Zonal Relations of Wallrock Alteration and Sulfide Distribution at Porphyry Copper Deposits[1]

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Abstract

Most of the porphyry copper deposits are characterized by a similar pattern of lateral zoning involving sulfides and silicate alteration assemblages. A central zone of biotite-orthoclase alteration is surrounded by a partial to complete halo of quartz-sericite alteration. Propylitic alteration commonly forms a further halo if rocks of appropriate composition are present. The hypogene sulfides also are zoned, from a central zone with a low pyrite/chalcopyrite ratio and generally low total sulfides, through a zone of moderate sulfides with dominant chalcopyrite, then to a halo of high pyrite/chalcopyrite and high total sulfides which grades outward to lower total sulfides. The highest copper content normally occurs within the biotite-orthoclase zone or at its outer borders with quartz-sericite alteration. The silicate and sulfide zoning is generally centered on a granitic porphyry stock.

Lead and sulfur isotope data, as well as the zoning, suggest that the ore fluid traveled outward from the porphyry, starting at high temperatures and relatively high K/H ratios in the orthoclase field, thereby forming the biotite-orthoclase alteration. In order to form the strong sericite alteration, cooling of the fluid is concluded to be the most probable means of changing mineral equilibria. A model calculation, for a large porphyry copper ore body, of heat losses to wall rock during outward flow of the solution shows that this mechanism cannot be the major means of cooling. The calculation also demonstrates that mineral deposition from solutions as dilute as 1–100 ppm base metals encounters grave difficulties in cooling from temperatures of 500° C or above, because of the huge volumes of solution involved to form a porphyry copper orebody, and the resulting huge amount of heat that must be dissipated. Copper concentrations in the ore fluid on the order of 1,000 ppm or higher are therefore suggested. Cooling by expansion or by mixing with cool ground water seems an attractive means of bringing the high temperature ore fluid into the muscovite stability field. These processes are probably also instrumental in causing metal sulfide precipitation.

Introduction

The recent publication of several papers on porphyry copper deposits has made available a considerable amount of new data on wallrock alteration and sulfide distribution in porphyry copper deposits. The intent of this paper is to utilize these and older data to point out some significant features at these important deposits. The emphasis is on district-scale patterns, as contrasted to alteration around individual veins. Although extremely significant data have been obtained from detailed studies of veins, the "disseminated" character of porphyry copper deposits and their large size suggest the value of a district-scale view of their characteristics. In addition, such a viewpoint can be of considerable value in exploration.

Supergene Alteration

A major problem in interpretation of alteration in porphyry copper deposits is the superimposition of supergene alteration on the preexisting hypogene hydrothermal alteration. The term supergene alteration denotes rock alteration in mineral deposits caused by weathering and related near-surface processes involving solutions of nearby surficial origin. In contrast, hypogene alteration is caused by higher temperature solutions at depth. Acid solutions derived from oxidation of pyrite are especially important in causing supergene alteration. The significance of the problem is grossly suggested by the economic significance of supergene sulfide enrichment at many porphyry copper deposits, as compared to the original hypogene protore. Although many workers undoubtedly recognize this problem (Meyer and Hemley, 1967, p. 185), the distinction between hypogene and supergene alteration is not easy. Supergene alteration effects are probably more prevalent in porphyry copper deposits than the literature indicates.

The discussion to follow is concerned mainly with hypogene alteration, but an interpretation of whether a particular mineral occurrence is hypogene or super-

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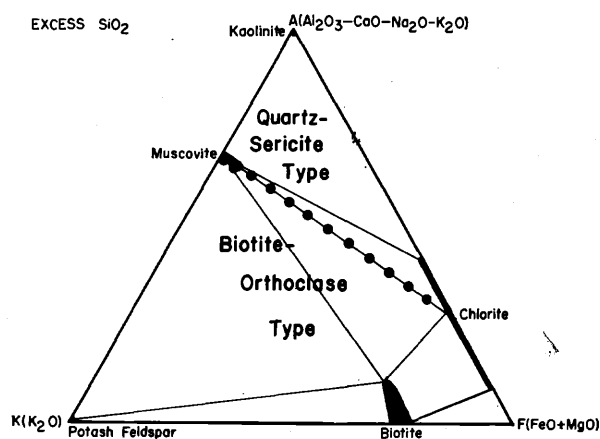
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FIG. 1. AKF diagram for minerals common in hydro-thermal alteration at porphyry copper deposits, with some equilibrium assemblages indicated. The dotted line separates the two alteration types distinguished in this paper.

gene is involved. A supergene origin for some kaolinite is widely accepted. Abrupt changes from sericite to biotite at the base of the leached capping at Safford, Arizona suggest to the writer that some sericite may be supergene. Field (1966b) suggests on the basis of sulfur isotope data that some alunite is supergene, and a similar origin seems possible for some chlorite and montmorillonite. For this reason, every attempt has been made to compare critically alteration well below the surface (and therefore presumably hypogene) with the more abundant data on alteration in the weathered zone.

Hypergene Alteration

Hydrothermally altered rocks are essentially a special type of metamorphic rock. As a result, it is convenient and meaningful to classify alteration on the basis of mineral assemblages (Creasey, 1959). However, in contrast to most metamorphic rocks, the hydrothermally altered rocks of porphyry copper deposits have undergone moderate to strong addition and leaching of elements by the hydrothermal fluid, and are therefore metasomatic rocks, rather than simply metamorphic rocks. In the more strongly altered rocks, differing mineral assemblages result predominantly from the extent and chemical character of metasomatism and only secondarily from temperature and total pressure.

In the highly altered zones of porphyry copper deposits, some of the critical mineral assemblages can be illustrated by an AKF diagram with excess SiO$_2$ and H$_2$O (Fig. 1). The projection includes K-feldspar, muscovite, kaolinite, biotite, and chlorite. However note that several of the minerals contain components or compositional variations not specifically included in this projection. Muscovite is known

to vary in Al/Si ratio, to accept Mg and other elements for Al, and in the form of illite to occur interlayered with montmorillonite. Chlorite and biotite vary in Al/Si, and in Mg/Fe, as well as other probable substitutions. K-feldspar commonly contains sodium in solid solution. Montmorillonite is not included in the diagram because the common types probably contain considerable Ca, Mg, and Na.

The most common and significant hypogene mineral assemblages of the AKF diagram in porphyry copper deposits are:

(1) Orthoclase-biotite-quartz
(2) Orthoclase-biotite-sericite-quartz
(3) Orthoclase-sericite-quartz
(4) Sericite-quartz
(5) Sericite-kaolinite-quartz

Sulfides may be present with all assemblages. Clays are common but may be of non-equilibrium, retrograde or supergene origin, and thus they are generally disregarded because of their uncertain significance. Chlorite is also common, but it commonly appears to be later than the above assemblages.

Based on the distribution of these assemblages in the deposits and correlations with sulfide abundance, two alteration types are recognized on the AKF projection. These are the biotite-orthoclase alteration type and the quartz-sericite alteration type. The advantage of using alteration mineral assemblages rather than mineral abundances is that abundance is dependent on initial rock composition and extent of metasomatism, but the assemblages are largely free of these complications.

The biotite-orthoclase alteration type is characterized by the presence of biotite or orthoclase (or both) as alteration products or vein minerals. Sericite may be present, but does not replace the secondary K-feldspar or biotite. Assemblage (2) above is most common; assemblages (1) and (3) are not uncommon. The K-feldspar is normally orthoclase, and the biotite is normally a medium brown pleochroic variety, but in some cases is greenish. Additional phases that may be present include pyrite, chalcopyrite, Ti oxides, plagioclase, magnetite, anhydrite, and siderite. Chlorite, montmorillonite, and kaolinite are not uncommon but probably involve later stages of alteration including retrograde and supergene alteration, formation as metastable phases, or the influence of components not explicitly shown on the AKF diagram. The critical feature of the biotite-orthoclase alteration type is the presence of K/H high enough in the ore fluid to stabilize and form biotite or orthoclase, and in the case of biotite, Mg/H high enough to avoid removal of Mg.

The quartz-sericite alteration type is characterized by quartz, sericite, and sulfides. Assemblages (4)

and (5) are typical. Normally, pyrite is the predominant sulfide. *K-feldspar and biotite are not stable* and are normally completely altered. Chlorite may be present. Kaolinite is commonly present in small amounts. Titanium oxides are usually present. The complete alteration of both K-feldspar and plagioclase to sericite and kaolinite is the criterion used to distinguish this type in the following pages. The critical chemical feature of this alteration type is almost complete leaching of Ca, Mg, and Na, and limitation of K content to muscovite.

The propylitic alteration type characteristically includes various combinations of chlorite, epidote, calcite, and albite. Montmorillonite, sericite, quartz, pyrite, and potash feldspar are locally present. Occasionally the presence of pale greenish biotite associated with a propylitic assemblage causes confusion, but the presence of other propylitic minerals can usually be used to resolve such conflicts. The distinguishing chemical feature of the propylitic type is the addition of H_2O and CO_2, and recrystallization without strong leaching of bases.

The propylitic type as discussed above agrees with the classifications of Creasey (1966) and Meyer and Hemley (1967). The quartz-sericite alteration includes Creasey's argillic alteration type plus the very common quartz-sericite assemblage that he includes in his potassic type. The biotite-orthoclase type is equivalent to Creasey's potassic type less the quartz-sericite assemblage, and is equivalent to the "potassium silicate" alteration of Meyer and Hemley (1967). The change from Creasey's classification

SANTA RITA — Alteration

⬭ Stock outline (6000' elev.)

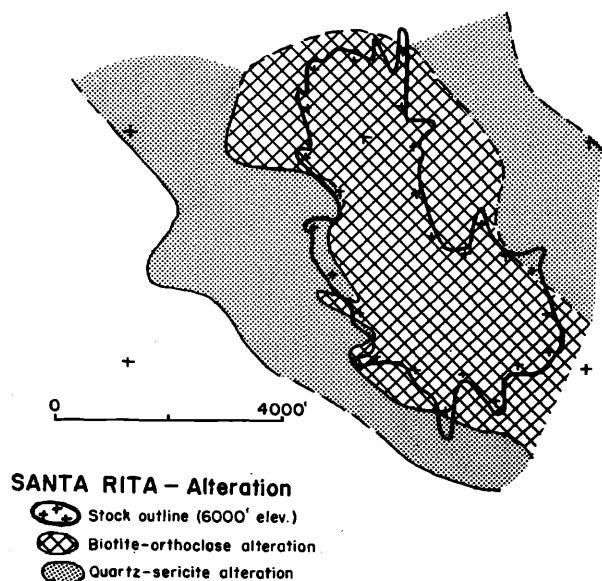⬭ Biotite-orthoclase alteration

⬭ Quartz-sericite alteration

Fig. 2. Alteration pattern at Santa Rita, N. Mex. Tactite alteration of limestone interrupts the pattern at the north end of the stock. After Nielsen (1968), Rose and Baltosser (1966), and Burnham (1962).

results in closer correlation with the sulfide distribution, as will be noted later.

