

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

**STABLE ISOTOPE SYSTEMATICS AND MAGMATIC AND  
HYDROTHERMAL PROCESSES IN THE SUMMITVILLE, CO  
GOLD DEPOSIT**

by

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Open-File Report 90-626

This report is preliminary and has not been edited or revised for conformity with U.S. Geological Survey standards and nomenclature

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*This report is a slightly modified and reformatted version of a poster presented at the annual meeting of the Geological Society of America in Dallas, Texas October 30, 1990 (Rye et al., 1990). We are releasing the study at this time because of the considerable interest in gold-bearing magmatic hydrothermal deposits.*

## ABSTRACT

The Summitville gold deposit occurs on the margin of the Platoro-Summitville caldera complex within the South Mountain quartz latite, a hypabyssal stock. Intense acid-leaching along fractures in the quartz latite has produced up to 70 m thick irregular pipes and lenticular pods of vuggy silica which are developed vertically over 300 m. The vuggy silica is enclosed sequentially by alteration zones of quartz-alunite, quartz-kaolinite, and clay; it hosts later gold mineralization with accompanying covellite, chalcopyrite, enargite, luzonite and minor kaolinite.  $\delta^{34}\text{S}$  values of sulfide in magnetite (-2.3‰) and of sulfate in apatite (5.4‰) in the quartz latite indicate  $\delta^{34}\text{S}_{\Sigma\text{S}} = 2 \pm 2\text{‰}$ .  $\delta^{34}\text{S}$  values of coexisting alunite and pyrite are 18.2 to 24.5‰ and -8.1 to -2.2‰, respectively, and indicate that the  $\text{H}_2\text{S}/\text{SO}_4$  of the system was probably  $4 \pm 2$ .  $\delta^{18}\text{O}_{\text{SO}_4}$  values (10.5 to 16.3‰) in alunite correlate with  $\delta\text{D}$  values (-70 to -39‰) as do  $\delta^{18}\text{O}$  values (5.3 to 12.3‰) and  $\delta\text{D}$  values (-60 to -103‰) of adjacent kaolinites. These data indicate that sulfate was derived from disproportionation of magmatic  $\text{SO}_2$  in both nearly pure magmatic water and in mixtures of magmatic and meteoric water at redox conditions below the  $\text{H}_2\text{S}/\text{SO}_4$  equivalence curve. Systematic  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  variations are not noticeable away from individual vuggy silica zones indicating that meteoric fluid compositions were buffered by wall rocks.  $\Delta^{34}\text{S}$  values between coexisting alunite and pyrite (16 to 30‰), define depositional temperatures (390° to 200°C) and permit reconstruction of the geothermal gradient and indications of a hydrostatic to lithostatic transition in the hydrothermal system at depth. Reflecting this geothermal gradient, the  $\delta^{18}\text{O}$  values of quartz (11.0 to 15.0‰) in the vuggy silica and quartz alunite zones generally increase with elevation.  $\Delta^{18}\text{O}_{\text{qtz-alunite}(\text{SO}_4)}$  values approach equilibrium but are generally not suitable for temperature determinations.  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  values in alunite are out of equilibrium because of retrograde  $^{18}\text{O}$  exchange in the OH site, and indicate only maximum temperatures of deposition.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of ore stage kaolinite (-98 to -122‰ and 7.3 to 9.7‰, respectively) suggest that exchanged meteoric water was dominant during ore deposition in contrast to the earlier magmatic water dominant acid-leaching event. However, the  $\text{H}_2\text{S}/\text{SO}_4$  ratio in the system appears to have remained relatively constant between the two stages, as evidenced by  $\delta^{34}\text{S}$  values for ore stage sulfides and barite similar to those for pyrite and alunite from the acid-leaching stage.

## INTRODUCTION

### **FIGURE 1: Air photo of the Summitville deposit**

The Summitville deposit is a classic example of epithermal Cu-Au-Ag mineralization associated with the advanced argillic (acid-sulfate) assemblage quartz+ alunite+kaolinite, and of a mixed magmatic-meteoric hydrothermal ore deposit in a relatively near surface (< 1km) environment. The deposit was worked episodically from 1870 to 1942 and produced about 260,000 oz of gold from underground workings. The Summitville Consolidated Mining Company, a subsidiary of Galactic Resources, Inc., currently operates an open pit mine with initial reserves of 12 MT of .043 oz/T Au. The active cooperation of the Galactic staff (particularly Mark Coolbaugh and Steve Enders), and of the preceding operator, the Anaconda company, has been critical to this study and the earlier study by Stoffregen (1987). Their provision of access to fresh exposures in the open cut, to extensive exploration drill core and cuttings, and extensive geologic mapping and interpretation has provided a documentation base unparalleled for this type of deposit.

The purpose of this study is twofold: 1) to further the understanding of the origin of the Summitville deposit through integrated stable isotope, geological and geochemical studies, with particular emphasis on the interaction of magmatic and meteoric processes throughout the history of hydrothermal activity, and 2) to evaluate the use of stable isotope data as temperature and process indicators for acid-sulfate alteration in magmatic-hydrothermal environments.

This poster is organized to first present the mineralogic, geologic and geochemical framework for the Summitville deposit including new sulfur isotope data on the unaltered host igneous rocks. This background is followed by presentation of the stable isotope data that constrain the temperature and  $H_2S/SO_4$  of the ore fluids and then the stable isotope data that constrain the origin and evolution of acid-sulfate alteration and mineralization fluids. The poster concludes with general models of acid-sulfate alteration and mineralization.

## BACKGROUND AND GEOLOGIC AND GEOCHEMICAL FRAMEWORK

### **FIGURE 2:** *San Juan volcanic field showing the location of the Summitville deposit*

The Summitville mining district is located at an elevation of about 12,000 feet in the Summitville-Platoro caldera complex of the San Juan volcanic field in southwestern Colorado. The Au-Cu-Ag ores of the Summitville district are hosted by the coarsely porphyritic quartz latite of the South Mountain volcanic dome (South Mountain Porphyry). The dome was emplaced along the coincident margins of the Platoro caldera and the younger, nested Summitville caldera at their intersection with the Pass Creek - Elwood Creek fault zone. This fault zone is a major graben cutting the Platoro - Summitville caldera complex, and running northwest toward the Mount Hope caldera.

### **FIGURE 3:** *Sequence of volcanic and hydrothermal events*

K/Ar dating of alunite and enclosing South Mountain Porphyry indicates that emplacement of the South Mountain volcanic dome and mineralization were nearly coincident at 22.5 Ma and followed subsidence of the Summitville caldera by approximately 6 Ma. (Mehnert, et al., 1973). Alteration and mineralization proceeded through 3 hypogene stages and a supergene stage distinguished by Stoffregen (1987) on the basis of mineralogy.

### **FIGURE 4:** *Schematic cross section of the South Mountain volcanic dome showing reconstructed topography at the time of mineralization*

Mineralization and alteration at Summitville occurs in fault controlled, sub-vertical tabular zones and pods within the South Mountain Porphyry. Currently known economic mineralization occurs within a thousand feet of the present surface, but drilling has shown that the hydrothermal system extended over a vertical range of at least 4500 feet. A quartz monzonite porphyry intrusion with Cu anomalies, phyllic alteration, and a stockwork zone with pyrite and minor quartz fillings occurs beneath the district at elevations below 10,000 ft. Although neither the quartz monzonite nor the sericitic alteration have been dated, they are probably genetically related to the overlying Au-Cu-Ag mineralization and associated acid-sulfate alteration because both the intrusion and acid-sulfate alteration cut the South Mountain Porphyry, and the acid-sulfate alteration and South Mountain Porphyry are nearly coeval.

### **FIGURE 5A:** *Schematic of alteration zoning*

### **FIGURE 5B:** *Photo of vuggy silica, quartz-alunite, and quartz-kaolinite zones*

The classic acid-sulfate alteration at Summitville, first described by Steven and Ratte (1960) has been interpreted by Stoffregen (1987) to have formed by extreme base and aluminum leaching by strongly acid fluids that formed by the condensation of an  $SO_2$ -rich magmatic vapor plume and subsequent disproportionation of  $SO_2$  to  $H_2S$  and sulfuric acid.

in magmatic or mixed magmatic-meteoric water fluids. Alteration preceded mineralization and consists of vuggy silica cores surrounded by successive zones: 1) quartz-alunite, 2) quartz kaolinite, 3) kaolinite-illite, and 4) smectite-chlorite. The first three zones are shown in the photo. The zoning reflects the progressive neutralization of the low pH fluids through reaction with wall rock and/or mixing with surrounding meteoric waters.

**FIGURE 6: Sulfur content and  $\delta^{34}\text{S}$  of minerals in the South Mountain Porphyry**

The South Mountain Porphyry is believed to be genetically related to the magma which produced the quartz monzonite encountered in deep exploration drilling and is most likely representative of the magma which was the ultimate source of sulfur for the mineralization. As shown in the table, sulfide sulfur occurs as chalcopyrite inclusions in biotite and magnetite, and as sulfate sulfur in apatite. Sulfur was extracted by KIBA reagent and analyzed as  $\text{Ag}_2\text{S}$ .

**STABLE ISOTOPE TEMPERATURES AND  $\text{H}_2\text{S}/\text{SO}_4$  OF FLUIDS**

**FIGURE 7:  $\delta^{34}\text{S}$  and calculated temperatures of sulfate and sulfide minerals from South Mountain Porphyry and acid-sulfate alteration showing  $\delta^{34}\text{S}_{\Sigma\Sigma}$  of system**

Temperatures based on sulfur isotope fractionations in coexisting sulfates and sulfides for igneous rocks, acid-sulfate alteration, and late mineralization are remarkably consistent with geologic occurrence whereby temperatures decrease from  $390^\circ$  at deepest levels to  $200^\circ\text{C}$  at higher elevations. Furthermore the temperatures of the acid-sulfate alteration are consistent with those observed in homogenization temperatures of fluid inclusions in quartz (Stoffregen, unpub. data, Bruha and Noble, 1983). The sulfur isotope data appear to be excellent indicators of primary temperatures and form the temperature framework of this study. The  $\delta^{34}\text{S}$  of the bulk sulfur in the magma, crystal, and exsolved fluid system can be estimated if data on the temperature, sulfur fugacity, and oxidation state of the magma are available. Currently such data do not exist for the South Mountain Porphyry. However, from the data on sulfate in apatite and sulfide sulfur in chalcopyrite inclusions in biotite and magnetite, the  $\delta^{34}\text{S}_{\Sigma\Sigma}$  must have been between 5.5 and  $-2.3\text{‰}$  and most likely was  $2 \pm 2\text{‰}$  (shaded in Figure 7). Using the range of  $\delta^{34}\text{S}_{\Sigma\Sigma}$  values as a fulcrum, the values of  $\delta^{34}\text{S}$  for coexisting sulfides and sulfates throughout the deposit require that  $\text{H}_2\text{S}/\text{SO}_2$  of the fluid was between 8 and 1, and most probably was  $4 \pm 2$ , a value typical of most I-type magmas. The difference between  $\delta^{34}\text{S}$  values for inclusions of chalcopyrite in biotite and those in magnetite may reflect loss of sulfur to the vapor phase or, less likely, assimilation of sulfur with resulting change in the bulk  $\delta^{34}\text{S}$  of the system.

**FIGURE 8:  $\Delta^{34}\text{S}_{\text{alun-py}}$  temperatures versus present elevation and relation to boiling curves**

Temperatures based on  $\Delta^{34}\text{S}_{\text{alun-py}}$  values show a correlation with elevation. Temperatures in the upper part of the deposit are consistent with those observed from filling temperatures of fluid inclusions, as noted above. When plotted as a function of elevation they fall close to, but below, a hydrostatic boiling curve calculated for a 10 wt. % NaCl equivalent brine and a water table at 13,300 ft. present elevation (approximately 300 feet below Steven and Ratte's (1960) reconstruction of the top of the volcanic dome of South Mountain. The sample at 9157 ft. elevation falls close to a lithostatic boiling curve calculated for the same conditions, suggesting that the transition from lithostatic to hydrostatic conditions occurred between approximately 9,000 and 10,000 ft. present elevation. A lower elevation for the 1 bar point could have been chosen so that the lithostatic boiling point curve would pass just above the lower temperature data points and through the 9157 ft. data point, but several lines of evidence, including the occurrence of breccias and stockworks deep in the system strongly argue against such a model.

