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Diverse origins of alunite and acid-sulfate alteration: stable isotope systematics

by

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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 Denver, Colorado, November 3, 1988 (Rye et al., 1988). We are releasing a preliminary report at this time because of expressions of interest and the obvious exploration implications of the study. This work is continuing. Present investigations are concentrated on understanding the  $\delta^{18}\text{O}$  systematics of OH in the alunites investigated in this study, the effects of compositional variations on the stable isotope systematics, and the stable isotope geochemistry of alunites in other areas.*

## ABSTRACT

Acid-sulfate wallrock alteration, characterized by the assemblage alunite+kaolinite+quartz $\pm$ pyrite, results from base-leaching by fluids concentrated in  $\text{H}_2\text{SO}_4$ . Requisite amounts of  $\text{H}_2\text{SO}_4$  can be generated by different mechanisms in 3 principal geological environments: 1) by oxidation of sulfides in the *supergene* environment, 2) by oxidation at the water table in the *steam-heated* environment, of  $\text{H}_2\text{S}$  released by deeper, boiling fluids, and 3) by the disproportionation of magmatic  $\text{SO}_2$  to  $\text{H}_2\text{S}$  and  $\text{H}_2\text{SO}_4$  at intermediate depths in *magmatic-hydrothermal* systems in silicic and andesitic volcanic terrains. In addition, vein alunite without substantial acid-sulfate alteration can form from the deep oxidation of  $\text{H}_2\text{S}$  in *magmatic steam* at temperatures  $< 300^\circ\text{C}$ . Furthermore, some alunites form in the sedimentary or diagenetic environment.

Detailed stable isotope data on alunite and associated kaolinite and pyrite are powerful tools in determining the environment of formation. Analyses of alunite from over 20 mining districts and geothermal fields suggest that the hydrogen isotopic fractionation factors between alunite and water appear to be small enough to be only a secondary factor in the interpretation of  $\delta\text{D}$  data, and that the  $^{18}\text{O}$  fractionations between sulfate oxygen in alunite and water can be approximated by those between dissolved sulfate and water. Alunite in *supergene* acid-sulfate alteration zones has  $\delta^{34}\text{S}$  virtually identical to precursor sulfides and  $\delta\text{D}$  close to that of meteoric water. Associated kaolinite has  $\delta\text{D}$  and  $\delta^{18}\text{O}$  near the kaolinite line of Savin and Epstein (1970). Alunite formed in the *steam-heated* environment also has  $\delta^{34}\text{S}$  near that of associated pyrite and  $\delta\text{D}$  close to meteoric water but associated kaolinite has low  $\delta^{18}\text{O}$  values that shift compositions from the kaolinite line. Alunite formed by disproportionation of  $\text{SO}_2$  in *magmatic-hydrothermal* environments has  $\delta^{34}\text{S}$  values 16 to 28‰ larger than associated pyrite,  $\delta^{18}\text{O}_{\text{SO}_4}$  of 10 to 15‰,  $\delta\text{D}$  of -45 to -80‰ and systematic covariance of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  reflecting variations in temperature and  $\text{SO}_2/\text{H}_2\text{O}$  fluid ratios. Alunite formed in the *magmatic steam* environment can usually be recognized by  $\delta^{34}\text{S}$  near hydrothermal  $\text{H}_2\text{S}$  and  $\delta\text{D}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  near magmatic values. Superposition of either *steam-heated* or *supergene* environments on the *magmatic-hydrothermal* environment may lead to difficulty in interpretation by isotope data alone.

## INTRODUCTION

Acid-sulfate alteration is a special case of advanced-argillic alteration (Meyer and Hemley, 1967) characterized by the assemblage: alunite + kaolinite + quartz  $\pm$  pyrite. It is a product of extreme base-leaching by fluids concentrated in  $\text{H}_2\text{SO}_4$ . Its occurrence indicates extreme conditions of very low pH and relatively oxidizing conditions (Hemley et al., 1969).

Requisite amounts of  $\text{H}_2\text{SO}_4$  to produce acid sulfate alteration may be generated by different mechanisms in three environments of interest in ore deposits: *supergene*, *steam-heated*, and *magmatic-hydrothermal*. Vein filling alunite without kaolinite may form by vapor transport in  $\text{H}_2\text{S}$  and/or  $\text{SO}_2$ -rich (*magmatic-steam*) environments. Because each of the three acid-sulfate environments may be associated with, but bear different genetic and geometric relationships to, ore (particularly gold) it is important to be able to distinguish between them. In combination with geologic characteristics, stable isotope data on alunite and associated kaolinite and pyrite can be powerful tools in making such distinctions (Field, 1966, Jensen et al., 1971, Bethke, 1984). Furthermore, an understanding of the stable

isotope systematics of the various environments can provide valuable clues about the processes operating within them and the role of such processes in ore-formation.

This study builds on the work of Field (1966) who first analyzed the  $\delta^{34}\text{S}$  of alunite, Cunningham et al. (1984) who added  $\delta\text{D}$  data, and Sheppard et al. (1969) who pointed out the environmental significance of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data on kaolinite. We here present a significant amount of data on the  $\delta^{18}\text{O}$  in the sulfate radical in alunite and bring together for simultaneous evaluation the  $\delta\text{D}$ ,  $\delta^{34}\text{S}$ , and  $\delta^{18}\text{O}_{\text{SO}_4}$  data on alunite, the  $\delta^{34}\text{S}$  data on associated pyrite and the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data on associated kaolinite.

To establish the isotope systematics, and evaluate their utility in recognizing environments of alunite formation, the sulfur, sulfate oxygen, and hydrogen isotopic compositions were determined on alunites (and in some cases the  $\delta^{34}\text{S}$  of associated pyrite and the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of associated kaolinites or halloysites) from several diverse and geologically well defined environments, most of which have been sampled in considerable detail by various colleagues. Samples from geologically less well defined environments were then analyzed, and predictions made as to their origin.

This report is organized to point out the value of alunite for stable isotope studies and then to examine the principles and predicted stable isotope systematics in the various environments. Next, examples of each environment are presented and evaluated, and finally the stable isotope systematics are combined with the geologic characteristics for each environment to present the conclusions of the study.

A number of colleagues have made significant contributions to this study by providing samples from, and sharing their knowledge of, well documented environments. These include Antonio Arribas, Roger Ashley, Bill Bagby, Dana Bove, Jeff Deen, Roger Stoffregen, and Peter Vikre. Each is specifically acknowledged at appropriate panels. Jim Goss assisted in the early stage of the development of the chemical separation of the sulfate from alunite and in the physical separation and characterization of many samples. Skip Cunningham and Paul Barton have contributed various insights in frequent discussions.

