineralization. Silicification was also well-developed in and near the pegmatitic zone. These alteration zones are irregularly distributed and not symmetrical as in the idealized model described
GENERALIZED ALTERATION PATTERN

Figure 4. Schematic illustration of generalized distribution of alteration zones in the New Cornelia Mine.

Potassic alteration has been separated into two types, K-feldspar-biotite and K-feldspar-chlorite. K = K-feldspar and biotite; K-chl = K-feldspar and chlorite; prop = propylitic; phyl = phyllic. Modified from maps made public by the Phelps Dodge Corporation.
by Lowell and Guilbert (1970). Figure 4 schematically illustrates the general distribution of alteration zones in the mine.

Potassic, phyllic, and propylitic alterations are all present, with potassic alteration as the most prominently developed. Strongly fracture-controlled, potassic alteration is centered in the intrusion but is concentrated more at its tip. It occurs primarily as K-feldspar veins or quartz veins with K-feldspar selvages, with K-feldspar replacing all the minerals adjacent to the veins. Other minerals such as chlorite, anhydrite, and biotite may also be present in the veins. Phyllic alteration is locally developed in the quartz monzonite but is far more common in the volcanic host rock. It, too, is a strongly fracture-controlled alteration, occurring primarily as quartz-pyrite veins with strongly sericitized alteration haloes. Zones of phyllic alteration can also be identified by sericitization of the feldspars and mafic minerals in the host rock. Propylitic alteration is expressed as saussuritization of plagioclase coupled with chloritization of mafic minerals. This alteration type is apparently more pervasive than either potassic or phyllic alteration; it is present as a broadly based host rock alteration and is not associated with a major stockwork. Epidote-bearing veins are uncommon except in the northern part of the pit, where copper values are not economic; chlorite-bearing veins are usually associated with potassic alteration.
Supergene processes affected only a small portion of the orebody. After displacement on the Gibson Fault and prior to the deposition of the fanglomerate, erosion exposed the mineralized apex to the atmosphere, and leaching and enrichment left a thin chalcocite blanket. After rotation on the Little Ajo Mountain Fault and further erosion, a second cycle of supergene processes began. This time, leaching was ineffective, and most of the copper remained as malachite and chrysocolla in the oxidized capping. This carbonate-silicate capping was the original ore mined at Ajo. Unlike most porphyry copper deposits, pyrite is a meager constituent at Ajo. This scarcity may have contributed to the inefficacy of supergene sulfide enrichment, but the presence of the first enrichment blanket indicates that it was not the only factor.

Sulfide Ore Mineralization

The hypogene sulfide minerals present at Ajo are chalcopyrite, bornite, and molybdenite. Chalcopyrite and bornite, in the approximate ratio 4:1, are the primary copper ore minerals. These sulfides occur in veins, veinlets, and as disseminated blebs in the host rock, usually in local replacement of chlorite and biotite. In general, copper grades are highest in the quartz monzonite, intermediate in the quartz diorite, and lowest in the volcanics (Dixon, 1966). Molybdenite appears in veins with quartz in both the quartz monzonite and volcanics. It also occurs as
disseminated blebs throughout the volcanics, where molybdenum values are highest.

Gilluly mentioned native gold derived from the oxidized ore; sulfide ore is also gold-bearing. From early recorded smelter production values, Gilluly surmised that gold values were more closely associated with copper sulfides than with pyrite.

Mineralization decreases in the direction of the "root zone" to the northwest.

Structure

Orthogonal joint sets in the Cornelia Pluton currently display east-northeast and north-northwest trending orientations that are similar to systematic orientations exhibited by many Laramide plutons of Arizona (Rehrig and Heidrick, 1972). As rotation of the fault block on the Little Ajo Mountain Fault was primarily vertical and not lateral, these orientations approximate their original directions. Establishment of more systematic fracture orientations within the mine itself was found by Gilluly to be difficult because of the extreme shattering of the orebody, which he described as "crackle breccia". This difficulty is compounded by complex post-mineralization faulting. Joralemon (1914) also noted, in the earliest published paper on the Ajo mining district, that in any portion of the porphyry there is generally a well-marked direction of strongest fracturing, but in the porphyry mass as a whole no such
generalization can be made. He did comment, however, that the larger fissures generally trend N20W.

While a strongly preferred direction in fracture orientations is difficult to determine for the New Cornelia orebody, some systematic variation is evident in the degree of fracturing experienced by the intrusion as its hydrothermal system evolved. This variation is a general trend toward a decrease in fracturing and is discussed in more detail later in this report.
CHAPTER 3

METHODS OF STUDY

**Sampling**

Over 70 samples were collected within the New Cornelia open pit; sample locations are shown in Figure 5. Sampling was not rigidly systematic, but care was taken that each alteration and rock type was adequately represented, with special attention given to collecting samples of potassic alteration. The eastern edge of the pit was avoided because of the presence of the supergene zone.

**Geological Observations**

Porphyry copper systems are characterized by intensive fracturing that is assumed to record the physiochemical conditions experienced by the system in the changing mineralogy, morphology, frequency, and orientation of crosscutting vein sets. Because potassic alteration is but one stage of this constantly evolving system, an understanding of the relationship between fractures containing potassic alteration assemblages and other vein types was necessary before undertaking analytical studies.

Each rock collected was first slabbed and then inspected under a binocular microscope for vein mineralogy and morphology, host rock mineralogy, and crosscutting relations among veins. In over
Figure 5. Sample location map.

Triangles enclose localities of the feldspars analyzed in this study. 1-12 samples were collected from each locality. Because the geology shown on Figure 2 is not current, it does not reflect the geological distribution of the samples and is thereby omitted from this map.
half of the samples, two or three dimensions exceeded 25 centimeters, providing a large cross-sectional area for the observation of all types and their structural relations. Polished thin sections were made for a selected majority of the samples, and these were examined with a standard petrographic microscope to verify observations on the macroscopic scale and to observe microscopic textures. Paragenesis among the vein types was established, particularly the placement of veins containing potassic alteration mineral assemblages. As noted in the preceding discussion of the geological background of this deposit, systematic fracture orientations could not be discerned within the orebody; however, the established vein paragenesis, together with observations of the mineralogy, morphology, and frequency of each vein type, sufficiently describes the nature of fracturing in the Ajo deposit and provides the necessary geological context developed below for interpretation of the analytical data.

Analytical Studies

In the quartz monzonite samples, veins containing potassic alteration minerals were found to occur in two closely related generations: The initial stage was deposition of vein-filling K-feldspar accompanied occasionally by biotite; deposition of quartz with K-feldspar restricted to vein selvages followed. In the pegmatite samples, this sequence is seen as deposition of coarse K-feldspar immediately adjacent to the host rock with coarse quartz deposited on it or veins of quartz cutting it. Quartz is sometimes
accompanied by anhydrite, chlorite, and rarely, biotite. Whether the chlorite is primary or an alteration product of biotite is difficult to ascertain. This pegmatitic zone contained high copper values and, as mentioned in the description of mine geology, was found by Gilluly to be the earliest manifestation of the hydrothermal system. He further concluded that the circulation of hydrothermal fluids commenced soon after the last stages of magmatic differentiation of the Cornelia Pluton. Deposition of K-feldspar and biotite during this stage may have occurred at near-magmatic temperatures, making them the highest-temperature hydrothermal minerals. Vein-filling K-feldspar was deposited earlier than the quartz during potassic alteration. Because the most common and widespread minerals of this assemblage are quartz and K-feldspar, the analytical studies were made on these two minerals.

Fluid inclusions in quartz from the pegmatitic zone analyzed for geothermometric information on potassic alteration also permitted approximation of the pressure at the time of formation. Fluid inclusions in K-feldspar would have been a valuable source of information, but none were discovered in these samples.

By solid solution, potassium feldspar can compositionally and structurally readjust toward equilibrium in response to changing temperature and pressure provided the required elements are present. Structural and compositional analysis of vein-filling potassium feldspars therefore allowed approximations of temperatures
prevailing during potassic alteration and chemical potentials of solution components. In addition, petrography revealed that these potassium feldspars were macroperthitic, simplifying interpretation of their structure and directing compositional studies toward coexisting alkali feldspars rather than potassium feldspar alone. Structural analysis by least squares refinement of X-ray diffraction data yielded geothermometric information interpreted from theoretical and experimental crystal chemistry of monoclinic potassium feldspars as summarized in Appendix A. Chemical compositions of coexisting potassic and sodic phases were obtained with the electron microprobe. Existing phase relations within the feldspars and among the minerals coexisting in the veins were combined with these chemical compositions to predict chemical potentials of solution components present during potassic alteration.