**FIGURE 9A and 9 B:** *Measured  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{SO}_4)}$  and  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{OH})}$  versus alunite-pyrite sulfur isotope temperatures and predicted  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{SO}_4)}$  values*

The  $^{18}\text{O}$  fractionations between coexisting quartz and alunite for both the  $\text{SO}_4$  and OH oxygen sites in alunite, measured on samples for which alunite-pyrite sulfur isotope temperatures are available are summarized in Figures 9A and 9B. In Figure 9A the measured fractionations are plotted against temperatures calculated from alunite-pyrite sulfur isotope data and compared with temperatures predicted from experimental curves of Stoffregen et al. (1989). In Figure 9B the measured fractionations are compared with the predicted fractionations. It is clear that the neither  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{SO}_4)}$  nor  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{OH})}$  is a good indicator of temperature of deposition. The  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{SO}_4)}$  fractionations approach equilibrium values (although they still exhibit considerable scatter), but the fractionation curve is much too insensitive to temperature to give meaningful temperatures. Also, the  $\delta^{18}\text{O}_{\text{SO}_4}$  values may not reflect equilibrium with water at the point of precipitation from a rapidly moving fluid due to the sluggishness of  $^{18}\text{O}$  exchange between aqueous sulfate and water. On the other hand, the  $\Delta^{18}\text{O}_{\text{qtz-alun}(\text{OH})}$  fractionation curve is sensitive enough as a function of temperature to be a geothermometer but observed fractionations are far from equilibrium values. The observed fractionations are much too small and give unrealistically high temperatures, probably due to retrograde  $^{18}\text{O}$  exchange between fluid and the OH site in alunite as the mineral cooled, as suggested in the next figure.

**FIGURES 10A and 10B:** *Measured  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  in alunite versus alunite-pyrite sulfur isotope temperatures and predicted  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  values*

In Figure 10A  $^{18}\text{O}$  fractionations between  $\text{SO}_4$  and OH in alunite are plotted versus the temperature of deposition as indicated by the alunite-pyrite sulfur isotope fractionations (or estimated for samples lacking sulfur isotope data on pyrite based on their elevation in deposit) and compared to the experimentally determined fractionation curve of Stoffregen et al. (1989). Also plotted (along the fractionation curve) is the field for  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  values for samples from steam-heated environments (Rye et al., 1990). In Figure 10B the measured versus predicted  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  values are plotted against one another for the same samples. Both figures illustrate that the observed  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  values are in poor agreement with the experimental curve. However, the measured values appear to approach the curve at lower temperature, and fall along a trend that will intersect the equilibrium curve at about the temperatures and fractionations observed for alunites from steam-heated environments (Rye et al., 1990). We interpret this departure of  $\Delta^{18}\text{O}_{\text{SO}_4\text{-OH}}$  from equilibrium as a result of exchange between the OH site and fluid as the system cooled.

**FIGURE 11:**  *$\delta^{34}\text{S}$  values and temperatures calculated from sulfur isotope fractionations between pyrite and ore-stage sulfur, sulfides, and barite*

This table shows the total range of  $\delta^{34}\text{S}$  values obtained on sulfides and barite. Most of the sulfides are from drill hole samples while most of the barites are from shallow, oxidized ores. Even though few of the samples are contemporaneous the sulfur isotope fractionations between ore stage minerals and pyrite are consistent and, except for the fractionations between pyrite and chalcopyrite give reasonable depositional temperatures. Even covellite in the deeper part of the deposit appears to have formed at higher temperatures than barite and sulfur at higher levels. The narrow range of  $\delta^{34}\text{S}$  values on ore stage minerals indicates that the  $\delta^{34}\text{S}_{\Sigma\text{S}}$  and the oxidation state of the fluids was buffered throughout mineralization.

**FIGURE 12:** *Conclusions about stable isotope temperatures and  $\text{H}_2\text{S}/\text{SO}_4$  of the system*

## STABLE ISOTOPE SYSTEMATICS, SOURCES AND EVOLUTION OF FLUIDS

**FIGURE 13A:**  $\delta^{34}\text{S}$  -  $\delta^{18}\text{O}_{\text{SO}_4}$  of alunite

**FIGURE 13B:**  $\delta\text{D}_{\text{H}_2\text{O}}$  -  $\delta^{18}\text{O}_{\text{SO}_4}$  of alunite and  $\delta\text{D}_{\text{H}_2\text{O}}$  -  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of parent fluids during acid-sulfate alteration

Figure 13 summarizes the  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$ , and  $\delta\text{D}$  on alunites from Summitville. The black squares represent values for alunites produced as part of the pre-ore acid-sulfate alteration (Main Alunite). The faded symbols (Late Alunite) in Figure 13A represent late, sugary alunites that cut vein mineralization, and are discussed later. Their relationship to the barite+jarosite+goethite+Au assemblage is unknown. The large  $\delta^{34}\text{S}$  values in Figure 13A for the main alunites support Stoffregen's (1987) conclusion that the sulfuric acid required for the acid-sulfate alteration was derived from the disproportionation of  $\text{SO}_2$ . The  $\delta\text{D}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  data (Figure 13B) provide strong evidence that the fluids (and by implication the  $\text{SO}_2$ ) that produced the acid-sulfate alteration were predominantly of magmatic origin. The trend of the data in Figure 13A probably reflects the temperature decrease between the deepest and shallow samples while  $\text{H}_2\text{S}/\text{SO}_4$  of the fluids remained constant. The alunite-pyrite temperatures are  $390^\circ\text{C}$  for the deepest sample and  $210^\circ\text{C}$  for the shallow samples, and the data parallel the fractionation curve for alunites precipitated from fluid of constant  $\delta^{34}\text{S}_{\Sigma\text{S}}$  and  $\text{H}_2\text{S}/\text{SO}_4$  over this temperature range. Deviation of  $\delta^{18}\text{O}_{\text{SO}_4}$  values from the trend resulted from variation of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  due to mixing with meteoric water and/or exchange with wall rocks as discussed below. The fact that the lowest  $\delta^{18}\text{O}_{\text{SO}_4}$  values have the lowest  $\delta\text{D}$  values in Figure 13B suggests that the disproportionation of  $\text{SO}_2$  may have occurred in mixtures of magmatic and meteoric water.

The  $\delta\text{D}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values of most alunite fluids (Figure 13B) fall outside of the magmatic water box (which would probably include the composition of fluids in equilibrium with magmas having the composition of the South Mountain Porphyry). The shallow alunites have larger  $\delta\text{D}$  values than the deeper ones. The  $\delta\text{D}$  values of the alunite fluids are greatly different than meteoric water at the time of mineralization as indicated by  $\delta\text{D}$  of ore stage kaolinites (Figure 16) and the fluids were predominately magmatic in origin. Some of the possible causes of the variations in alunite fluid compositions are indicated by the arrows. The  $\delta\text{D}_{\text{H}_2\text{O}}$  of magmatic fluids can decrease by mixing with exchanged meteoric water.  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values can also decrease by exchange with wall rocks, and at very low water/rock ratios the  $\delta\text{D}_{\text{H}_2\text{O}}$  of the fluid can increase as well. Almost all  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values fall within the range of those predicted for equilibrium with feldspar in the South Mountain Porphyry between  $250^\circ$  and  $600^\circ\text{C}$  and it is clear that  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of the alunite fluids, whether magmatic or mixed magmatic-meteoric, was controlled by exchange with wall rocks.

**FIGURE 14:**  $\delta\text{D}$  -  $\delta^{18}\text{O}$  of wall rock kaolinite and  $\delta\text{D}_{\text{H}_2\text{O}}$  -  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of parent fluids

The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values of fluids responsible for the acid-sulfate alteration calculated from the alunite (Faded symbols) and wall rock kaolinite isotope data using alunite-pyrite sulfur isotope temperatures are similar, but the  $\delta\text{D}_{\text{H}_2\text{O}}$  values calculated from kaolinite data are distinctly lower than those calculated from alunite data - even when kaolinite and alunite are in the same hand specimen. Almost all  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values fall within the range of those predicted for equilibrium with feldspar between  $250^\circ$  and  $600^\circ\text{C}$ . The H-O isotope systematics for kaolinite and alunite shown in the figure are typical of all acid-sulfate alteration zones from magmatic-hydrothermal deposits studied to date (Rye et al., 1989). There are two interpretations of the differences between alunite and kaolinite fluids: 1) alunite formed from dominantly magmatic water and kaolinite formed in dilution zones as magmatic fluids mixed with surrounding meteoric water, 2) both alunite and kaolinite formed from dominantly magmatic water, but kaolinite  $\delta\text{D}$  values have undergone retrograde D exchange with meteoric waters after formation. Present data are insufficient to choose between the two possibilities, but Kharaka and O'Neil (1976) demonstrated that

clays are more susceptible to D than  $^{18}\text{O}$  exchange and that the rate of exchange is a function of temperature and grain size. The possibility of such exchange with later fluids has been demonstrated in fine-grained alunites experimentally (Stoffregen, et al., 1990), but the alunites of the acid-sulfate alteration zones are much coarser-grained than the kaolinite and therefore much less susceptible to retrograde exchange with later fluids. In any event, the correspondence of the  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of the alunite and kaolinite fluids indicates that both were buffered to the same degree by exchange with wall rocks.

**FIGURE 15A:  $\delta^{18}\text{O}$  of quartz versus elevation**

$\delta^{18}\text{O}$  values determined on fine-grained quartz in the ground mass of vuggy silica, quartz-alunite and quartz-kaolinite alteration zones are similar at a given locality, and drusy quartz in vugs has the same value as does quartz from the fine-grained ground mass. The values overlap those reported by Larson and Taylor (1987) for similar material. The  $\delta^{18}\text{O}$  values of quartz from the upper (main) portions of the system form a broad band that follows the quartz-water fractionations calculated for the hydrostatic boiling curve of Figure 8, using the fractionation factors of Matushisa, et al. (1979), and assuming a  $\delta^{18}\text{O}$  of the fluid of 6‰. This indicates that the first order variations in the quartz  $\delta^{18}\text{O}$  values reflect the temperature gradient in the upper part of the deposit. The variation in  $\delta^{18}\text{O}$  values at a given elevation probably reflects variations in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  due to exchange of the fluids with the wall rocks and boiling. The sample at 9157 foot elevation appears, from Figure 8, to represent pressures close to lithostatic, and is best referred to the lithostatic boiling curve. It comes from a mainly pyrite-filled stockwork zone suggesting it may represent the transition from a lithostatic to a hydrostatic pressure regime.

**FIGURE 15B:  $\delta\text{D}$  of alunite versus elevation**

$\delta\text{D}$  values of alunite also appear to increase with elevation. This increase cannot be due to the temperature decrease which governs the  $^{18}\text{O}$  data, because hydrogen isotope fractionation factors do not increase with decreasing temperature. Rather, it must be due to a complex combination of water/rock effects and mixing with exchanged meteoric water. A quantitative understanding of the H-O isotope data will require computer-based modeling incorporating the effects of temperature, mixing, and water/rock exchange.

**FIGURE 16:  $\delta\text{D} - \delta^{18}\text{O}$  of ore-stage kaolinite fluids and  $\delta\text{D}_{\text{H}_2\text{O}} - \delta^{18}\text{O}_{\text{H}_2\text{O}}$  of parent fluids**

Fluids that formed kaolinite associated with ore mineralization are shown in heavy symbols (solid symbols represent mineral data; open symbols are calculated values for fluids). Faded symbols represent values for alunite and kaolinite formed during the pre-mineralization acid-sulfate alteration shown in previous figures. The kaolinites formed during mineralization have  $\delta\text{D}_{\text{H}_2\text{O}}$  values much lower than those formed during pre-ore alteration, reflecting the dominant role of meteoric water in the system during mineralization. It is very interesting that these late meteoric water ore fluids have the same  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values as the magmatic acid-sulfate fluids. Thus the meteoric waters in the Cu-Au stage (as well as those that mixed with magmatic waters during acid-sulfate alteration) appear to have been highly  $^{18}\text{O}$  exchanged, presumably as a result of low water/rock ratios. This implies a substantially different hydrologic system from classic adularia-bearing bonanza gold vein systems such as proposed for the Bodie mining district where the initial low  $\delta^{18}\text{O}$  of the meteoric water are imposed on the rock (O'Neil et al., 1973).