## BACKGROUND

### **FIGURE 1** *Unit cell of alunite emphasizing the value of the mineral for isotope studies*

Alunite has been used successfully for geochronology (e.g., Mehnert et al., 1973). As shown on the diagram it also offers four stable isotope sites, more than any other common mineral. Stable isotope data on these sites, especially when accompanied with stable isotope data on coexisting minerals, can provide information on origins of components, processes (including rates), physical-chemical environments, and temperatures of formation. Field (1966) first used sulfur isotope data to distinguish between primary and secondary alunite. Cunningham et al. (1984) combined sulfur and hydrogen isotope data to distinguish between different origins of alunite in the Marysvale, Utah district. Pickthorn and O'Neil (1985) determined the fractionation between OH and sulfate oxygen and indicated its potential use in geothermometry. This study combines sulfur, hydrogen, and sulfate oxygen isotopic data to establish the stable isotope systematics in various alunite forming environments in order to develop a basis for investigating processes operating within the environments, and to develop isotopic criteria for distinguishing between them.

### **FIGURE 2a-b** *pH- $f\text{O}_2$ diagrams showing alunite stability*

pH- $f\text{O}_2$  diagrams showing that alunite stability range at 250° and 100°C is limited to regions of low pH and relatively high  $f\text{O}_2$  for geologically reasonable conditions. The stability of alunite has been determined by Hemley et al. (1969) and the influence of sulfur concentration and chemistry of solutions on alunite stability has been reviewed by Stoffregen (1985).

## FIGURES 3a-d Characteristics and $H_2SO_4$ -forming reactions of alunite-forming environments

*Supergene* alunite, often with halloysite and hydrous iron oxides, forms topographically controlled blankets during the weathering of sulfides and is best distinguished by dating. *Magmatic-hydrothermal* alunites are characterized by vertical aspect and lateral zoning (often with vuggy silica cores), the presence of coeval pyrite and possibly  $PO_4$  and F-rich alunite analogs and later gold, pyrite, enargite and covellite. *Steam-heated* alunites are characterized by vertical zoning that follows paleo-topography. Gold and base-metals may be present in underlying alteration zones and veins. *Magmatic steam* alunites are characterized by coarsely crystalline monomineralic alunite veins without substantial alteration of the host rock.

## ASSUMPTIONS

In the following diagrams theoretical mineral stable isotopic compositions were determined by assuming fluid compositions in various alunite-forming environments, and by making certain assumptions about temperature, fractionation factors, and degree of equilibrium. The following fractionation factors were used: kaolinite-water oxygen (Kulla and Anderson, 1978); kaolinite-water hydrogen (Liu and Epstein, 1984); sulfate/alunite- $H_2S$ /pyrite sulfur (Ohmoto and Rye, 1979); alunite-water oxygen and hydrogen in the temperature range 250°-400°C (R.E.Stoffregen, R.O. Rye and M.D. Wasserman unpublished data); alunite-water hydrogen at low temperatures (Bird et al., in press). Observations based on data of natural samples in this study indicate that dissolved sulfate-water oxygen fractionations (Lloyd, 1968) and anhydrite-water oxygen fractionations (Chiba et al., 1981) can be used to approximate alunite-water oxygen fractionations between 200 and 400°C. and that alunite-water hydrogen fractionations are small (<10 per mil) at all temperatures. The assumed temperatures and fluid compositions are indicated on each diagram and are typical of the various environments encountered in Tertiary deposits of the western U.S. Exchange rates for sulfur isotopes between aqueous sulfur species and for oxygen isotopes between sulfate and  $H_2O$  are kinetically inhibited but reach a maximum for a given temperature at the low pH of alunite formation (Ohmoto and Lasaga, 1982). In the following diagrams both sulfur and oxygen isotopic equilibrium is assumed for the magmatic-hydrothermal environment, whereas, complete kinetic control of isotopic compositions is assumed for the supergene environment. Our data suggest that retrograde isotope exchange between alunite and later fluids does not normally occur in geologic environments.

## PRINCIPLES

### FIGURE 4a-b Predicted $\delta D$ , $\delta^{18}O_{SO_4}$ and $\delta^{34}S$ systematics of supergene alunites

The  $\delta^{34}S$  and  $\delta^{18}O_{SO_4}$  of supergene alunite are kinetically controlled. Under supergene conditions the oxidation of pyrite (and, probably other sulfides) is microbially-mediated (Taylor et al., 1984). Application of the experiments of Taylor et al. (1984) to the supergene environment indicates that, for microbially-mediated oxidation, substantial kinetic fractionation of oxygen occurs between sulfate and water, with the sulfate enriched in  $^{18}O$  by a maximum of approximately 18 per mil. In contrast, sulfur undergoes essentially zero fractionation during supergene oxidation (Field, 1966). Alunite formed by supergene oxidation appears to have  $\delta D$  values similar to that of local groundwater (Bird et al., in press). Globally, supergene alunites should define a zone parallel to the METEORIC WATER LINE (MWL) but about 18 per mil or less removed. We define this as the ALUNITE LINE, but because, unlike for the kaolinite, the sulfate oxygen-water fractionation is kinetically controlled, the ALUNITE LINE probably cannot be as well defined as the KAOLINITE LINE of Savin and Epstein (1970). It appears, however, that *supergene* alunite compositions will fall on or to the left of the ALUNITE LINE, whereas those from *steam-heated* environments (next figure) will fall to the right of the line. Associated kaolinites will have  $\delta D$ - $\delta^{18}O$  values close to the KAOLINITE LINE (Sheppard et al., 1969) and alunites will yield K/Ar ages younger than those of primary mineralization.

**FIGURE 5a-b** *Predicted  $\delta D$ ,  $\delta^{18}O_{SO_4}$  and  $\delta^{34}S$  systematics of magmatic hydrothermal alunites*

Magmatic-hydrothermal alunites derive their sulfate from the disproportionation of  $SO_2$  derived from a magma. At the temperature and pH of this environment, equilibrium conditions in the fluids are likely. Disproportionation may take place in magmatic (e.g., Julcani) or mixed magmatic-meteoric (e.g., Summitville) water surrounding the magmatic vapor plume. Dark shading indicates compositions of alunites deposited from purely magmatic water. Graduationly lighter shadings show displacement of compositions with increasing proportions of  $^{18}O$ -depleted meteoric water. For a given unmixed system the  $\delta^{34}S$  of alunite as well as that of pyrite (shown schematically by arrow) will track the initial  $H_2S/SO_4$ , and the change in the ratio due to  $SO_2$  disproportionation and sulfide (e.g., pyrite) and alunite deposition.  $\delta^{18}O$  will track the temperature of deposition and mixing. Associated kaolinites (not shown on the diagram) will normally have lower  $\delta D$  and a range of  $\delta^{18}O$  values reflecting mixing with meteoric water (e.g., Red Mountain, Summitville). Assumed isotopic compositions of magmatic and exchanged meteoric water are arbitrary. Assumptions:  $T = 400^\circ$  to  $200^\circ$  C (Stoffregen, 1985; Bove et al., 1988);  $H_2S/SO_4 = 1$  to  $8$  (Stoffregen, 1985; Bove et al., 1988, Brimhall and Ghiorso, 1983);  $\delta^{34}S_{SS} = 0\text{‰}$ . Changes in assumptions will change positions, but not relationships, of fields.