Description of Alteration at Some Deposits

The following sections summarize available data on alteration types and sulfide distribution at some porphyry copper deposits where sufficient data are available to make a meaningful presentation. The maps illustrate the predominant features of various parts of the deposits as based on either grid sampling results, geologic mapping, or studies of deep drill cores. Local deviations from the patterns clearly exist along veins and shears, but the patterns shown probably typify 95 percent of the rock.

Santa Rita

A recent study of hypogene alteration at Santa Rita by Nielsen (1968) furnishes clear data for the existence of biotite-orthoclase alteration in most of the porphyry stock, and hypogene quartz-sericite alteration in adjacent quartz diorite sills to the southwest. Earlier reports by Rose and Baltosser (1966) and Burnham (1962), based on instrumental (X-ray diffraction and infrared spectrophotometry) and thin section studies of several hundred rock samples collected on a grid, indicate the presence of similar quartz-sericite alteration at the surface of the northeast and east of the stock, and a propylitic zone located at still greater distances from the stock (Fig. 2). Nielsen's drill hole data do not extend far enough east to confirm the hypogene origin of all the quartz-sericite alteration, but a trend toward sericitic alteration of feldspar certainly exists in that direction. The north and south borders are not considered because of tactite alteration of limestone and post-ore cover, respectively.

In the biotite-orthoclase alteration zone, much of the plagioclase is altered to montmorillonite and kaolinite, especially adjacent to the boundary with quartz-sericite alteration. Although Ca and Na might stabilize montmorillonite, the kaolinite-orthoclase pair should not be stable together according to any phase equilibrium data presently known. The kaolinite is therefore regarded either as a nonequilibrium alteration product of plagioclase, perhaps controlled by high silica activity (Fournier, 1967), or as a retrograde alteration controlled by the survival of plagioclase from the earlier orthoclase alteration, or as superimposed argillic alteration of either hypogene or supergene origin. The isotopic results of Sheppard, Nielsen, and Taylor (1969) indicate a hypogene origin for some clay, but they do not demonstrate an origin as an equilibrium phase formed during the major episode of sulfide deposition. Thin section studies by the writer indicate that much of

SANTA RITA — Sulfide distribution

Stock outline (6000' elev.)
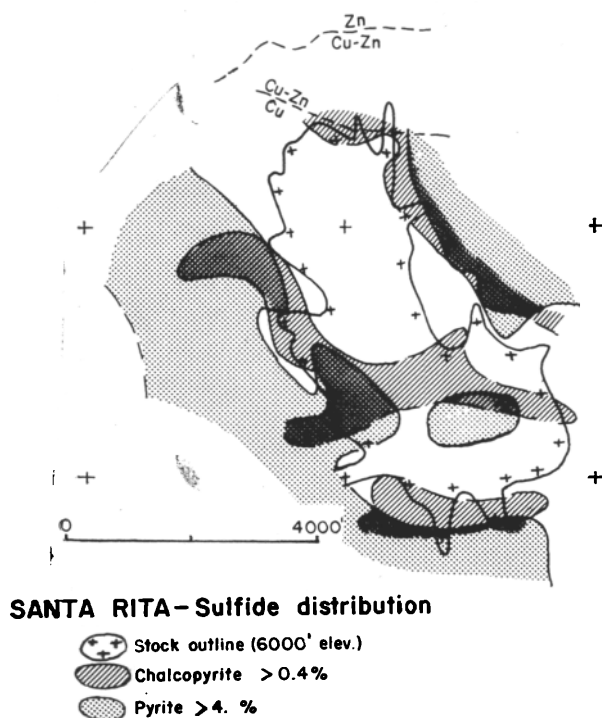
Chalcopyrite > 0.4%

Pyrite > 4. %

Fig. 3. Sulfide distribution at Santa Rita, N. Mex., after Nielsen (1968).

the chalcopyrite occurs in or adjacent to veinlets containing orthoclase. The part of the argillized zone containing secondary K-feldspar is included with the biotite-orthoclase alteration type on the above reasoning.

Nielsen (1968) also gives data on sulfide distribution. Pyrite is abundant (4–8 wt %) in a zone largely coinciding with the quartz-sericite alteration, and in a patch in the south-central part of the stock (Fig. 3). In contrast, chalcopyrite tends to be most abundant in a zone approximately along the boundary between the biotite-orthoclase and quartz-sericite alteration types, and in a zone extending east-west through the central part of the stock (bordered on the south by the pyritic patch noted above). Chalcopyrite and pyrite are both low in areas at the north-central and south-central portions of the stock, i.e., the stock has two centrally-located, relatively barren zones. The sulfide distribution can be generalized as grading from low pyrite and chalcopyrite in a central zone in the stock, through relatively high chalcopyrite near the contacts, to low chalcopyrite and very high pyrite in a zone peripheral to the contact. The picture is complicated by the east-west zone through the center of the stock, but within this zone, the chalcopyrite-pyrite relations fit a picture of zoning outward from the northern center of low sulfides. It is possible that two stages of

mineralization have been superimposed at Santa Rita to result in the zone cutting through the stock as proposed by Wallace et al. (1968) for Climax.

San Manuel

The recent description by Lowell (1968) of the mineralization and alteration in the Kalamazoo orebody at San Manuel, in combination with earlier descriptions by Creasey (1965) and Schwartz (1953), furnishes an excellent picture of the interrelations of alteration, sulfides, and porphyry.

After restoration of movement on the San Manuel fault, the alteration and sulfide patterns are concentric cylindrical shells. A central zone of the San Manuel-Kalamazoo orebody exhibits alteration of the biotite-orthoclase type, in which biotite and orthoclase of alteration origin are accompanied by varying amounts of quartz, sericite, chlorite, relict (?) sodic plagioclase, and other minerals (Fig. 4). At depth, chlorite apparently takes the place of biotite in this assemblage. A relatively sharp boundary separates the biotite-orthoclase alteration from a halo of intense quartz-sericite alteration, called the sericite-

SAN MANUEL — KALAMAZOO

Biotite-orthoclase alteration

Chlorite-orthoclase "

Quartz-sericite alteration
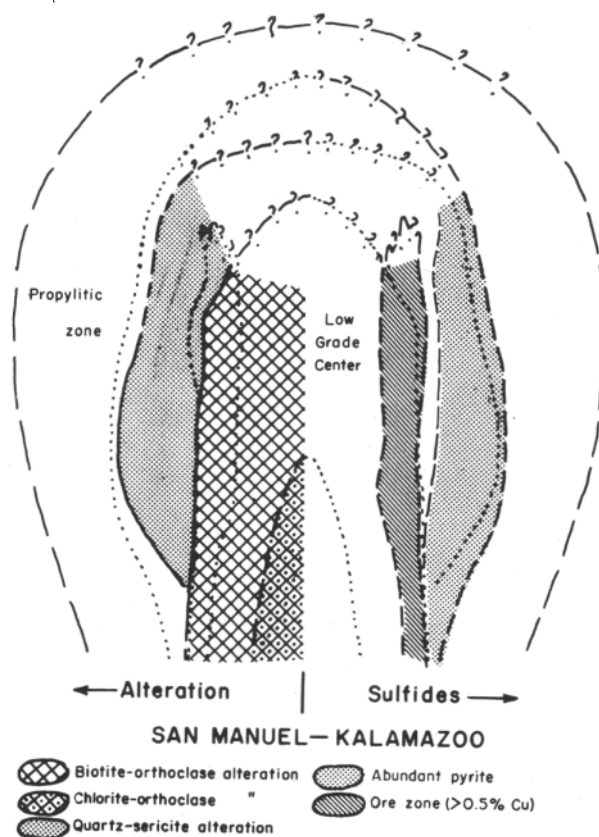
Abundant pyrite

Ore zone (>0.5% Cu)

Fig. 4. Diagrammatic section along the original vertical axis of the restored San Manuel-Kalamazoo orebody, Arizona, modified after Lowell (1968).
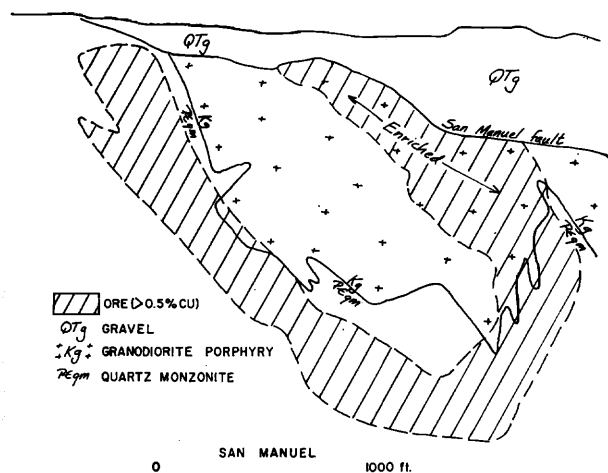
Fig. 5. Vertical section through the San Manuel orebody, showing relationship of primary ore to granodiorite porphyry contact. Because the orebody has been tilted 70°, this section is equivalent to a horizontal section of the original orebody. After Creasey (1965).

kaolinite assemblage by Creasey (1965). A wide zone of propylitic alteration surrounds the other two types.

Zoning of sulfide minerals dovetails well with the alteration pattern. When tilting and inferred movement on the San Manuel fault are removed, the orebody in horizontal cross section is ring-shaped with a barren center. This barren center with its low sulfide content (0.3% Cu, and pyrite/chalcopyrite about 1:2, according to Lowell, 1968) lies entirely within the biotite-orthoclase alteration zone. The ore zone, averaging 0.7% Cu as chalcopyrite, lies mainly in the biotite-orthoclase alteration zone, extending a short distance out into the quartz-sericite zone (Fig. 4). Lowell (1968) indicates pyrite/chalcopyrite of about 1:1. Outside the orebody a strongly pyritized zone largely coincides with the quartz-sericite alteration. This zone contains 6 to 25 wt % pyrite, averaging about 10%, and only 0.03% Cu, indicating pyrite/chalcopyrite of above 100. The pyritic zone fades out into the propylitic halo which grades from 4% down to traces of pyrite.

Geological evidence discussed by Lowell (1968) indicates that the San Manuel orebody has been tilted about 70° since its original formation so that the orebody is now lying almost on its side. If restored to the original attitude, the concentric zones of alteration and mineralization have a nearly vertical axis. In most of the San Manuel portion of the orebody, the ore lies near the contact of the porphyry intrusive with the Precambrian granite host rock (Fig. 5). The western portions of both orebodies are concentric to a small stock of granodiorite porphyry. Much of this stock occupies the low grade center of the orebody. The implication is

clear that this small stock or intrusive center is a controlling feature for the concentric ore and alteration patterns.

