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Petrology and Geochemistry of Propylitic Alteration at Southwest Tintic, Utah

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Abstract

Systematic variations in mineral assemblages, fluid inclusion characteristics, mineral chemistry, and isotopic ratios document the chemical and thermal evolution of hydrothermal fluids responsible for late alteration in a small porphyry copper system near Tintic, Utah. Propylitic alteration of volcanic rock can be subdivided into actinolite, epidote, and chlorite subzones. An actinolite subzone containing actinolite, epidote, chlorite, and calcite extends 250 m away from the secondary biotite zone. An epidote subzone containing epidote, chlorite, and calcite is present up to 500 m away from the secondary biotite zone. A chlorite subzone of chlorite and calcite is present up to 2 km from the secondary biotite zone. Chlorite which occurs in each subzone varies systematically in Fe, Mg, and Mn content. The ratio Fe/(Fe + Mg) increases from 0.27 at the secondary biotite zone to 0.48 in the outer propylitic zone accompanied by a decrease in activity of clinochlore from 0.15 to 0.02. MnO increases from 0.23 to 0.44 wt percent. The Fe^{+3} content of epidote also systematically decreases from the actinolite subzone outward. The activity of clinozoisite in the epidote ranges from 0.038 at the secondary biotite zone to 0.21 700 m away from the secondary biotite zone in the outer epidote subzone. Systematic changes in chlorite and epidote compositions reflect increasing log $a_{Mg^{+2}}/a^2_{H^+}$ and log $a_{Fe^{+2}}/a^2_{H^+}$ with increasing distance from the hydrothermal biotite zone and decreasing temperature and salinity.

Fluid inclusion homogenization temperatures decrease away from the secondary biotite zone with a horizontal thermal gradient of 78°C/km. Temperatures range from 351° to 160°C in propylitic alteration. Salinities also decrease outward from 7.3 to 0.0 equiv wt percent NaCl.

Hydrothermally altered rocks are systematically depleted in ^{18}O outward from the phyllic alteration zone into the chlorite subzone, as recorded by whole-rock samples (10.9 to −1.7‰), calcite (10.4–1.6‰), and quartz veins (2.8 to −0.8‰). Calculated $\delta^{18}O$ and δD values for the actinolite subzone are +5 and −55 per mil, respectively; values as low as −15.1 and −120 per mil are recorded at the outer limits of sampling in the chlorite subzone.

These latter values indicate that outer propylitic alteration is dominated by isotopically unevolved local meteoric water. However, the large variations in hydrogen and oxygen isotope compositions recorded across the zoned propylitic alteration are too large to have been produced from an isotopically homogeneous fluid, given the measured range of alteration temperatures (350°–200°C). Rather, the variations in isotopic compositions and salinity of the propylitic alteration fluids are consistent with the progressive mixture of unevolved (^{18}O- and D-depleted), low-salinity local meteoric water with a much more ^{18}O- and D-enriched, higher salinity fluid. The later phyllic alteration also formed from a similar, ^{18}O- and D-enriched fluid. We suggest that these isotopically enriched fluids more likely evolved from local meteoric water through extensive exchange at very low water/rock ratios with the igneous rocks at depth in the hydrothermal system at Tintic. An alternative explanation is that ^{18}O- and D-enriched fluids represent a late incursion of magmatic water unlike many other porphyry copper systems.

Participation of such ^{18}O- and D-enriched fluids in the waning stages of hydrothermal alteration at Tintic contrasts with the usual domination of isotopically unevolved meteoric water at these stages (e.g., propylitic, phyllic) in many porphyry copper systems (Sheppard et al., 1971; Taylor, 1974; Gustafson, 1978). At Tintic, isotopically enriched fluids coexist with and even displace meteoric water during propylitic and phyllic alteration, respectively.

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Introduction

HYDROTHERMAL fluids in many porphyry Cu systems evolve from an early, high-temperature, high-salinity fluid derived from magmatic sources to a later, lower temperature, lower salinity fluid with a dominant meteoric water component (Sheppard et al., 1971, Titley and Beane, 1981, Bowman et al., 1987). Such variations would be expected to induce mineralogical, chemical, and isotopic zoning in porphyry systems. Ballantyne (1981) has shown that systematic mineral and chemical variations occur in the propylitically altered rocks of the Silver Bell, Safford, and Christmas porphyry copper deposits in Arizona. First, alteration mineral subzones exist within the propylitic zone. These zones include an actinolite zone, an epidote-bearing zone, and an epidote-free zone. The actinolite zone is confined to an area of less than 1,200 m from the hydrothermal biotite zone. Actinolite is not always present and may be notably absent in felsic rocks. Epidote subzones are also highly variable and can occur up to 4 km from the secondary biotite zone. Second, chlorite and epidote show variations in composition with respect to distance from the hydrothermal biotite zone. The most consistent variations in the Arizona porphyries that Ballantyne (1981) has studied are in Mn, Fe, and Mg in chlorites. Third, fluid inclusion studies indicate that the temperature decreases outward. Fourth, isotopic analyses show ^{18}O depletion due to the influx of meteoric water in the propylitic zone. The most intensely propylitized rocks have the lowest $\delta^{18}O$ values; away from the center of mineralization the $\delta^{18}O$ values grade back into the normal igneous values of 6 per mil.

A two-stage evolution of fluid sources from magmatic to meteoric water may be too simple for actual porphyry copper systems. Recent studies of the Bingham, Utah, porphyry Cu deposit by Bowman et al. (1987) have documented a systematic trend of ^{18}O depletion and D enrichment with decreasing temperature in the propylitic mineral assemblage. This trend is inconsistent with a progressive influx of local meteoric water and is produced by either an influx of D-enriched formation water or isotope exchange of meteoric water with rock at very low water to rock ratios in the deeper parts of the system. These highly exchanged fluids would then be focused upward into the present exposure of the deposit. The Bingham study emphasizes that evolving hydrothermal fluids in porphyry systems may contain important components in addition to magmatic and meteoric water. These additional fluids may initially be meteoric waters that attain their chemical and isotopic signature, including D/H ratio, in a rock-dominated (very low W/R ratio) exchange zone in the roots of a hydrothermal system. Flow of these highly exchanged fluids may then be focused upward to create hydrothermal alteration and mineralization in water-dominated (locally high W/R ratio) zones of discharge in the hydrothermal system.

Alternatively, if sedimentary formation waters (e.g., Hitchon and Friedman, 1969) are involved directly at Bingham, then the Oquirrh basin (Jordan and Douglass, 1980) in which Bingham is located provides a potential source of such fluids. The Bingham igneous complex intrudes a 7.5-km-thick sequence of limestone, quartzites, and related sedimentary rocks of Upper Pennsylvanian age of the Oquirrh basin. Formation water from Oquirrh basin sediments or highly exchanged meteoric waters may be involved in other hydrothermal ore deposits in and near the Oquirrh basin.

The southwest Tintic porphyry copper system in the Tintic mining district, Utah, is one of several diverse hydrothermal deposits in the district. The Main Tintic district includes replacement deposits of Pb-Zn-Ag in carbonate host rocks. In East Tintic, deposits of Pb-Zn-Ag-Au are localized by reactive carbonate rocks, thrust faults, high-angle faults, fissures, and breccia zones and are overlain by hydrothermally altered volcanic rocks. The southwest Tintic area includes a porphyry Cu-type hydrothermal system where latite volcanic rocks and a related monzonite intrusion have been altered to zoned assemblages of hydrothermal minerals that include a central zone of hydrothermal biotite, orthoclase, quartz, anhydrite, and sulfides (secondary biotite zone). An envelope of quartz, sericite, chlorite, tourmaline, and pyrite (phyllic zone) overlies potassic alteration and overprints parts of propylitic alteration and is usually present between them. Outer propylitic alteration consists of epidote, chlorite, sericite, calcite, albite, and actinolite and represents the outer limit of perceptible fluid-rock interaction.

Relatively little attention has been given to physical-chemical and isotopic properties of the fluids responsible for propylitic alteration at Tintic. The purpose of this study is to determine the geologic, geochemical, and isotopic characteristics of propylitic alteration in latite tuffs surrounding an Oligocene quartz monzonite intrusion at southwest Tintic. Mineralogy, mineral chemistry, fluid inclusions, and oxygen and hydrogen isotope compositions in the propylitic assemblage are used to estimate the physical and chemical conditions of hydrothermal alteration, the origin and evolution of the hydrothermal fluids, and chemical relationships among fluids producing propylitic, phyllic, and potassic alteration.