**FIGURE 17:  $\delta^{34}\text{S} - \delta^{18}\text{O}_{\text{SO}_4}$  of ore-stage barite and late alunite**

The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  of barite and late, sugary alunite (black symbols) are compared to the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  of alunite formed during pre-ore acid-sulfate alteration (faded symbols). Although the  $\delta^{34}\text{S}$  values for barite span a larger range, and  $\delta^{18}\text{O}_{\text{SO}_4}$  values are slightly lower than those for pre-ore alunite, the data show a similar correlation between  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ . Some of the barites occur in the upper levels of the deposit and were

almost certainly formed during mixing of the mineralizing fluids with overlying, steam-heated meteoric water. The barite with lower  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  reflects contributions of sulfate from the oxidation of isotopically light  $\text{H}_2\text{S}$  at or above the water table. The lower  $\delta^{18}\text{O}_{\text{SO}_4}$  for barites as compared to pre-ore alunite of a given  $\delta^{34}\text{S}$  reflect: 1) the difference between alunite-water and barite-water  $^{18}\text{O}$  fractionation factors, and 2) the influence of meteoric water on the  $\delta^{18}\text{O}_{\text{SO}_4}$  of the barites. The large  $\delta^{34}\text{S}$  values for the barite and  $\Delta^{34}\text{S}$  between barite and coexisting sulfides are similar to those for the pre-ore alunite and coeval pyrite and indicate that the ore fluids had the same sulfur isotope geochemistry as did the acid-sulfate fluids. This is also true for the late alunite fluids although the relationship of these alunites to the pre-ore alunites and barites is not clear.

**FIGURE 18:**  $\delta^{34}\text{S}$  and calculated temperatures of coexisting sulfate and sulfide from South Mountain porphyry, acid-sulfate alteration and ore-stage mineralization

Figure 18 compares the  $\delta^{34}\text{S}$  of coexisting ore-stage sphalerite and barite with those shown in Figure 7 where sulfate-sulfide sulfur isotope temperatures were calculated from the  $\delta^{34}\text{S}$  of igneous rocks and acid-sulfate alteration. The  $\delta^{34}\text{S}$  values of the coexisting ore stage sphalerite and barite (as well as those of other ore stage minerals in Figure 11) are similar to those formed in the earlier acid-sulfate alteration stage indicating little change in  $\delta^{34}\text{S}_{\Sigma\text{S}}$  or in  $\text{H}_2\text{S}/\text{SO}_4$  of the system during hydrothermal activity. Most of the change in  $\delta^{34}\text{S}$  was in the sulfate, indicating that the  $\text{H}_2\text{S}/\text{SO}_4$  of fluids was buffered at some value  $>1$  - most likely about 4 - throughout the period of hydrothermal activity. If the  $\delta^{34}\text{S}$  data of the South Mountain Porphyry is typical of the magmatic source of hydrothermal sulfur, then the  $\delta^{34}\text{S}_{\Sigma\text{S}}$  was between 5.5 and -2.3 ‰ and most likely close to 2‰.

## MODELS OF ACID-SULFATE ALTERATION AND MINERALIZATION

**FIGURE 19A:** Schematic model of acid-sulfate alteration showing interfacing of magmatic and meteoric fluid and phase of fluid

**FIGURE 19B:** Schematic model of gold mineralization showing dominant meteoric water fluids with sulfur from magmatic source

The stable isotope data provide quantitative documentation of the hydrology of the magmatic hydrothermal system and establish the geothermal gradient in which the system operated. These data also establish that the sulfur isotope geochemistry of the system remained constant though the transition from acid-sulfate alteration to copper-gold mineralization. The data require that, although dominated by magmatic fluids, the acid-sulfate alteration stage involved some meteoric waters, particularly around the margins of the veins in the quartz-kaolinite and outer zones, and that these meteoric fluids exchanged with wall rocks at high temperatures.

The acid-sulfate alteration in Figure 19A formed as a consequence of the sudden ascent of magmatic fluids. The sulfuric acid required formed from the disproportionation of  $\text{SO}_2$  to  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  upon condensation of the vapor plume at shallow levels in the system. This vapor plume was surrounded by a sheath of meteoric fluids that were close to  $^{18}\text{O}$  equilibrium with volcanic rocks at high temperatures. The fractures that allowed the ascent of the vapor plume, and the volume reduction produced by the extreme base leaching during acid-sulfate alteration, provided a "chimney" of vertical permeability. The dashed arrows in Figure 19A indicate movement of meteoric water toward the "chimney" but do not necessarily imply large fluxes of meteoric water in the acid-sulfate alteration stage. The degree of circulation of meteoric waters in the wall rocks marginal to the fractures is uncertain. The increase in exchanged meteoric water involvement away from the veins may reflect: 1) large chemical but small fluid fluxes away from the veins, or 2) physical mixing of magmatic fluids with a large flux of exchanged meteoric water. Detailed studies of alteration halos and combined chemical isotopic and hydrologic modeling are necessary to resolve this important question.

During the ore stage, following collapse of the magmatic vapor plume, exchanged meteoric water occupied the "chimney" and dominated the system (Figure 19 B). The magma continued to supply sulfur and other volatiles to these meteoric fluids, providing the chemistry sufficient to transport metals to high permeability zones at higher levels.

**FIGURE 20:** *Conclusions about the Summitville system*

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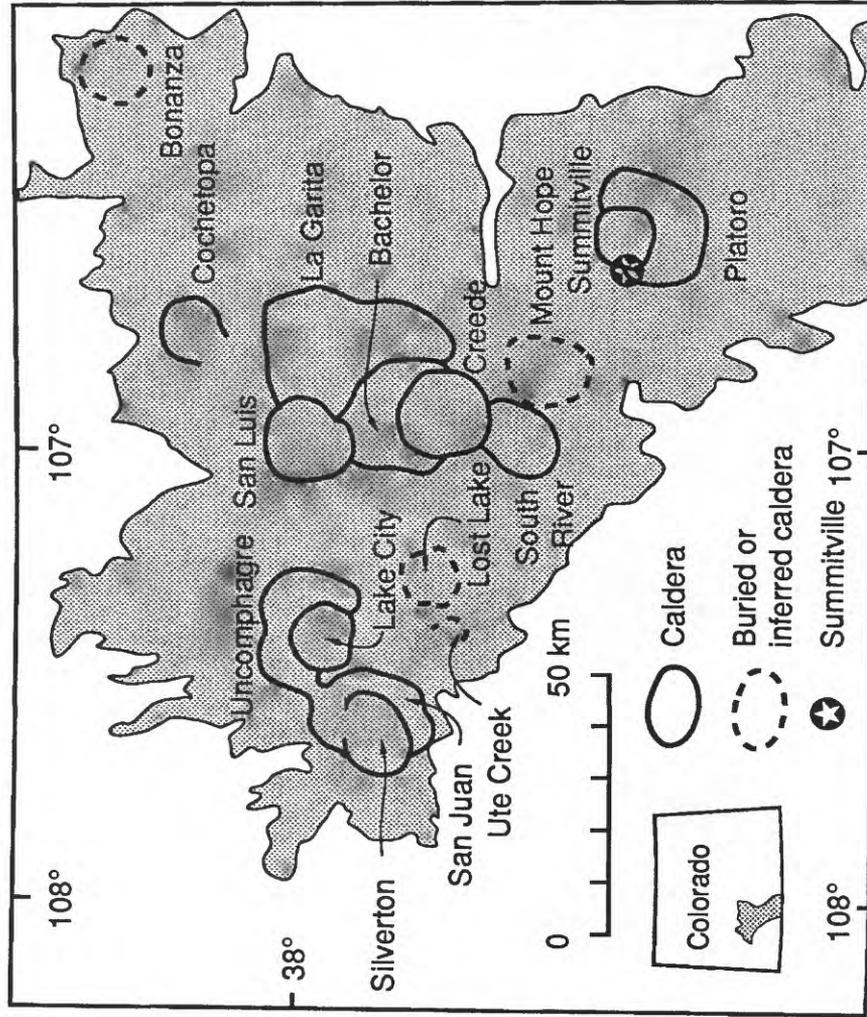
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SUMMITVILLE MINE  
(LOOKING SOUTHEAST; OCTOBER, 1989)



FIGURE 1

SAN JUAN VOLCANIC FIELD SHOWING LOCATION OF THE SUMMITVILLE DEPOSIT

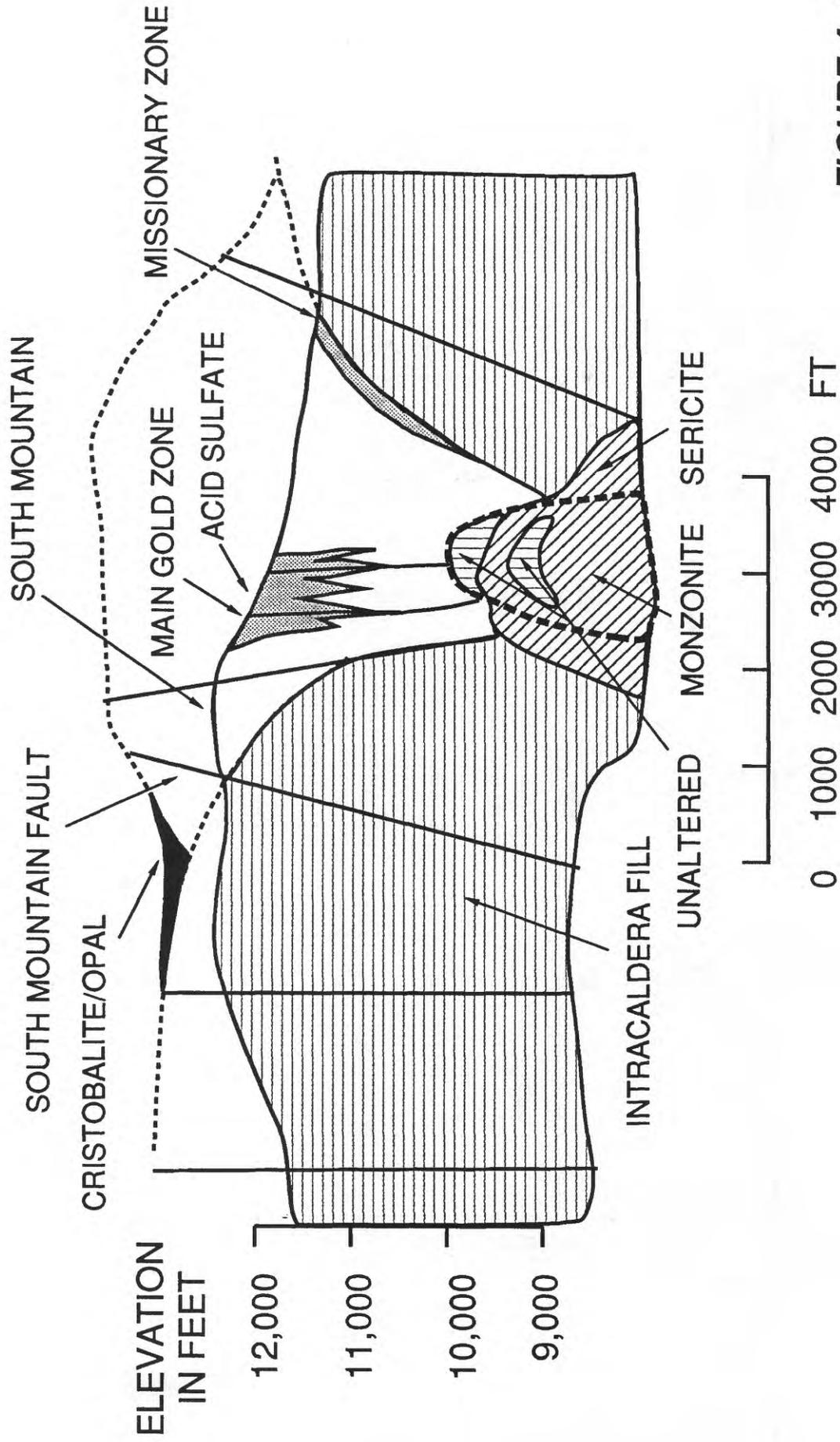


## SEQUENCE OF VOLCANIC AND HYDROTHERMAL EVENTS IN THE SUMMITVILLE DISTRICT

AGE Ma	EVENT	PRODUCTS
28-29	COLLAPSE OF PLATERO-SUMMITVILLE CALDERA COMPLEX	TREASURE MOUNTAIN TUFF
22.8	SOUTH MOUNTAIN VOLCANIC DOME	SOUTH MOUNTAIN PORPHYRY
22.3	ACID SULFATE ALTERATION	STAGE 1 Quartz+alunite+kaolinite+pyrite alteration
22.3?	MINERALIZATION	STAGE 2 Deep: Chalcopyrite+tennantite+pyrite STAGE 2 Shallow: Kaolinite+covellite+ enargite/luzonite+pyrite+gold STAGE 3 Surficial: Barite+gold+sulfides+jarosite(?) + goethite(?) +alunite(?)
5-0?	SUPERGENE OXIDATION	STAGE 4 Goethite+chalcocite+jarosite(?) +gold(?)