The analytical techniques themselves are described in detail in Appendix B.
CHAPTER 4

FRACTURE-CONTROLLED MINERALIZATION AT AJO

Mineral assemblages in veins at Ajo exhibit complicated relationships resulting from the reopening of veins, in many cases several times. In some fractures more than one generation of quartz can be distinguished. Open-space-filling textures are common and serve as useful indicators of depositional sequence, particularly for veins that were later filled in and sealed; many veins contain a center zone of different mineralogy from that at the edge of the vein. These textures and the major vein types are illustrated in Figures 3a, 3b, 6, 7, 8 and 9.

Vein Paragenesis

The following sequence was established for hypogene, fracture-controlled, hydrothermal mineral assemblages at Ajo. The minerals are listed in their approximate order of volumetric abundance; "(s)" indicates the mineral is found primarily in the selvage and not within the vein itself.

(1) K-feldspar ± biotite
(2) Quartz ± anhydrite ± K-feldspar(s) ± chalcopyrite ± bornite ± chlorite ± biotite(s)
Figure 6a. Pegmatite displaying sequential deposition of early K-feldspar, quartz, and chalcopyrite-borneite veins.

ksp = K-feldspar; qtz = quartz; cpy = chalcopyrite; bn = bornite.

Figure 6b. Vein type 2 quartz vein with K-feldspar selvage.

Branching pattern is common in this vein type.
qtz = quartz; ksp (s) = K-feldspar selvage;
cpy = chalcopyrite; chl - chlorite.
Figure 6a. Pegmatite displaying sequential deposition of early K-feldspar, quartz, and calcopyrite-bornite veins.

Figure 6b. Vein type 2 quartz vein with K-feldspar selvage. Branching pattern is common in this vein type.
Figure 7a. Chalcopyrite vein with K-feldspar selvage, transitional from vein type 2 to vein type 3.

Figure 7b. Chalcopyrite vein of vein type 3 offsetting a K-feldspar-quartz vein (vein type 2).
Figure 8. Vein containing several generations of quartz.

Earlier K-feldspar veinlets are altered to sericite where overlapped by sericitic envelope. Other side of the vein is sealed off from destructive sericitization. cpy = chalcopyrite
Figure 9. Pyrite-Chalcopyrite vein in propylitized quartz monzonite.

py = pyrite; cpy = chalcopyrite; qtz = quartz; prop = propylitized quartz monzonite.
Figure 9. Pyrite-chalcopyrite-quartz vein in propylitized quartz monzonite.
(3) Chalcopyrite ± bornite ± quartz ± pyrite ± K-feldspar(s) ± muscovite

(4) Quartz ± pyrite + sericite(s) ± chlorite(s) ± chalcopyrite ± epidote(s) ± molybdenite

5) Calcite

In addition to the 5 vein types listed, discontinuous biotite-chlorite veinlets are present but occur only rarely and do not persist for more than a few centimeters; consequently they are difficult to place in the major vein chronology. These veinlets appear to have been first deposited after the early K-feldspar (vein type 1) and then sporadically deposited through all of the succeeding mineralizing and altering events. Most of the veinlets contain only chlorite; biotite is rare and is usually found altering to chlorite. This group may actually consist of biotite-altering-to-chlorite veinlets and primary chlorite veinlets rather than one group of original biotite veinlets in varying states of alteration to chlorite. This distinction is not verifiable from these samples.

Propylitic alteration is pervasive in many areas of the pit, and the majority of these tiny veinlets may be chlorite deposited during propylitic alteration.

Magnetite veining that Gilluly found strongly developed in and near the pegmatite zone is not present in these samples.

The suggested comparative duration of deposition of each mineral as determined from Gilluly's observations and textural
relations seen in these samples is depicted in Figure 10. These
textures and a detailed description of the mineralogy and morphology
of each vein type follows.

Vein Mineralogy and Morphology

K-Feldspar ± Biotite Veins

The K-feldspar ± biotite assemblage is the earliest fracture-
related hydrothermal mineralization and was particularly well
developed in the pegmatitic zone. There it did not occur primarily as
distinct veins, but as linear zones of coarse-grained masses of
reddish pink K-feldspar that replace the host rock and are
accompanied by minor amounts of biotite. Most of the biotite was
later chloritized, perhaps during the later stages of potassic
alteration or at the onset of propylitic alteration. In other areas
of the deposit this assemblage appears as K-feldspar and biotite
crystals in open spaces or solid veins of K-feldspar up to 1
centimeter wide that are often reopened and filled with later quartz,
anhydrite, or sulfides. Hairline fractures showing only a line of
replacement K-feldspar without other minerals are also common.

In some of the samples, plagioclase adjacent to the vein is
altered to a soft, white mixture of montmorillonite-sericite-quartz-
kaolinite, listed in order of abundance as determined from X-ray
diffraction. This alteration is always associated with K-feldspar or
quartz veins and not with sericite-bearing veins; it is converted to
sericite where overlapped by phyllic alteration. Although this
SEQUENCE OF HYDROTHERMAL MINERALIZATION IN VEINS AT AJO

K-feldspar  EARLY  LATE
Biotite
Quartz
Anhydrite
Pyrite
Chalcopyrite
Bornite
Chlorite
Sericite
Epidote
Molybdenite
Calcite

Based on Gilluly (1946, p. 75) and samples of this study.

Diagrammatic representation of the duration of deposition of fracture-controlled mineralization.
alteration of plagioclase appears to be controlled by fluids from the same conduit as the vein-filling minerals its occurrence is irregular and therefore may result from later, probably lower-temperature fluids. This type of alteration is restricted to local areas within the deposit; it is not found with all K-feldspar or quartz veins and is not accompanied by the host rock silicification and chloritization that is common at Ajo. It is also best developed in the pegmatitic zone; a pegmatite sample is shown in Figure 6a.

Quartz ± Anhydrite ± K-Feldspar(s) ± Chalcopyrite
± Bornite ± Chlorite + Biotite(s) Veins

This assemblage, designated "late potassic", composes the most widespread and common vein type. Quartz is the primary vein-filling mineral and is often accompanied by purple anhydrite, a rare leaf of chlorite or biotite, or a bleb of chalcopyrite or bornite. Quartz and chlorite, deposited on K-feldspar in the pegmatite (Fig. 6a) are considered part of this assemblage. K-feldspar forms as an alteration halo to the vein and is not usually a vein-filling mineral except in the quartz diorite. In the quartz diorite biotite forms the selvage and K-feldspar is found among the vein-filling minerals. In some veins, initial deposition of quartz displaying comb structure and euhedral terminations is followed by deposition of a mixture of K-feldspar and quartz that seals the fracture.
Late potassic veins show widths up to 10 centimeters and commonly have narrower branches striking off the main vein (Fig. 6b). The extent of the K-feldspar mineralization seems to be related to the number of fractures transecting a given area rather than the size of any individual vein; many quartz veins that are several centimeters wide display K-feldspar selvages similar in extent to those on veinlets a millimeter wide, whereas areas with numerous fractures, however narrow, showed widespread replacement by K-feldspar.

Chalcopyrite ± Bornite ± Quartz ± Pyrite ± K-Feldspar(s) Veins

This group constitutes the major ore depositional event, with chalcopyrite and bornite being the most common sulfide minerals. Pyrite makes up less than 5 percent of this assemblage. Quartz is often present. Some veins of this set display a K-feldspar selvage; it is not unusual to find a solid chalcopyrite vein with a K-feldspar selvage. Flakes of muscovite sometimes occur within chalcopyrite grains. Chalcopyrite is the most abundant sulfide and varies considerably in occurrence. It is present as pods or clumps associated with K-feldspar-chlorite alteration, in veins that attain widths of over 1 centimeter, and with or without bornite in narrow (< 1 mm width) stringers that form local stockworks. These stringers repeatedly cut potassic veins and traverse their interiors. In many veins the sulfides were deposited later than the quartz; in some veins, sulfides and quartz are interlocked and appear
to be coeval. Chalcopyrite continued through the stage of phyllic alteration, during which it formed in veins with pyrite and quartz. Chalcopyrite is also more common than pyrite as a disseminated mineral, usually replacing chlorite or biotite in the host rock.