The Tintic mining districts are in the central portion of the eastern margin of the Basin and Range province, Utah and Juab counties, Utah (Fig. 1), about 90 km south of Salt Lake City and 70 km south of Bingham. The oldest rocks exposed in the East Tintic Mountains are Lower Cambrian to Upper Mississippian sedi-

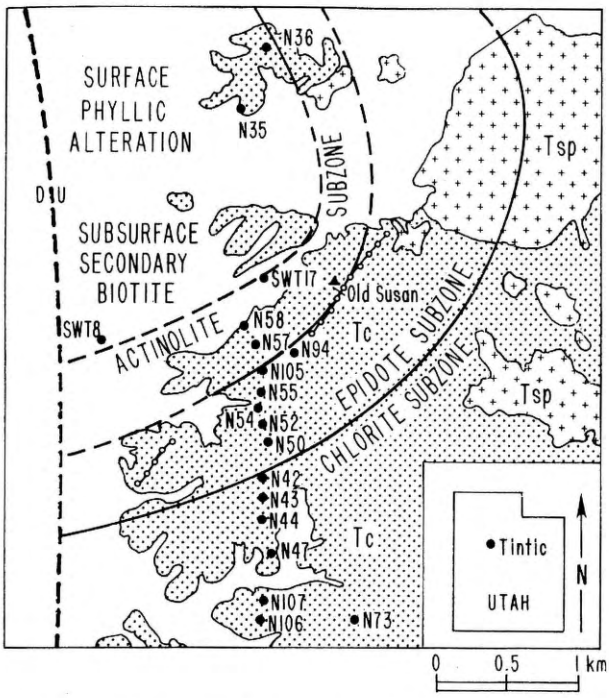

FIG. 1. Geologic map of the southwest Tintic area modified from Morris (1975). Also shown are the areas of the Diamond Gulch porphyry copper deposit and the phyllic and propylitic alteration zones. The secondary biotite zone is projected from drill hole information. The phyllic zone is approximately coincident with the surface projection of the secondary biotite zone. The propylitic zone is subdivided into an actinolite subzone, an epidote subzone, and a chlorite subzone. Sample locations are shown as numbered dots. Map symbols are as follows: T_c, Copperopolis Latite (dot patterns); T_{sp}, Sunrise Peak monzonite porphyry (+ pattern); open areas are alluvium and colluvium; the Old Susan vein is shown by connected open circles.

mentary rocks which consist of 3.4 km of quartzite, limestone, dolomite, and shale that have been folded and thrust faulted during the late Mesozoic Sevier orogeny (Morris and Lovering, 1979).

Tertiary igneous rocks cover much of the deeply eroded Paleozoic strata and Mesozoic structure in the area. Oligocene volcanic rocks consist largely of latite tuffs. Intrusive equivalents of the latites are extensive and occur as sills, stocks, plugs, and dikes in the southern part of the East Tintic Mountains.

The youngest structures in the area are Basin and Range normal faults cutting the volcanics which first formed in the early Miocene. Normal faulting has continued to the present. The geology of the East Tintic Mountains is described in detail by Morris and Lovering (1979).

Analytical Techniques

Electron microprobe analysis

Analysis of the chlorite, epidote, and calcite for Si, Ti, Al, Mg, Fe, Mn, K, Ca, and Na in polished thin sections were performed using a three-channel ARL model EMX electron microprobe operated at 15 kV and a sample current of 0.03 μA. Counts accumulated for a constant integrated beam current were achieved in approximately 12 seconds. Five spots were analyzed for each grain and a beam approximately 1 μ in diameter was used. Background-corrected probe data were corrected for matrix effects using the factors of Bence and Albee (1968) and Albee and Ray (1970) and the correction algorithm of J. Nicholls et al. (unpub. data). Standards used were clinopyroxene, cummingtonite, kaersutite, and calcite. Because of the matrix effects of (OH) in hydrous minerals an iterative process was used for matrix corrections described by Parry and Downey (1982). A structural formula was first computed from microprobe analysis, wt percent water was calculated from that structural formula, followed by recalculation of matrix effects, composition, and a new structural formula. Three iterations usually produced satisfactory convergence. Thus water not measured during microprobe analysis was included in the matrix correction and an estimate of wt percent water consistent with mineral composition is included in the tables.

Fluid inclusion measurements

Heating measurements were made on a Roman Science Model 3 heating stage. Temperatures for heating measurements were recorded by an Omega 2809 digital thermometer connected to an ungrounded chromel-alumel thermocouple. Freezing measurements were made on a Chaixmeca stage mounted on a Leitz Sm-Lux-Pol microscope. Heating measurements are accurate to ±5°C with a precision of ±1°C. Freezing measurements are accurate to ±1°C and are precise to ±1°C. Repeat measurements were usually within 1° of the first measurement.

Calcite abundance

Samples were analyzed for wt percent calcite by two independent methods: fusion in a Leco carbon analyzer and reaction of the carbonate with phosphoric acid. Both techniques show similar amounts of calcite present in each sample.

Isotope extraction techniques

Standard extraction (McCrea, 1950; Friedman, 1953; Taylor and Epstein, 1962; Clayton and Mayeda, 1963) and mass spectrometry techniques were used in stable isotope analyses. Hydrogen and oxygen isotope data are reported relative to SMOW (Craig, 1961b); the carbon isotope data are reported relative to PDB (Craig, 1957). The analytical error for carbon and oxygen isotope data is ±0.1 per mil (±0.2‰ for silicates), and the error for hydrogen isotope data is ±1.5 per mil.

Calculation of mole fraction and activity

Calculation of activities of clinozoisite and epidote in the analyzed epidotes followed procedures of Bird and Helgeson (1980). Octahedral M(2) sites are assumed to contain only Al, M(1) sites are completely filled with Al and Fe, and remaining Al, Fe, other octahedral species, and vacancies are assigned to M(3) sites. Assignment of Al and Fe to M(1) and M(3) sites is dependent on an ordering parameter σ calculated to be 0.90 at 300°C and 0.95 at 200°C using equations in Bird and Helgeson (1980).

Activities of clinochlore (Mg chlorite) and chamosite (Fe chlorite) were calculated using the solid solution model and equations of Walshe (1986). Ideal ionic mixing is assumed on six octahedral sites and two tetrahedral sites; no mixing is assumed on the remaining two tetrahedral sites. Activities were calculated from computed structural formulas.

Geology, Alteration, and Mineralogy of Southwest Tintic

Geology

The Tintic area contains the Main Tintic mining district (Lindgren and Loughlin, 1919) and the East Tintic mining district (Morris and Lovering, 1979). The southwest Tintic area is located 10 km south and west of the Main Tintic district. In the southwest Tintic area, a series of middle Oligocene latite volcanics have been intruded by quartz monzonite stocks, dikes, and sills. The Copperopolis Latite is host for extensive hydrothermal alteration centered around the Diamond Gulch porphyry intrusion and dates at approximately 32 Ma (Laughlin et al., 1969). Unaltered Copperopolis Latite contains about 25 percent phenocrysts of plagioclase, biotite, augite, hypersthene, orthoclase, and magnetite. The largest and most abundant phenocrysts in the latite are plagioclase (Morris and Lovering, 1979).

Alteration zones and mineralogy

Phyllic and propylitic alteration zones of the southwest Tintic copper porphyry system are exposed at the surface. Potassic alteration was observed below the surface in drill core. Potassic alteration consists of biotite, pyrite, orthoclase, quartz, anhydrite, amphibole, magnetite, chalcopyrite, and molybdenite (Ramboz, 1979). Propylitic alteration that surrounds and is locally in contact with the potassic alteration can be divided into three subzones: actinolite, epidote, and chlorite (Fig. 1). The actinolite subzone at southwest Tintic is defined by the presence of actinolite with abundant epidote, chlorite, and calcite. The actinolite zone extends 250 m outward from the secondary biotite and copper sulfide zone. The epidote subzone contains abundant epidote, chlorite, and calcite and is present up to 500 m away from the secondary biotite zone. The chlorite subzone contains chlorite and calcite and extends at least 2 km from the secondary biotite zone. Propylitic alteration consist of epidote, chlorite, calcite, actinolite, albite, pyrite, magnetite, hematite, and sericite. Phyllic alteration overlies potassic alteration and crosscuts both potassic and propylitic alteration. Mineralogy of phyllic alteration is quartz, sericite, pyrite, rutile, chlorite, apatite, and tourmaline.

Temporal and spatial association of hydrothermal alteration mineral zones and sulfide mineralization in a large number of porphyry copper deposits worldwide has established a genetic relationship (Titley and Beane, 1981).

Hydrothermal Mineral Chemistry

Samples were collected from outcrops of the latite volcanics along traverses outward from the intrusive center. One traverse chosen for detailed study (Fig. 1) represents the most continuous outcrop of propylitically altered rock. Chemical compositions of chlorite, epidote, and calcite were determined in order to establish mineral chemistry and to determine chemical trends in the propylitic zone. Because chlorite and epidote compositions can be a function of the host-rock composition, samples were taken from rocks with the same initial bulk composition. Compositions of chlorite, epidote, and calcite from each subzone are given in Table 1.