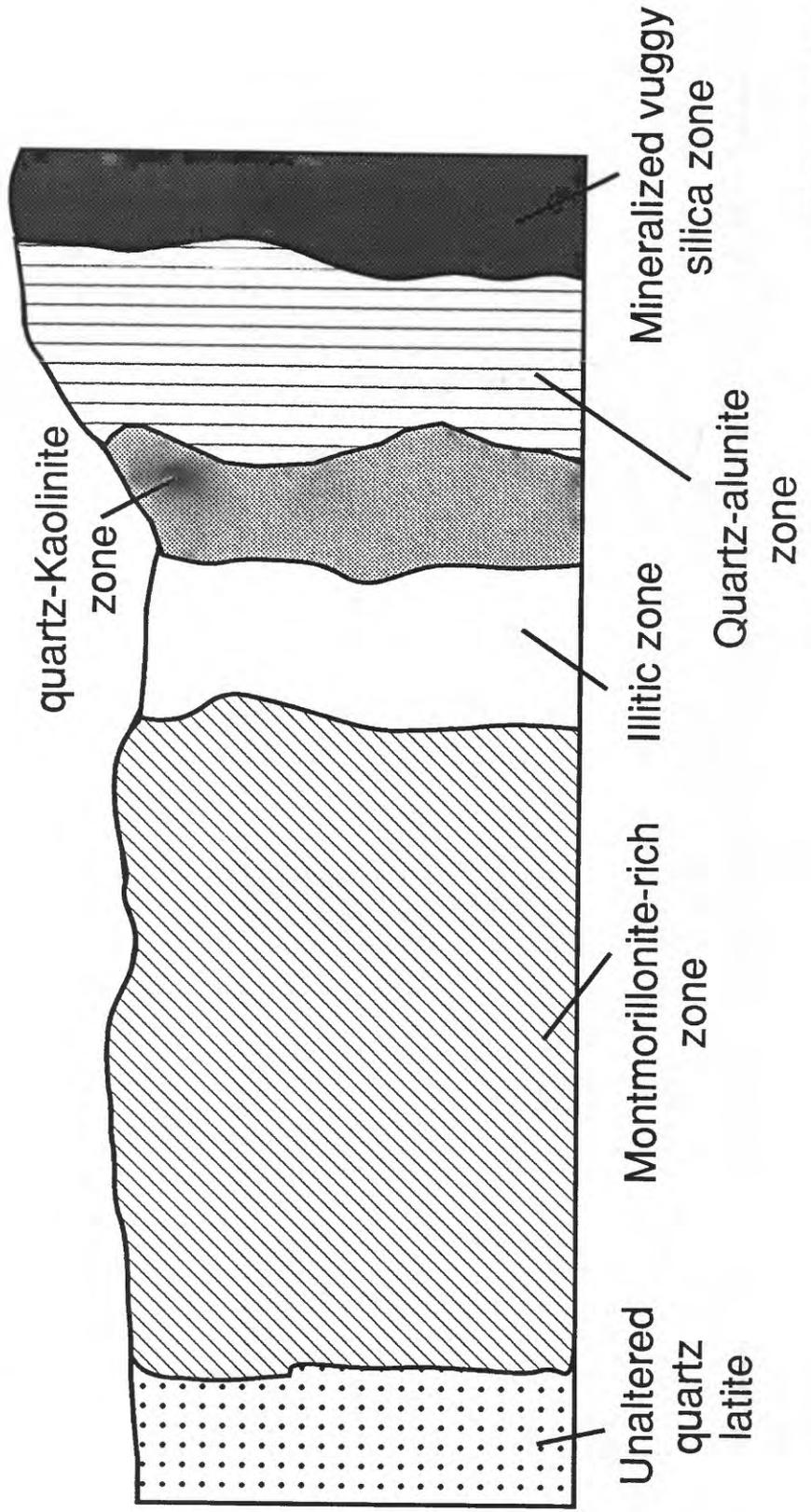
**FIGURE 3**

SCHEMATIC CROSS SECTION - SUMMITVILLE DISTRICT SHOWING  
 RECONSTRUCTED TOPOGRAPHY AT TIME OF MINERALIZATION  
 (modified from Steven and Ratte, 1960; Enders and Coolbaugh, 1987 with post  
 mineralization fault displacement removed)



# SCHEMATIC OF ALTERATION ZONING (Modified from Steven and Ratte, 1960)

Boundaries between clay zones are transitional



ACID-SULFATE ALTERATION SHOWING VUGGY SILICA,  
QUARTZ-ALUNITE, AND QUARTZ-KAOLINITE ZONES



QUARTZ-KAOLINITE

QUARTZ-ALUNITE

VUGGY SILICA

FIGURE 5B

SULFUR CONTENT AND  $\delta^{34}\text{S}$  OF MINERALS IN  
THE SOUTH MOUNTAIN PORPHYRY

MINERAL	ppm S	$\delta^{34}\text{S}$
SO <sub>4</sub> in Apatite	1300	5.5
Chalcocopyrite in biotite	150	-2.3
Chalcocopyrite in magnetite	80	-6.3
Whole rock	100	1.0

FIGURE 6

$\delta^{34}\text{S}$  AND CALCULATED TEMPERATURES OF COEXISTING SULFIDE AND SULFATE MINERALS FROM SOUTH MOUNTAIN PORPHYRY AND VARIOUS LEVELS OF ACID-SULFATE ALTERATION

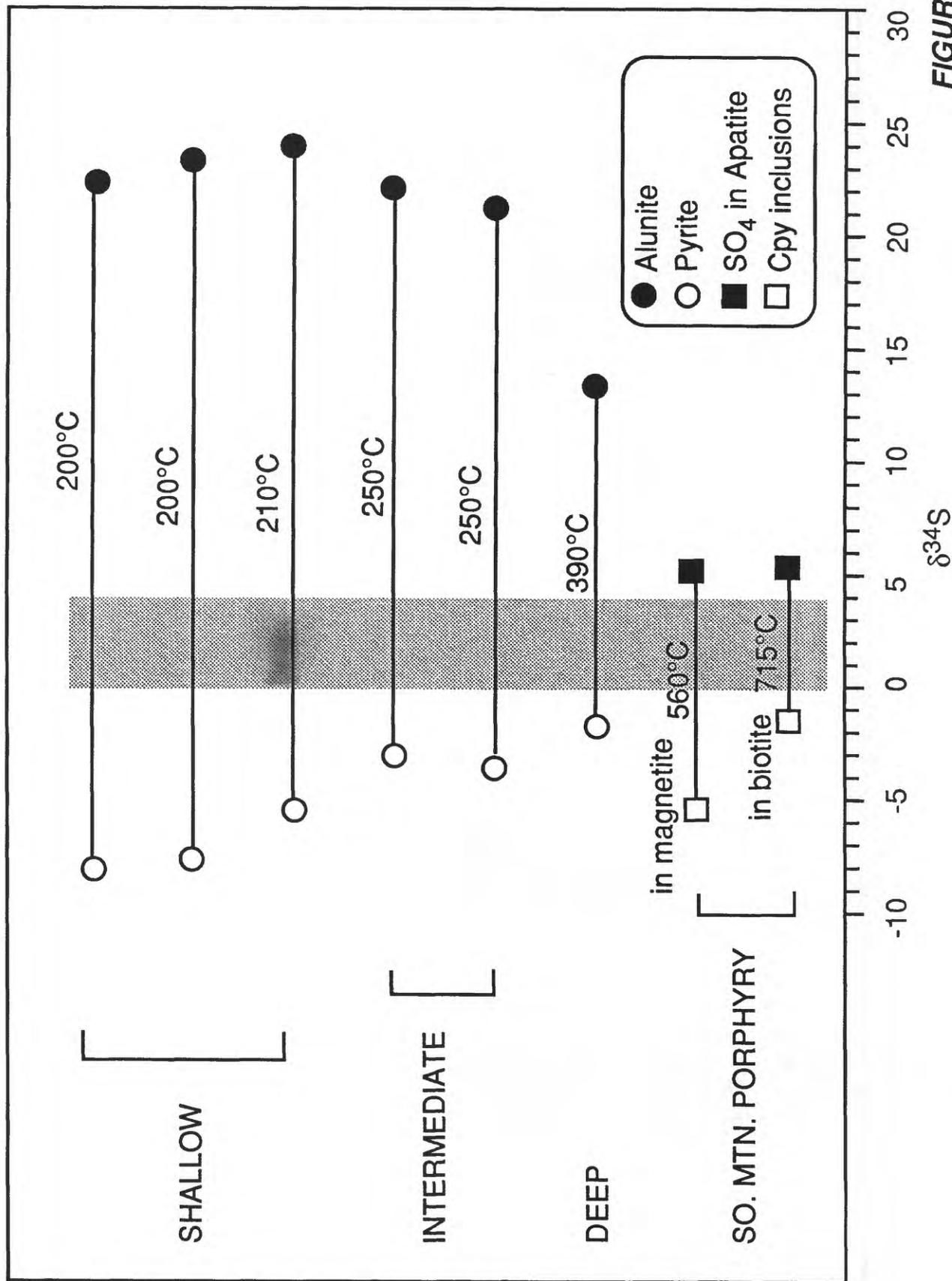


FIGURE 7

ALUNITE - PYRITE SULFUR ISOTOPE TEMPERATURES  
 VERSUS PRESENT ELEVATION:  
 RELATION TO BOILING CURVES

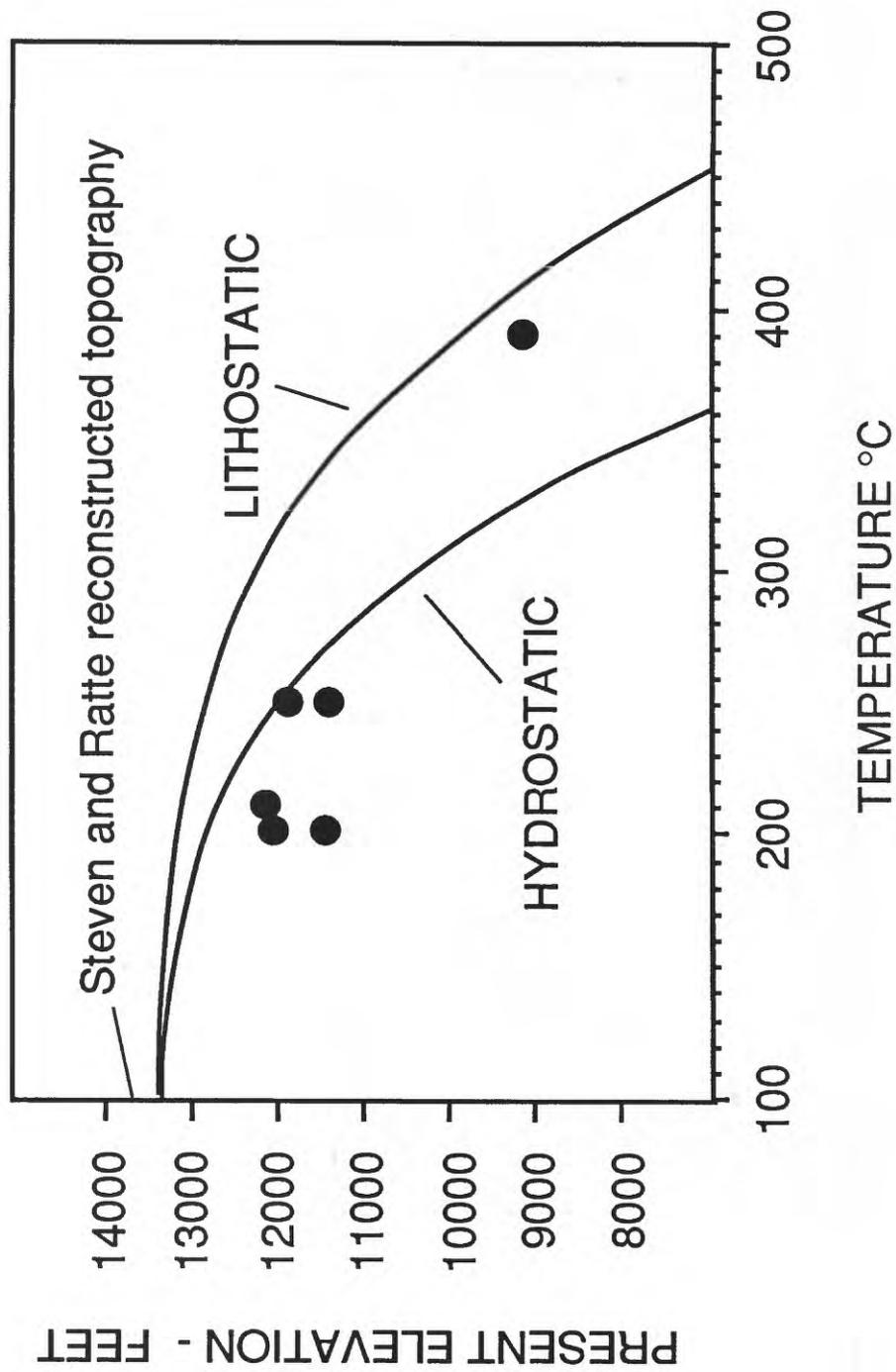


FIGURE 8

MEASURED  $\Delta^{18}\text{O}_{\text{qtz-alun}}$  VERSUS ALUNITE-PYRITE FROM ALUNITE-PYRITE SULFUR ISOTOPE TEMPERATURES