Bingham, Utah

Aspects of the Bingham deposit have been described by Peters, James, and Field (1966), Moore, Lanphere, and Obradovich (1968), James, Smith, and Bray (1961), Bray (1969) and Stringham (1953). Two main types of intrusive igneous rock are present in the district. The Last Chance stock and the southern and eastern portions of the Bingham stock are composed of a relatively dark equigranular to seriate porphyritic rock which probably averaged quartz monzonite in composition before alteration and has been called "dark porphyry" and "granite." A second body, called "granite porphyry" or "light porphyry," intrudes the north side of the "dark porphyry." This intrusive has the typical porphyry texture with an aphanitic quartz-feldspar groundmass as found at other porphyry copper deposits, and it appears to form a center for the alteration and mineralization patterns of the district.

The alteration, based on instrumental studies of rock samples taken on a grid, consists of a central zone within the intrusives of biotite-orthoclase alteration, with accompanying quartz and local sericite, sodic plagioclase, chlorite, sulfides, and other minerals (Fig. 6). Partly surrounding this zone, and occurring mainly in the quartzite country rock, is a zone of quartz-sericite alteration in which all feldspar

BINGHAM-Alteration
- Granite porphyry
- "Granite" (dark porphyry)
- Biotite-orthoclase alteration
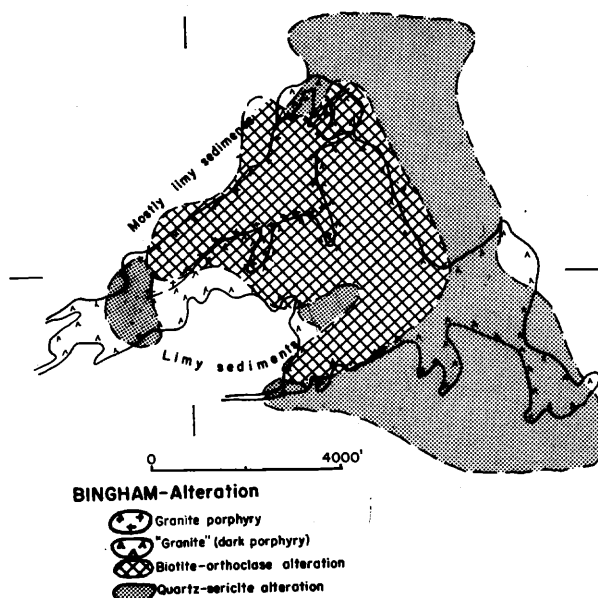- Quartz-sericite alteration

Fig. 6. Alteration pattern at Bingham, Utah. Tactite alteration of limestones interrupts the continuity of the peripheral alteration pattern. Modified after Peters, James, and Field (1966).

in the originally arkosic sandstone is altered to sericite. Tactite assemblages interrupt the completeness of the quartz-sericite zone. At still greater distances, some rocks show propylitic alteration.

Sulfides exhibit similar zoning concentric to the granite porphyry part of the stock (Fig. 7). The central zone is highest in chalcopyrite, bornite, and molybdenite, with low pyrite. Outward, the content of bornite diminishes and pyrite increases. The ore zone, defined by the limit of abundant chalcopyrite, approximately coincides with the area of the "granite porphyry" and immediately adjacent "dark porphyry," but it only locally extends appreciably into the quartzite. The ore zone also approximately coincides with the biotite-orthoclase alteration. Outside the ore is a zone of abundant pyrite and only traces of copper. Still farther out are lead-zinc-silver replacement and vein ores.

The Bingham orebody is thus seen to have the same type of zoning as the San Manuel and Santa Rita orebodies, except that the central zone is ore grade rather than low grade. At depth a barren center appears, and thus the pattern is exactly analogous to the others (James, 1969).

Ray, Arizona

Geology and alteration at Ray have been described by Metz and Rose (1966). Alteration data, based on instrumental and thin section studies of 250 samples, were obtained mainly from rocks that have undergone some supergene alteration, and interpretations of hypogene alteration are thus subject to some uncertainty. However, a large area of biotite-orthoclase alteration clearly exists (Fig. 8) and is interpreted to be partially surrounded by a quartz-sericite halo. Spot checks in drill holes indicate that the gross pattern is hypogene, although locally supergene effects are superimposed. A propylitic halo nearly surrounds the ore.

The several small quartz monzonite porphyry stocks in the ore zone generally have low contents of both chalcopyrite and pyrite along with relatively weak biotite-orthoclase alteration. Schist and diabase, the main ore hosts, generally have moderate sulfide contents with relatively low pyrite/chalcopyrite ratios and exhibit moderate to strong biotite-orthoclase alteration. In the West pit area, schist with a high pyrite content and some chalcopyrite produced good enriched ore in highly sericitized rock. Farther west, not enough chalcopyrite is present to form significant enriched ore despite abundant pyrite.

Although a single centrally-located stock does not exist at Ray, the general pattern of a central biotite-orthoclase zone with a low pyrite/chalcopyrite ratio

BINGHAM—Sulfide distribution

Granite porphyry
"Granite" (dark porphyry)
Bornite or "chalcocite" present
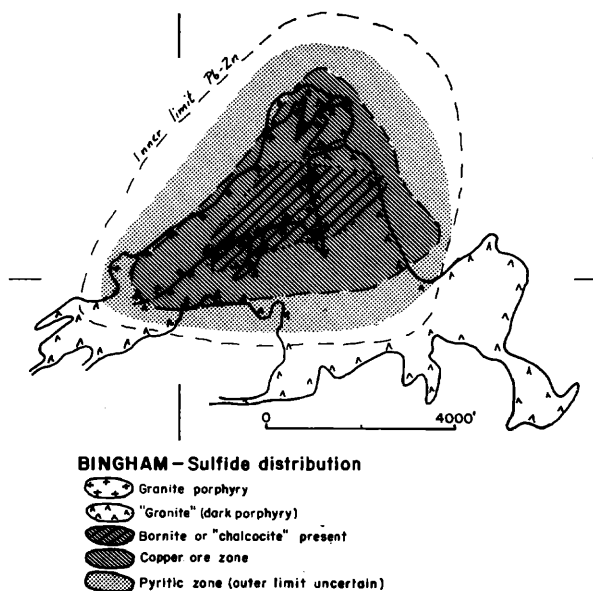Copper ore zone
Pyritic zone (outer limit uncertain)

FIG. 7. Sulfide distribution at Bingham, Utah, showing zoning from high Cu/Fe ratios at the center to low ratios on the periphery of the deposit. After James and others (1961) and Rose (1967).

passing outwards to a peripheral quartz-sericite zone with high pyrite can be recognized.

Ely

Studies by Fournier (1967) and Bauer et al. (1966), plus observations by the writer, show that alteration in porphyry and shale of the Liberty pit, Tripp pit, and Veteran pit areas is predominantly of the biotite-orthoclase type. Clay (mainly montmorillonite) is present where plagioclase was not altered to sericite or orthoclase, and it appears to be at least partly hypogene. Relatively small amounts of quartz-sericite alteration are present along veins in the southwestern Liberty pit. Chalcopyrite and pyrite are of approximately equal abundance in the biotite-orthoclase alteration zone.

Farther east in the district, strong quartz-sericite alteration is evident in the vicinity of the Ruth, Kimbley, and Wedge orebodies. Some of the sericite may be produced by supergene alteration of biotite, but much of it appears to be hypogene in origin. Jasperoids, representing strong silicification of limestone, also are abundant in this area, and may be equivalent to quartz-sericite alteration of aluminous rock types. Pyrite is abundant, both compared to chalcopyrite and in absolute amounts. Silicified sandstone, jasperoid, and other possible equivalents of quartz-sericite alteration are present locally along the south and west sides of the Liberty-Tripp-Veteran pit areas. The quartz-sericite alteration can thus be considered as peripheral to the biotite-ortho-
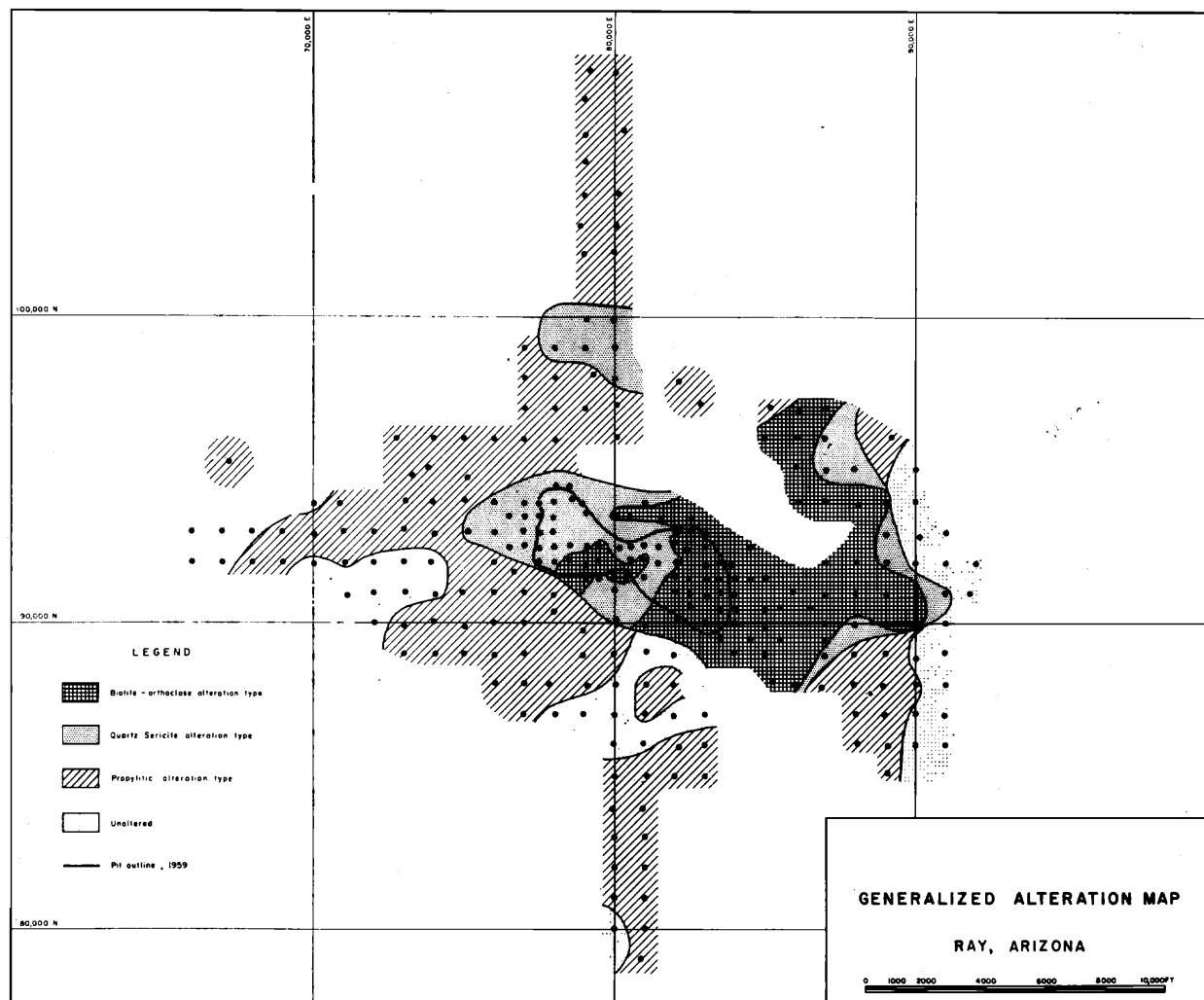
FIG. 8. Alteration pattern at Ray, Arizona, showing sample localities. After Metz and Rose (1966).

clase type, although the zones are greatly elongated in an east-west direction.