Bornite deposition, thought by Gilluly (1946) to have been initiated later than chalcopyrite deposition, terminates with this main sulfide event and is more restricted in distribution. It may occur alone or with chalcopyrite as a vein-filling mineral but is never found replacing chlorite or biotite. Bornite is most common in the south and southwest sections of the mine, toward the original tip of the intrusion. There is some supergene bornite at Ajo (Gibson, 1981) but in these samples the bornite is clearly hypogene.

The morphology of the stockwork sulfide veinlets can be straight or sinuous and irregular, often thickening and thinning. Many are simply linear series of unconnected sulfide blebs. Larger veins are straighter in overall shape but also have irregular edges (Figs. 7a and 7b).

Quartz ± Pyrite ± Sericite(s) ± Chlorite(s) ± Chalcopyrite ± Molybdenite ± Epidote(s) Veins

These veins compare in persistence and width to potassic veins but are limited in extent. They are also more common in the volcanic host rocks than in the intrusion. Sericitization of plagioclase, often in an albite matrix, is present to some degree everywhere, but the typically destructive sericitic selvage on a
quartz-pyrite vein (phyllic alteration *sensu stricto* as defined in Rose (1970) and Beane (1982)) is only locally developed. Where these veins cut across potassic veins, all minerals encompassed by the sericitic selvage are converted to sericite or sericite-chlorite (Fig. 8).

Quartz and pyrite may be accompanied by chalcopyrite in the vein (Fig. 9). Chlorite and epidote are present in the selvage where the host rock is more mafic in composition. In the quartz monzonite, molybdenite forms as "moly paint" between the edge of a quartz vein and a sericitic selvage or as a thin line in the center of a quartz vein. Molybdenite is rare except in the volcanic host rocks where it appears primarily as disseminated blebs.

**Calcite Veins**

Hypogene calcite veins, generally less than 5 millimeters in width, crosscut all other vein types. They are far more numerous on a microscopic scale than on a macroscopic scale. Gilluly mentioned occasional sulfides associated with these veins but this association was not seen in these samples.

**Fracture Densities**

Fracture density measurements, where fracture density = total length of fractures (cm) / unit area (cm²) (Haynes and Titley, 1980), were taken on samples collected from the pit and augmented by several outcrop measurements.
The outcrop measurements were taken by measuring the integrated lengths of macroscopic veins within a 1 meter square area on the outcrop face. Sample measurements were taken on the slabbed surfaces, 64 cm$^2$ or greater, of hand samples. The total number of outcrop and sample measurements is 52.

Fracture densities were measured for each vein type present in a sample. The apparent trend with increasing time is one of decreasing fracture abundance, a trend illustrated in Figure 11. At Ajo, fracturing was well-developed during potassic alteration, increased slightly during sulfide deposition, then tapered off during phyllic alteration (Fig. 11). Owing to the occurrence of K-feldspar and biotite primarily as coarse-grained masses rather than veins and the scarcity of macroscopic calcite veins in these samples, fracture density measurements are restricted to vein types 2, 3, and 4, which together constitute over 90% of the macroscopic fracturing in these samples, with the exception of the pegmatitic masses. Quartz-anhydrite-K-feldspar veins (vein type 2) of the potassic alteration assemblage had an average fracture density of 0.31 cm$^{-1}$ (6 outcrop measurements, 30 hand sample measurements). Chalcopyrite-bornite veins and veinlets (vein type 3) average 0.33 cm$^{-1}$ (18 hand sample measurements). Phyllic quartz-sericite-pyrite veins (vein type 4) average 0.22 cm$^{-1}$ (8 hand sample measurements). At Ajo, ore values are spatially associated with potassic alteration. Temporally, sulfide deposition followed, and may have slightly overlapped, late-
Figure 11. Fracture densities for vein types 2, 3 and 4 at Ajo.
stage potassic alteration. It is therefore not unexpected that the fracture abundances of vein types 2 and 3 (0.31 cm\(^{-1}\) and 0.33 cm\(^{-1}\) respectively) are similar. These values are slightly higher than the fracture densities reported by Haynes and Titley (1980) for the Ruby Star Granodiorite, associated with the Sierrita porphyry copper deposit, which also show similar trends.

Since the geologic map is not current and the majority of samples are of one rock type, quartz monzonite, fracture densities were not evaluated by rock type or geological setting. However, extrapolation of the fracture density values specific to each vein type to the areas in the pit where those vein types are dominant (based on the general geology and alteration in Figures 2 and 4) points out several trends borne out by geological observations: fracturing is strongest at the tip of the intrusion, decreasing toward the "root zone", and is also more abundant in the intrusion than in the host rock.
CHAPTER 5

FLUID INCLUSIONS IN QUARTZ

Fluid inclusions in quartz adjacent to early K-feldspar in the pegmatitic zone were analyzed in order to establish the temperature of the onset of quartz deposition and to characterize the temperatures and salinities of fluids circulating during this stage of potassic alteration. However, because of multiple refracturing of the quartz, evident from the numerous, crosscutting planar arrays of secondary fluid inclusions, only the highest temperature fluids could be assigned with any certainty to potassic alteration alone.

Terminology described by Nash (1976) is used here to classify the fluid inclusions. Type I inclusions are liquid-rich and homogenize to a liquid. Type II inclusions are vapor-rich and homogenize to a vapor. Of his Type III inclusions, which contain a halite daughter salt, two types were observed at Ajo: In the first category, the salt dissolved before the vapor bubble disappeared; in the second type, the salt dissolved after the vapor bubble disappeared. These inclusions are designated Type IIIa and Type IIIb, respectively. The homogenization temperatures for Type III inclusions can be the temperature of vapor bubble disappearance or of salt dissolution, whichever is higher.
All the inclusions were conservatively considered to be secondary inclusions because of the extensive fracturing (Roedder, 1979). The hottest, hypersaline (see Fig. 12) inclusions were found in a pocket of quartz embaying the K-feldspar in the sample AJ-Peg (Fig. 6a), and within the pocket there were no visible fractures. These inclusions might be primary, but because the designation would not be unequivocal, they were also classified as secondary.

All hypersaline inclusions were found in groups of 3 or more, and some contained a flake of hematite or an unidentifiable daughter mineral. Unfortunately the majority of inclusions of all types were less than 10 microns in diameter, so that optical resolution for salt dissolution and homogenization to a vapor phase were extremely limited. Also, in most of the Type II inclusions, the vapor phase composed up to 90 percent of the visible surface, making it impossible to establish the filling temperature with any acceptable degree of accuracy. Many inclusions appeared to contain only a vapor phase, being completely dark at room temperature.

Decrepitation of individual inclusions and planes of inclusions was common at temperatures over 400°C. This rupturing seemed to be more prevalent among vapor-rich and hypersaline inclusions. Occasionally an inclusion would decrepitate before the salt dissolved in a Type IIIb inclusion.
SECONDARY FLUID INCLUSIONS IN QUARTZ FROM THE PEGMATITE ZONE AT AJO, ARIZONA
Numerous solid inclusions were present, both within the fluid inclusions and more often, in patches throughout the quartz. Most were anhedral, dark, and unidentified. Only hematite could be readily identified by its red color.

**Homogenization Temperatures**

The distribution of the homogenization temperatures of all four types of fluid inclusions is given in Figure 12. These temperatures are raw data collected at 1 atmosphere pressure. The hottest fluids are in type IIIb inclusions that homogenized at an average temperature of 420°C. A minimum pressure of formation can be obtained for these multi-phase inclusions (Roedder and Bodnar, 1980) and was calculated to be 650 bars. This pressure falls within Gilluly's (1946) estimated range of 300-1000 bars at the time of intrusion. The temperature correction for 650 bars, extrapolated from temperature-pressure-salinity curves in Potter (1977), is around +50°C. This correction is only a first approximation because experimental data for the NaCl-H2O system are collected at vapor saturation, and therefore salinities for Type IIIb inclusions are themselves approximations. Applying the correction of +50°C raises the hottest homogenization temperature to 470°C. This temperature is taken to be the temperature of the onset of quartz deposition in the pegmatitic zone.

The major peak centered around 230°C in the histogram represents a significant event in the hydrothermal history. Again as
a first approximation the correction of +50°C is applied, raising this temperature to 280°C. This invokes the further assumption that the pressure at the time these fluids circulated was not significantly different from the pressure existing when the hottest fluids circulated, a reasonable assumption for the epizonal porphyry copper environment (Beane, 1982). Because the samples analyzed were not affected by phyllic alteration, it is difficult to attribute this peak to a phyllic event. At 280°C potassic alteration may still have been in progress. These and other possibilities are discussed in Chapter 7.