**FIGURE 6a-b** *Predicted  $\delta D$ ,  $\delta^{18}O_{SO_4}$  and  $\delta^{34}S$  systematics of steam-heated alunites*

Steam-heated alunites and associated kaolinites probably form over the temperature range of  $90$  to  $150^\circ\text{C}$  in waters acidified by atmospheric oxidation, at the water table, of  $H_2S$  distilled off of a deeper hydrothermal system. It is not possible to predict the  $\delta^{18}O_{SO_4}$  of steam-heated alunite with certainty. The value will reflect the ratio of air to water oxygen involved in the oxidation, the  $\delta^{18}O$  of the water, the degree of equilibration of the sulfate with the water and the temperature of deposition. If oxidation involves largely air oxygen ( $\delta^{18}O = 23\text{‰}$ ) and equilibration with water does not occur, the  $\delta^{18}O_{SO_4}$  values may be quite large. The  $\delta^{34}S$  of alunite will normally be that of the  $H_2S$  that boiled off of the hydrothermal fluid, but given enough time the  $SO_4$  could begin to equilibrate with the  $H_2S$  resulting in larger values (e.g., Marysville Figure 10a). Steam-heated alunites should have  $\delta D$  similar to that of the paleo-groundwater (Bird et al., in press; R.E. Stoffregen, R.O. Rye, and M.D. Wasserman unpublished data).  $\delta D$ - $\delta^{18}O$  values for steam-heated alunites will fall to the right of the alunite line, and the values for associated kaolinites will be to the left of the kaolinite line (Marumo et al., 1981). Compare with the positions of these fields for supergene alunites. The difference in orientation of the alunite and kaolinite fields is due to the difference in temperature dependence of mineral-water hydrogen isotope fractionations which is very small for alunite.

**FIGURE 7a-b** *Predicted  $\delta D$ ,  $\delta^{18}O_{SO_4}$  and  $\delta^{34}S$  systematics of magmatic steam alunites*

The principles of  $\delta^{18}O_{SO_4}$  and  $\delta^{34}S$  systematics in magmatic steam alunites are similar to those for steam-heated alunites. The magmatic steam alunite, however, forms at higher temperature possibly in a volcanic edifice that allows atmospheric  $O_2$  to oxidize the  $H_2S$  and  $SO_2$  in the steam and the alunite grows directly from the vapor (Cunningham et al., 1984). Because oxidation to sulfate is essentially quantitative, the  $\delta^{34}S$  of the alunite will be identical to that of the bulk sulfur in the magma. At these temperatures the oxygen in the sulfate will probably equilibrate with the magmatic steam in most cases. Magmatic steam alunites can be distinguished from steam-heated alunites by their having  $\delta D$  values in the magmatic range except when local meteoric waters have  $\delta D$  values in the primary magmatic range.

## EXAMPLES

### **FIGURE 8a-b** *Stable isotope systematics of supergene alunites and halloysites: Creede, CO*

The Creede alunites have been dated between 3.1 and 4.8 Ma (Lanphere, pers. comm.) and are definitely supergene. Many are intergrown with halloysite.  $\delta D$  data of halloysite are not very reliable and typically are about 20 per mil heavier than coexisting kaolinites (Marumo et al., 1981, Lawrence and Taylor, 1971). During ore deposition at 25 Ma the  $\delta D$  of meteoric water was about -110‰ (Rye et al., 1988). What is surprising about the data is the wide range of  $\delta D$  values of the alunite that suggests that the fluid history of the supergene alunite was not simple. Note position of  $\delta^{18}O$  -  $\delta D$  data relative to the ALUNITE and KAOLINITE LINES.

### **FIGURE 9a-b** *Stable isotope systematics of steam-heated alunites and kaolinites: Buckskin Mtn., National district, NV*

The National district has been well documented by the comprehensive studies of Vikre (Vikre, 1985 and 1987). A 250 foot thick quartz+alunite+pyrite zone underlies an ~250 foot thick zone of cinnabar-bearing chalcedonic sinter. The quartz+alunite+pyrite zone grades downward into a quartz+kaolinite+pyrite zone. These zones overlie base- and precious metal veins of the adularia-sericite type with kaolinite-dominated alteration selvages adjacent to the vein. K/Ar dating of alunite and vein-related muscovite yield consistent ~15 Ma ages.  $\delta^{34}S$  values of the two alunites analyzed fall in the upper range of values for associated pyrite.  $\delta^{18}O_{SO_4}$  values fall to the right of the alunite line and would be in equilibrium (at 100°C) with exchanged meteoric water of  $\delta^{18}O = \sim -3.5$ ‰. Kaolinite data from the quartz+kaolinite+pyrite zone beneath the quartz+alunite+pyrite zone are from Vikre (1987) and fall to the left of the kaolinite line. Pyrite data is also from Vikre (1987). Alunite samples were provided by Peter Vikre.

### **FIGURE 10a-b** *Stable isotope systematics of steam-heated alunites: Marysvale, UT*

The replacement alunite deposits at Marysvale, Utah, have most recently been described by Callaghan (1973) and Cunningham et al. (1984). The alunite replaces intermediate composition volcanic rocks in several cells up to 3 km diameter ringing the 23 Ma Central Intrusive. K/Ar ages of alunite are coincident with that of the Central Intrusive (Steven et al., 1979). The alteration cells are zoned vertically from a flooded silica cap down through a hematite zone, then a jarosite zone, into an alunite zone, and finally into a propylitic zone. The alunite zone is ringed laterally by a kaolinite zone (Cunningham et al., 1984). It is clear that the alunite formed in a steam-heated environment of a fossil geothermal system. The  $\delta^{34}S$  values for alunites are much larger than those of all of the pyrites in the underlying propylitic zone but it is not clear that these minerals formed at the same time. The sulfur isotope data may represent: 1) different sources of sulfur for the alunite and pyrite as proposed by Cunningham et al. (1984), 2) partial equilibration of the sulfate with the  $H_2S$  in the system. The  $\delta^{18}O_{SO_4}$  values of the alunites would be in equilibrium (at 100°C) with exchanged meteoric waters with  $\delta^{18}O$  ranging from -7 to 0‰. Note that the  $\delta^{18}O_{SO_4}$  -  $\delta D$  values of alunite fall to the right of the alunite line. Compare with supergene alunite from Creede.