Safford, Arizona

The effects of deep supergene oxidation and alteration are of critical importance in deciphering the hypogene alteration pattern at Safford. In addition, although orthoclase is known to be present in sericitized dikes and plugs, detailed data on its distribution are not available. A pattern of alteration inferred from the published material (Robinson and Cook, 1966) plus unpublished observations in some drill holes is shown as Figure 9.

The ore is clearly associated with pervasive biotitic alteration of andesites and with sericitic alteration of quartz latite accompanied at least locally by orthoclase. Some plagioclase is albitized or locally altered to kaolin-group clays in the biotitized rock but much plagioclase remains unaltered. A large

sericitized zone on the southwest side of the orebody is known from drilling to be at least partly hypogene in origin, although drill holes in adjacent areas passed from sericitic to biotitic alteration at depth. Strong chloritic alteration and pyritization are peripheral to the quartz-sericite alteration on the southwest. Muscovite accompanies the chlorite in at least part of the zone, and the assemblage is equivalent to the quartz-sericite type as modified by the mafic character of the andesite.

Sulfide distribution (Fig. 10) largely parallels the alteration pattern. As shown by Robinson and Cook (1966), chalcopyrite is dominant over pyrite in an area encompassing the orebody and the biotite-orthoclase alteration. The sericitic and chloritic zones southwest of the orebody are strongly pyritized, as are a few other localities mainly on the periphery or just outside of the orebody, but also along dikes and shears through the biotitized zone.

Although the orebody occurs in andesite cut by a quartz latite dike swarm, no central stock is evident within the ore area, and the largest areas of quartz latite and brecciated quartz latite occur on the southwest margin of the mineralized area. Perhaps the alteration is centered on a larger intrusive at depth. Such a pattern of dikes coalescing into a larger intrusive at depth would be consistent with the apparent shallow depth of ore deposition, as indicated by the associated volcanic features (fine grain size of dikes, possible volcanic neck containing bedded sediments).

Cerrillos, New Mexico

A small non-economic disseminated copper deposit near Cerillos, New Mexico, has been described by Wargo (1964). The area is a center of laccolithic and crosscutting intrusions of monzonite and syenite into Cretacous sediments. The copper mineralization occurs as a ring-shaped zone in monzonite porphyry surrounding a coarse-grained monzonite plug. Adjacent to the coarse monzonite, the pyrite/chalcopyrite ratio is low, and the rock is altered to biotite and orthoclase. Farther from this center, pyrite is abundant, and plagioclase is altered to clay in patchy areas. Though no quartz-sericite alteration is recognized,

SAFFORD, ARIZONA—Alteration

Quartz latite porphyry
Latitic tuff and breccia
Biotite-orthoclase alteration
Quartz-sericite alteration
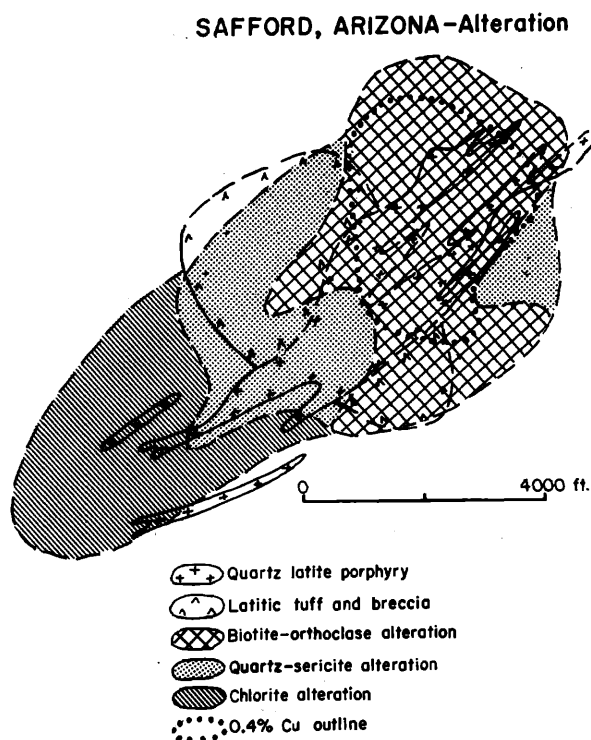Chlorite alteration
0.4% Cu outline

FIG. 9. Alteration pattern at Safford, Arizona, modified from Robinson and Cook (1966). The chlorite alteration is probably analogous to the quartz-sericite type as modified by the mafic-rich country rock (andesite).

SAFFORD, ARIZONA—Sulfide distribution

Quartz latite porphyry
Latitic tuff and breccia
Chalcopyrite and pyrite subequal
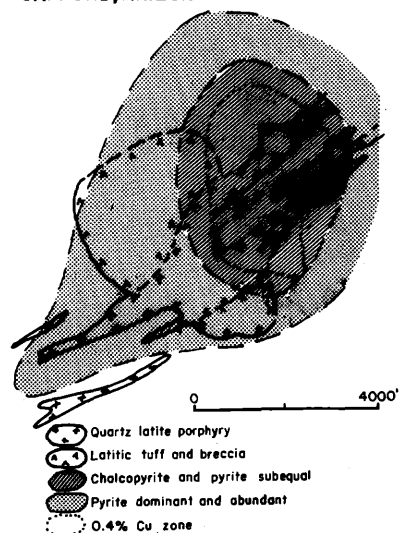Pyrite dominant and abundant
0.4% Cu zone

FIG. 10. Sulfide distribution at Safford, Arizona, after Robinson and Cook (1966).

the sulfide zoning and the biotitic alteration fit the common pattern.

San Juan, Arizona

This sub-economic deposit near the Kennecott Safford deposit (Robinson and Cook, 1966) is similar in many ways to the Cerrilos deposit. A central, weakly mineralized quartz monzonite porphyry plug, in which plagioclase is partly altered to sericite and clay, is surrounded by strongly biotitized andesite containing a low chalcopyrite content, with approximately a 1:1 pyrite/chalcopyrite ratio (Figs. 11, 12). Andesite in an incomplete ring of still larger diameter is strongly altered to chlorite accompanied by abundant pyrite. Strong propylitic alteration (epidote, chlorite, carbonate) is locally peripheral to the chlorite alteration. It seems possible that this center is also the root zone of a San Manuel-type or orebody. The chlorite zone is perhaps equivalent to quartz-sericite alteration, as modified by a mafic host rock. At any rate, the area shows a very clear zonal pattern of alteration centered on a small stock, and an outward increase of the pyrite/chalcopyrite ratio.

Butte

New data on the alteration and mineralization at Butte, especially at deep levels, have been presented recently by Meyer et al. (1968). Molybdenite- and chalcopyrite-bearing veins with associated biotite-orthoclase alteration envelopes occupy a part of the central portion of the district at depth. Quartz-sericite alteration forms halos around pyrite-rich veins that have their strongest development above and
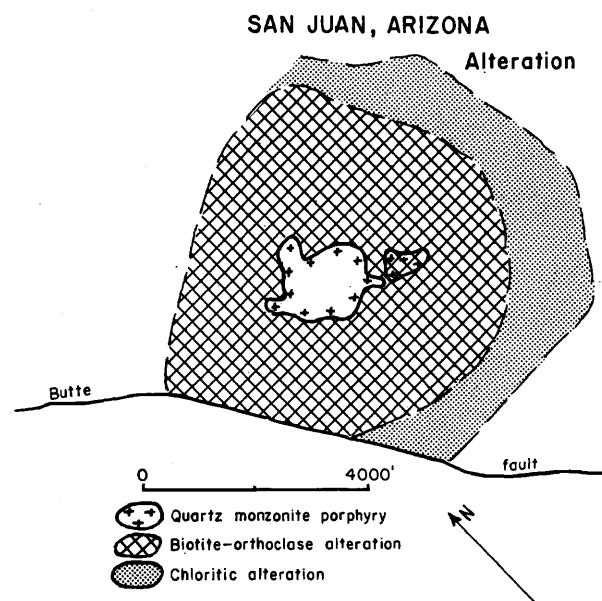
SAN JUAN, ARIZONA

Alteration

FIG. 11. Alteration at the San Juan prospect near Safford, Arizona, modified after Robinson and Cook (1966).

peripheral to the deep biotite-orthoclase alteration. The pyrite-rich veins and associated alteration cut the biotite-orthoclase alteration envelopes, but the age relations of strong quartz-sericite alteration at shallow levels to biotite-orthoclase alteration at depth remain uncertain.

No definite intrusive center is recognized at Butte, but a cluster of quartz porphyry dikes and pods does occur within the central molydenite zone.
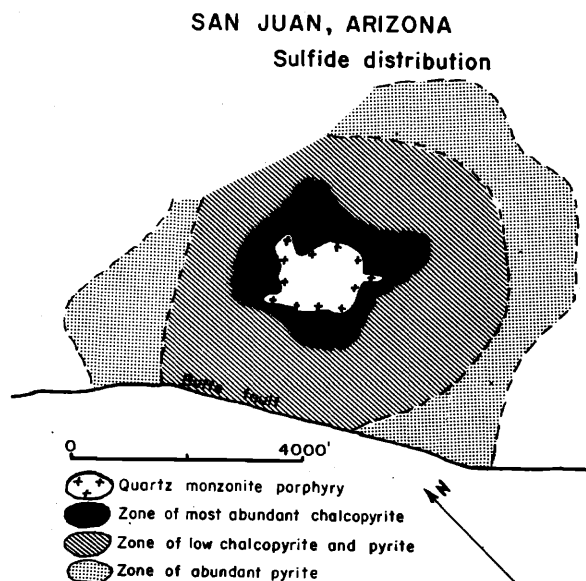
SAN JUAN, ARIZONA
Sulfide distribution

FIG. 12. Sulfide distribution at the San Juan prospect near Safford, Arizona, after Robinson and Cook (1966).