**Salinities**

Obtaining salinities by measuring freezing point depression (Potter, Clynne, and Brown, 1978) proved difficult for the vast majority of fluid inclusions because of their small size. Even the larger, > 10 micron, inclusions often did not freeze. This resistance might be attributable to the inability of the inclusion to overcome the kinetics of ice nucleation. Most of the salinities were obtained from Type III inclusions (Potter, Babcock, and Brown, 1977) and, as stated before, salinities for Type IIIb inclusions are approximate.

Salinity data are given in Table 1. There are not enough points to make a significant temperature-salinity curve. The salinities show extensive variations which preclude the association of a specific salinity range with a specific thermal event.
Table 1. Fluid Inclusion Salinities in Pegmatitic Quartz.

<table>
<thead>
<tr>
<th>Method of Establishing Salinity</th>
<th>Temp. of Vapor Bubble Disappearance (°C)</th>
<th>Temp. of Freezing or Halite Dissolution (°C)</th>
<th>Salinity (wt. %)</th>
<th>Molality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fz. Pt. Dep.</td>
<td>-</td>
<td>-4.9</td>
<td>7.72</td>
<td>1.43</td>
</tr>
<tr>
<td>Fz. Pt. Dep.</td>
<td>225</td>
<td>-13.9</td>
<td>17.83</td>
<td>3.71</td>
</tr>
<tr>
<td>Fz. Pt. Dep</td>
<td>-</td>
<td>-20.7</td>
<td>23.29</td>
<td>5.19</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>210</td>
<td>125</td>
<td>28.77</td>
<td>16.91</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>198</td>
<td>172</td>
<td>30.59</td>
<td>7.54</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>170</td>
<td>246</td>
<td>34.40</td>
<td>8.97</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>313</td>
<td>286</td>
<td>36.95</td>
<td>10.03</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>331</td>
<td>369</td>
<td>43.31</td>
<td>13.07</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>282</td>
<td>413</td>
<td>47.27</td>
<td>15.34</td>
</tr>
<tr>
<td>Salt Diss.</td>
<td>264</td>
<td>424</td>
<td>48.33</td>
<td>16.00</td>
</tr>
</tbody>
</table>
CHAPTER 6

VEIN-FILLING POTASSIUM FELDSPAR STUDIES

Six fracture-filling potassium feldspars from the early potassic alteration assemblage were chosen for detailed structural and compositional analysis. One of these samples was collected from the pegmatitic zone that is now mined out; it was donated for study by Dr. Richard Beane. These samples are cut by later potassic minerals and sulfides, and four of them show slightly sericitized plagioclase adjacent to the vein. Late stage potassic alteration (vein type 2), marked by the initiation of quartz deposition, is represented by only one sample. In type 2 veins, K-feldspar is present primarily as selvages on quartz-anhydrite veins and is not easily separable from the host rock, raising the possibility of contamination by plagioclase. The chosen sample is intimately intergrown with quartz in the vein, but because quartz peaks are readily identified in X-ray diffraction patterns, the sample was thought to be acceptable. All of the samples are free from destructive effects of subsequent phyllic alteration. The location of each sample, with the exception of the sample donated by Dr. Beane, is shown on the sample location map in Figure 5. The mineralogic setting of each sample, as well as other notable
features, is given in Table 2. Quartz monzonite is the host in all cases.

Morphologically, the early potassic feldspar samples can be divided into a pegmatitic group (AJ-Peg, AJ-13), an open-space-filling group (AJ-12a, AJ-5b), and a vein group (AJ-17, AJ-15c) (Table 2). The K-feldspar of R-4-F fills a vein center, formerly an open space left by the comb quartz that fills most of the vein. Reddish tones in the feldspars may be caused by ferric iron oxide, presumably as hematite (Smith, 1974b), but this correlation is not substantiated by observations in this study or studies of K-feldspars in other porphyry copper deposits (Chivas, 1978).

Each sample is macroperthitic, and both the sodic and potassic phases were analyzed for chemical composition. Unfortunately none of the samples displayed more than five albite peaks in the X-ray diffraction patterns so that information on the structural state of the exsolved albite was not obtained.

Details of the analytical procedures are given in Appendix B, and a summary of the crystal chemistry of potassium feldspars is given in Appendix A.

**Significance of Microtextures**

Petrographic studies of the feldspars revealed microscopic textures of significance to the understanding of the subsolidus history of the crystals and the interpretation of the chemical and structural data. Two important microscopic textures are present:
Table 2. Descriptions of Analyzed Perthitic Feldspars

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elevation (feet)</th>
<th>Color</th>
<th>Alteration Type</th>
<th>Perthitic Texture (% of surface area; varieties given in order of abundance)</th>
<th>Turbidity (% of surface area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AJ-Peg</td>
<td>unknown</td>
<td>Reddish pink</td>
<td>Early potassic</td>
<td>$&lt; 20$; patch and string, in equal amounts</td>
<td>$&gt; 80$</td>
</tr>
<tr>
<td>AJ-13</td>
<td>890</td>
<td>Reddish pink</td>
<td>Early potassic</td>
<td>$&lt; 20$; string, patch, braid</td>
<td>$&gt; 80$</td>
</tr>
<tr>
<td>AJ-12a</td>
<td>890</td>
<td>Dark pink</td>
<td>Early potassic</td>
<td>$&lt; 15$; string, patch, lamellae</td>
<td>$&gt; 80$</td>
</tr>
<tr>
<td>AJ-5b</td>
<td>885</td>
<td>Dark pink</td>
<td>Early potassic</td>
<td>$&lt; 10$; string, patch, lamellae, and incipient braiding</td>
<td>$&gt; 80$</td>
</tr>
<tr>
<td>AJ-17</td>
<td>1180</td>
<td>Dark pink</td>
<td>Early potassic</td>
<td>$&lt; 5$; tiny patches</td>
<td>$&lt; 50$</td>
</tr>
<tr>
<td>AJ-15c</td>
<td>1180</td>
<td>Dark pink</td>
<td>Early potassic</td>
<td>$&lt; 5$; lamellae, some patch and string; kinking and incipient braiding</td>
<td>$&lt; 50$</td>
</tr>
<tr>
<td>R-4-F</td>
<td>1180</td>
<td>Pink</td>
<td>Later potassic</td>
<td>$&lt; 5$; string, patch, and lamellae</td>
<td>$&gt; 50$</td>
</tr>
</tbody>
</table>
turbidity, or cloudiness, and macroperthite. Both are present in all samples but to varying degrees (see Table 2). Turbidity has been attributed to the presence of numerous, sub-microscopic, fluid-filled vacuoles (Folk, 1955) or to the water-catalyzed exsolution of transition metal oxides from the feldspar structure (Smith, 1974b). It has also been associated with oxygen isotope exchange in feldspars (O'Neill and Taylor, 1967). Any or all of these factors may be operative at Ajo; there is no evidence favoring one effect over the others. The presence of turbidity, however, does indicate subsolidus interaction with fluids. Such interaction enhances the maintenance of equilibrium between crystal and fluid in a cooling hydrothermal system.

Possibly the more informative texture is macroperthite. The feldspars exhibit, in order of abundance, the following varieties: string perthite, patch perthite, lamellae, and braid perthite (nomenclature after Smith, 1974b). Photomicrographs in Figures 13 and 14 illustrate these textures. A study by Lorimer and Champness (1973) suggests that these varieties of perthite represent stages of coarsening during spinodal decomposition, beginning with lamellar exsolution and progressing to wavy lineations of string perthite which eventually develop kinks to form a braidlike pattern. Rafting into separate, rhombic-shaped patches is the final stage. While these perthites are not exactly rhombic, and their outlines are
Figure 13a. Albitic lamellae in macroperthite showing incipient broadening to string perthite.

Figure 13b. Wavy string perthite beginning to kink.
usually obscured by turbidity, the textures present resemble the textures of this sequence (Figs. 13 and 14).

Preservation of the original Al-Si ordering state is favored by spinodal decomposition. During this process, separation of a sodic phase occurs in an essentially immobile Al-Si-O framework. Furthermore, the absence of lattice strain at the interface of the sodic and potassic phases is evidenced by the coarseness of the perthite and the visible albite twinning in the triclinic phase. These physical characteristics are essential to a reasonable interpretation of the data. Since only the most important points can be given here, a more detailed discussion of the limits of Al-Si geothermometry and the main theories of subsolidus processes in alkali feldspars is provided in Appendix A.