Chlorite

Chlorite is the most common mineral in propylitic alteration and variations in abundance and composition are a useful index to fluid evolution. Chlorite occurs in hydrothermal veins and as replacement of original igneous phenocrysts. Point counting established that chlorite abundance diminishes outward through epidote and chlorite subzones (Fig. 2). Chlorite compositions also change systematically through these zones. Mean values for each zone are given in Table 1. Magnesium values decrease outward from a maximum of 25 wt percent at the propylitic-sericite boundary to a minimum of 16 wt percent in the outer chlorite subzone. Total iron increases from 15 to 25 wt percent outward through the chlorite subzone. A similar trend is observed at North Silver Bell, Safford, and Christmas, Arizona (Ballantyne, 1981), and Bingham, Utah (Bowman et al., 1987). Manganese also increases outward from 0.23 to 0.44 wt percent Mn.

Calculated activities of clinochlore in the chlorite decrease from 0.132 to 0.032 (Fig. 2), and activity of chamosite increases from 0.00019 to 0.0016 outward.

Epidote

Green epidote most commonly occurs as a replacement of plagioclase and in veins at southwest Tintic

TABLE 1. Microprobe Analyses of Hydrothermal Minerals from Southwest Tintic

	Chlorite			Epidote			Calcite		
	Actinolite subzone (5)	Epidote subzone (8)	Chlorite subzone (5)	Actinolite subzone (8)	Epidote subzone (7)	Chlorite subzone (3)	Actinolite subzone	Epidote subzone	Chlorite subzone
Weight percent									
SiO_2	28.0	29.9	29.3	38.0	38.7	38.5			
TiO_2	0.06	0.04	0.05	0.08	0.12	0.32			
Al_2O_3	19.4	17.5	17.7	21.2	22.2	22.1			
FeO	13.2	15.6	17.0				0.56	0.62	0.27
Fe_2O_3	6.3	7.4	8.1	15.4	14.1	14.2			
MnO	0.23	0.39	0.44	0.55	0.27	0.24	0.86	0.21	0.08
MgO	19.8	17.0	16.0	0.20	0.18	0.10	0.17	0.22	0.09
CaO				22.2	22.1	22.5	55.6	55.6	56.0
H_2O	11.9	11.8	11.7	1.87	1.88	1.88	43.5	44.1	43.8
Total	98.9	99.6	100.0	99.5	99.6	99.8	101.0	101.0	100.0
				Number of ions					
Si	2.82	3.01	2.97	3.05	3.07	3.06			
$Al^{(IV)}$	1.18	0.99	1.03						
$Al^{(VI)}$	1.11	1.09	1.09	2.01	2.08	2.07			
Fe^{+2}	1.11	1.31	1.44						
Fe^{+3}	0.48	0.56	0.62	0.93	0.84	0.85			
Mg	2.96	2.56	2.41						
Ca				1.91	1.89	1.92			
OH	8.00	8.00	8.00	1.00	1.00	1.00			

and decreases in abundance outward from the secondary biotite zone (Fig. 2). Epidote decreases in both Fe and Mn content outward. Calculated activity of clinozoisite increases from 0.038 at the innermost actinolite subzone to 0.21 at the outermost epidote subzone shown in Figure 2. Ferric iron decreases with distance from the secondary biotite zone. Calculated activity of epidote decreases from 0.98 to 0.73. Beyond 1 km the modal percent of epidote decreases to 1 percent. MnO in epidote ranges from a maximum of 1.18 wt percent in the actinolite subzone to 0.15 wt percent in the outer chlorite subzone.

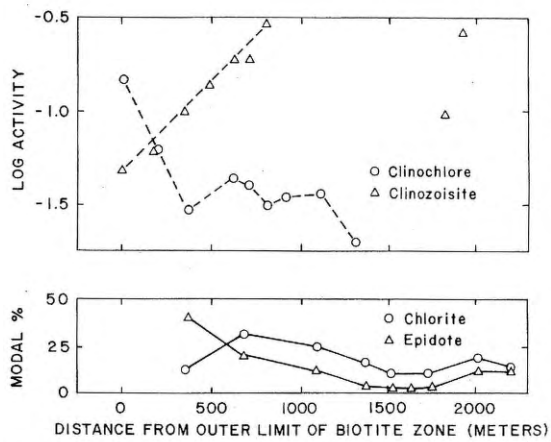

FIG. 2. Modal abundance of chlorite and epidote, logarithm of the activity of clinochlore in chlorite, and logarithm of the activity of clinozoisite in epidote versus distance from the secondary biotite zone. Activities were calculated using procedures outlined in the text.

Calcite

Calcite abundances varied from 1 to 5 percent and showed no spatial variation with respect to distance from the intrusion. Mean values of electron microprobe analysis of calcite are shown in Table 1 for each subzone. Calcites were analyzed for nine elements but only the four shown to be significant are reported here. Fe/(Fe + Mg) ratios increase with distance away from the secondary biotite zone. Although not as conclusive as the Fe and Mg variations in chlorite, the spatial variations of Fe and Mg in calcite are similar. Manganese decreases from a value of 0.86 wt percent near the secondary biotite zone to 0.07 wt percent at a distance of 1.5 km. The low manganese values at the outer limits of alteration is similar to observations in both epidote and chlorite.

Fluid Inclusions

At southwest Tintic quartz, epidote, and calcite veins contain useable fluid inclusions. Quartz veins occur throughout the propylitic zone. Primary inclusions in quartz, calcite, and epidote were chosen for heating and freezing measurements.

Classification and description

Two types of fluid inclusions are present at southwest Tintic. Measurements have been made on these two types in seven quartz veins, one calcite vein, and one epidote vein from the propylitic zone. A third type is also present in quartz veins in potassic and phyllic alteration. Type I inclusions are low-salinity inclusions, lack daughter salts, and are the most abundant. They contain approximately 30 percent vapor by volume and homogenize to a liquid phase. Type II inclusions are gas-rich inclusions which contain approximately 80 vol percent vapor, lack daughter minerals, and homogenize to a vapor phase. The phase proportions and homogenization to the vapor phase at temperatures similar to those of liquid-rich inclusions indicate that the fluid was originally trapped as steam from a boiling solution. Type II inclusions are more common near the secondary biotite zone and are present but rare at the outer limits of the propylitic zone. Type III inclusions described by Ramboz (1979) are high-salinity multiphase inclusions. In addition to the liquid and vapor phases, several daughter minerals are present including halite which is always present, sylvite, chalcopyrite, hematite, and other unidentified phases. Type III inclusions homogenize to the liquid phase (Ramboz, 1979). At southwest Tintic, type III inclusions occur only in potassic and phyllic alteration. We have made no measurements on type III inclusions.

Fluid inclusions range from 5 to 20 μ in diameter with most in the 5- to 7-μ range. Angular and ellipsoidal shapes were common. Most inclusions were either solitary or in small groups of less than five. These were the main criteria that established the inclusions as primary. Inclusions in obvious trains along fractures were considered secondary and avoided, following recommendations and criteria of Roedder (1979).

Heating measurements

Homogenization temperatures for 123 fluid inclusions in the propylitic zone and 14 in the phyllic zone were measured. Temperatures ranged from 160° to 351°C in propylitic alteration and 267° to 339°C for phyllic alteration with all but three homogenizing to the liquid phase. In Figure 3 the inclusions are divided into two types based on phase proportions and homogenization. They are divided further by the host mineralogy. The histograms in Figure 3 show a range of homogenization temperatures for each sample. Reasons for these ranges include (Ahmad and Rose, 1980):

1. Leakage occurring naturally or during heating. If leakage was observed, the temperatures were discarded.
2. Trapping of both steam and liquid would give anomalously high homogenization temperatures.

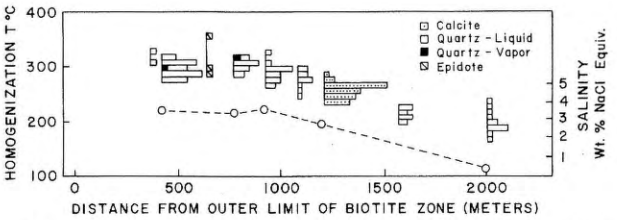

FIG. 3. Histograms of homogenization temperatures of fluid inclusions in calcite, quartz, and epidote, and a plot of NaCl equivalent salinity versus distance from the secondary biotite zone.

3. Low temperatures might result from measuring secondary or pseudosecondary inclusions. As discussed these were avoided.
4. Fluctuations in both pressure and salinity would affect the filling temperature.

Pressure changes are a reasonable explanation for the range of temperatures observed. Pressure increases and subsequent release of pressure can be expected in some vein systems. Liquid- and vapor-rich inclusions are commonly seen in the epidote and actinolite subzone, but vapor-dominated inclusions are rarely seen in the outer chlorite subzone. Boiling occurred in most of the southwest Tintic system but may not have been sustained more than a kilometer away from the secondary biotite zone, hence the rarity of vapor-dominated inclusions.