Other Deposits

A large number of deposits have a central zone of biotite-orthoclase alteration (Table 1). These include Yerington, Bagdad, Esperanza, the Phelps Dodge orebody at Safford, Braden, and probably Mission, Miami-Inspiration, Cuajone, Rio Blanco, El Salvador, and Potrerillos. In most of these deposits, biotite-orthoclase alteration is centered on a porphyry intrusion and largely coincides with the best primary ore.

Sericite is widespread as an alteration product but most descriptions do not specify whether orthoclase of alteration origin accompanies it. According to present data, it seems likely that quartz-sericite alteration is the main alteration type at Ithaca Peak and Bisbee. No central biotite-orthoclase zone is recognized at these deposits, but it could be present at depth. At other deposits, a peripheral relation to biotite-orthoclase alteration seems possible, but this is complicated by sericitized zones cutting through biotite-orthoclase alteration, and by supergene effects as previously discussed.

Discussion of Alteration Pattern

A large proportion of the well-studied deposits show a consistent pattern of lateral (and possible vertical) zoning of both alteration and sulfides. A central area of biotite-orthoclase alteration, usually coinciding with an intrusive center, has a low pyrite/ chalcopyrite ratio and may constitute primary ore if enough sulfides are present. Molybdenite and bornite, if present, are typically most abundant in this central zone. A barren center may be present within the biotite-orthoclase zone, and if present, is within

TABLE 1. Occurrence of Alteration Types at Porphyry Copper Deposits. "X" Indicates that Significant Alteration of the Designated Type is Present at the Deposit

Deposit	Biotite-orthoclase	Quartz-sericite
Yerington	X	
Bagdad	X	
Ithaca Peak		X
Miami-Inspiration	X	
Castle Dome		X
Copper Cities		X
Silver Bell	?	X
Esperanza	X	X
Mission	X	
Bisbee		X
Safford (P.D.)	X	
Morenci		X
Cananea	?	X
Cuajone	X	
Chuquicamata	X	X
El Salvador	X	X
Potrerillos	X?	
Rio Blanco	X	
Braden	X	X?

the porphyry intrusive (Santa Rita, Ray, Bingham, San Manuel, Cerillos).

Quartz-sericite alteration is generally peripheral to the biotite-orthoclase zone, and it includes high pyrite but low copper except adjacent to the boundary with the biotite-orthoclase alteration. Variable amounts of quartz-sericite alteration also occur within the biotite-orthoclase area along veins and faults (Butte, Safford, Ely). The sericitic alteration along faults and shears is later than biotite-orthoclase alteration it cuts, but the relative ages of pervasive biotite-orthoclase and quartz-sericite alteration are uncertain in that much quartz-sericite alteration may be contemporaneous with biotite-orthoclase.

Within the biotite-orthoclase zone, chalcopyrite commonly occurs in and adjacent to small veins containing orthoclase or with orthoclase-rich or biotite-rich alteration halos. This texture indicates the coexistence and probable contemporaneity of at least some of the copper sulfides with the biotite-orthoclase alteration. Similar relations exist with respect to pyrite-rich veins and peripheral quartz-sericite alteration. In the porphyry hosts, common control of alteration and sulfides by veinlets indicates that much of the copper was introduced after consolidation of the exposed intrusive.

The two alteration types (biotite-orthoclase and quartz-sericite) can be understood in part with reference to the K/H (actually total KCl/HCl) vs. temperature diagram (Fig. 13). In order for orthoclase to form stably, as it appears to in both veins and wallrock, the combination of K/H and temperature must be high enough to be in the K-feldspar field of the diagram, or on the K-feldspar muscovite boundary. In contrast, where silicates, including K-feldspar, are altered to the quartz-sericite assemblage, the temperature and/or K/H ratio must be lower than the K-feldspar-muscovite boundary. The zoning from biotite-orthoclase alteration outward to quartz-sericite alteration thus represents an outward decrease in temperature or K/H or both.

Further discussion of the alteration and sulfide zoning is facilitated by knowing the direction of solution transport. The presence of a considerable meteoric component in the ore fluid is suggested by oxygen and hydrogen isotope studies at porphyry copper deposits (Sheppard, Nielsen, and Taylor, 1969). Although oxygen and hydrogen in some alteration minerals may reflect meteoric water, the isotopic compositions for lead and sulfur are generally not those expected as a result of leaching from country rocks, but are consistent with a deep-seated origin in the lower crust or mantle (Doe et al., 1968, Stacey et al., 1968, Kulp et al., 1956, Field, 1966a, 1966b). Also, the lead isotope studies at Bingham and Butte demonstrate a close similarity or identity
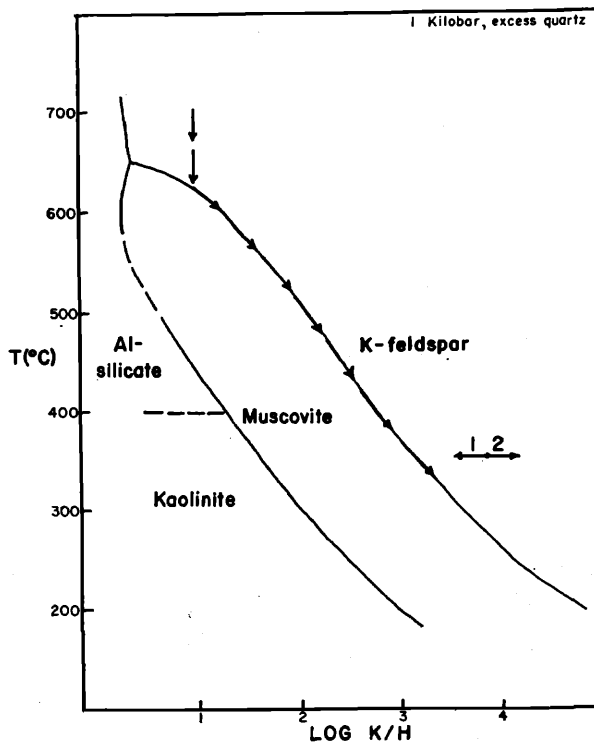

Fig. 13. Stability relations of kaolinite, muscovite, and K-feldspar in chloride solutions with respect to temperature and KCl/HCl ratio, after Hemley (1959) and Shade (1968). See text for significance of arrows.

between the ore lead and lead in associated igneous rocks. It thus appears that, whatever the source of the water, the metals and sulfur have a deep-seated source in common with the granitic intrusive. The consistent association of porphyry copper deposits with granodioritic intrusives with a limited compositional range tends to support an igneous source for the ore constituents. The discussion to follow therefore assumes that ore transport is outward from a' magmatic source because the metals and sulfur seem most reasonably attributed to such a source. The oxygen and deuterium effects may result from retrograde or meteoric processes, or from admixture of meteoric water with magmatic fluids.

The lateral and vertical zoning from orthoclase to quartz-sericite can be explained in two contrasting ways, involving the relative ages of the alteration types:

1. The pervasive quartz-sericite alteration developed essentially at the same time as the biotite-orthoclase alteration it surrounds, in the manner of zoning around veins (Sales and Meyer, 1948) but on a larger scale.

2. The quartz-sericite alteration is completely earlier or later than the biotite-orthoclase alteration.

At least some quartz-sericite alteration is apparently later than biotite-orthoclase alteration, as indicated by the cross-cutting relations along veins as found at Butte (Meyer et al., 1968) and elsewhere. However, these might be explained as late-stage features resulting from a "retreating source," i.e., the altering solution at a late stage differs in K/H or temperature because it has traveled farther from its source or the entire system has cooled, but the alteration is the same type earlier produced farther from the source.

If the prevasive alterations differ significantly in age (Case 2), this implies the release of two different ore fluids from the magmatic source. Based on the observed age relations, the first would presumably be hot and/or alkali-rich; the second relatively more acid and/or cooler, at least by the time it accomplishes the quartz-sericite alteration. But in view of the pervasive alteration characterizing both types, how does the second acid-rich solution attain a peripheral location with little or no effect on the older biotite-orthoclase zone? This inner zone has been highly shattered, as evidenced by the presence of a multitude of chalcopyrite bearing veinlets, yet re-alteration to quartz-sericite has occurred only locally. Laboratory data (Fig. 13) shows that cooling of a concentrated alkali chloride solution initially in equilibrium at high temperatures with both feldspars and muscovite (as observed in many biotite-orthoclase zones) will tend to produce muscovite-rich alteration from the feldspars, especially if the cooling rate is moderately rapid. It therefore requires some special condition to avoid forming sericitic alteration during cooling of a fluid in the orthoclase field. In addition, the presence of the highest copper contents at the outer margin of the biotite-orthoclase zone overlapping into the quartz-sericite alteration, as well as the gradual sulfide zoning (especially at Bingham) and the consistent zonal relations of the two alteration types at many deposits suggests that the two alteration types develop at the same time as part of the same process.
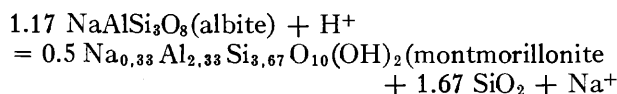
Based on the relations of K/H with mineral stability, the possible effects of changes in K/H ratio by reactions with wallrock need to be considered as an explanation for the zoning. Meyer and Hemley (1967, p. 206–207) and Hemley and Jones (1964) have discussed some such reactions; for instance, chloritization of biotite uses H and releases K which will tend to keep the fluid in the feldspar field.

In the biotite-orthoclase zone, the major observed alteration processes are normally the following:

1. Replacement of plagioclase by orthoclase, by a reaction such as:

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+$$
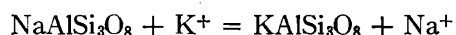
2. Replacement of plagioclase by clays. The reaction is illustrated by the following, after Hemley and Jones (1964);

$$1.17\ NaAlSi_3O_8(albite) + H^+$$
$$= 0.5\ Na_{0.33}\,Al_{2.33}\,Si_{3.67}\,O_{10}(OH)_2(montmorillonite$$
$$+ 1.67\ SiO_2 + Na^+$$

3. Replacement of hornblende or pyroxene by biotite. Reactions are complicated but involve consumption of K, and in the case of hornblende might either consume or release H.

Argillization of plagioclase (Reaction 2) may well be a later superimposed feature but is included in view of the possibility that it is a nonequilibrium process controlled by high SiO_2 activity. The reaction would use H^+ and thereby increase K/H, tending to keep the fluid in the orthoclase field (trend 2, Fig. 13). Therefore, this reaction cannot be responsible for the observed zoning from orthoclase to sericite.