**Chemical Compositions**

Compositions of coexisting albite and orthoclase determined by electron microprobe in these perthitic feldspars are close to their respective endmember compositions in all the samples (Fig. 15). The exsolved albite is slightly more homogeneous than the orthoclase host. FeO and BaO were also analyzed for, but neither was usually present to even a hundredth of a mole percent, and neither showed any consistent presence or pattern. Representative analyses are given in Appendix C.
Figure 14. Isolated patch perthite in turbid host.
Figure 15. Distribution of electron microprobe analyses of perthitic feldspars.
The subsolidus equilibrium curve of coexisting alkali feldspars is the solvus shown in Figure 16. This solvus is calculated from activity coefficients and data given in Thompson and Waldbaum (1968, 1969). Compositions of two-phase feldspars, located by solid dots on the solvus, are listed at temperatures of interest discussed throughout this text. With decreasing temperature the composition of each phase becomes respectively more sodic or more potassic.

The most sodic and most potassic compositions attained in each sample are listed in Table 3. These compositions, particularly of the orthoclase host, exceed the equilibrium compositions of Ab$_{96}$ and Or$_{92}$ shown on the solvus at 25°C. Given the distribution of spot analyses shown in Figure 15, a possible explanation of this disparity may be that it is the average composition of each phase across the crystal that more closely approaches the equilibrium composition, and the excessively, or insufficiently, sodic or potassic compositions are attained only on a local scale of 2 microns (size of the electron beam). It should be noted that a statistically acceptable average composition, or bulk composition, for each phase would require either a statistically valid pattern for taking electron microprobe analyses or bulk chemical analyses, neither of which was feasible for this study of perthitic feldspars. However, the structurally derived compositions are essentially average, or bulk, compositions because X-ray diffraction measures an average structural state for a crystal
Figure 16. Strain-free solvus for alkali feldspars calculated from Thompson and Waldhauser (1968, 1969).
Table 3. Sodic and Potassic Compositions in Perthitic Feldspars

<table>
<thead>
<tr>
<th>Sample</th>
<th>Most Sodic $X_{Ab}$</th>
<th>Most Potassic $X_{Or}$</th>
<th>Potassic (cell volume) $X_{Or}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AJ-Peg</td>
<td>.97</td>
<td>.96</td>
<td>.93</td>
</tr>
<tr>
<td>AJ-13</td>
<td>.98</td>
<td>.97</td>
<td>.95</td>
</tr>
<tr>
<td>AJ-12a</td>
<td>.99</td>
<td>.97</td>
<td>.92</td>
</tr>
<tr>
<td>AJ-5b</td>
<td>.99</td>
<td>.97</td>
<td>.94</td>
</tr>
<tr>
<td>AJ-17</td>
<td>.95</td>
<td>.93</td>
<td>.91</td>
</tr>
<tr>
<td>AJ-15c</td>
<td>.99</td>
<td>.95</td>
<td>.92</td>
</tr>
<tr>
<td>R-4-F</td>
<td>-</td>
<td>.96</td>
<td>.96</td>
</tr>
</tbody>
</table>
that contains complex domains of varying composition (Stewart, 1975). When the highest mole percent \( \text{KAlSi}_3\text{O}_8 \) for each sample is graphed against the composition calculated from its cell volume, the structurally derived compositions are generally lower and closer to the equilibrium compositions (Fig. 17). This difference might be attributed to strain in the crystal lattice undetected by the X-ray technique used here; however, the presence of macroperthite argues against lattice strain. (This criterion for the absence of lattice strain is elucidated in Appendix A).

The presence or absence of alkali equilibrium significantly affects the interpretation of the structural data presented in the following section because the results of Al-Si order/disorder experiments vary according to the status of the alkali exchange. Attainment of alkali equilibrium is assumed for these samples.

Experimental and theoretical studies of substitutional order/disorder in potassium feldspars are also based on an Al-Si stoichiometry of 1:3, for Al and Si respectively. The \( \text{Al}/(\text{Al} + \text{Si}) \) ratios depicted in Figure 18 cluster around 0.25 with a very slight increase in the sodic phase attributable to coupled substitution of Ca-Al for Na-Si in the albite. These ratios demonstrate the adherence of these natural, hydrothermal alkali feldspars to stoichiometric tetrahedral site occupancy.
Figure 17. Comparison of maximum orthoclase content determined from electron microprobe and orthoclase content calculated from cell volumes (Stewart and Wright, 1974).

Large circles are error circles.
Figure 18. Al-Si stoichiometry of perthitic feldspars.
Structural States

Unit cell edges, the Z ordering parameter, and the mole percent KAlSi₃O₈ calculated from the cell volumes are listed for each sample in Table 4. As order increases, \( c \) increases and \( b \) decreases (Stewart, 1975) so that plotting these lattice parameters against each other reveals their general structural state. The \( b - c \) plot in Figure 19 shows the early potassic feldspars clustered together within a narrow range at a structure intermediate between that of high sanidine and maximum microcline. Error bars for R-4-F, the later feldspar, are much larger than those of the other samples, which fall within the ranges found in the published literature. Because the K-feldspar in this sample is intimately intergrown with quartz, interference from quartz peaks, originally assumed to be negligible, may have caused the large errors. It may also be that, for unknown reasons, this sample which crystallized later in the hydrothermal history has a more complex structure than the others, and this structure is accordingly less resolvable. Bearing this qualification in mind it can be said that R-4-F appears to be more ordered than the early potassic samples, but the exact extent of this difference is difficult to ascertain.

The absence of lattice strain as evidenced by the coarseness of the perthitic textures is critical to the correct evaluation of lattice parameters. Strained lattices commonly yield anomalous cell parameters that cannot be used for assessment of ordering states
Table 4. Direct Cell Parameters for Vein-Filling Potassic Feldspars

<table>
<thead>
<tr>
<th>Sample</th>
<th>0.00a(A)</th>
<th>0.0ob(A)</th>
<th>0.0oc(A)</th>
<th>0.00b(deg.)</th>
<th>Volume (Å³)</th>
<th>Mole% KAlSi3O8</th>
<th>Z</th>
<th>* No. of Peaks Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>AJ-Peg</td>
<td>8.576</td>
<td>12.988</td>
<td>7.201</td>
<td>116.04</td>
<td>720.7</td>
<td>93.4</td>
<td>.4400</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
<td>0.02</td>
<td>0.2</td>
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<td></td>
</tr>
<tr>
<td>AJ-13</td>
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<td>721.2</td>
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<td>.4475</td>
<td>15</td>
</tr>
<tr>
<td></td>
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<td>0.003</td>
<td>0.001</td>
<td>0.02</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AJ-12a</td>
<td>8.579</td>
<td>12.983</td>
<td>7.198</td>
<td>116.05</td>
<td>720.3</td>
<td>92.4</td>
<td>.4404</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
<td>0.02</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AJ-5b</td>
<td>8.581</td>
<td>12.983</td>
<td>7.200</td>
<td>116.00</td>
<td>721.0</td>
<td>94.5</td>
<td>.4535</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
<td>0.02</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AJ-17</td>
<td>8.572</td>
<td>12.983</td>
<td>7.198</td>
<td>116.02</td>
<td>719.9</td>
<td>91.3</td>
<td>.4367</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
<td>0.02</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AJ-15c</td>
<td>8.575</td>
<td>12.984</td>
<td>7.199</td>
<td>116.03</td>
<td>720.2</td>
<td>92.1</td>
<td>.4388</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
<td>0.02</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-4-F</td>
<td>8.591</td>
<td>12.978</td>
<td>7.204</td>
<td>116.03</td>
<td>721.7</td>
<td>96.5</td>
<td>.5035</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>0.007</td>
<td>0.007</td>
<td>0.002</td>
<td>0.04</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* LCLSQ eliminates all observations that deviate from the calculated d-spacing of monoclinic orthoclase by more than 1%; this number listed is the number of A or B quality (Orville, 1967) peaks that was actually incorporated into the refinement.
Figure 19. Structural states of vein-filling K-feldspars.