The horizontal temperature gradient at southwest Tintic is between 71° and 85°C/km with an average gradient of 78°C/km. An obvious systematic decrease in temperature occurs across the propylitic zone (Fig. 3).

Freezing measurements

Freezing point depression measurements were made on 22 inclusions from four quartz veins and one calcite vein. Salinities are low and range from 0.0 to 7.3 equiv wt percent NaCl. The mean salinities are shown in Figure 3. In most of the propylitic zone there is probably only one type of fluid present since salinities are similar. Near the center of the system, however, there are at least two types of fluids with different salinities ranging from 6.5 to 25.0 wt percent NaCl and 31.9 to 48.9 wt percent NaCl (Ramboz, 1979).

Pressure corrections and fluid pressures

Samples N-84 and N-61 contain type II fluid inclusions that homogenize to the vapor phase at nearly the same temperature as type I inclusions. Since these inclusions are primary and appear to have been trapped simultaneously with the liquid-dominated ones from boiling fluids, no pressure correction is required and the temperature measured is the entrapment temperature. Boiling of a 5 wt percent NaCl solution at 320°C indicates a pressure of 109 bars (Haas, 1971) and a depth of 1,350 m (hydrostatic) or

385 m (lithostatic) using an average density of 2.61 (andesite).

Geochemical Model

The alteration assemblage of chlorite, epidote, calcite, and actinolite is evaluated to indicate the nature of the hydrothermal fluids that altered the Copperopolis Latite at southwest Tintic. End-member compositions of minerals were used in calculations and solid solution effects on phase equilibria were taken into consideration. Clinochlore shows a systematic decrease in activity whereas clinozoisite shows an increase with distance from the secondary biotite zone except for the two most remote samples. These two epidote samples may represent hydrothermal alteration that was not part of the southwest Tintic system. Variations in fluid composition from interaction with the host latite tuffs and dikes and varying temperatures and pressure may be responsible for variations in chemical composition reflected in the alteration minerals chlorite, epidote, and calcite.

We have attempted to estimate solution parameters from mineral assemblages, mineral compositions, and appropriate phase diagrams. Mineral assemblages used for these estimates occur in contact with one another and microprobe analyses show that mineral grains are relatively homogeneous (Parry et al., 1984), and systematic variation in compositions of epidote, chlorite, and calcite with distance from the biotite zone suggest that the assumption of equilibrium is a good approximation. The minimum log fugacity of oxygen is estimated from hematite and magnetite equilibria and ranges from −31 at 300°C to −40 at 200°C (Fig. 4A). Equilibria among calcite, CO_2, and water were used to estimate pH at 5.63 at 300°C to 5.82 at 200°C; these values are near neutrality at these temperatures.

Stability relationships among muscovite, clinochlore, phlogopite, and K feldspar are shown in Figure 4B from which log a_{K^+}/a_{H^+} is estimated to be constant at 3 for 300° to 200°C. This estimate would correspond to the innermost propylitic subzone adjacent to the secondary biotite zone. Stability relationships for clinozoisite, muscovite, and clinochlore are shown in Figure 4C. Tremolite saturation is also shown and calcite saturation at various values of P_{CO_2} are shown. Because epidote, chlorite, and muscovite coexist, log $a_{Mg^{+2}}/a^2_{H^+}$ and log $a_{Ca^{+2}}/a^2_{H^+}$ can be estimated from Figure 4C at a temperature of 300°C. Log $a_{Mg^{+2}}/a^2_{H^+}$ is 4.8 and log $a_{Ca^{+2}}/a^2_{H^+}$ is 6.6 at 300°C. Figure 5 represents the relations between epidote, chlorite, and solution compositions at southwest Tintic. Equilibrium among clinochlore, calcite, clinozoisite, and solution can be represented as:

$$2Ca_2Al_3Si_3O_{12}(OH) + 4CO_2 + 26H_2O + 3SiO_2 + 15Mg^{+2} = 3Mg_5Al_2Si_3O_{10}(OH)_8 + 4CaCO_3 + 30H^+. \quad (1)$$

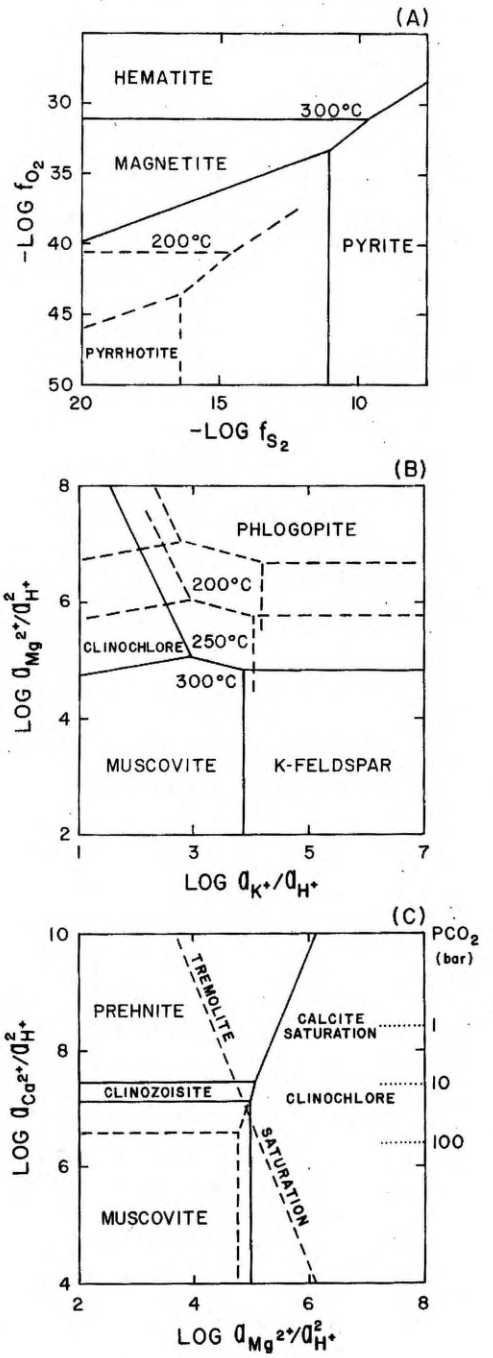

FIG. 4A. Log f_{O_2} versus log f_{S_2} for hematite, magnetite, and pyrite equilibria at 300° and 200°C. B. Log $a_{Mg^{2+}}/a^2_{H^+}$ versus log a_{K^+}/a_{H^+} at 300°, 250°, and 200°C at pressures of liquid-vapor equilibrium for pure water for clinochlore, muscovite, phlogopite, and K feldspar. C. Log $a_{Mg^{2+}}/a^2_{H^+}$ versus log $a_{Ca^{2+}}/a^2_{H^+}$ for coexisting end-member clinozoisite, muscovite, and clinochlore at 300°C and pressure of liquid-vapor equilibrium for pure water and log a_{K^+}/a_{H^+} = 3.0. Deviation from end-member composition is shown by dash lines. Also shown are tremolite saturation and calcite saturation at various values of P_{CO_2} (dotted lines). Equilibrium constants for these diagrams were calculated using the computer program SUPCRT, thermodynamic data, and equations of Helgeson and Kirkham (1974a, 1974b, 1976), Walther and Helgeson (1977), Helgeson et al. (1978), and Helgeson et al. (1981).

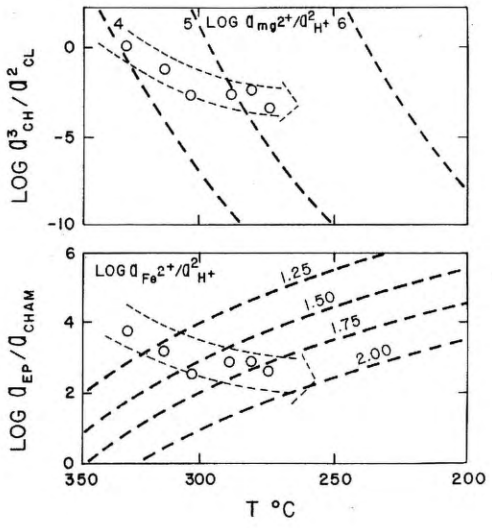

FIG. 5. Top. Log ($a^3_{\text{clinochlore}}/a^2_{\text{clinozoisite}}$) of coexisting chlorite-epidote pairs for six samples (shown as dots) with log $a_{Mg^{2+}}/a^2_{H^+}$ contours shown as dashed lines. Bottom. Log ($a_{\text{epidote}}/a_{\text{chamosite}}$) for chlorite-epidote pairs (dots) with log $a_{Fe^{2+}}/a^2_{H^+}$ contours. Dashed arrows show trends with decreasing temperatures. Entropy, volume, and heat capacity for chamosite are from Helgeson et al. (1978), free energy data are from Anovitz and Essene (1982).