Replacement of plagioclase by orthoclase (Reaction 1) consumes K with no effect on H; therefore it could move the fluid from the orthoclase field to the muscovite field (trend 1, Fig. 13), although it would more likely stay in a feldspar field since there is no net consumption of base cation. There might also be sericitization of plagioclase with or without attack on orthoclase. However, the latter reaction, which is observed in the quartz-sericite zone and sometimes in the biotite-orthoclase zone, tends to consume more H than K and therefore tends to keep the fluid on the muscovite-orthoclase boundary, with stability of both minerals. The observations indicate that orthoclase is completely destroyed in the quartz-sericite zone, and thus some other factor must be operative.

Biotitization of mafic minerals is complicated by the variable composition of the minerals. However, zoning from biotite-orthoclase to quartz-sericite alteration is observed for cases where mafic minerals are sparse, and thus biotitization does not seem a general control for the change of alteration types.

An additional reason for rejecting chemical exchange with wallrock as a control of the zoning is the high absolute values of the K/H ratio. At 625° C, this ratio is 10 on the muscovite-orthoclase boundary (Fig. 13), and at 350° C the ratio is about 1,000. High alkali chloride contents of ore fluids are indicated by the presence of alkali chloride crystals in some inclusions from porphyry copper deposits (Roedder, 1963). The K/H ratio is therefore much more sensitive to changes in H than K, but the observed changes involving H tend to keep the fluid in the feldspar field. We therefore discuss
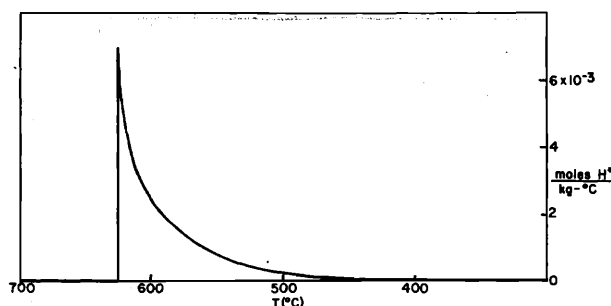
Fig. 14. Moles of hydrogen ion available for alteration of K-feldspar to sericite during cooling of a 2M chloride solution with an initial K/H of 10.

next the effects of cooling, the other major variable controlling orthoclase-muscovite stability.

Figure 13 illustrates the effect of cooling on a hypothetical solution of HCl and KCl in contact with a quartz-orthoclase rock. The solution is characterized by a total chloride content of 2 molal, a K/H ratio of 10, an initial temperature of 700° C and a pressure of 1,000 bars. This composition is in the K-feldspar field but near the boundary with aluminum silicates (Shade, 1968; Burnham and Shade, 1966). As the fluid is cooled from 700° C to about 625° C, it remains in the K-feldspar field. Although alterations of the type discussed above might affect the K/H ratio, we assume for simplicity that these processes have no significant effect. Upon reaching the muscovite-K-feldspar boundary and cooling a small additional amount, the equilibrium with the solid phases changes drastically. K-feldspar is no longer stable, and is altered to muscovite (as may be other phases). These reactions consume H and the solution moves to higher K/H ratios, near or on the curve, if the reactions take place fast enough. However, any further cooling must result in additional muscovite alteration, and K-feldspar, although it may be stable, will not be formed as long as cooling continues. Eventually the HCl content of the fluid is essentially used up, and although further cooling requires changes in K/H, the concentration of H in the fluid at temperatures of 200° C or less is so small that the ratio is changed by consuming only infinitesmal amounts of H.

Figure 14 summarizes the amount of H available for alteration to mica per degree of cooling of the above fluid, assuming that changes in K content are insignificant (i.e., perhaps K entering fluid from K-feldspar alteration is used in sericitization of plagioclase). It is seen that the largest amounts of H are available just below the temperature at which the mica-feldspar boundary is crossed. This pattern of H availability matches very closely the observed alteration pattern; a central biotite-orthoclase alteration, with a rapid transition to pervasive and complete sericitization, grading outward to weakly propylitized rock, in which strong alteration is localized by fissures. The close analogy indicates that cooling of a single fluid during flow is a likely means of producing the observed alteration, in contrast to the effects found for chemical reaction with wallrock on the K/H ratio.

Heat Effects.—Toulmin and Clark (1967) have shown that for an ore fluid flowing through a large vein, heat transfer to the wall rocks is not an effective cooling process, unless ore deposition is very rapid or involves only a small amount of fluid. The above mechanism involves cooling the ore fluid to move
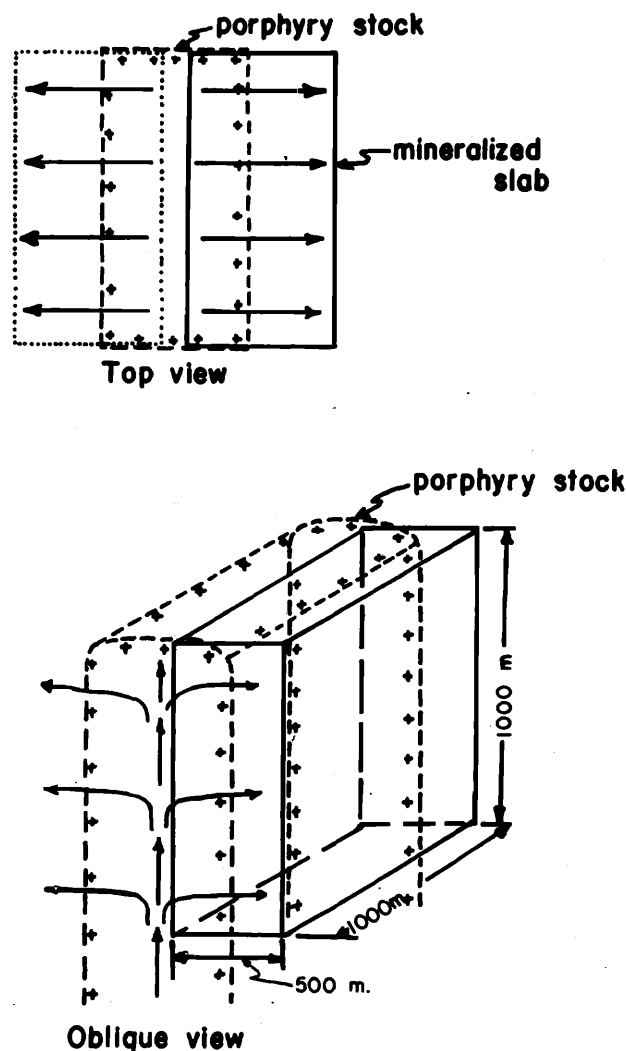

Top view

Oblique view

Fig. 15. Diagram of model for thermal calculation. The 500 × 1,000 × 1,000 m block is assumed to average 0.4% Cu deposited by a hydrothermal fluid moving upward through a highly-fractured porphyry intrusive (indicated by + symbols) and then outward laterally into country rock. Although actual fluid flow would probably be oblique, the overall results would be similar to the model.

from the K-feldspar field into the muscovite field, and for this a cooling process must be available.

As a model to test the cooling effects, we take a slab-shaped mineralized and altered block illustrated in Figure 15. The block is 500 meters wide and 1,000 meters square. This block lies along one side of slightly elongate porphyry stock, with one face well inside the stock and the other outside the zone of intense alteration. Ore fluid moves up the interior of the stock and then outward in a horizontal direction. This slab is the zone within which ore deposition and alteration is concentrated, and approximately fits the dimensions of some of the larger porphyry copper deposits. The final copper content is assumed to average 0.4% Cu (some zones may be higher, and some are certainly lower) to give a total copper content of about 5×10^6 metric tons in about 1.3×10^9 tons of rock.

Hemley et al. (1967) have found solubilities for ZnS of thousands of ppm in solutions at 300–500° C in equilibrium with quartz-muscovite-K-feldspar. Solubilities in this range are also suggested by considerable other data (Barnes and Czamanske, 1967, p. 369). On this basis a solution containing 2,000

Table 2. Calculation of heat transfer from fluid to country rock.

A. Heat transfer coefficient for fluid flowing through aggregate of 20 cm cubes separated by 0.4 cm open fractures (Perry, 1963).

$$h = (\frac{c\mu}{k})^{2/3} \cdot (\frac{L}{D})^{1/3} \cdot (\frac{\mu_w}{\mu})^{0.14} \cdot (\frac{\mu}{DG})^{2/3} \cdot \frac{cG}{1.86}$$

h = heat transfer film coefficient (cal-cm^{-2} - sec^{-1}- °C^{-1}

k = thermal conductivity of fluid (2×10^{-3} cal-cm^{-2} - sec^{-1}- °C^{-1})

c = specific heat of fluid (1.0 cal-gm^{-1} - °C^{-1})

μ = viscosity (5×10^{-4} gm-sec^{-1} - cm^{-1})

L = length of undisturbed flow (20 cm)

D = width of open fracture (0.4 cm)

μ_w = viscosity of fluid at wall (assumed equal to μ)

G = mass velocity (gm-cm^{-2} - sec^{-1})

Results:

Flow velocity	h
1 cm-sec^{-1}	3×10^{-3} cal-cm^{-2}-sec^{-1}-°C^{-1}
10^{-2}	6.8×10^{-4}
10^{-4}	1.6×10^{-4}

B. Temperature vs. distance calculations (Furnas, 1932)

$$y = \frac{Px}{C_g G} \qquad z = \frac{P}{C_s(1-f)} (t - \frac{fx}{G})$$

P = heat transfer coefficient (cal-cm^{-3}-°C^{-1}- sec^{-1})

x = distance from inlet point (cm)

C_s = heat capacity of solid (0.8 cal-cm^{-3}-°C^{-1})

C_g = heat capacity of fluid (0.5 cal-cm^{-3}-°C^{-1})

t = time (sec)

f = porosity, fraction of rock through which fluid flows (0.02)

h and G as in part A; P derived from h by conversion from surface area (20 cm. cube) to volume.

y and z are dimensionless parameters graphed by Furnas (1932).

ppm Cu is not unreasonable, though probably higher than many past conceptions. To deposit the copper in the ore body described above would require about 2.5×10^9 metric tons of solution containing 2,000 ppm Cu, or a flow of about 2.5×10^5 gm H$_2$O per square centimeter of cross section of the slab. A body of magma of about 92 km^3 (a cube 4.5 km or 2.8 mi on a side) losing 1% H$_2$O and 20 ppm Cu could provide the water and copper. The large amount of rock that must be depleted of H$_2$O and Cu furnishes an argument for a magmatic process of concentration of the metals rather than a post-magmatic leaching of the consolidated igneous rock by heated waters of a non-magmatic source.

Toulmin and Clark (1967) in their discussion of heat effects in ore deposits find that cooling of a hydrothermal solution by the following processes can be significant:

1. Irreversible adiabatic expansion ("throttling," or expansion due to a sudden pressure drop).
2. Mixing with cool ground water.
3. Under certain conditions, heat exchange with wallrocks.