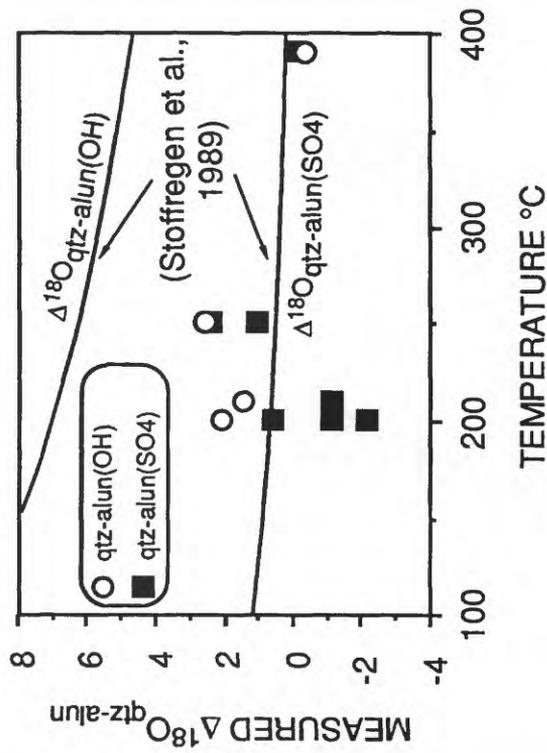


FIGURE 9A

MEASURED  $\Delta^{18}\text{O}_{\text{qtz-alun}}$  VERSUS PREDICTED VALUES FROM ALUNITE-PYRITE SULFUR ISOTOPE TEMPERATURES

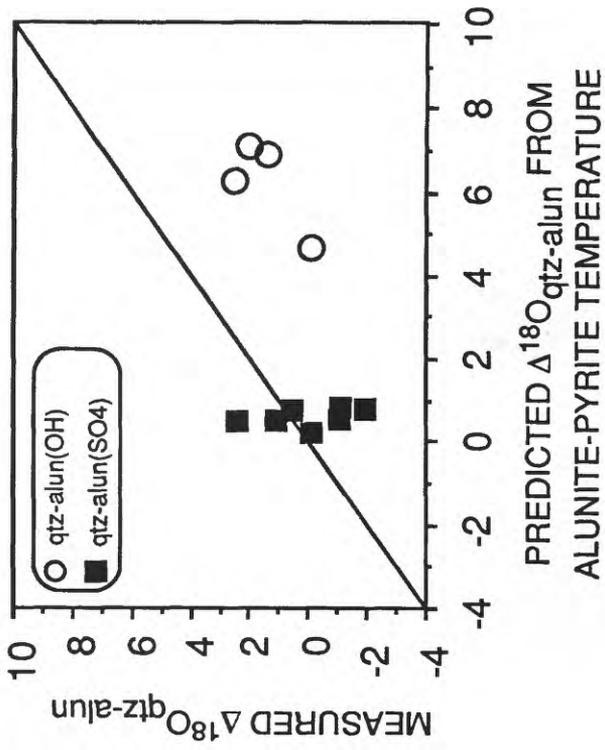


FIGURE 9B

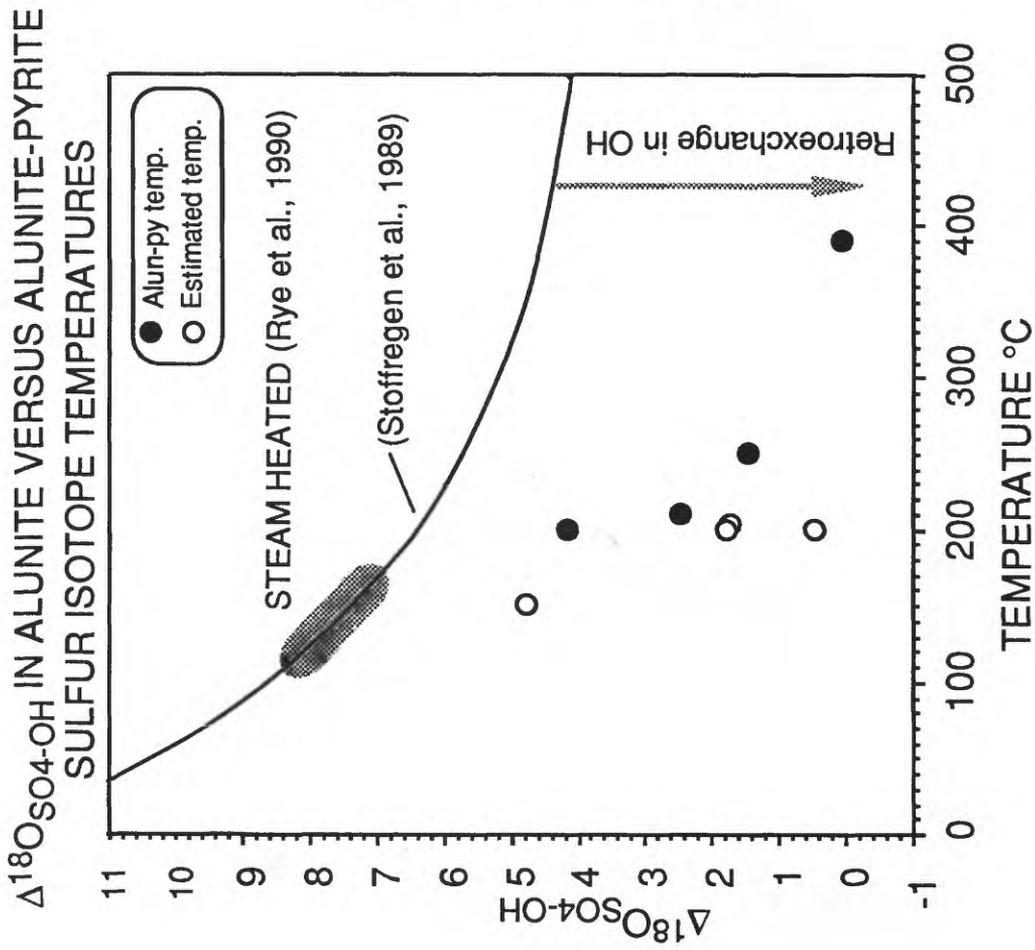


FIGURE 10A

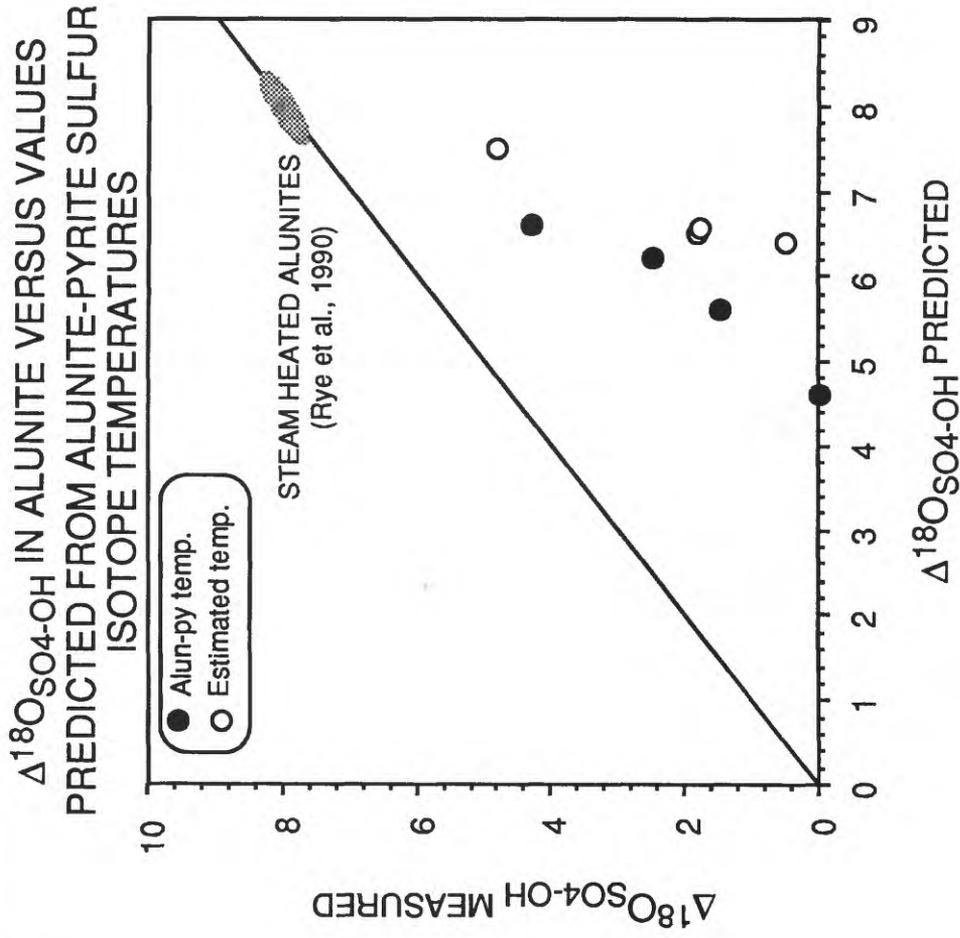


FIGURE 10B

TEMPERATURES CALCULATED FROM SULFUR  
ISOTOPE FRACTIONATIONS BETWEEN PYRITE AND  
ORE-STAGE SULFUR, SULFIDES AND BARITE

MINERAL	$\delta^{34}\text{S}$	$\Delta_{\text{py-min}}$	TEMPERATURE °C
Pyrite	-1.9 to -3.0		
Sphalerite	-4.2	2.3-1.2	90-230
Sulfur	-5.3	3.4-2.3	132-220
Galena	-6.6 to -7.0	5.1-3.6	174-259
Chalcopyrite	-5.7	3.8-2.7	71-135
Covellite	-6.7	4.8-3.7	216-284
Barite	26.6 to 24.3	29.6-26.2	172-208

FIGURE 11

## CONCLUSIONS ABOUT GEOTHERMOMETERS, TEMPERATURES AND H<sub>2</sub>S/SO<sub>4</sub> OF THE SYSTEM

- THE SULFUR ISOTOPE FRACTIONATION BETWEEN COEXISTING ALUNITE AND PYRITE IS A SUPERB GEOTHERMOMETER FOR APPLICATION TO ACID-SULFATE ENVIRONMENTS AND CAN BE USED TO RECONSTRUCT THE GEOTHERMAL GRADIENT DURING ACID-SULFATE ALTERATION.
- THE  $\delta^{34}\text{S}$  VALUES OF COEXISTING ALUNITE AND PYRITE, WHEN COMPARED WITH DATA ON SULFATE AND SULFIDE IN THE IGNEOUS ROCK, INDICATE THAT THE H<sub>2</sub>S/SO<sub>4</sub> OF THE ACID-SULFATE SYSTEM WAS BETWEEN 2:1 AND 8:1.
- QUARTZ-ALUNITE (SO<sub>4</sub>) OXYGEN ISOTOPE FRACTIONATIONS DO NOT PROVIDE USEFUL TEMPERATURE INFORMATION IN MAGMATIC HYDROTHERMAL ACID-SULFATE ENVIRONMENTS BECAUSE THE FRACTIONATIONS ARE TOO INSENSITIVE TO TEMPERATURE.
- QUARTZ-ALUNITE (OH) OXYGEN ISOTOPE FRACTIONATIONS DO NOT PROVIDE USEFUL TEMPERATURE INFORMATION IN MAGMATIC HYDROTHERMAL ACID-SULFATE ENVIRONMENTS BECAUSE RETROGRADE EXCHANGE OCCURS IN THE OH SITE OF ALUNITE AS THE SYSTEM COOLS.
- OXYGEN ISOTOPE FRACTIONATIONS BETWEEN SO<sub>4</sub> AND OH IN ALUNITE GIVE ONLY MAXIMUM TEMPERATURES OF DEPOSITION IN MAGMATIC HYDROTHERMAL ACID-SULFATE ENVIRONMENTS BECAUSE RETROGRADE EXCHANGE OCCURS IN THE OH SITE OF ALUNITE AS THE SYSTEM COOLS.