This reaction is used to evaluate the compositional variation in alteration minerals in propylitic alteration at southwest Tintic. Log ($a^3_{\text{clinochlore}}/a^2_{\text{clinozoisite}}$) versus temperature is plotted for mineral pairs of known composition. The changes in composition of the two minerals show systematic variation with distance and therefore with temperature. Log $a_{Mg^{+2}}/a^2_{H^+}$ contours are also shown on the diagram. A restricted value between 4 and 5 at 350° to 300°C accounts for observed mineral compositions. The relations between chamosite (Fe chlorite), epidote, calcite, and hematite are used to evaluate variation in iron content of solutions at southwest Tintic. This relation is represented as:

$$Fe_5Al_2Si_3O_{10}(OH)_8 + 2CaCO_3 + \tfrac{1}{4}O_2 + 8H^+ = Ca_2Al_2FeSi_3O_{12}(OH) + 2CO_2 + 4Fe^{+2} + 7.5\ H_2O. \quad (2)$$

CO_2 and f_{O_2} are buffered by calcite-water-CO_2 and hematite-magnetite, respectively. Log ($a_{\text{epidote}}/a_{\text{chamosite}}$) versus temperature is plotted for mineral pairs, and log $a_{Fe^{+2}}/a^2_{H^+}$ contours are shown in Figure 5. The range in log $a_{Fe^{+2}}/a^2_{H^+}$ of 1.25 to 1.75 is attributed to changes in ferrous iron activity because pH for calcite-water-CO_2 equilibria is nearly constant in the propylitic zone. P_{CO_2} is estimated to be 18 bars at 300°C from Figure 4C and coexistence of calcite, epidote, muscovite, and chlorite with prehnite absent. Log f_{S_2} estimated from Figure 4A is approximately −10 for equilibria among pyrite, hematite, and magnetite at 300°C and −15 at 200°C.

Oxygen, Hydrogen, and Carbon Isotope Data

Oxygen, hydrogen, and carbon isotope analyses were made of whole-rock samples, vein quartz, vein epidote, and chlorite and calcite mineral separates from vein-free whole-rock samples. The locations of these samples are shown in Figure 1. These analyses are tabulated in Table 2 and are plotted as a function of distance from the outer limit of secondary biotite alteration in Figure 6. In addition, four samples of spring water were analyzed to determine the present-day hydrogen and oxygen isotope compositions of local meteoric water.

Oxygen and carbon isotope compositions

The $\delta^{18}O$ values of samples from the phyllic zone range from 8.0 to 10.9 per mil; these are equivalent to or somewhat enriched in ^{18}O compared to normal igneous values for intermediate rock compositions (Taylor, 1977). The $\delta^{18}O$ values of the whole-rock samples from the propylitic zone range from 10.9 to −1.7 per mil, decreasing systematically outward from the edge of secondary biotite (Fig. 6). Between samples N-57 and N-55, there is a significant drop in the $\delta^{18}O$ value of the whole rock, from 5.7 (N-57) to 1.4 (N-55) per mil. These two samples are separated by the Old Susan vein (Fig. 1), one of the largest veins in this area. This break in oxygen isotope composition also corresponds in location to the boundary between the epidote and actinolite subzones of the propylitic alteration. The two outermost samples in the epidote subzone, N-50 and N-51, have the lowest $\delta^{18}O$ values; the two samples from the chlorite subzone are somewhat higher, although both have $\delta^{18}O$ values less than 2 per mil. The oxygen isotope compositions of the minerals also record the outward decrease in ^{18}O through the propylitic zone. The $\delta^{18}O$ values of epidote and chlorite decrease outward from 5.4 to −5.0 and 8.0 to 1.6 per mil, respectively.

The oxygen and carbon isotope compositions of hydrothermal calcite are tabulated in Table 2. The $\delta^{18}O$ values of calcite decrease outward within the propylitic zone, from a high of 10.4 to as low as 1.6 per mil in the outer chlorite subzone of propylitic alteration. The calcites also record a break between samples N-55 and N-57 (e.g., the approximate contact between the actinolite and epidote subzones). All calcite samples from N-57 and closer to the edge of secondary biotite alteration (e.g., potassic alteration) have $\delta^{18}O$ values higher than 10.0 per mil; those from sample N-55 and outward have $\delta^{18}O$ values less than 5.0 per mil.

Carbon isotope compositions of calcite record no systematic variation with distance from potassic alteration and range from −2.4 to −6.7 per mil (Table 2). Carbon in carbonate in porphyry systems may be derived from magmatic sources, CO_2 released from

TABLE 2. Oxygen, Hydrogen, and Carbon Isotope Compositions of Minerals, Fluid Inclusions, and Calculated Values of Water in Exchange Equilibrium with Minerals

						Calculated water[1]	
Sample no.	T (°C)	Mineral	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	δD (‰)
Phyllic alteration							
N-36	300	Whole rock	8.9			4.8	
		Sericite		−74			−61
N-35	300	Whole rock	10.9			6.8	
		Calcite	13.1		−3.5	7.5	
		Sericite		−68			−55
SWT-8		Whole rock	8.1			4.0	
		Sericite		−72			−59
Actinolite subzone							
SWT-17	350	Whole rock	8.0			6.3	
		Carbonate	10.4		−6.7	4.8	
N-58	330	Whole rock	6.8			4.8	
		Calcite	10.0		−6.0	3.9	
		Epidote	4.9	−98		4.7	−62
		Chlorite	8.0	−89		5.9	−51
N-57	320	Whole rock	5.7			3.4	
		Calcite	10.4		−5.6	3.9	
		Epidote	3.0	−94		1.8	−58
		Chlorite	6.3	−84		4.1	−50
Epidote subzone							
N-55	300	Whole rock	1.5			−1.2	
		Calcite	5.0		−5.7	−2.2	
		Epidote	−3.4			−3.8	
N-54	295	Whole rock	2.9			0.1	
		Calcite	4.1		−6.7	−3.3	
N-51	280	Whole rock	−1.7			−4.8	
		Calcite	1.6		−4.4	−6.4	
		Chlorite	−0.8	−115		−3.8	−78
N-50	270	Whole rock	−0.8			−4.2	
		Calcite	3.5		−2.4	−4.9	
Chlorite subzone							
N-42	260	Whole rock	1.5			−2.2	
		Calcite	3.4		−4.6	−5.4	
		Chlorite		−112			−83
N-43	255	Whole rock	0.4			−3.4	
		Calcite	1.6		−5.4	−7.5	
		Chlorite	1.2	−105		−2.3	−76
Quartz veins-epidote subzone							
N-94	294	Quartz	2.8			−5.8	
N-61	301	Quartz	0.6			−7.7	
N-52b	287	Quartz	0.4			−8.5	
(Fluid inclusion crush)		Water		−105			
Quartz veins-chlorite subzone							
N-47	207	Quartz	0.0			−13.3	
(Fluid inclusion crush)		Water		−120			
N-73	193	Quartz	−0.8			−15.1	
Local meteoric water							
Water Canyon			−15.5	−105			
Hannibal Spring			−14.3	−111			
Dennis Spring			−14.2	−115			
Jameson Spring			−12.8	−96			

[1] The fractionation factors used to calculate $\delta^{18}O$ values for water are from Clayton et al. (1989) for quartz, calcite, and plagioclase; Matthews et al. (1983) for epidote; and Wenner and Taylor (1971) as modified by Harper et al. (1988) for chlorite. The hydrogen isotope fractionation factors are extrapolated from the high-temperature (>400°C) experimental results of Suzuoki and Epstein (1976), using the lower temperature results of Liu and Epstein (1984) for kaolinite-H_2O and the methods and assumptions presented by Bowers and Taylor (1985) and Harper et al. (1988)

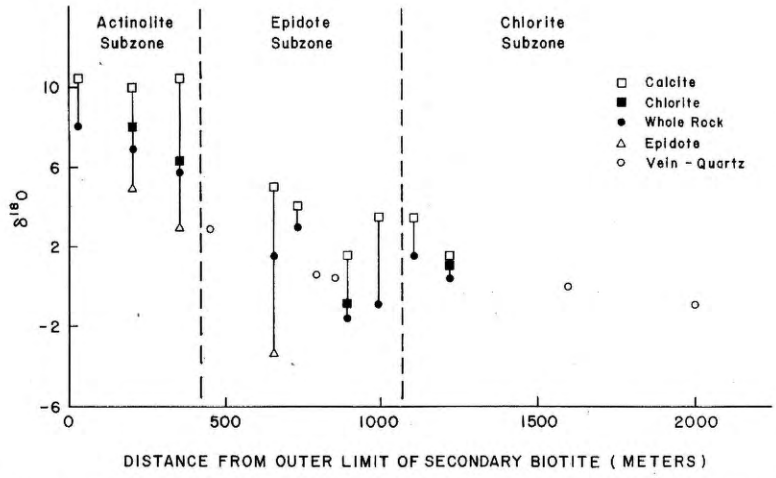

FIG. 6. Plot of the measured $\delta^{18}O$ value of whole-rock and mineral samples from zoned propylitic alteration versus distance from the secondary biotite zone.

sediments by decarbonation reactions, oxidation of reduced carbon species, or carbonate from mixed crustal sources dissolved by meteoric or formation water. The hydrothermal calcites at Tintic have $\delta^{13}C$ values intermediate between those corresponding to magmatic or deep crustal sources (Deines, 1970) and those corresponding to Paleozoic marine carbonate sources (Veizer and Hoefs, 1976) and may represent mixtures of these components.