### **FIGURE 11a-b** *Stable isotope systematics of pure magmatic hydrothermal alunites: Julcani district, Peru*

The Julcani district has been described by Petersen et al. (1977), and Deen et al., (1987, 1988). The district consists of zoned base- and precious-metal mineralization associated with a Miocene volcanic dome complex. Mineralization occurred within 0.5 m.y. of latest dome formation and was interrupted by emplacement of an anhydrite-bearing dike. Pre-ore acid-sulfate alteration produced zones with vuggy silica cores and successive alunite+quartz+pyrite and kaolinite+quartz+pyrite envelopes up to 400 m deep. (Deen et al., 1988). The subsequent ore fluids can be shown by isotopic evidence to have been derived

from a magma that had a composition similar to the magmas that produced the earlier biotite-bearing dacitic domes and mineralization can be shown to be largely the result of mixing of the magmatic fluids with isotopically light meteoric water (Deen et al., 1987; 1988). Note the narrow range of isotopic compositions for the alunite indicating that the magmatic component dominated the fluids during alunite formation. Associated kaolinites have  $\delta D$  values of -70 to -75‰ while late-stage fluids have  $\delta D$  as low as -140‰. The sulfur isotope fractionations between coeval pyrite and alunite are nearly constant and give an average temperature of about 250° C. Alunite fluid  $\delta D_{H_2O}$  and  $\delta^{18}O_{H_2O}$  values calculated from the fractionation factors of R.E. Stoffregen, R.O. Rye, and M.D. Wasserman. (unpublished data) and are nearly identical to those calculated for fluids in equilibrium with igneous biotites in the district. This is a cooperative study with Jeff Deen to understand the role of magmatic fluids in the origin of the Julcani deposit, and is part of his Ph.D. thesis at the University of Colorado.

**FIGURE 12a-b** *Stable isotope systematics of mixed magmatic-meteoric magmatic-hydrothermal alunites and kaolinites: Summitville, CO*

The acid sulfate alteration at the Summitville, Colorado, Au-Cu-Ag deposit has been described by Steven and Ratte (1960) and its genesis recently been discussed by Stoffregen (1987). At Summitville irregular pipes and lenticular pods of vuggy silica, which are developed vertically over 300 meters and reach thickness of up to 70 m, are enclosed sequentially by zones of quartz-alunite, quartz-kaolinite and clay alteration. Mineralization occurred in the vuggy silica zones subsequent to the acid-sulfate alteration. Sulfur isotope fractionations of coeval alunite and pyrite indicate average temperatures of about 250°C and this temperature is assumed in the calculation of the fluid compositions. The large  $\delta^{34}S$  values for the alunites support Stoffregen's (1987) conclusion that the acid-sulfate was derived from the disproportionation of  $SO_2$ . The large  $\delta D$  and  $\delta^{18}O_{SO_4}$  values support the derivation of the  $SO_2$  from a magma. However, the range of these values is larger than for Julcani (shown above) and the lowest  $\delta D$  values correlate with the lowest  $\delta^{18}O_{SO_4}$  values indicating that the disproportionation of some of the  $SO_2$  occurred in mixtures of magmatic and meteoric water. The low  $\delta D$  values of the kaolinites indicate that kaolinite formation was related to even greater dilution of the low pH magmatic fluids by low  $\delta D$  meteoric water in the quartz-kaolinite zone. This study is part of a cooperative effort with Roger Stoffregen to determine the environment of mineralization and acid-sulfate alteration at Summitville and most of the samples in this study were collected and described by him.

**FIGURE 13a-b** *Stable isotope systematics of multiple-stage magmatic-hydrothermal alunites: Red Mountain, Lake City, CO*

The alunite deposit at Red Mountain, Lake City, Colorado has recently been described and its origin discussed by Bove et al. (1987, 1988). The deposit, which is one of the largest in the U.S., consists of two roughly conical centers with roots extending more than 250 m beneath the surface. Alunite+quartz+pyrite rock changes outward into argillized and propylitized dacitic volcanics and downward through argillic, sericitic, and potassic zones in dacite intrusions. Deep drilling indicates a molybdenum-bearing porphyry system at depth. Paragenetic relationships within the quartz-alunite zone indicate at least 4 stages of alunite. Sulfur isotope data on coeval alunite and pyrite indicate bulk  $\delta^{34}S$  of ~0‰ and temperatures of ~400° and ~200°C and  $H_2S/SO_4$  ~1 and ~8, for stage 1 and 2 fluids, respectively. The data further indicate an  $H_2S/SO_4$  >8 for the stage 3 and 4 fluids. Calculations based on the  $\delta^{18}O_{SO_4}$  values indicate the  $\delta^{18}O_{H_2O}$  of fluid was ~4‰ for stages 1 and 2. The large  $\delta^{34}S$  values indicate that stage 1 and 2 sulfate was derived from the disproportionation of  $SO_2$ . The  $\delta D$  values of the alunite indicate derivation from magmatic fluids. The  $\delta D$  values of kaolinite are consistent with meteoric water derivation as would be expected on the margins of the hydrothermal system. Stage 3 and 4 alunites are restricted spatially. Their spatial relationships and  $\delta^{34}S$  and  $\delta D$  data indicate formation as the result of the quantitative oxidation of sulfur species in a magmatic steam or a steam-heated environment that was

superimposed on the earlier magmatic-hydrothermal environment as the hydrothermal system collapsed. Their fluid compositions are not shown because the temperatures needed for  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  calculations are not known. This study is part of cooperative investigation with Dana Bove (Bove et al., 1988) to determine the origin of the Red Mountain alunite.