FIGURE 12

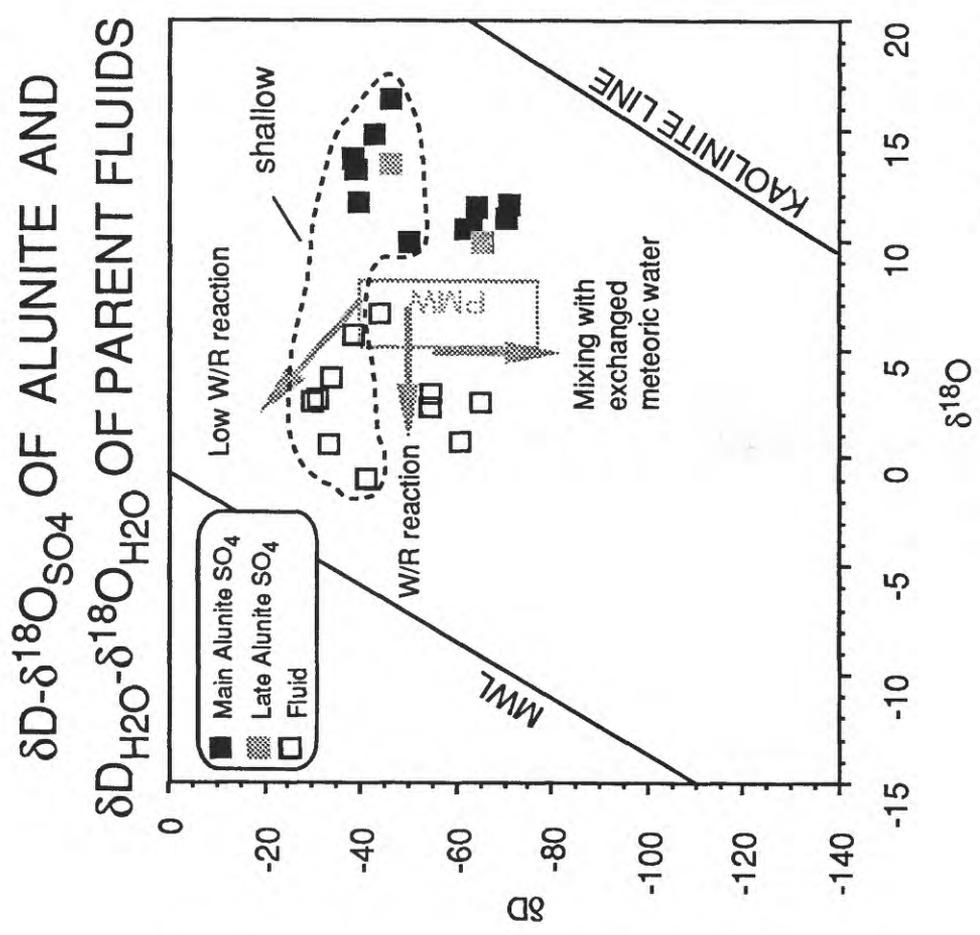


FIGURE 13B

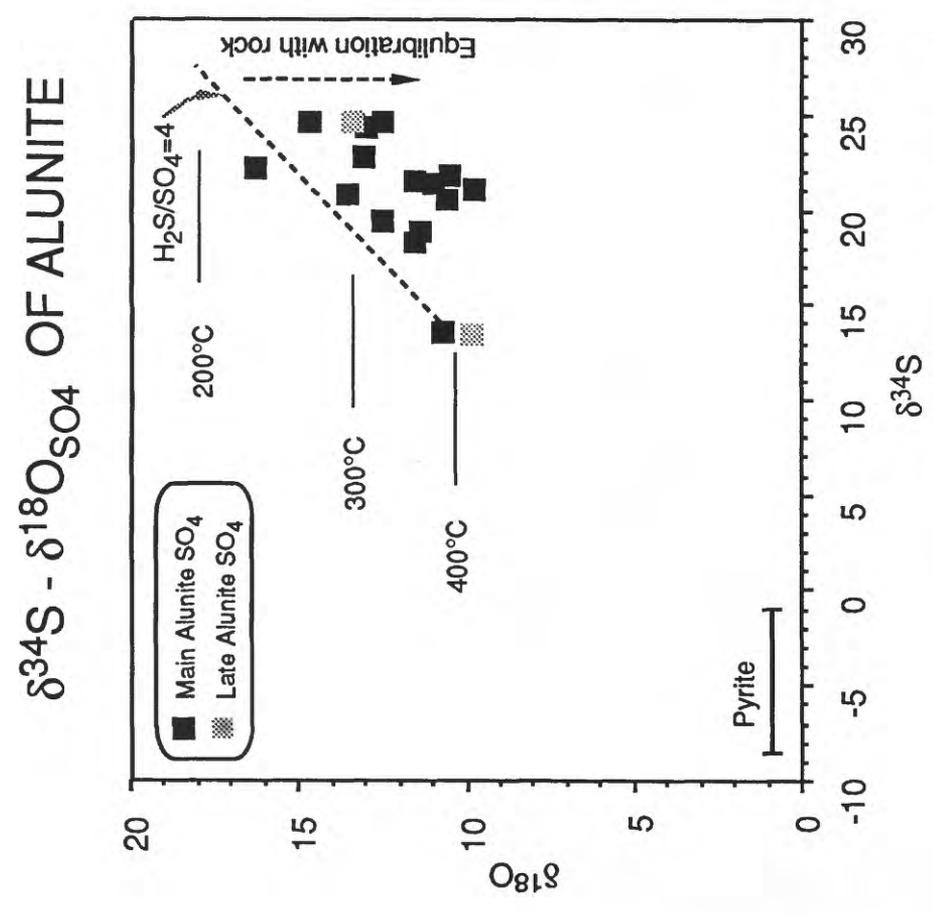


FIGURE 13A

# δD-δ<sup>18</sup>O OF WALL ROCK KAOLINITE AND δD<sub>H2O</sub>-δ<sup>18</sup>O<sub>H2O</sub> OF PARENT FLUIDS

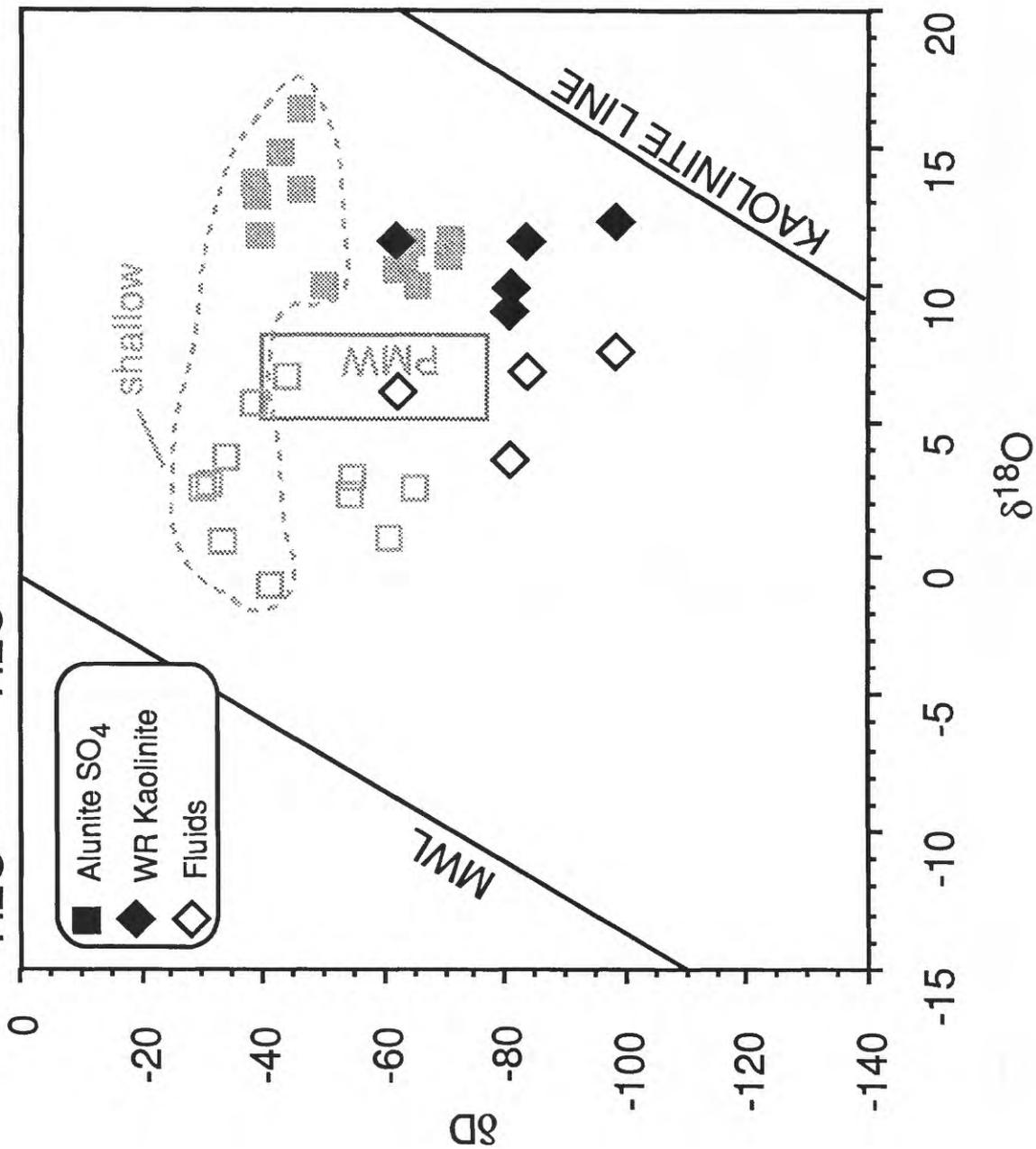


FIGURE 14

$\delta^{18}O$  QUARTZ VERSUS ELEVATION

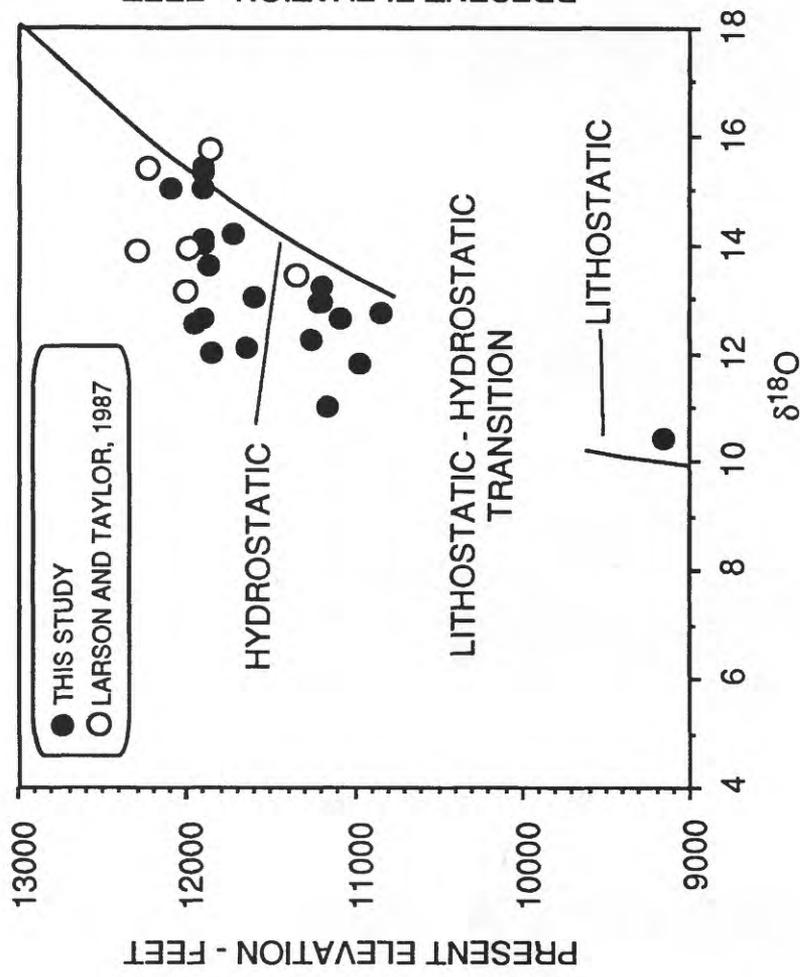