Comparative structural states of the orthoclase hosts in perthitic feldspars. Data points are at intersections of crosshairs; extent of crosshairs indicates size of errors.
Figure 19. Structural states of vein-filling K-feldspars from Ajo, Arizona.
(Brown and Willaime, 1974; Stewart, 1975). All the samples exhibit macroperthite although it is present to the least degree in R-4-F, which may account for the high errors of that data point.

The temperatures at which the observed ordering states are in equilibrium are given in Figure 20. These temperatures are derived from the results of calorimetric experiments by Hovis (1974) in conjunction with the theory outlined in Appendix A. The early potassic feldspars are in equilibrium at approximately 580°C, and the later feldspar is in equilibrium at 530°C. These temperatures fall within the range established by other methods for potassic alteration (Sheppard, 1971; Jacobs and Parry, 1976, 1979).
Figure 20. Temperatures at which the observed potassium feldspar ordering states are in equilibrium (curve from Hovis, 1974).
CHAPTER 7

DISCUSSION

Temperature and Pressure of Potassic Alteration at Ajo

The pressure of formation calculated from the apparent highest temperatures of multi-phase fluid inclusions is approximately 650 bars. Although this is an approximate figure, it is some tribute to the validity of qualitative geological observation that this figure is midway in Gilluly's estimated range of 300-1000 bars based on his reconstruction of the original roof cover at the time of intrusion. Feldspar studies provided no further geobarometric information on this epizonal system because feldspars are not pressure-sensitive except on the order of kilobars.

The temperature range indicated from both the quartz and the feldspar studies can be summarized as follows: Potassic alteration, beginning with the earliest deposition of K-feldspar, was in progress when the system was at 580°C, continued through the onset of quartz deposition at 470°C, and may have persisted all the way down to 280°C. Not mentioned in this scenario is the 530°C temperature obtained for the late potassic K-feldspar, R-4-F, the only analyzed sample in which K-feldspar is coeval with quartz. The equilibrium temperature of 530°C for the late-stage K-feldspar R-4-F does not fit in because it is higher than the 470°C for quartz and physically it
appears to be later than the quartz. The point should again be raised that the resolution of the structure of R-4-F is problematic, and the errors are unacceptably high when compared to published values, so that this is probably not a valid data point. However, similar discrepancies of 50-100°C have been found between feldspar equilibrium temperatures and fluid inclusion temperatures in coexisting quartz from other magma-hydrothermal systems (Sierrita, Santa Rita, Four Metals Breccia) (Dr. Dennis K. Bird, writ. comm., 1982). The reason for this difference may be that the greatest quartz solubility in water at 650 bars is around 450°C (Walther and Helgeson, 1977; Helgeson et al, 1978), and fluids that circulate above this temperature are less likely to be trapped as inclusions. This could be the case at Ajo, where only 2 inclusions were found to homogenize at temperatures greater than 450°C (adding the pressure correction +50°C to the data in Figure 12).

The lower temperature limit on potassic alteration is more uncertain because the event represented by the fluid inclusion temperature peak at 280°C is difficult to evaluate. The alteration events affecting the analyzed samples are the introduction of K-feldspar, followed by quartz and chlorite deposition, with all 3 minerals cut by chalcopyrite-bornite veins, i.e. the paragenesis of vein types 1, 2 and 3 but involving only the major minerals of each type. This succession is best illustrated in Figure 6a, which shows the pegmatite sample from which most of the fluid inclusion
temperatures were taken (the chlorite is not seen in this photograph). Phyllic alteration is not abundantly present. The peak at 280°C must signify an event later than the K-feldspar mineralization because the textural relationship between the early K-feldspar and the quartz indicates that the quartz was deposited later. In addition, the equilibrium temperatures determined from the structural states of the early K-feldspars (vein type 1), including AJ-Peg (Fig. 6a), predict that they formed at the much higher temperature of 580°C.

Which of the succeeding events in this sample, then, is recorded by the peak centered on 280°C? Because the fluid inclusions analyzed were secondary inclusions, most of the quartz was probably already deposited. As previously stated, the highest fluid inclusion homogenization temperature of 470°C is assumed to be the temperature of the onset of quartz deposition at Ajo. These observations, however, do not preclude the possibility that quartz continued to be the major mineral deposited at 280°C as pre-existing quartz was fractured and hydrothermal solutions circulated through it. Quartz is deposited in fractures throughout most of the life of the Ajo hydrothermal system. Where in this continuum of quartz deposition the associated chlorite was deposited cannot be evaluated here. Another possibility is that the peak at 280°C records the temperature of formation of the chalcopyrite-bornite veins that transect the quartz and the K-feldspar. It should be emphasized here that the
vein paragenesis shows that although some chalcopyrite and bornite is found in apparent equilibrium with K-feldspar-quartz (vein type 2), and some chalcopyrite seems also in equilibrium with quartz-pyrite (vein type 4, Fig. 9), in the samples collected for this study a volumetrically significant proportion of the copper sulfides appears simply as chalcopyrite-bornite ± quartz veins (vein type 3, Figs. 6a, 7a, 7b). Thus, as expressed in the veins, hypogene copper mineralization at Ajo appears to have originated during potassic alteration and terminated during phyllic alteration, occurring meanwhile as a discrete, transitional event. The occasional presence of both K-feldspar and muscovite in this vein type emphasizes its transitional nature. From the above discussion it can be concluded that if this major peak centered on 280°C represents quartz (and possibly chlorite) deposition that preceded sulfide deposition, potassic alteration was still in progress at this temperature. If the peak represents formation of the chalcopyrite-bornite veins, potassic alteration may or may not have been in progress, but a temperature range can be tentatively assigned to a significant proportion of the copper mineralization in the pegmatitic zone.

**Equilibrium Phase Relations and Solution Composition**

Figure 21. Equilibrium phase relations in the K-Na-Si-Al-O-H system at 650 bars.

Activity-activity diagrams in the Na-K-Al-Si-O-H system at 650 bars and temperatures of interest for the Ajo hydrothermal system.
SOLID SOLUTION PHASE RELATIONS IN THE Na-K-Al-Si-O-H SYSTEM AT 650 BARS

Figure 21. Equilibrium phase relations in the K-Na-Si-Al-O-H system at 650 bars.
and Helgeson, Kirkham and Flowers (1981), are shown in Figure 21. These logarithmic activity diagrams are calculated at temperatures of interest discussed throughout the text and represent changing phase relations among K- and Na- silicates during the cooling history of the Ajo hydrothermal system. Subsolidus textures and equilibrium order/disorder in the feldspars are specifically accounted for by using the equilibrium compositions on the solvus in Figure 16 and activity coefficients and data in Thompson and Waldbaum (1968, 1969).

These diagrams predict that the stability fields of albite and K-feldspar become restricted with decreasing temperature and that higher activities of Na+ and K+ in solution, or decreasing activity of H+ ion, are required to maintain alkali feldspar stability. In the veins containing early K-feldspar found to have formed at temperatures of 580°C or higher, neither andalusite or albite is present, restricting the equilibrium values of log $a_{K^+}/a_{H^+}$ and log $a_{Na^+}/a_{H^+}$ to those in the K-feldspar stability field. The minimum values of log $a_{K^+}/a_{H^+}$ and log $a_{Na^+}/a_{H^+}$ at 580°C predicted from the phase boundaries are 2.6 and 2.7 respectively. Later during potassic alteration, when quartz is beginning to be deposited at 470°C, these minimum values rise to 3.2 for log $a_{K^+}/a_{H^+}$ and 3.8 for log $a_{Na^+}/a_{H^+}$. As the system cools, the minimum values of log $a_{K^+}/a_{H^+}$ and log $a_{Na^+}/a_{H^+}$ required to maintain K-feldspar stability are predicted to continue to rise.
These diagrams also show that muscovite can be a stable phase at 470°C, but because it is not present in these vein samples, the log \(a_{K^+}/a_{H^+}\) in solution must have been higher than the value fixed by the muscovite-K-feldspar phase boundary.