**FIGURE 14a-b** *Stable isotope systematics of magmatic steam alunites: Marysvale, UT*

The vein alunite deposits in the Marysvale volcanic district, Utah, have recently been described by Callaghan (1973) and their origin discussed by Cunningham et al. (1984). This type of alunite deposit is rare and the ones along Alunite Ridge are the largest, purest, most coarsely crystalline veins of alunite in the U.S and possibly in the world. Alunite Ridge is located at the center of a radial fracture pattern that resulted from the forceful injection of an underlying stock believed to contain porphyry-type mineralization. The veins, which contain virtually no coeval quartz, pyrite or kaolinite, formed 14 m.y. ago as open-space filling as much as 20 m wide and 100 m deep in extension fractures. Fluid inclusion evidence indicates that the alunite formed from low density vapor. The  $\delta\text{D}$  values are substantially larger than those for the replacement alunites in the district (see above) and strongly suggest a magmatic component in the hydrothermal fluids. The  $\delta^{34}\text{S}$  values of the alunite are the same as the bulk sulfur in the fluids responsible for the nearby Deer Trail Mountain manto deposits. These fluids are believed to have been derived from a coeval intrusion (Cunningham et al., 1984; Beatty et al., 1986). The  $\delta^{18}\text{O}_{\text{SO}_4}$  values could reflect precipitation over a temperature range of about 220° to 330°C if the  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of the hydrothermal fluid was about 3-4‰. We believe that the open structure of the vein system permitted the entrainment of atmospheric oxygen in a high-temperature magmatic vapor-plume that led to the quantitative oxidation of sulfur species in the plume and the precipitation of alunite. Most of the  $\delta^{34}\text{S}$  data are from Cunningham et al. (1984). The  $\delta^{18}\text{O}_{\text{SO}_4}$  and  $\delta\text{D}$  data are from the same samples used by Cunningham et al. (1984).

**FIGURE 15a-b** *Stable isotope systematics of alunites from multiple acid-sulfate environments: Rodalquilar gold alunite deposit, Almeria, Spain*

The Rodalquilar gold-alunite deposit (Almeria, S.E. Spain) has recently been studied by Rytuba et al. (1988) and Arribas et al. (1988). Au - Ag chalcedony veins fill ring and radial fractures associated with a Miocene caldera. Mineralization is associated with a core of acid-sulfate alteration (stage 1 alunite) that extends several hundred meters below the surface and contains cores of vuggy silica. This central zone is surrounded by younger barren alunite - jarosite veins (stage 2 alunite). Most of these veins are shallow, but barren veins of alunite have also been recognized at deeper levels. It is clear from the sulfur isotope data that stage 1 alunite formed in a magmatic-hydrothermal environment. Sulfur isotope data on coexisting pyrite and alunite indicate average temperatures of ~ 250° C. The large  $\delta^{34}\text{S}$  values for the stage 1 alunite and pyrite reflect the large  $\delta^{34}\text{S}$  value for the total sulfur in the hydrothermal system (typical of Miocene hydrothermal systems in this part of Spain). The high  $\delta\text{D}$  values reflect the proximity of the area to the ocean and possible involvement of sea water in the system. Stage 2 alunites have  $\delta^{34}\text{S}$  values slightly larger than most of the pyrites in the mineralized zone and their  $\delta\text{D}$ - $\delta^{18}\text{O}$  values lie to the left of the alunite line. These alunites have the same age as the mineralization and formed from the oxidation of  $\text{H}_2\text{S}$  in a steam-heated environment. The  $\delta^{18}\text{O}$  data indicate these alunites precipitated over a considerable temperature range in unexchanged meteoric water. The deep stage 2 alunites probably formed when the steam-heated environment was superimposed over the central magmatic-hydrothermal environment during the collapse of the hydrothermal system. This study is sponsored by the U.S./Spain Joint Committee for Scientific and Technical Cooperation as a project to understand the origin of Spanish-United States epithermal quartz-alunite deposits and is part of a Ph.D thesis study by Antonio Arribas at the University of Michigan. Many people have contributed to this project and are mentioned in the authorship of Rytuba et al. (1988) and Arribas et al. (1988)



**FIGURE 16a-b** *Stable isotope systematics of diverse acid-sulfate environments: Nevada, Tertiary hydrothermal deposits*

Without detailed geologic information on these samples interpretations based on limited isotope data is tenuous. We would like to point out, however, that the data fall into two groups. The alunites with large  $\delta^{34}\text{S}$  and relatively large  $\delta\text{D}$  from Comstock, Virginia Range, Ramsey and Goldfield presumably formed in a magmatic-hydrothermal environment. The low  $\delta^{18}\text{O}$  of some of these alunites indicates that the disproportionation of  $\text{SO}_2$  occurred in relatively unexchanged meteoric waters. The alunites with smaller  $\delta^{34}\text{S}$  and lower  $\delta\text{D}$  at Goldfield, Maggie Creek, and Virginia Range formed in a steam-heated or possibly a supergene environment. Jensen et al. (1971) previously demonstrated the presence of two generations of alunite at Goldfield on the basis of  $\delta^{34}\text{S}$  data. The Comstock, Virginia Range, and Ramsey samples were provided by Peter Vikre. The Goldfield and Maggie Creek samples were provided by Roger Ashley and Bill Bagby, respectively.

### CONCLUSIONS

The combined use of sulfur, sulfate oxygen, and hydrogen isotopes in alunite, and oxygen and hydrogen isotopes in coeval kaolinite group minerals and sulfur in coeval pyrite is a powerful tool to be used in conjunction with geological, mineralogical and geochronological studies in distinguishing between the diverse origins of acid-sulfate alteration and alunite formation, and in elucidating the processes involved in their genesis. Both identification of type and understanding of process can make important contributions to exploration and assessment efforts.

**FIGURE 17a-b** *Summary of predicted  $\delta^{18}\text{O}_{\text{SO}_4}$ ,  $\delta\text{D}$ , and  $\delta^{34}\text{S}$  systematics of alunite in diverse environments*

SUPERGENE acid-sulfate assemblages may form over any sulfide mineralized zone (particularly those that are pyrite-rich) when it is raised above the water table by tectonics or exposed by erosion. Obviously, supergene assemblages may overprint other acid-sulfate assemblages, particularly the magmatic-hydrothermal assemblages which are pyrite-rich. Often jarosite will be present. Supergene alunite is best recognized by dating.  $\delta^{34}\text{S}$  values will be the same as precursor sulfides. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values will be to the left of the alunite line and  $\delta\text{D}$  values will near that of meteoric water during weathering. Stable isotope data will be definitive only if coeval kaolinite has  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values near the kaolinite line.