Although they find that process 3 is effective only in unrealistic cases for large veins, the porphyry copper environment differs from the vein situation because of the intimate permeation of fluid through the highly fractured country rock. Heat transfer is more effective in this case, so some discussion seems necessary.

No exact treatment of heat transfer in this situation is available. However, an approximate result can be found from the work of Schumann (1929) and Furnas (1932). Schumann (1929) developed the mathematics for heat transfer from a flowing fluid to a mass of fragments of uniform size under the following assumptions:

1. The fragments are small or have high enough thermal diffusivity that they have a uniform temperature throughout.
2. Heat conduction in the direction of fluid flow may be neglected.
3. The heat transfer rate from fluid to solid is proportional to the average temperature difference at the point.
4. There is no change of volume of the fluid or solid.
5. The thermal constants are independent of temperature.

These assumptions appear to be approximately met if flow velocities are slow, say between 10^{-4} cm/sec and 1 cm/sec, and the total time involved is less than a few thousand years. For longer times heat

transfer by conduction through the rock becomes dominant over heat transfer by convection. Furnas (1932) provides curves for graphical solution of the equations of Schumann (1929). In order to use the Schumann-Furnas results, values for the heat transfer coefficient from fluid to solid are needed. These have been calculated using a Colburn-type equation for heat transfer through a surface film (Perry et al., 1963). Table 2 lists values of the various parameters used to calculate the heat transfer coefficient and the distance vs. temperature curves. Most of the parameters are taken from Toulmin and Clark (1967).

Three flow velocities have been studied; 10^{-4} cm/ sec, 10^{-2} cm/sec, and 1 cm/ sec. The 2.5×10^9 tons of solution has been allowed to flow at the above rates until exhaustion, equivalent to times of about 10,000 years, 100 years, and 1 year. The 10^{-4} cm/sec flow rate seems unrealistically slow, mainly because of the possibility of faster velocities caused by thermally driven convection, as discussed by Toulmin and Clark (1967), and because the pressure gradient involved would be extremely low for the presumed combination of hypabyssal environment and high-temperature fluid near its boiling point. In addition, the approximation becomes inaccurate because heat transfer by conduction is important, and because the rates found for diffusion transport of elements in experiments by Burnham (1967, p. 57–60) appear to be of nearly this order of magnitude. Because of these factors, further work is needed to evaluate diffusion and conduction in an essentially stagnant fluid. However, in view of the reasons cited above, as well as others, such slow flow rates seem unlikely as predominant feature of mass transfer in porphyry copper deposits. No special justification can be made for 1 cm/sec as an upper limit except that 1 year seems a short time for deposition, although not impossible.

Unfortunately, the temperature-distance profiles demanded for the above situation exceed the range of graphical solutions given by Furnas (1932), which is not surprising since he was dealing with industrial equipment. Values for Bessel functions of the required size are not available for mathematical evaluation. However, by extrapolation of his curves and by analogies with solutions for shorter times a solution has been approximated in Figure 16, and is seen to be close to a step function. Near the fluid source a large body of rock has been heated to the temperature of the incoming fluid. A narrow zone of heating (the step) separates the heated zone from a cold zone. The zone of heating is widest for the fastest (1 cm/sec) flow rate, but even in this case the transition zone is only a few tens of meters thick, based on calculations for smaller times. At
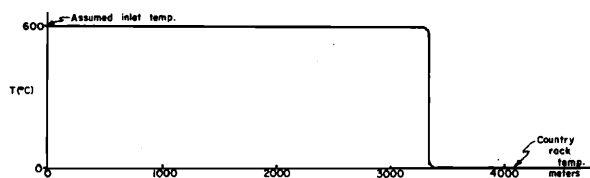

Fig. 16. Temperature profile from inner edge of ore zone outward into country rock after deposition of ore by hydrothermal fluid containing 2,000 ppm Cu and flowing 10^{-2} cm/ sec. The ore fluid is assumed to be initially at 600° C and the country rock at 0° C, but the shape of the curve would be little altered by changes of initial temperature of several hundred degrees (though the location of the temperature step would change appreciably). For slower flow rates the step would be rounded off because of heat conduction through the rock.

the scale of the ore body, the zone of heating thus moves as a thermal front, as does the cooling zone in the fluid (the temperatures of the fluid and solid are essentially the same at the scale of the figure). Undoubtedly this simple picture would be modified by chemical heat effects, variations in initial temperature, flow pattern, permeability and other aspects of the plumbing, but for a wide variety of conditions the volume of rock heated and the advancing step character would be approximately preserved.

A critical feature of the temperature-distance profile is the location of the step. The distance where $(Tg - To)/T_f - To) = 0.5$ (the half height of the step) can be approximated by setting $y = z$ in Furnas' equations (Table 2). This gives a distance for the step at the end of fluid flow of about 3,150 meters for all three cases, and is not dependent on the heat transfer coefficient, only on the total volume of fluid, the relative heat capacities of fluid and rock, and the proportion of voids.

The large volume heated according to this model conflicts with field observation, and therefore casts doubt on the effectiveness of heat conduction to wall rocks in cooling the solution. According to this result our relatively concentrated ore solution (2,000 ppm Cu) has heated up a huge volume of rock (1,000 × 1,000 × 3,150 meters) to the inlet temperature of the solution. Evidence for heating of such a large volume of rock does not appear to exist in the deposits, at least not to temperatures as high as 500–700° C, which are implied by the inferred magmatic source. Note that more dilute ore solutions would considerably increase the volume of rock heated. In the case of a flow rate of 10^{-4} cm/sec, there would be a significant heat loss by conduction through the rocks; however, as noted above, conclusions from this flow rate are probably unrealistic and the gross results would still be similar. The 10^{-2} cm/sec and 1 cm/sec flow rates would not be affected appreciably by conduction, because heat transfer by flow predominates.

An additional argument against cooling by this mechanism is furnished by the alteration pattern and age relations expected from the model based on the K/H vs. temperature plot. The model would give an advancing temperature front, along which the fluid would accomplish sericitic alteration as the step passed a point, but at a slightly later time the sericitized rock at that point would be in contact with fluid at the inlet temperature, and presumably in the K-feldspar stability field. If the fluid were able to convert some sericite back to K-feldspar, the final result would be a vast area of biotite-orthoclase alteration, and a very narrow zone of quartz-sericite alteration. Sericite would be replaced by K-feldspar throughout the felspathized zone. In actuality, the K-feldspar is almost always a vein filling or a direct replacement of plagioclase, and sericitic alteration appears to encroach on K-feldspar alteration.

One is thus driven to the conclusion that simple cooling of hydrothermal fluid by conduction to wall-rock is no more tenable for the porphyry copper deposit than for the simple vein, although for different reasons. A very concentrated ore solution flowing very rapidly (>1 cm/sec) would appear to be the only feasible mechanism for producing the observed pattern of alteration and mineralization by a wall-rock cooling process, and even in this case the age relations of K-feldspar and sericite are a problem.

The other two mechanisms (irreversible adiabatic expansion, and mixing with ground water) thus become candidates for cooling the fluid. Significant cooling by irreversible adiabatic expansion (throttling) requires relatively large pressure differences, according to the data presented by Toulmin and Clark (1967). A number of the porphyry copper deposits appear to have developed at relatively shallow depths in the crust, on the order of a few thousand to perhaps 10,000 feet. Lithostatic loads of $\frac{1}{4}$ to $\frac{3}{4}$ kilobars are thus indicated. If the fluid (assumed for simplicity as pure H_2O) is cooled by expansion from 750 bars and 600° C to 250 bars (i.e., change from lithostatic to hydrostatic load) its temperature is about 450° C, according to Toulmin and Clark (1967). This appears sufficient to cause the observed alteration change, although the pressure decrease would shift the K/H boundaries slightly in a direction tending to keep K-feldspar stable (Shade, 1968). The common occurrence of breccias and pebble dikes is suggestive of the considerable pressure gradients implied by throttling. This mechanism thus seems a possible means of producing the alteration pattern.

If throttling is the main cooling process, one is left with a fluid at 350–500° C (depending on initial temperature and the pressure drop). A means for disposing of a considerable amount of heat is still necessary. At some deposits a wide zone of propylitic alteration is present around the deposit. Temperatures represented by propylitic alteration (essentially equivalent to greenschist facies metamorphism) remain uncertain. Winkler (1967, p. 175–8) suggests that temperatures of at least 360° C up to about 525° C are necessary, but Muffler and White (1969) find the greenschist mineral assemblage forming at 300° C in the Salton Sea geothermal system. The extensive propylitic alteration can be conveniently attributed to heating of wallrocks by the expanded hydrothermal fluid, accompanied by addition of H_2O and CO_2. The extent of propylitic alteration in at least some districts is adequate to allow for cooling for the relatively concentrated hydrothermal fluid used in our example (2,000 ppm Cu), but probably not more dilute solutions. The extent and nature of the now-eroded rocks above the ore deposit remain a partial unknown that might have promoted cooling.

Mixing with meteoric or other cold water also is capable of causing the cooling. According to this hypothesis, the quartz-sericite zone is the zone of mixing of a hot hydrothermal fluid of magmatic origin with cooler water. The oxygen-18 and deuterium data so far available suggest the presence of a large meteoric component in the hydrothermal fluid in the quartz-sericite zone (Garlick and Epstein, 1966; Sheppard et al., 1967). Isotopic data are lacking for the biotite-orthoclase zone. Essentially any degree of cooling can be accomplished by mixing. If the cool water is low in dissolved solids relative to the hydrothermal fluid, no significant change in K/H ratio is involved. The main problem seems to be a means of mixing the fluids gradually over a distance of many hundreds of feet.

In view of the convective instability of hot fluids relative to cold fluids in the country rocks, it seems certain that the hydrothermal fluids will circulate and mix with ground waters if any access of cool waters is possible. The highly fractured nature of porphyry copper districts suggests that ground waters will have access to the hydrothermal area at some stage in the process of cooling. The main problems are the proportions of hot and cool fluids and the location of mixing as a function of time. It seems possible that the zone of throttling may coincide with the zone of mixing, so that the effects of two processes are superimposed. As the influx rate of hydrothermal fluid decreases, the zone of throttling and/or mixing might retreat to give the quartz-sericite alteration along veins and shears in the biotite-orthoclase zone.

In the present state of knowledge it does not seem possible to choose between the later two cooling processes, if indeed a choice is possible. Very likely all three cooling processes are involved, with the

relative importance varying in different cases. Mixing with cold water has the advantage of great flexibility, but it remains to be determined whether this process is responsible for the change to the quartz-sericite alteration. The oxygen and deuterium data suggest that meteoric water has been important at some stage, but perhaps only during a retrograde exchange process during cooling, after the basic features are formed.