As can be seen in Figure 22, the \(a_{K^+}/a_{H^+}\) ratio in solution is predicted to decrease with decreasing temperature. This diagram is calculated from the equilibrium constants at 650 bars for the reaction

\[
\text{KAlSi}_3\text{O}_8 + \text{Na}^+ = \text{NaAlSi}_3\text{O}_8 + \text{K}^+
\]

where \(a_{\text{stoichiometric minerals}} = 1\)

and \(\log K_{eq} = \log \frac{a_{K^+}}{a_{\text{Na}^+}}\)

This diagram also shows that accounting for solid solution in alkali feldspars permits the prediction of lower equilibrium \(a_{K^+}/a_{\text{Na}^+}\) ratios at 580°C and 470°C. In this temperature range, \(a_{K^+}/a_{\text{Na}^+}\) changes more rapidly, from 0.8 at 580°C to 0.3 at 470°C, than at any other time in the system's history. This high rate of change in the equilibrium constant for reaction (1) indicates rapid alkali cation exchange, facilitating maintenance of alkali equilibrium during potassic alteration. In addition, as cooling proceeds toward 470°C the extreme in quartz solubility is approached. Such rapidly changing
Reaction:
\[ \text{KAlSi}_3\text{O}_8 + \text{Na}^+ = \text{NaAlSi}_3\text{O}_8 + \text{K}^+ \]

\[ \log k_{eq} = \log \frac{a_{K^+}}{a_{Na^+}} \]

Figure 22. Changing \( \frac{a_{K^+}}{a_{Na^+}} \) with temperature in the K-Na-Si-Al-O-H system at 650 bars.

Squares indicate regions of feldspar stability.
chemical conditions probably affect the tetrahedral ordering state, but the nature and magnitude of the effect, if any, is unknown.

In summary, during potassic alteration, when K-feldspar was a stable phase, the minimum equilibrium value of $\log a_{K^+}/a_{H^+}$ in solution is predicted to have been 2.6 at 580°C and 3.2 at 470°C. $\log a_{Na^+}/a_{H^+}$ is predicted to have gone from 2.7 at 580°C to 3.8 at 470°C. In this temperature range the ratio $a_{K^+}/a_{Na^+}$ changed drastically, facilitating alkali cation exchange, but if it also affected Al-Si exchange, that effect is not understood.
Phase relations in crosscutting veins, fracture density measurements, results of analyses of K-feldspar and quartz from the potassic alteration zone, and interpretation of textures resulting from subsolidus reactions in potassium feldspars permit the following conclusions to be drawn concerning physiochemical conditions that prevailed during potassic alteration at Ajo:

(1) Fracturing persisted throughout the life of the hydrothermal system, beginning strongly during potassic alteration at a fracture density of 0.31 cm⁻¹, continuing through sulfide mineralization at 0.33 cm⁻¹, and decreasing during phyllic alteration to an abundance of 0.21 cm⁻¹.

(2) Pressures during potassic alteration were approximately 650 bars.

(3) Potassium metasomatism began in the earliest stages of fracturing, starting at a minimum temperature of 580°C and progressing through 470°C. This is the temperature range indicated by analysis of early K-feldspar and fluid inclusions in later quartz; it does not take into account the problematic 530°C temperature obtained for the later K-feldspar. This 50-100°C discrepancy in the temperatures of
coexisting potassic feldspar and quartz may arise from increased quartz solubility at temperatures greater than 450°C at 650 bars or an unreliable feldspar temperature attributable either to a highly complex feldspar structure or contamination. The fluid inclusion data does, however, permit the designation of a minimum of temperature of 470°C for the onset of quartz deposition and therefore the continuation of potassic alteration. Potassic alteration may still have been in progress when the system cooled at 280°C, but this lower temperature limit is uncertain. 280°C may instead indicate the temperature of formation of the chalcopyrite-bornite veins in the pegmatite zone, veins that formed during a significant period of ore deposition.

Ratios of potassium ion and sodium ion to hydrogen ion in the solutions that formed potassic alteration were maintained at progressively higher levels as the system cooled. Equilibrium values of log $a_{K^+}/a_{H^+}$ changed from 2.6 to 580°C to 3.2 at 470°C. Equilibrium values of log $a_{Na^+}/a_{H^+}$ went from 2.7 at 580°C to 3.8 at 470°C. The alkali cation ratio of $a_{K^+}/a_{Na^+}$ radically decreased from 0.8 to 0.3 in this temperature range.
Appendix A

CRYSTAL CHEMISTRY OF MONOCLINIC POTASSIUM FELDSPARS

Structural states of alkali feldspars are reflected in their unit cell dimensions (Smith, 1974): the $a$ cell edge is proportional to the K and Na concentrations and $b$ and $c$ can be correlated with the degree of Al-Si distribution in the tetrahedral sites. Monoclinic C2/m feldspars have two energetically distinct tetrahedral sites, designated $T_1$ and $T_2$ (notation after Megaw, 1956). High sanidine is the completely disordered potassium feldspar and is characterized by

$$X_{Al, T_1} = X_{Al, T_2}$$

where $X_{Al}$, considered the mole fraction of Al, actually represents the statistical probability of finding an atom of Al in the subscripted site. Ordering proceeds by the preferential migration of Al into the two $T_1$ sites and Si into the two $T_2$ sites in order to satisfy electrostatic charge balance constraints. This migration results in the intermediate structure of low sanidine, or orthoclase, in which

$$0.5 > X_{Al, T_1} > X_{Al, T_2} > 0.25$$
Thompson (1969) has defined the long-range tetrahedral ordering parameter \( Z \) in terms of Al distribution in monoclinic alkali feldspars as

\[
Z = 2 \left( \frac{X_{Al,T_1}}{X_{Al,T_2}} - \frac{X_{Al,T_2}}{X_{Al,T_1}} \right)
\]  

(3)

where \( Z \) equals unity for ordered and zero for disordered site distributions. Equations and data reported by Hovis (1974) permit calculation of the tetrahedral site distributions of Al, and thus \( Z \), from direct lattice constants for monoclinic potassium feldspars by

\[
Z = 7.6344 - 4.3874 b - 6.861 c
\]  

(4)

Equilibrium distributions of Al and Si in alkali feldspars can be represented by the intra-crystalline reaction

\[
\begin{align*}
\text{Al}_{T_1} + \text{Si}_{T_2} & \rightleftharpoons \text{Al}_{T_2} + \text{Si}_{T_1}
\end{align*}
\]  

(5)

Theoretical and experimental evaluation of the thermodynamic and calorimetric properties of reaction (5) in monoclinic \( KAlSi_3O_8 \) by Thompson (1969) and Helgeson et al (1978) indicates that the intracrystalline equilibrium constant for this reaction can be represented by
\[
\ln K(5) = \ln \frac{X_{AlT_2} - X_{SiT_2}}{X_{AlT_1} - X_{SiT_2}} = -2 \arctanh Z + \arctanh \frac{Z}{3}
\]

\[
= \frac{-\Delta H^o(5)}{R} \left( \frac{1}{T} - \frac{1}{T_{ds}} \right)
\]

where \(K(5)\) and \(\Delta H^o(5)\) are the intra-crystalline standard equilibrium constant and enthalpy for reaction (5) and \(T_{ds}\) is the temperature where \(Z = 0\) (~ 1432°K). Equations (5) and (6), together with the stoichiometry of \(KAlSi_3O_8\), permit calculation of the long-range ordering parameter \(Z\) and the appropriate equilibrium ordering temperature from X-ray measurements of natural feldspars.

**Limits of Al-Si Geothermometry**

The theory and experiments correlating Al-Si ordering states in monoclinic potassium feldspars with temperatures of equilibration are an accepted branch of feldspar research. Limits on the applications of theory and experimental results to "real-life" feldspars lie primarily in the interpretation of what the existing ordering states represent. Factors such as deformation, cooling rate, or hydrothermal activity can affect a crystal's structure such that the observed ordering state may not be the ordering state existing at the time of formation of the crystal.
The ability of an ordering state to maintain equilibrium at a given temperature depends on the cooling rate and the kinetics of ordering, which decreases exponentially with temperature. As the system "slows down", it diverges from the equilibrium ordering path and asymptotically approaches a constant ordering state (Ganguly, 1982). Extrapolating the observed ordering state back to the equilibrium path gives a minimum temperature of formation, called the closure temperature (Dodson, 1976). This relationship to the true temperature of formation is illustrated in Figure 23. The faster the cooling rate, the closer the closure temperature is to the actual formation temperature. One possibility, therefore, is that the equilibrium temperatures established for the Ajo feldspars represent minimum values of the temperatures of crystallization.

A second possibility is that the observed ordering states result from retrograde disordering. Experiments by O'Neill and Taylor (1967) on alkali feldspars reacting with chloride solutions showed that whereas alkali and oxygen isotope exchange reached equilibrium quickly, Al-Si exchange did not. They postulated solution-redeposition as the exchange process and found that the redeposited phase was always monoclinic sanidine, even at 350°C, at which temperature it is metastable. In these experiments the alkalis in the feldspars and the chloride solutions were far out of equilibrium. In similar experiments that did maintain alkali equilibrium, Yund and Anderson (1974) concluded that oxygen isotope
Figure 23. Ordering behavior in cooling crystals.