MAGMATIC-HYDROTHERMAL acid-sulfate assemblages in near-surface epithermal environments such as Summitville, Julcani, or Red Mountain, Lake City, the examples shown result from the disproportionation of magmatic  $\text{SO}_2$  in magmatic water or mixed magmatic-meteoric water. Such assemblages also occur as late stages deeper in the porphyry-copper environment as at Butte (Meyer and Hemley, 1967), and El Salvador, (Gustafson and Hunt, 1975). In these deeper porphyry environments it has been suggested that the requisite sulfuric acid is generated during the remobilization of the primary ore minerals by meteoric hydrothermal fluids contaminated by magmatic  $\text{SO}_2$  (Brimhall, 1980; Brimhall and Ghiorso, 1983). In both cases the temperatures are high enough that both sulfur and oxygen in the sulfate can be expected to equilibrate with the fluid, and their isotopic systematics will reflect equilibrium exchange between aqueous  $\text{H}_2\text{S}$  and  $\text{SO}_4^{2-}$ . Large values of  $\delta^{34}\text{S}$  in alunite are almost always diagnostic and may vary with changes in temperature and  $\text{H}_2\text{S}/\text{SO}_4$  ratio. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values may reflect equilibration with magmatic or meteoric-hydrothermal fluid depending on in what part of the system the magmatic derived  $\text{SO}_2$  disproportionates.

STEAM-HEATED acid-sulfate assemblages form near the water table by the attack of sulfuric acid formed from the oxidation, in the vadose zone, of  $\text{H}_2\text{S}$  derived from the degassing of underlying hydrothermal fluids. They are characterized by pronounced vertical zoning (eg., Cunningham et al., 1984; Vikre, 1987) in paleogeothermal environments. Initial  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  values are kinetically controlled, but  $\delta^{18}\text{O}$  may reach equilibrium with fluid and even  $\delta^{34}\text{S}$  values may reach partial equilibrium with  $\text{H}_2\text{S}$  in some cases. The steam-heated assemblage can be recognized isotopically by  $\delta^{34}\text{S}$  the same as precursor  $\text{H}_2\text{S}$  (and as related sulfides, if present), possibly large  $\delta^{18}\text{O}$ , and  $\delta\text{D}$  the same as meteoric water. Coeval kaolinites will have  $\delta^{18}\text{O}$  and  $\delta\text{D}$  to the left of the meteoric water line.

MAGMATIC STEAM alunite forms from the oxidation of  $\text{H}_2\text{S}$  and or  $\text{SO}_2$  in a volcanic edifice that permits atmospheric oxygen to mix with high temperature magmatic steam. This type of alunite is characterized by monomineralic veins of alunite such as occur at the Alunite Ridge deposits at Marysvale (Cunningham et al., 1984) without pyrite or extensive wall rock alteration.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  will reflect a magmatic water component, and  $\delta^{34}\text{S}$  will have the value of the bulk sulfur in the system.

Although the various environments are treated individually above, in nature two or more of them may occur together in the same district, either as parts of the same system or separated in time. Further, both the STEAM-HEATED and MAGMATIC-HYDROTHERMAL occur in more than one type of hydrothermal system. Some of the possible geologic relationships of the various environments are shown schematically in the diagrams below.

**FIGURE 18** *Model of volcano-related hydrothermal systems showing possible steam-heated, magmatic-hydrothermal and magmatic steam environments*

Hydrothermal systems in stratovolcanic edifices (as shown above, and typical of the Pacific Rim environments) or volcanic domes (more typical of continental environments) can be expected to develop both MAGMATIC-HYDROTHERMAL and STEAM-HEATED environments. The deeper MAGMATIC-HYDROTHERMAL environment results from the disproportionation of magmatic  $\text{SO}_2$  as discussed above, whereas the overlying STEAM-HEATED environment is a product of the oxidation of  $\text{H}_2\text{S}$  at the water table. Acid lakes may develop in the craters of stratovolcanoes (Henley, 1985; Brantley et al, 1987). It is possible that the overlying steam-heated waters may mix with the deeper magmatic-hydrothermal fluids along the top of the zone of condensation. Overprinting of the early-formed magmatic-hydrothermal assemblage by steam-heated waters during the waning stages of hydrothermal activity is also possible. This diagram also illustrates the geologic relationships of the MAGMATIC STEAM environment as interpreted by Cunningham et al. (1984), but does not imply any necessary relationship to the magmatic-hydrothermal environment.

**FIGURE 19** *Model of near-neutral hydrothermal system showing shallow steam-heated acid-sulfate environment above adularia-sericite epithermal system*

STEAM-HEATED acid sulfate assemblages occur above many near-neutral geothermal systems (Henley and Ellis, 1983) and adularia-sericite type epithermal ore zones (Heald et al., 1987, Hayba et al., 1985). Buckskin Mountain in the National district, Nevada, is an excellent, and well documented example (Vikre, 1985, 1987). The superjacent, low pH, sulfate-rich, steam-heated waters may mix with the top of the underlying near-neutral, chloride waters. During the waning stages of the hydrothermal system, the acid-sulfate waters may descend into the ore zone and overprint the adularia-sericite assemblage.