Conclusions

A consistent general pattern of hypogene silicate and sulfide zoning is indicated at the best-described porphyry copper deposits (San Manuel, Santa Rita, Bingham, perhaps Butte). Other deposits seem to fit the pattern if the various permutations of multiple stages of mineralization, retreating source, supergene alteration, etc. are added.

Although the halos of quartz-sericite and propylitic alteration are not perfect rings in many cases, this is to be expected if the hydrothermal fluid is channeled by fractures and other permeable conduits. An unfractured rock, or one not part of the main plumbing system, would not develop much alteration. It is entirely possible to have biotite-orthoclase alteration in contact with unaltered or propylitically altered rocks. However, there should be an outlet for the hydrothermal fluid in some direction, with appropriate alteration and thermal effects. If the main direction of fluid flow is upward, this portion of the plumbing may have been removed by erosion. A wide variety of alteration patterns is therefore possible in detail.

The correlation of sulfide abundance with silicate alteration as described here, and discussed by Meyer and Hemley (1967) in more comprehensive terms, suggests that changes in the factors affecting the stability of silicates relative to the hydrothermal fluid (temperature, activities of H^+, K^+, Na^+, etc.) are accompanied by changes in stability of metal complexes in the fluid. Activity of H^+, as determined by dissociation on cooling, is an obvious parameter in this regard, as it is involved in H_2S-HS^--$S^=$ equilibria.

Given the observed correlation of sulfides and silicates, the model for alteration during cooling proposed here implies that ore deposition and strong alteration are critically dependent on availability of a process for cooling the ore fluid, as well as on the fluid composition. In view of the limitations on cooling summarized here, it is apparent that significant cooling occurs only in relatively unusual situations, i.e., zones of mixing with cool waters, zones of pressure release, or zones of extremely slow flow (which need further study).

REFERENCES

Barnes, H. L., and Czamanske, G. K., 1967, Solubilities and transport of ore minerals, *in* Geochemistry of Hydrothermal Ore Deposits, ed. by H. L. Barnes: New York, Holt, Rinehart and Winston, p. 334–381.

Bauer, H. L., Breitrick, R. A., Cooper, J. J., and Anderson, J. A., 1966, Porphyry copper deposits in the Robinson mining district, Nevada, *in* Geology of the Porphyry Copper Deposits, ed. by S. R. Titley and C. L. Hicks: Tucson, Univ. of Ariz. Press, p. 233–244.

Bray, R. E., 1969, Igneous rocks and hydrothermal alteration at Bingham, Utah: Econ. Geol., v. 64, p. 34–49.

Burnham, C. W., 1962, Facies and types of hydrothermal alteration: Econ. Geol., v. 57, p. 768–784.

Burnham, C. W., 1967, Hydrothermal solutions at the magmatic stage, *in* Geochemistry of Hydrothermal Ore Deposits, ed. by H. L. Barnes: New York, Holt, Rinehart, and Winston, p. 34–76.

Burnham, C. W., and Shade, J., 1966, Hydrolysis equilibria in the system K_2O-Al_2O_3-SiO_2-H_2O (abst.): Geol. Soc. Am., Sp. Paper 101, p. 32–33.

Creasey, S. C., 1959, Some phase relations in hydrothermally altered rock of porphyry copper deposits: Econ. Geol., v. 54, p. 354–373.

Creasey, S. C., 1965, Geology of the San Manuel area, Pinal County, Arizona: U. S. Geol. Surv., Prof. Paper 471.

Creasey, S. C., 1966, Hydrothermal alteration, *in* Geology of the Porphyry Copper Deposits, ed. by S. R. Titley and C. L. Hicks: Tucson, Univ. of Ariz. Press, p. 51–75.

Doe, B. R., Tilling, R. I., Hedge, C. E., and Klepper, M. R., 1968, Lead and strontium isotope studies of the Boulder Batholith, southwesetrn Montana: Econ. Geol., v. 63, p. 884–906.

Field, C. W., 1966a, Sulfur isotope abundance data, Bingham district, Utah: Econ. Geol., v. 61, p. 850–871.

Field, C. W., 1966b, Sulfur isotopic method for discriminating between sulfates of hypogene and supergene origin: Econ. Geol., v. 61, p. 1428–1435.

Fournier, R. O., 1967, The porphyry copper deposit exposed in the Liberty pit mine near Ely, Nevada: Econ. Geol., v. 62, p. 57–81, 207–227.

Furnas, C. C., 1932, Heat transfer from a gas stream to a bed of broken solids: U. S. Bur. of Mines, Bulletin 361, 88 pp.

Garlick, G. D., and Epstein, S., 1966, The isotopic composition of oxygen and carbon in hydrothermal minerals at Butte, Montana: Econ. Geol., v. 61, p. 1325–1335.

Hemley, J. J., 1959, Some mineralogical equilibria in the system K_2O-Al_2O_3-SiO_2-H_2O: Am. J. Sci., v. 257, p. 241–270.

Hemley, J. J., and Jones, W. R., 1964, Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism: ECON. GEOL., v. 59, p. 538–569.

Hemley, J. J., Meyer, C., Hodgson, C. J., and Thatcher, A. B., 1967, Sulfide solubilities in alteration-controlled systems: Science, v. 158, p. 1580–1582.

James, A. H., 1969, Hypothetical diagrams of several porphyry copper deposits (abst.) : Geol. Soc. of Amer., Program for 1969 Annual meeting, p. 114.

James, A. H., Smith, W. H., and Bray, R. E., 1961, The Bingham district—a zoned porphyry ore deposit, in Geology of the Bingham Mining District and Northern Oquirrh Mountains, ed. by D. R. Cook: Guidebook 16, Salt Lake City, Utah Geol. Soc., p. 49–70.

Kulp, J. L., Ault, W. U., and Feely, H. W., 1957, Sulfur isotope abundances in sulfide minerals: ECON. GEOL., v. 51, p. 139–149.

Lowell, J. D., 1968, Geology of the Kalamazoo orebody, San Manuel district, Arizona: ECON. GEOL., v. 63, p. 645–654.

Metz, R. A., and Rose, A. W., 1966, Geology of the Ray copper deposit, Ray, Arizona, in Geology of the Porphyry Copper Deposits, ed. by S. R. Titley and C. L. Hicks: Tucson, Univ. of Ariz. Press, p. 177–188.

Meyer, C., and Hemley, J. J., 1967, Wall rock alteration, in Geochemistry of Hydrothermal Ore Deposits, ed. by H. L. Barnes: New York, Holt, Rinehart and Winston, p. 166–235.

Meyer, C., et al., 1968, Ore deposits at Butte, Montana, in Ore Deposits of the U. S., 1933–1967, ed. by J. D. Ridge: New York, AIME, p. 1373–1416.

Moore, W. J., Lanphere, M. A., and Obradovich, J. D., 1968, Chronology of intrusion, volcanism and ore deposition at Bingham, Utah: ECON. GEOL., v. 63, p. 612–621.

Muffler, L. J. P., and White, D. E., 1969, Active metamorphism of upper Cenozoic sediments in the Salton Sea geothermal field and the Salton trough, southeastern California: Geol. Soc. Am. Bull., v. 80, p. 157–182.

Nielsen, R. L., 1968, Hypogene texture and mineral zoning in a copper-bearing granodiorite stock, Santa Rita, New Mexico: ECON. GEOL., v. 63, p. 37–50.

Perry et al., 1963, Chemical Engineers' Handbook, 4th edition: New York, McGraw-Hill, Section 10, p. 13.

Peters, W. C., James, A. H., and Field, C. W., 1966, Geology of the Bingham Canyon porphyry copper deposit, in Geology of the Porphyry Copper Deposits, ed. by S. R. Titley and C. L. Hicks: Tucson, Univ. of Ariz. Press, p. 165–176.

Robinson, R. F., and Cook, A., 1966, The Safford Copper deposit, Lone Star mining district, Graham County, Arizona, in Geology of the Porphyry Copper Deposits, ed. by S. R. Titley and C. L. Hicks: Tucson, Univ. of Arizona Press, p. 251–266.

Roedder, E. W., 1963, Studies of Fluid Inclusions II, Freezing data and their interpretations: ECON. GEOL., v. 58, p. 178.

Rose, A. W., 1967, Trace elements in sulfide minerals from the central district New Mexico and the Bingham district, Utah: Geoch. et Cosmoch. Acta, v. 31, p. 547–585.

Rose, A. W., 1969, Origin of wallrock alteration at porphyry copper deposits: Geol. Soc. of Amer., Program for 1969 Annual Meeting, p. 192.

Rose, A. W., and Baltosser, W. W., 1966, The porphyry copper deposit at Santa Rita, New Mexico, in Geology of the Porphyry Copper Deposits, ed. by S. R. Titley and C. L. Hicks: Tucson, Univ. of Ariz. Press, p. 205–220.

Sales, R. H., and Meyer, C., 1948, Wallrock alteration at Butte, Montana: AIME Trans., v. 178, p. 9–35.

Schumann, T. E. W., 1929, Heat transfer: a liquid flowing through a porous prism: J. Franklin Inst., v. 208, p. 405–416.

Schwartz, G. M., 1953, Geology of the San Manuel copper deposit, Arizona: U. S. Geol. Surv., Prof. Paper 256, 65 pp.

Shade, J., 1968, Hydrolysis equilibria in the system K_2O-Al_2O_3-SiO_2-H_2O: Ph.D. Thesis, Pennsylvania State Univ., 172 pp.

Sheppard, S. M. F., Nielsen, R. L., and Taylor, H. P., Jr., 1969, Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits: ECON. GEOL., v. 64, p. 755–777.

Stacey, J. S., Zartman, R. E., and Nkomo, I. T., 1968, A lead isotope study of galenas and selected feldspars from mining districts in Utah: ECON. GEOL., v. 63, p. 796–814.

Stringham, B., 1953, Granitization and hydrothermal alteration at Bingham, Utah: Geol. Soc. Am. Bull., v. 64, p. 945–991.

Toulmin, P., and Clark, S. P., 1967, Thermal Aspects of Ore Formation, in Geochemistry of Hydrothermal Ore Deposits, ed. by H. L. Barnes: New York, Holt, Rinehart and Winston, p. 437–462.

Wallace, S. R., et al., 1968, Multiple intrusion and mineralization at Climax, Colorado, in Ore deposits of the U. S. 1933–1967, ed. by J. D. Ridge: AIME, New York, p. 605–640.

Wargo, J. G., 1964, Geology of a disseminated copper deposit near Cerrillos, New Mexico: ECON. GEOL., v. 59, p. 1525–1538.

Winkler, H. G. F., 1967, Petrogenesis of metamorphic rocks, 2nd ed.: Springer-Verlag, New York, 237 pp.