E = equilibrium ordering path; K = kinetically controlled ordering path; T_{closure} = final ordering state extrapolated back to the equilibrium cooling path.
exchange operated by volume diffusion and not solution-redeposition, and that no change in the existing Al-Si structural state occurred. Similar results were reported by Hovis and Perkins (1978).

Another argument in favor of the preservation of an existing ordering state is the difficulty of Al-Si migration. Sipling and Yund (1974) estimated an activation energy of ~99 kcal/mole for Al-Si exchange in potassium feldspar, about 25 kcal/mole higher than Na-K exchange in potassium feldspars. With such a high activation energy, under anhydrous conditions complete ordering would take 150 billion years to accomplish at 500°C (Sipling and Yund, 1974) and even longer at lower temperatures. This extremely high activation energy, the probability of alkali equilibrium, and the results of diffusion experiments favor the assumption that the structural state of these hydrothermal feldspars is not one of retrograde disorder but rather of some ordering state achieved at a closure temperature, or minimum temperature of formation.

Alkali feldspar geothermometry is also complicated by problems in obtaining a true structural state. Lattice strain, created in the crystal's lattice during its subsolidus history, has been cited as the main obstacle to the accurate assessment of ordering states.

The processes affecting this history are discussed in the next section.
Subsolidus Processes in Alkali Feldspars

Subsolidus behavior in alkali feldspars is controlled by the existing thermal regime and interaction with an aqueous phase, that is, its hydrothermal history (Parsons, 1978). As the crystal cools, its composition moves toward more sodic and potassic compositions in order to minimize the Gibbs free energy of the crystal. The temperature-composition curve defined by the minimum free energy is the strain-free, or binodal, solvus in Figure 16 that was introduced earlier.

The segregation of a sodic phase within an originally "homogeneous" alkali feldspar is believed to proceed by one or both of two processes: nucleation and growth or spinodal decomposition. In nucleation and growth, cooling conditions initiate compositional perturbations that cause ions to move and congregate, forming sodic patches that may or may not be triclinic. Spinodal decomposition is a process in which initial compositional inhomogeneities on the scale of perhaps a few unit cells are continuously amplified (Owen and McConnell, 1974). It can be pictured as a sinusoidal wave in which amplitude is analogous to composition (sodic), and wavelength represents length in the crystal. As the crystal cools, this wave increases in both amplitude and wavelength.

Spinodal decomposition is the mechanism of unmixing considered most likely by many workers (Lorimer and Champness, 1973; Robin, 1974; Owen and McConnell, 1974; Yund, 1974, 1975; Parsons,
1978) because it requires only alkali migration in an essentially immove Al-Si-O framework. Nucleation and growth involves migration of all the ions and is thereby limited by Al, Si, and O movements, which are much slower than alkali migration, even in the presence of an aqueous phase (Sipling and Yund, 1974; Yund, 1975).

Spinodal decomposition originates in a coherent lattice, i.e. the Al-Si-O framework is continuous across the sodic-potassic interface. Strain energy exists in the lattice because the Al-Si-O framework is unable to collapse around the smaller Na+ ion. The crystal attempts to reduce the strain by increasing the size of the sodic areas, which decreases the total interfacial area between the two phases (Lorimer and Champness, 1983). Eventually the bonds between the two phases break, allowing triclinic albite to form within a monoclinic orthoclase host. Qualitatively this breaking point is thought to be the transition from cryptoperthite to microperthite (Robin, 1974; Yund, 1974; Parson, 1978). Once this state is passed, the lattice is thought to be strain-free.

Coarsening of the exsolved albite is facilitated by interaction with an aqueous phase (Parsons, 1978). Unless subjected to a hydrothermal regime such as that found in a porphyry copper ore-forming system, crystals that decompose by spinodal unmixing may remain cryptoperthitic with a coherent lattice for millions of years even at or near the earth's surface (Yund, 1975). Even in this environment, textures that are less microperthitic and possibly even
cryptoperthitic are found to occur in alteration K-feldspars (Dr. Dennis K. Bird, pers. comm., 1982).
Appendix B

ANALYTICAL PROCEDURES

Electron Microprobe Analysis

Mineral compositions are obtained using an Applied Research Laboratories Scanning Electron Microprobe Quantometer (SEMQ) with Tracer Northern NS-880 TN-1310 automation. Samples are primarily polished thin sections; a few are polished chips. All feldspars were analyzed for K, Na, Ca, Ba, Fe, Al, and Si using a beam width of < 2 microns and a beam current of 25 nanoamperes. Sr, Rb, Pb were analyzed for initially but were not detected (detection limits for these elements in this system are 40-200 ppm with 800 seconds of counting time). Standards used were microcline (K), albite (Na), anorthite (Ca, Al), diopside glass (Si, Mg), Ba-silicate glass (Ba), and chromite (Fe). Data were reduced with Tracer Northern's software, the ZAF program based on principles described in Beaman and Isasi (1972). Over 400 analyses were collected but only analyses for which the total weight percent oxides sum to 100 ± 1 percent were accepted.

X-Ray Diffractometry

Samples for X-ray analysis were prepared by first separating feldspar grains from contiguous minerals, then grinding them as finely as possible together with an industrial grade silicon
standard. Feldspar to standard ratio was approximately 4:1. The powder was then slurried with acetone on a flat glass slide and allowed to dry or pressed into a shallow well on a glass slide. Analyses were made on a Siemens D-500 X-ray diffractometer with CuKα radiation, a graphite monochromator filter, and a scintillation detector. Each scan ran forward from 20° 2θ to 52° 2θ and back with a goniometer speed of 0.5° 2θ per minute, a chart speed of 2 centimeters per minute, at a full scale of 400 impulses per second and a time constant of 2.

Peaks were measured by taking the average of 3 points at half-width between 1/2 and 3/4 of the peak height and indexing them according to tables in Borg and Smith (1969) and Wright and Stewart (1968a). Peak quality was judged according to guidelines described in Orville (1967). Only A or B peaks were considered, where A peaks have their upper 1/10 restricted to 0.1° 2θ, and B peaks are slightly broader with their upper 1/10 greater than 0.1° 2θ. Indexed measurements were input to the LCLSQ Mark IV program (Burnham, 1962) which calculated d-spacings and lattice constants, tetrahedral site distributions, the long-range ordering parameter Z (Hovis, 1974), and mole percent KAlSi₃O₈ (Stewart and Wright, 1974). Several refinements were made for each sample using different combinations of peaks: A peaks only; A and B peaks only; only peaks whose d-spacings more closely approached orthoclase d-spacings than intermediate
microcline d-spacings. In almost every case, the lowest errors were obtained when only orthoclase peaks were included.

**Fluid Inclusion Analyses**

Heating and freezing tests on fluid inclusions in quartz were made on a gas flow heating/freezing stage originally set up by Werre et al (1979) and developed further by SGE, Inc. Temperature gradients in the 6-tiered sample chamber were 1.0°C over 3/4 of the viewing area at temperatures up to 300°C and 2°C over the same area at temperatures over 300°C (Werre et al, 1979). Sample temperatures were directly measured by an iron-constantan or chromel-alumel thermocouple attached to a Doric Digital Trendicator model 400A Type J. N₂ gas was flushed through the chamber for freezing tests and for heating above 500°C. Air was used for heating runs below 500°C. Calibrations with distilled water and powdered tin in sealed capillary tubes indicated an accuracy and precision of ± 0.1°C in the approximate range of -50°C to 50°C. From 50°C up to 300°C accuracy is ± 0.5°C, and at temperatures over 300°C, it is as high as ± 3°C. Precision and reproducibility can be maintained at ± 0.1°C below 500°C and at ± 0.2°C above 500°C.
Appendix C

REPRESENTATIVE ELECTRON MICROPROBE ANALYSES
FOR THE ORTHoclase HOST IN VEIN-FILLING
K-FELDSPARS AT AJO

(Tables follow)
Appendix C. Representative Electron Microprobe Analyses for the Orthoclase Host in Vein-Filling K-Feldspars at Ajo.

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Stoichiometry

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**Weight Percent Oxides**

**Stoichiometry**

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References—continued
References—continued


References—continued


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