The $\delta^{18}O$ values of quartz veins range from 2.8 per mil at the actinolite-epidote subzone boundary (the Old Susan vein) down to −0.8 at the outer margins of observable propylitic alteration. These values also decrease across the propylitic zone (Fig. 6).

Hydrogen isotope compositions

Hydrogen isotope compositions were determined on seven epidote and chlorite separates from the propylitic zone, fluid inclusion extractions from two quartz veins, and three samples of sericite from the phyllic zone (Table 2). The δD values of the three sericite samples range between −68 and −74 per mil, whereas the epidote and chlorite samples have δD values ranging from −84 to −115 per mil. The chlorites from the epidote and chlorite subzones of the propylitic alteration have somewhat lower δD values than those from the inner actinolite subzone. The fluid inclusion extract from the chlorite zone (N-47) has a lower δD value, −120 per mil, than the extract from the epidote subzone (N-52b), −105 per mil.

Isotopic compositions of hydrothermal fluids

The oxygen and hydrogen isotope compositions of water in exchange equilibrium with the altered rock and vein quartz were calculated from the isotopic data, using the temperatures defined for the phyllic and propylitic alteration by the fluid inclusion data (Table 2, Fig. 7). The fractionation factors used for these calculations are compiled in Table 2. The oxygen isotope fractionation between quartz latite rock and water can be approximated reasonably by the fractionation between anorthite and water. Hydrogen isotope fractionation between water and many hydrous silicates, including chlorite, is not well established below 400°C. We have assumed that the temperature dependence of D-H fractionation between chlorite and water parallels that experimentally confirmed by Liu and Epstein (1984) for kaolinite-water but is offset to more negative values at all temperatures by the amount (20‰) established experimentally at 400°C (Suzuoki and Epstein, 1976). This is the approach adapted by Bowers and Taylor (1985) and Harper et al. (1988).

The alteration fluids in the phyllic zone have relatively high $\delta^{18}O$ values ranging from 4.8 to 6.8 per mil. The $\delta^{18}O$ values of hydrothermal fluid in the propylitic zone are plotted as a function of increasing distance from the limit of secondary biotite in Figure 7. The calculated $\delta^{18}O$ values for the hydrothermal fluids in exchange equilibrium with the whole-rock samples decrease outward from the edge of secondary biotite, and with declining temperature, from as high as 6.3 per mil in the actinolite subzone to as low as −4.8 per mil in the outer epidote subzone. Still farther out in the chlorite subzone, the $\delta^{18}O$ values level off in the range between −2.2 and −4.2 per mil. North of the actinolite-epidote boundary and the Old Susan vein (between samples N-57 and N-55), the calculated $\delta^{18}O$ values of the hydrothermal fluids are 3.6 per mil or higher. To the south, all but one of these fluids have $\delta^{18}O$ values below −1.2 per mil.

The $\delta^{18}O$ values of water in exchange equilibrium with vein quartz also decrease outward from a value of −5.8 per mil within the epidote subzone to very

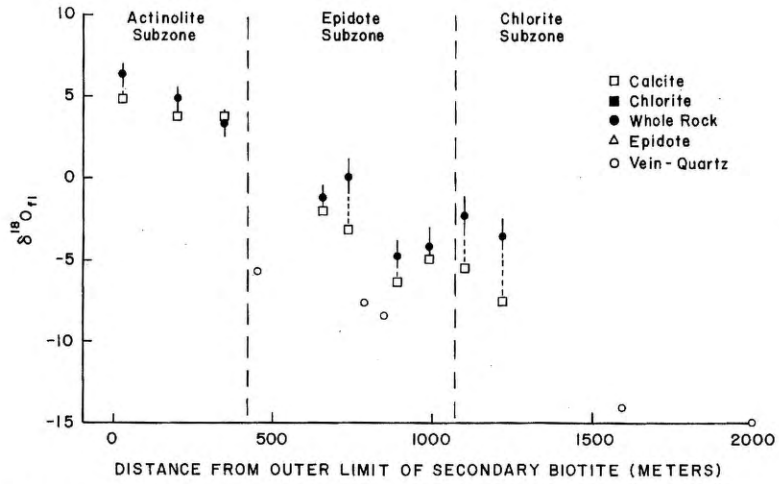

FIG. 7. Plot of calculated $\delta^{18}O$ values of hydrothermal fluids in exchange equilibrium with whole rock (solid circles), calcite (open squares), and quartz (open circles) versus distance from the secondary biotite zone. The solid portion of the lines connecting values from common samples is the estimate of error (1σ) for the calculated $\delta^{18}O$ values of water in equilibrium with the whole-rock samples.

low values (−15.1‰) in the outer limit of the propylitic zone. These latter values are within the range of present-day local meteoric waters, also shown in Figure 7. Fluid inclusion water was extracted from two of the quartz veins; the analyzed δD values are −105 and −120 per mil, near the δD values of present-day local meteoric water.

The $\delta^{18}O$ values of water calculated to be in exchange equilibrium with the vein quartz appear to be 2 to 4 per mil lower than values in exchange equilibrium with nearby calcite or whole-rock samples at any given location within the propylitic zone. There are four possible explanations for this difference:

1. The vein fluids may have become enriched in ^{18}O through fluid-rock interaction as these fluids percolated from the veins into the host rock along microfractures. Such enrichment would reduce the potential for ^{18}O depletion during fluid-rock interaction away from the major veins.

2. Either the calcite and whole rock or the quartz may have undergone retrograde exchange with declining temperature. Retrograde exchange of the vein quartz with a more ^{18}O-depleted fluid would have occurred as well. Calcite is vulnerable to retrograde exchange, but both the whole rock and calcite should have undergone similar degrees of retrograde exchange for both phases to be enriched in ^{18}O. Quartz on the other hand is much less vulnerable to retrograde exchange at temperatures less than 400°C (Clayton et al., 1968; Cole and Ohmoto, 1986).

3. During infiltration of the ^{18}O-depleted fluids responsible for the quartz veins, one or more minerals in the host-rock matrix did not attain isotopic exchange equilibrium with these infiltrating fluids. This possibility has serious implications for attainment of chemical equilibrium, for rates of reaction, and for rates of fluid infiltration.

4. The calculated difference in ^{18}O values between vein and rock matrix domains may reflect the existence of significant temperature gradients away from the veins. Differences in temperature of 100°C or greater would be necessary to account for the 2- to 4-per mil difference in calculated $\delta^{18}O$ values; such temperature changes would require the existence of significant local thermal gradients in this altered volcanic sequence.

At this point, none of these possibilities can be discounted.

Origins and evolution of hydrothermal fluids

The hydrogen and oxygen isotope compositions of hydrothermal solutions at southwest Tintic are compared to genetically different types of water in Figure 8. The δD values of the hydrothermal fluids are based on the measured δD values of both chlorite and sericite separates and extracted water from the quartz veins. The box labeled magmatic water refers to fluid that has equilibrated with an isotopically normal magma or igneous rock in the area (6–9‰) at $T \geq 650°C$. The δD values of local meteoric water from four springs in the southern Oquirrh Mountains range from −96 to −115 per mil.