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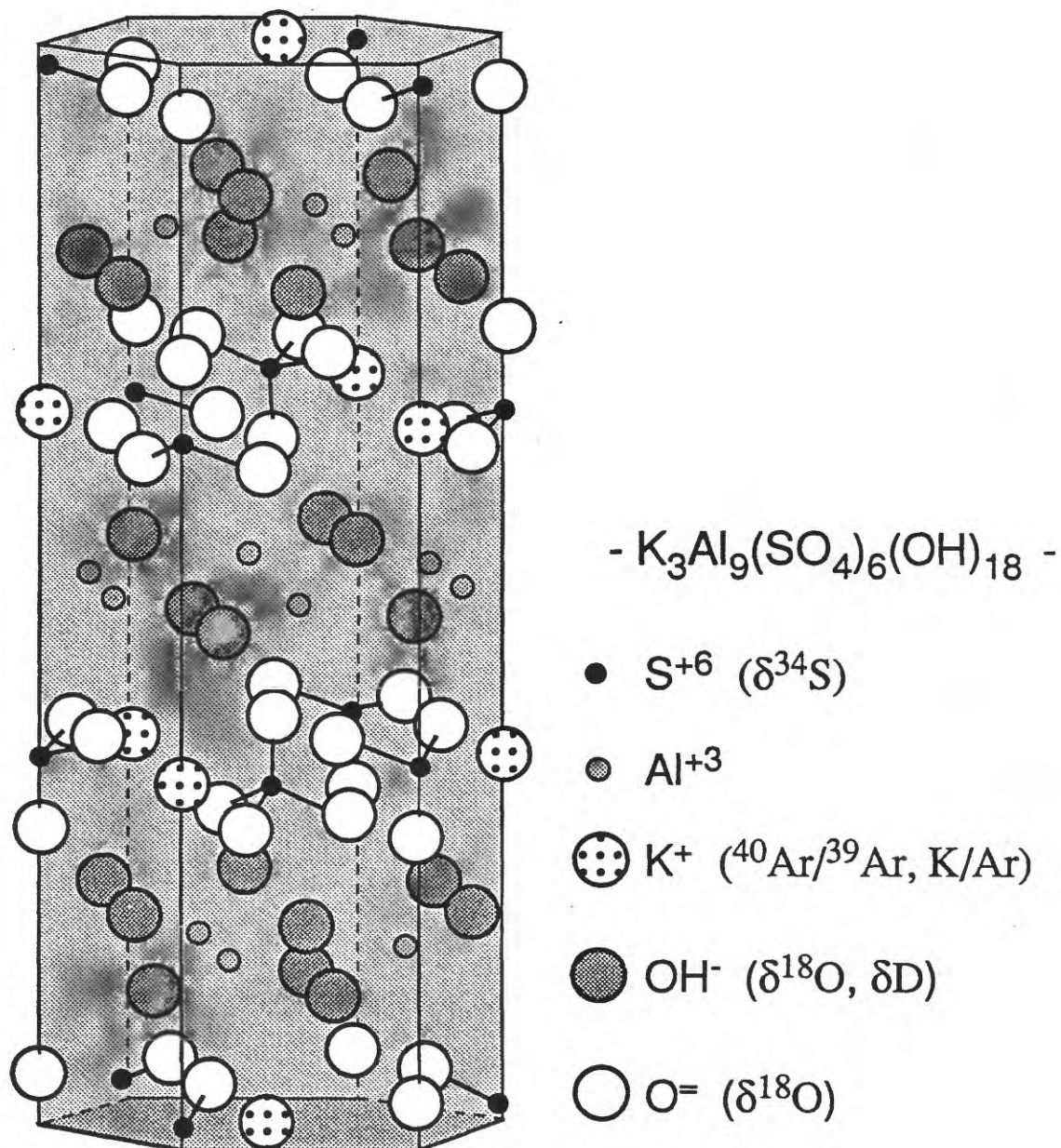
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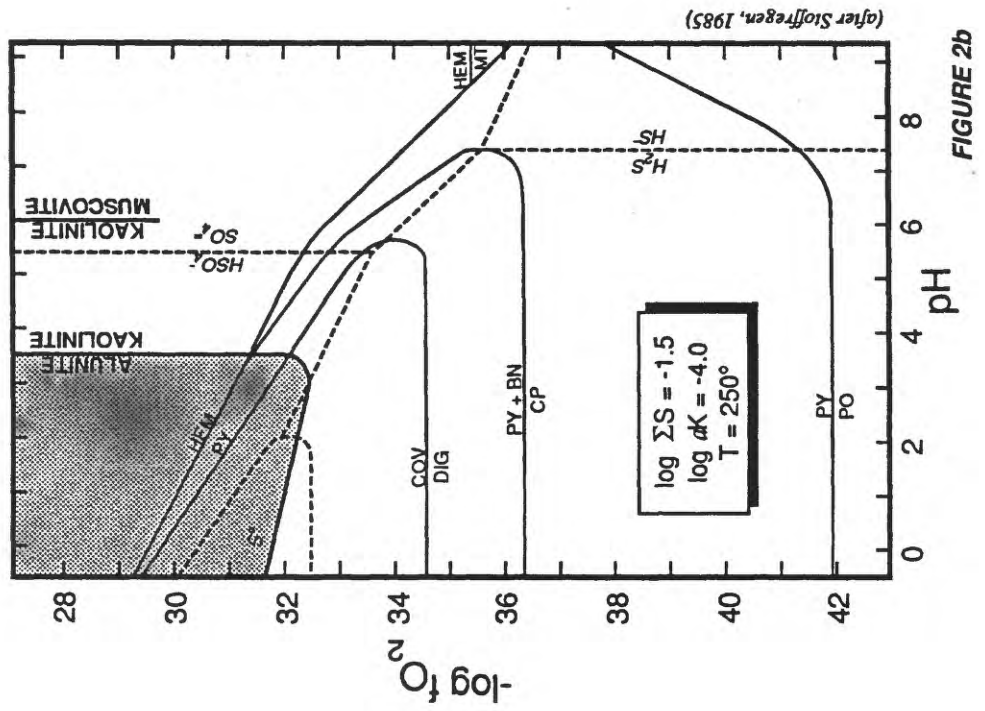
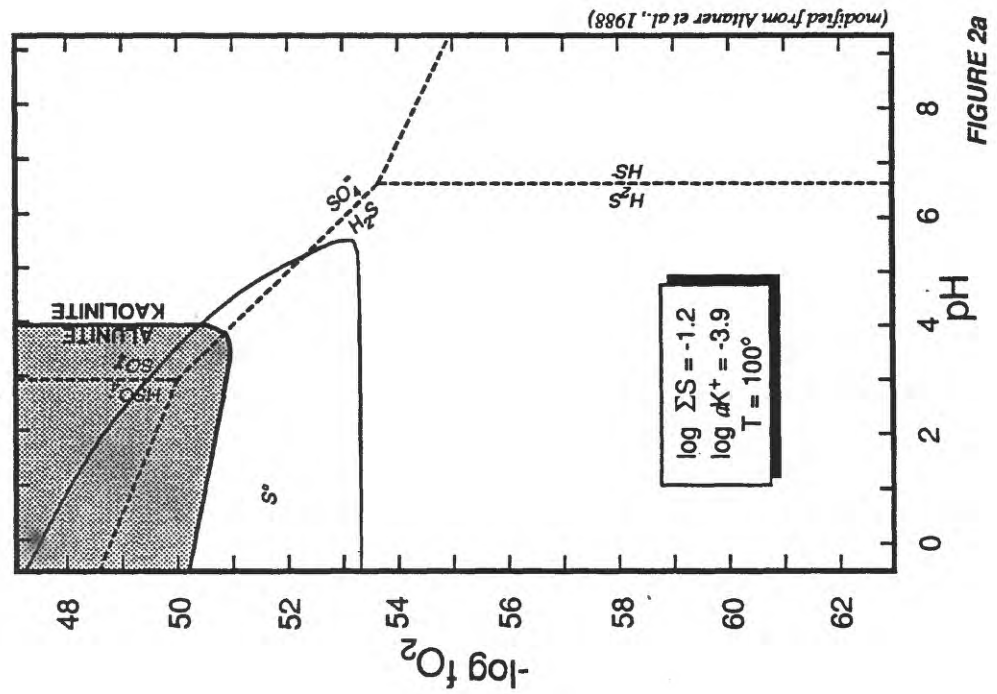
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# ISOTOPIC AND CRYSTAL CHEMISTRY OF ALUNITE



(modified from Brophy et al., 1962)