FIGURE 15A

$\delta D$  OF ALUNITE VERSUS ELEVATION

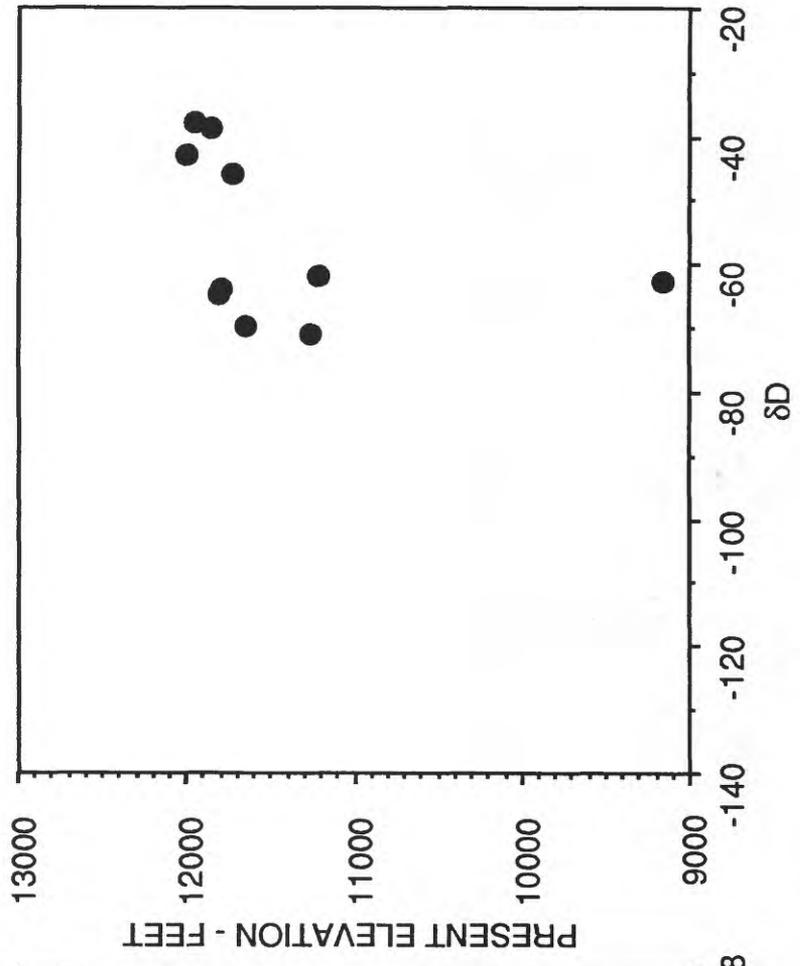


FIGURE 15B

# $\delta D$ - $\delta^{18}O$ OF ORE-STAGE KAOLINITE AND $\delta D_{H_2O}$ - $\delta^{18}O_{H_2O}$ OF PARENT FLUIDS

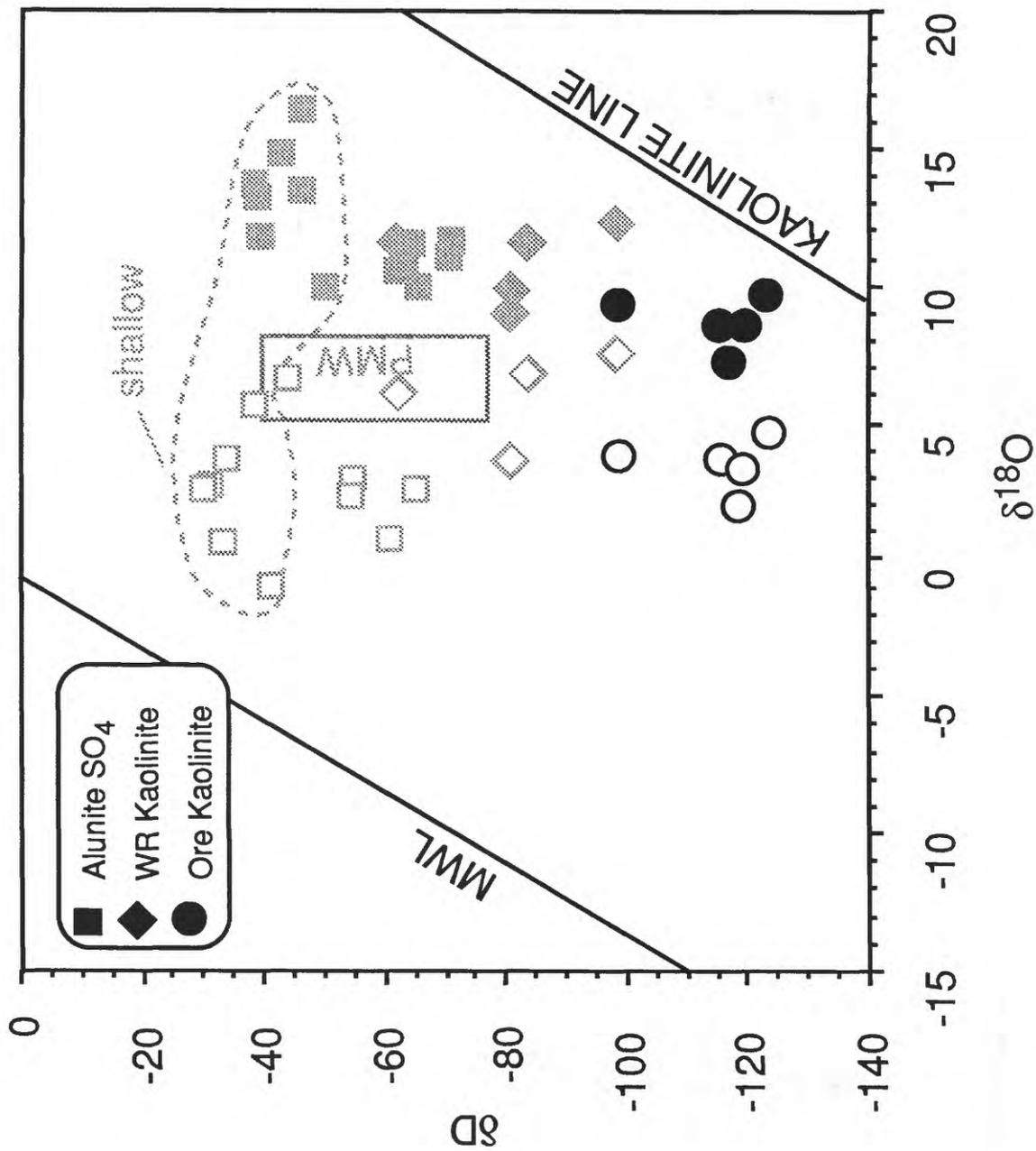


FIGURE 16

$\delta^{34}\text{S}-\delta^{18}\text{O}_{\text{SO}_4}$  OF BARITE AND LATE ALUNITE