The calculated $\delta^{18}O$ and δD values of water responsible for alteration in the inner actinolite subzone of propylitic alteration are 3.5 to 4.8 and −51 to −48 per mil, respectively. Proceeding outward through the epidote and chlorite subzones of propylitic alteration, both the $\delta^{18}O$ and δD values of hydrothermal fluids decrease, accompanied by decreases in temperature (from 350° to 200°C) and salinity. The di-

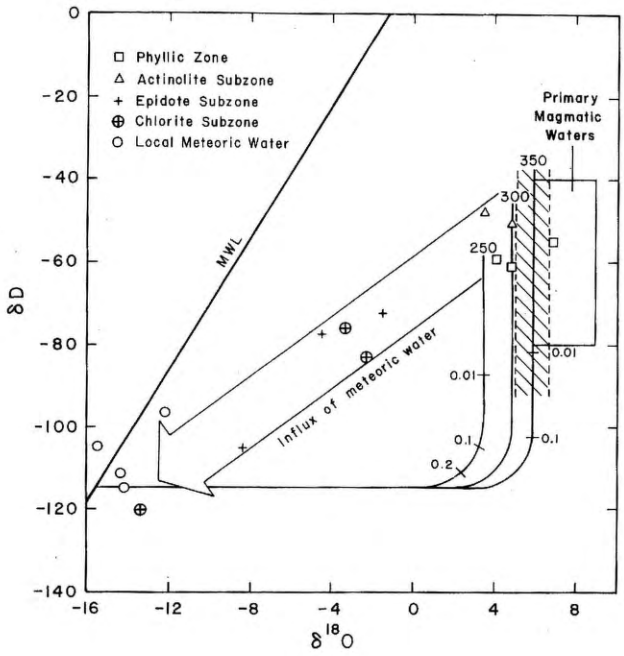

FIG. 8. Plot of calculated δD and $\delta^{18}O$ values of hydrothermal fluids of southwest Tintic. The meteoric water line (Craig, 1961a) and the field for primary magmatic water (Taylor, 1974, 1977) are also shown. Superimposed on this plot are exchange curves which illustrate the progressive changes in δD and $\delta^{18}O$ values that meteoric water would undergo through isotopic exchange with igneous rock ($\delta^{18}O$ = 7.5, δD = −80) as a function of temperature (250°, 300°, 350°C) and variable water/rock ratio. Only selected hash marks defining water/rock ratios (atomic oxygen) are shown for clarity. The diagonal line pattern centered on the vertical portion of the 350°C exchange curve illustrates the variations in $\delta^{18}O$ values of exchanged fluid that will result from variation in the $\delta^{18}O$ value (6.5 to 8.5) of the igneous rock with which these fluids exchange.

rection of these decreases is toward local meteoric water and indeed the outermost and lowest temperature quartz veins in the chlorite subzone have very low oxygen (−15‰) and hydrogen (−120‰) isotope compositions closely approaching those of local meteoric water. The trend of D and ^{18}O depletion outward through propylitic alteration can be easily explained by the progressive influx of cooler, D- and ^{18}O-depleted meteoric water diluting a hotter, more saline, and D- and ^{18}O-enriched hydrothermal fluid present in the center of the system. This fluid mixing could also account for the concurrent drop in temperature and decrease in salinity observed in fluid inclusions. The outermost fluids are so depleted in both D and ^{18}O that they are clearly dominated by meteoric water.

South of the actinolite-epidote boundary, there is a significant drop in both the $\delta^{18}O$ and δD value of the hydrothermal fluid, suggesting a significant increase in the amount of the meteoric water component across this boundary. The large (≤1.3 m thick) Old Susan vein also occurs at this location; to the south, in the epidote and chlorite subzones, there is a noticeable increase in the abundance of quartz veins and igneous dikes. The increase in these features implies greater permeability, consistent with the lower ^{18}O values, temperatures, and salinities recorded for the hydrothermal fluids to the south. The data suggest the existence of a mixing boundary or discontinuity in the thermal, physical (density, salinity), and isotopic characteristics of hydrothermal fluids at Tintic.

Subsequent to the progressive influx of local meteoric water responsible for the zoned propylitic alteration, phyllic alteration began. However, the calculated $\delta^{18}O$ and δD values of water responsible for the later phyllic alteration range from 4.2 to 6.8 and −61 to −55 per mil, respectively, and are similar to the fluids responsible for alteration in the actinolite subzone. In many porphyry copper systems, the hydrothermal fluids responsible for late phyllic alteration are depleted in both D and ^{18}O and are clearly derived from and dominated by local meteoric water (Sheppard et al., 1971; Bowman et al., 1987). However, it is clear that hydrothermal alteration in the phyllic zone at southwest Tintic is characterized by fluids much more enriched in both ^{18}O and D than those responsible for outer propylitic alteration. Phyllic alteration marks the return to the importance of hydrothermal fluids that are isotopically similar to those responsible for the earlier actinolite alteration. Such fluids either are from a different, nonmeteoric source or are derived from meteoric water that is far more evolved isotopically than that responsible for the outer propylitic alteration.

There are several possible origins of the D- and ^{18}O-enriched fluids responsible for the central actinolite and later phyllic zone alteration. These fluids have δD values identical with those expected for magmatic fluids; they also have $\delta^{18}O$ values similar to, or somewhat depleted relative to, magmatic fluids. One possibility therefore is that these fluids are magmatic waters, somewhat cooled and equilibrated at lower temperatures (and hence lower $\delta^{18}O$ values) than their igneous rock parents.

However, these fluids may also have been derived from meteoric water, as is the case for phyllic alteration in many other porphyry copper systems, and have become enriched in both ^{18}O and D through exchange at low water (W)/rock (R) ratios with the volcanic-sedimentary section in the southwest Tintic area. This process is also illustrated in Figure 8, where the hydrogen and oxygen isotope evolution of local meteoric water (δD = −115‰), resulting from progressive isotopic exchange with igneous rock ($\delta^{18}O$ = 7.5‰ δD = −80‰), is plotted as a function of W/R ratio at 250°, 300°, and 350°C. These curves were calculated by methods described by Taylor (1971, 1979). In the temperature range of 300° to 350°C

defined by fluid inclusion data for the formation of the actinolite and phyllic alteration episodes, water-rock exchange can produce, at W/R ratios < 0.01, fluids with the observed hydrogen and oxygen isotope compositions. Variation in the $\delta^{18}O$ values of alteration fluids within both actinolite and phyllic alteration zones may result from isotopic exchange with rock sections of somewhat different isotopic composition. A 2-per mil variation in the isotopic composition of rock (6.5–8.5‰) produces an equivalent variation in the $\delta^{18}O$ values of fluid equilibrated with this rock, as illustrated in Figure 8 (diagonally lined field) for fluid-rock exchange at 350°C.

Mechanisms of fluid-rock isotopic exchange at very low W/R ratios have been suggested to account for the presence of D-enriched hydrothermal fluids in tungsten vein deposits (Campbell et al., 1984) and specifically in porphyry copper-type deposits (Bowman et al., 1987). In these examples and at southwest Tintic, the temperatures required to reproduce the $\delta^{18}O$ and δD values of the hydrothermal fluids by fluid-rock interaction are in reasonable agreement with the estimated temperatures of alteration based on fluid inclusion measurements, lending support to this mechanism as a plausible process for isotopic evolution in hydrothermal systems. However, this mechanism requires very low W/R ratios to produce the D enrichment observed in these hydrothermal systems; it is not yet established whether such low W/R ratios (<0.01) are plausible in actual advective or convective hydrothermal systems. Given these severe constraints on W/R ratios, it is almost certain that any such fluid-rock exchange would take place at depth in the hydrothermal systems, below the exposed levels of alteration. This is because even the minimum abundance of alteration and quartz veining observed in either propylitic or phyllic alteration of Tintic is much greater than would be expected from the very low W/R ratios required to produce the necessary D enrichment in local meteoric water.

Fluid-rock exchange can explain the hydrogen and oxygen isotope characteristics of both the phyllic alteration fluids and those responsible for earlier actinolite zone alteration at Tintic. However, this process alone cannot explain the full range of hydrogen and oxygen isotope compositions recorded by the zoned propylitic alteration. In the Bingham Canyon porphyry system, the trends of D enrichment and ^{18}O depletion that characterize the zoned array of early potassic and propylitic alteration could be explained by fluid-rock exchange operating at different temperatures; higher temperatures (>500°C) to explain higher $\delta^{18}O$ and lower δD values in the potassic zone, lower temperatures (<450°C) to explain the lower $\delta^{18}O$ and higher δD values in the propylitic zone (Bowman et al., 1987). However at Tintic, fluid-rock interaction over the measured range of temperatures from 200° to 350°C can produce only about a 3-per mil decrease in the $\delta^{18}O$ values of hydrothermal fluids. This decrease is only a small fraction of the total decrease in $\delta^{18}O$ value for hydrothermal fluids recorded across the propylitic zone at Tintic. Clearly, fluid-rock exchange alone cannot explain the full range of hydrogen and oxygen isotope variations in the propylitic hydrothermal fluids at Tintic; fluid mixing involving an additional fluid type must also occur. These two fluid components may be meteoric waters that have circulated at different depths and exchanged with significantly different amounts of rock (and therefore attained very different isotopic compositions) or alternatively the mixing may involve magmatic fluids.