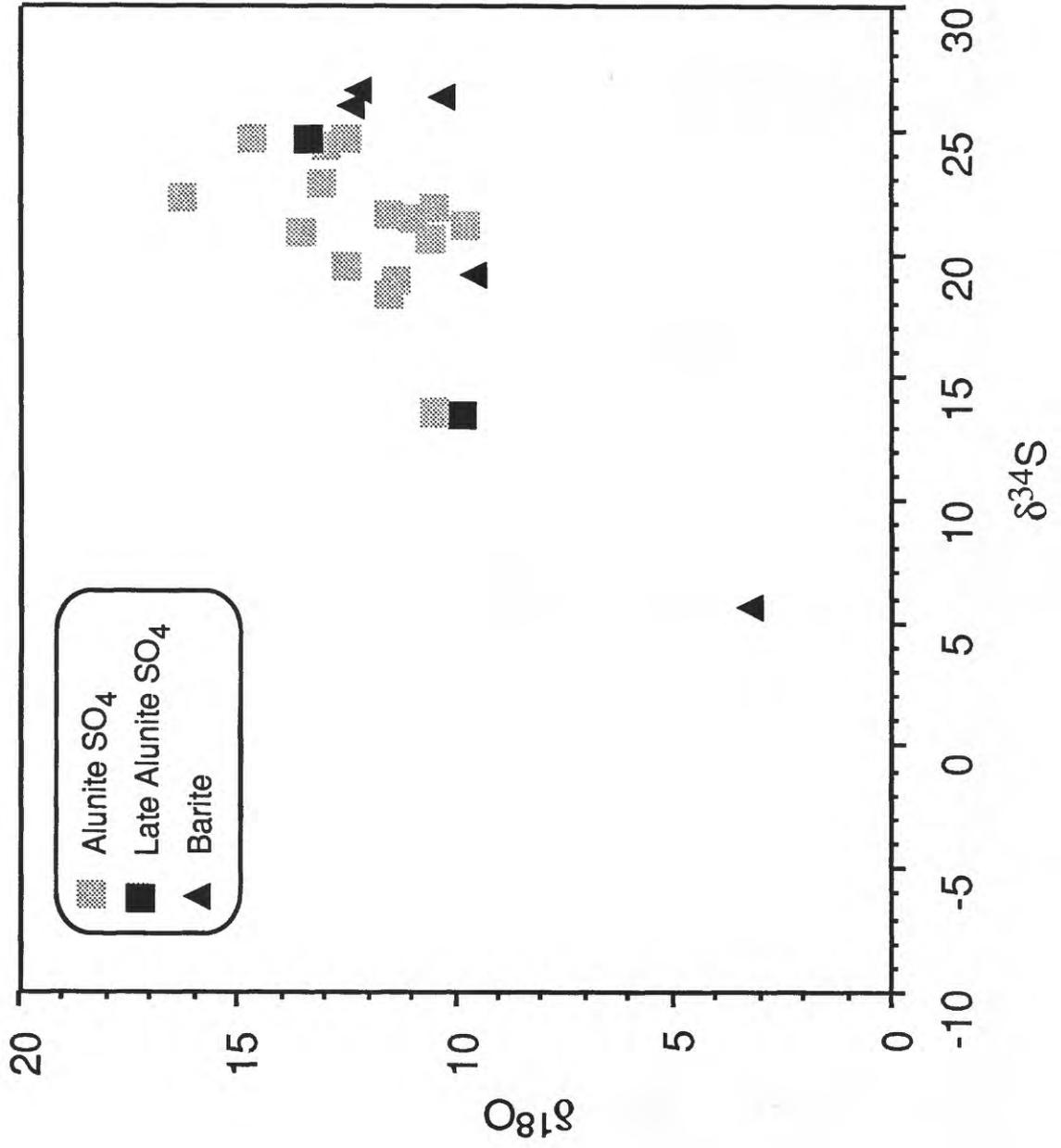
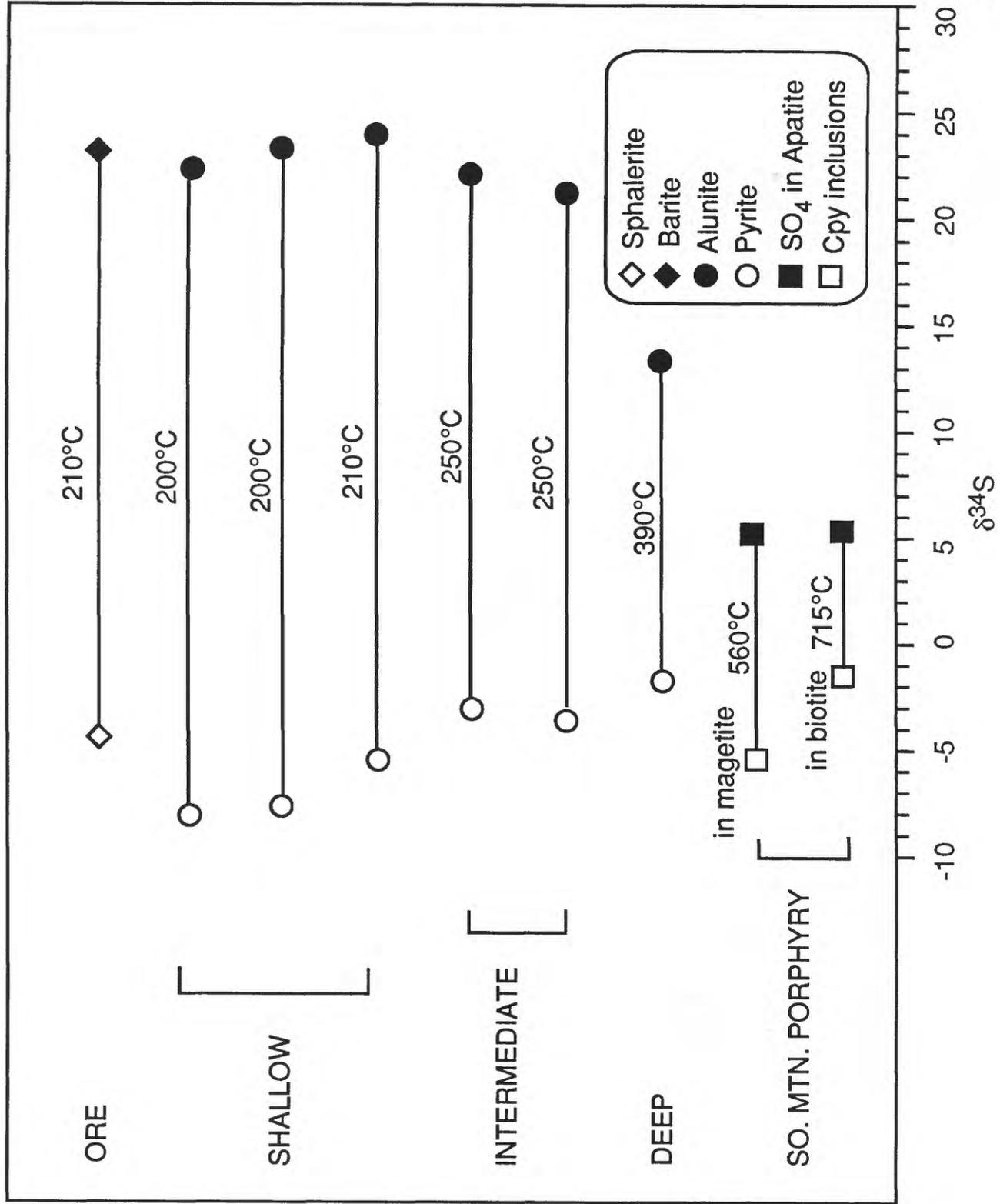
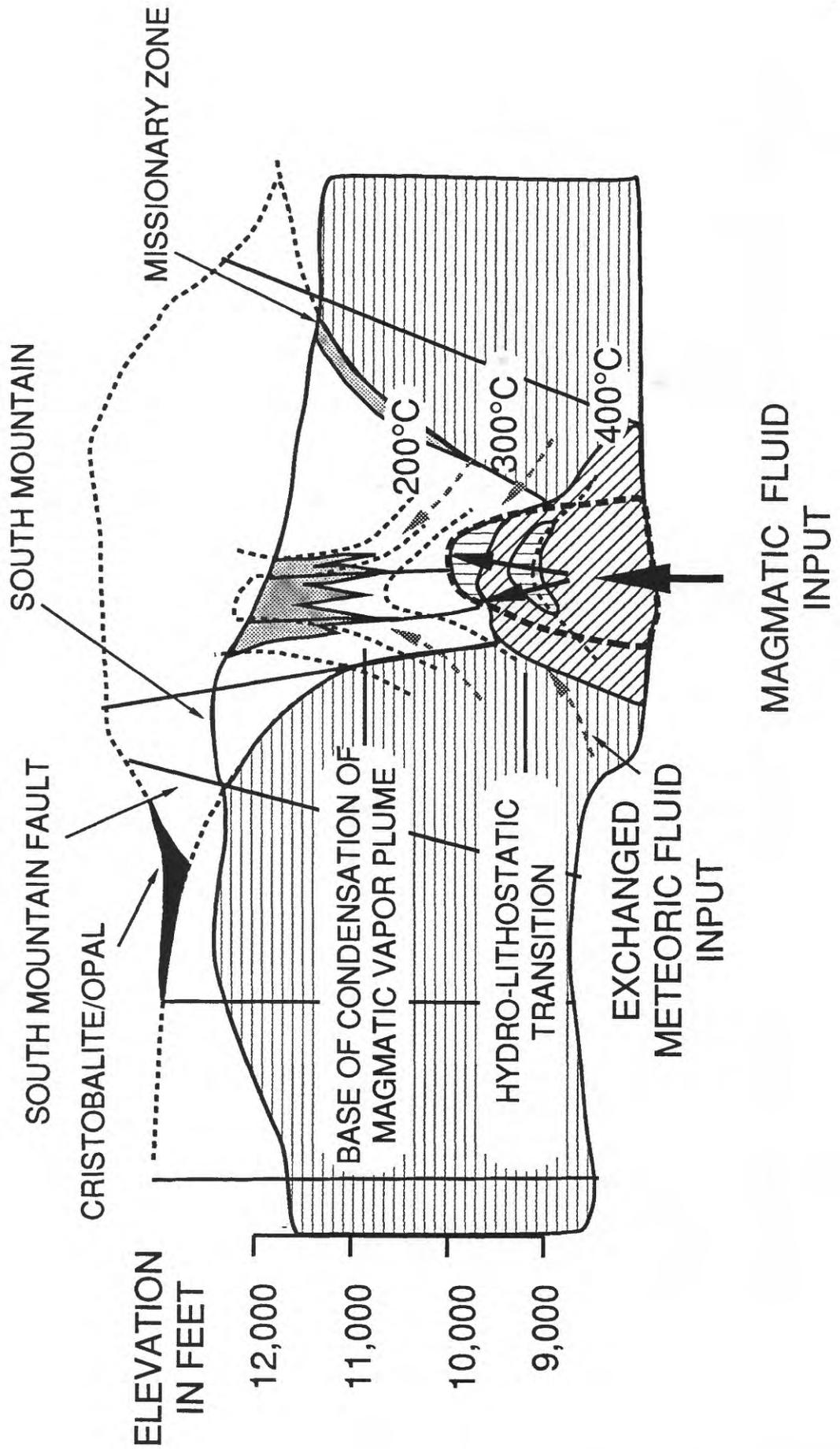


FIGURE 17

$\delta^{34}\text{S}$  AND CALCULATED TEMPERATURES OF COEXISTING SULFIDE AND SULFATE MINERALS FROM SOUTH MOUNTAIN PORPHYRY, ACID-SULFATE ALTERATION, AND ORE-STAGE MINERALIZATION

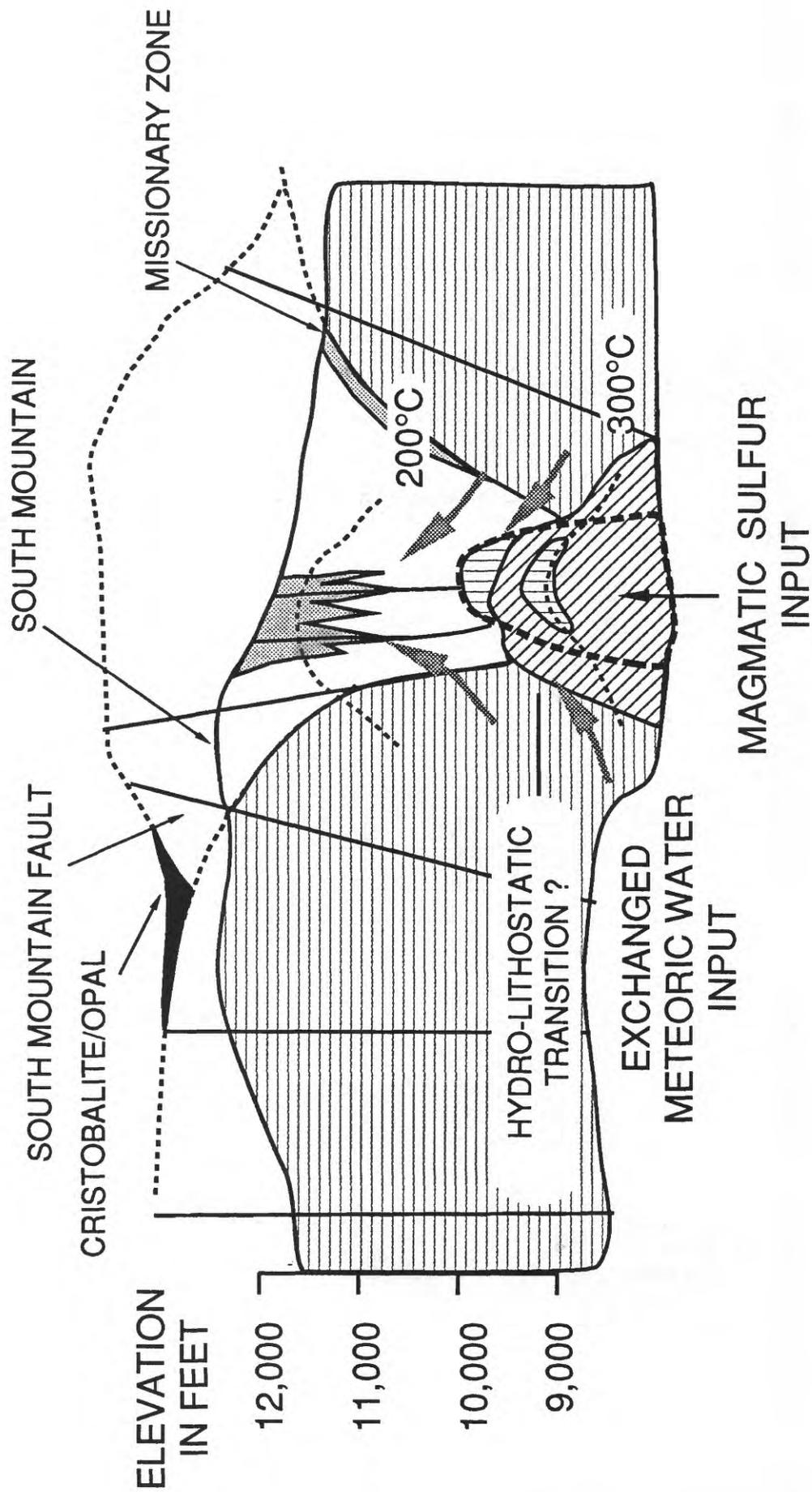


**SCHEMATIC MODEL OF ACID-SULFATE ALTERATION  
SHOWING INTERFACING OF MAGMATIC AND METEORIC  
FLUID AND PHASE OF FLUID**



**FIGURE 19A**

SCHEMATIC MODEL OF GOLD MINERALIZATION SHOWING  
DOMINANT METEORIC WATER FLUIDS WITH SULFUR  
FROM MAGMATIC SOURCE



## CONCLUSIONS ABOUT THE SUMMITVILLE SYSTEM

- ALUNITE FORMED FROM THE DISPROPORTIONATION OF MAGMATIC SO<sub>2</sub> IN MAGMATIC FLUIDS WHOSE ISOTOPE COMPOSITIONS WERE MODIFIED THROUGH EXCHANGE WITH ROCKS, HYDROUS MINERAL PRECIPITATION, AND MIXING WITH EXCHANGED METEORIC WATER.
- DURING ACID-SULFATE ALTERATION, THE HYDROTHERMAL SYSTEM WAS HYDROSTATIC AT SHALLOW LEVELS AND LITHOSTATIC AT DEEPER LEVELS WITH THE TRANSITION OCCURRING BETWEEN ABOUT 9000 AND 10000 FEET PRESENT ELEVATION.
- KAOLINITE FORMED DURING ACID-SULFATE ALTERATION WHERE THE LOW pH MAGMATIC FLUIDS WERE DILUTED BY HIGHLY EXCHANGED METEORIC FLUIDS AS WELL AS NEUTRALIZED BY REACTION WITH WALL ROCKS.
- THE LATE STAGE Cu-Au-Ag MINERALIZATION FORMED FROM METEORIC WATER DOMINATED HYDROTHERMAL FLUIDS THAT HAD ALSO EQUILBRATED WITH WALL ROCKS AND HAD DERIVED THEIR SULFUR FROM THE SAME MAGMATIC SOURCE.

*FIGURE 20*