Possible significance of the Old Susan vein as a record of a fluid-mixing interface

As noted above, the location of the Old Susan vein and the actinolite-epidote subzone boundary in the propylitic zone are also marked by significant changes in the isotopic compositions and salinities of the hydrothermal fluids. North of this location, the alteration fluids are significantly enriched in both ^{18}O and D and are noticeably more saline, relative to alteration fluids to the south. These decreases indicate a significant increase in the amount of unevolved, less saline meteoric water component in the hydrothermal fluids to the south of these features.

The Old Susan vein is a major vein feature in the Tintic hydrothermal system, is up to 1.3 m thick, and extends from Sunrise Peak west-southwest to the edge of Tintic Valley where it is cut by Basin and Range faulting and buried by alluvium, a distance of over 2 km. The Old Susan vein is mineralized (copper, lead, zinc, silver); south of the vein, in the epidote and chlorite subzones, there is a noticeable increase in the abundance of quartz veins and igneous dikes. These geologic and geochemical features suggest that the Old Susan vein marks a discontinuity or boundary between hotter, isotopically more evolved and more saline fluids to the north and cooler, more dilute fluids dominated by little-evolved meteoric waters to the south. Further, the greater degree of ^{18}O depletion and more abundant veins and dikes to the south suggest both greater permeability and higher fluid fluxes in the outer propylitic zone. The deposition of the Old Susan vein and its base metal mineralization could well be in response to mixing of these two chemically, physically, and isotopically distinct fluids.

If two fluids of different salinities and temperatures mix, it is possible to precipitate quartz. An estimate of how much quartz would precipitate is provided by using quartz solubility and an estimate of temperature from fluid inclusions. If two equal amounts of liquids mix, one at 150°C and the other at 400°C and both are saturated with respect to silica, then 7.2×10^{-8}

moles quartz/g of water will precipitate at the resultant 275°C. The Old Susan quartz vein has 3.3×10^{10} moles of quartz (using an estimated depth of 300 m, width of 1.3 m, and length 2 km) which would require a minimum of 4.6×10^{17} g of water. A minimum estimate of 5×10^{17} g of water is required to alter the rock at southwest Tintic, based on conventional calculations of W/R (Taylor, 1971) and on the observed ^{18}O depletion in the volcanic rocks in the vicinity of the Old Susan vein; significant amounts of water were channeled into the southwest Tintic system at this location to precipitate quartz in the Old Susan vein. Therefore, mixing a higher salinity, higher temperature fluid with a low-salinity, lower temperature fluid could produce ore deposition and precipitation of quartz by lowering the temperature.

The size and physical extent of the Old Susan vein may reflect the persistence of this mixing and fluid flow interface at this location over much of the duration of hydrothermal alteration and fluid circulation-advection in the Tintic district. Recent numerical modeling studies of fluid advection in intrusive-volcanic systems predict the existence of long-term boundaries between shallower and deeper circulation systems (Birch and Forster, 1989). The Old Susan vein may represent such an interface, which in this particular case separates a shallow circulation system dominated by relatively cooler, less saline, and unevolved meteoric water from a relatively deeper circulation system characterized by hotter, more saline, and much more isotopically evolved meteoric waters.

Summary of Geological-Geochemical Evolution

A simplified outline of the sequence of events at southwest Tintic is (1) the deposition of the Paleozoic sedimentary section, (2) folding and faulting during the Sevier orogeny, (3) the intrusion of Copperopolis Latite dikes and the stock at Sunrise Peak with equivalent extrusion of tuffs at 32 Ma, (4) the emplacement of a quartz monzonite stock near the center of the secondary biotite zone, (5) early-stage potassic and zoned propylitic alteration resulting from varying mixtures of either highly evolved meteoric or magmatic water and unevolved meteoric fluids, (6) formation of the Old Susan vein at the mixing interface between highly saline, high $\delta^{18}O$ and δD water and low $\delta^{18}O$ and δD, low-salinity meteoric water, (7) the formation of late-stage phyllic alteration, and (8) subsequent faulting and erosion to the present level.

The mineral subzones of propylitic alteration at southwest Tintic are at increasing distances from the intrusive center: (1) the actinolite subzone, (2) the epidote subzone, and (3) the chlorite subzone. These subzones are significant for exploration. At southwest Tintic the zones are a function of temperature, pressure, and composition of the fluids that altered the volcanics. Altering fluids are increasing in $a_{Mg^{+2}}/a^2_{H^+}$ and $a_{Fe^{+2}}/a^2_{H^+}$ with decreasing temperature. Mg decreases in chlorite and calcite with distance from the secondary biotite zone and Fe increases. In epidote, ferric iron decreases with distance from the secondary biotite zone. This is the expected elemental variation that is observed in chlorite, calcite, and epidote.

Propylitic alteration is also zoned isotopically with respect to the central zone of secondary biotite. The calculated $\delta^{18}O$ and δD values of water in isotopic exchange equilibrium with whole-rock samples, mineral separates, and vein quartz all decrease systematically outward, from relatively heavy values (6 to 8, −50 to −60) in the actinolite subzone to very much more depleted values (−8 to −15, −105 to −120) in the outermost chlorite subzone. The heavy fluids in the actinolite subzone are compatible with equilibration with the igneous rocks in the Tintic system at the temperatures estimated for alteration (300°–350°C). The fluids in the outer chlorite subzone are virtually identical with local meteoric water. In addition, the measured salinities of fluid inclusions from quartz veins decrease systematically outward through the propylitic alteration from about 7 percent (equiv wt % NaCl) to near zero. These large and systematic isotopic and salinity variations across propylitic alteration can be explained by the progressive mixture of unevolved, low-salinity local meteoric water with a much more D- and ^{18}O-enriched, higher salinity fluid. There is a large decrease in the $\delta^{18}O$ values of the hydrothermal fluids across a relatively short interval corresponding to the location of the Old Susan vein and the boundary between actinolite and epidote alteration subzones. This interval may represent a mixing interface between dominantly unevolved meteoric waters to the south and much more evolved meteoric waters or magmatic waters to the north. The mineralized Old Susan vein may represent the depositional response to this mixing interface. The later phyllic alteration, superimposed on potassic alteration inside the peripheral propylitic zone, also formed from a fluid similar in hydrogen and oxygen isotope compositions to those enriched fluids responsible for actinolite alteration.

The origin of this ^{18}O- and D-enriched fluid is not completely clear. The hydrogen isotope composition of this fluid (−55) is indistinguishable from magmatic water, but the low temperatures (<350°C) of alteration suggest that a direct connection via evolution from crystallizing magma is unlikely. We suggest that this fluid evolved from local meteoric water, which became significantly enriched not only in ^{18}O but D as well through extensive exchange with the igneous rocks at depth in this system. The temperatures required by the fluid-rock exchange calculations to produce the ^{18}O values observed in the actinolite and phyllic alteration zones agree well with those suggested for the alteration by the fluid inclusion data,

lending support to this fluid-rock exchange model. These fluids must exchange at very low water (W)/rock (R) ratios (<0.01) at depth in the hydrothermal system in order to produce significant D enrichment. These highly exchanged fluids subsequently would be focused upward into higher levels now represented by the observed actinolite and phyllic zones of alteration, producing extensive alteration at locally high W/R ratios. This type of fluid-rock exchange model distinguishes between locally high W/R ratios in the exposed alteration zones and the very low W/R ratios characteristic of cumulative exchange along the entire pathlength of fluid flow lines at deeper levels in the hydrothermal system (Bowman et al., 1987). It is this latter region of dispersed flow and rock-dominated exchange which acts as a source or exchange zone and which determines in large part the isotopic and chemical characteristics of the discharging hydrothermal fluids.

Most previous studies of later stages of alteration in porphyry systems have demonstrated or interpreted propylitic and phyllic alteration to result dominantly from the incursion of relatively unevolved meteoric water (Sheppard et al., 1971; Taylor, 1974; Gustafson and Hunt, 1975; Gustafson, 1978). In particular, Taylor (1974) has proposed that phyllic alteration represents the inward incursion of meteoric or possibly formation water hydrothermal convection cells during the waning stages of hydrothermal alteration; the so-called "meteoric collapse." The stable isotope data from the southwest Tintic system demonstrate that the hydrothermal fluids responsible for the inner (e.g., actinolite) propylitic alteration and later phyllic alteration are not relatively unevolved meteoric water. In addition, the participation of ^{18}O- and D-enriched fluids in phyllic alteration after the incursion of relatively unevolved local meteoric waters during development of the zoned propylitic alteration indicates that the thermal collapse of such hydrothermal systems (e.g., recorded by the incursion of unevolved meteoric water) is not always an irreversible, single-stage process. The participation of ^{18}O- and D-enriched fluids in latest phyllic alteration suggests either a return to much more highly evolved meteoric waters which have circulated to much greater depths and exchanged isotopically with much greater quantities of rock or an influx of magmatic water. Such a change implies significant changes in the fluid flow geometries and paleo-plumbing system at southwest Tintic during the waning stages of hydrothermal alteration.

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