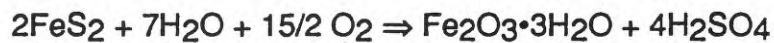




## SUPERGENE

- Age younger than mineralization
- Topographically controlled blanket
- Disordered kaolinite, halloysite
- Hydrous iron oxides and jarosite common

Representative reaction:

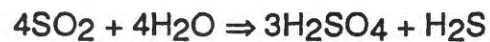


**FIGURE 3a**

## MAGMATIC-HYDROTHERMAL

- Vertical aspect; pods and lenses
- Horizontal alteration zoning
- Vuggy silica common
- Coeval pyrite; later pyrite, enargite, covellite common
- Zunyite, high PO<sub>4</sub> contents of alunite common
- Age coeval with intrusion

Representative reaction

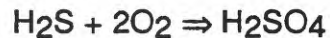


**FIGURE 3b**

### STEAM-HEATED

- Paleo-topographic control
- Age coincident with mineralization
- Vertical zoning
- Opaline silica, chalcedony, sinter common
- Jarosite, hematite common
- Base-precious metal sulfides may occur deeper in system

Representative reaction

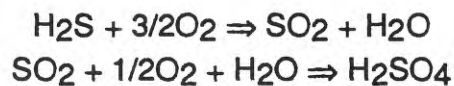


**FIGURE 3c**

### MAGMATIC STEAM

- Vertical aspect-veins
- Monomineralic alunite veins
- Kaolinite, sulfides absent
- Minor hematite may be present

Representative reactions



**FIGURE 3d**

# PREDICTED $\delta D$ - $\delta^{18}O_{SO_4}$ - $\delta^{34}S$ OF SUPERGENE ALUNITE

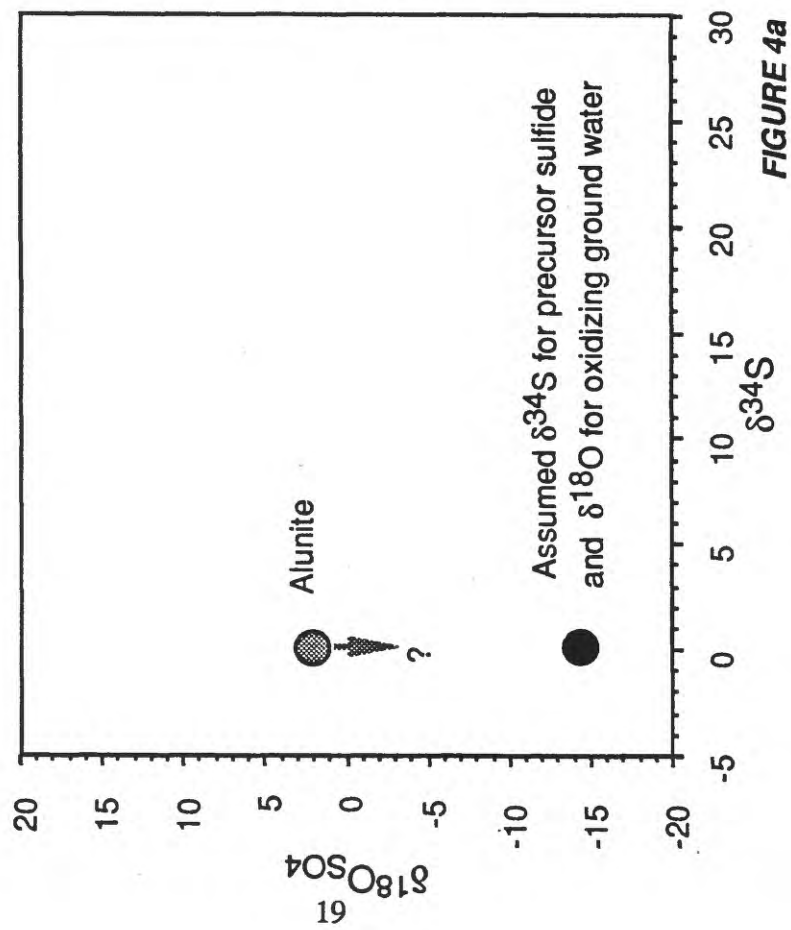


FIGURE 4a

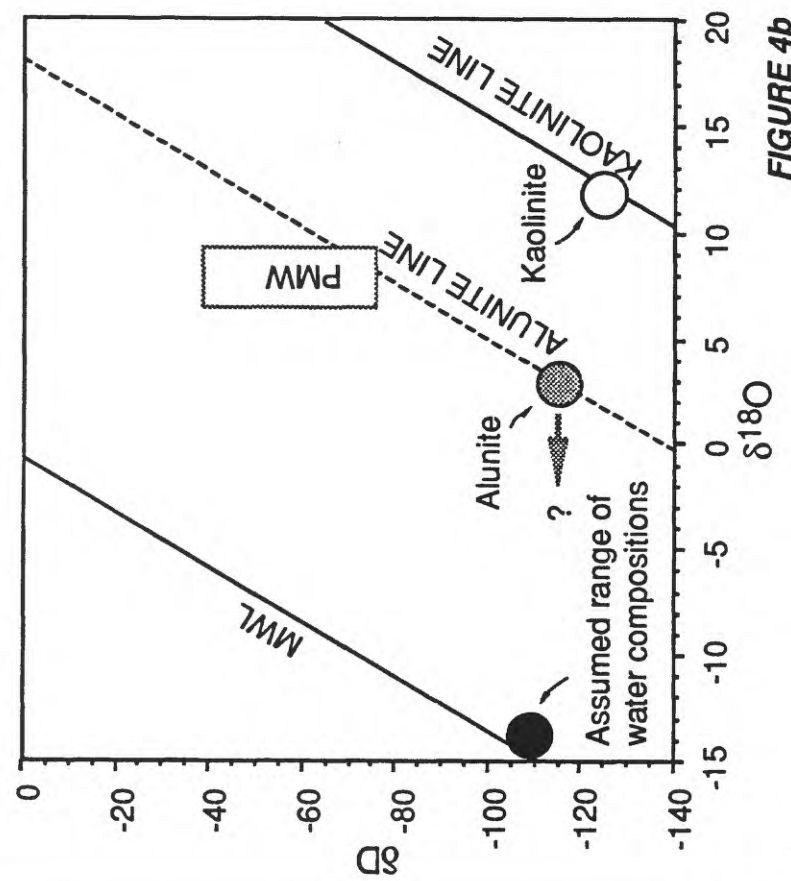


FIGURE 4b

# PREDICTED $\delta D$ - $\delta^{18}O_{SO_4}$ - $\delta^{34}S$ SYSTEMATICS FOR MAGMATIC-HYDROTHERMAL ALUNITE

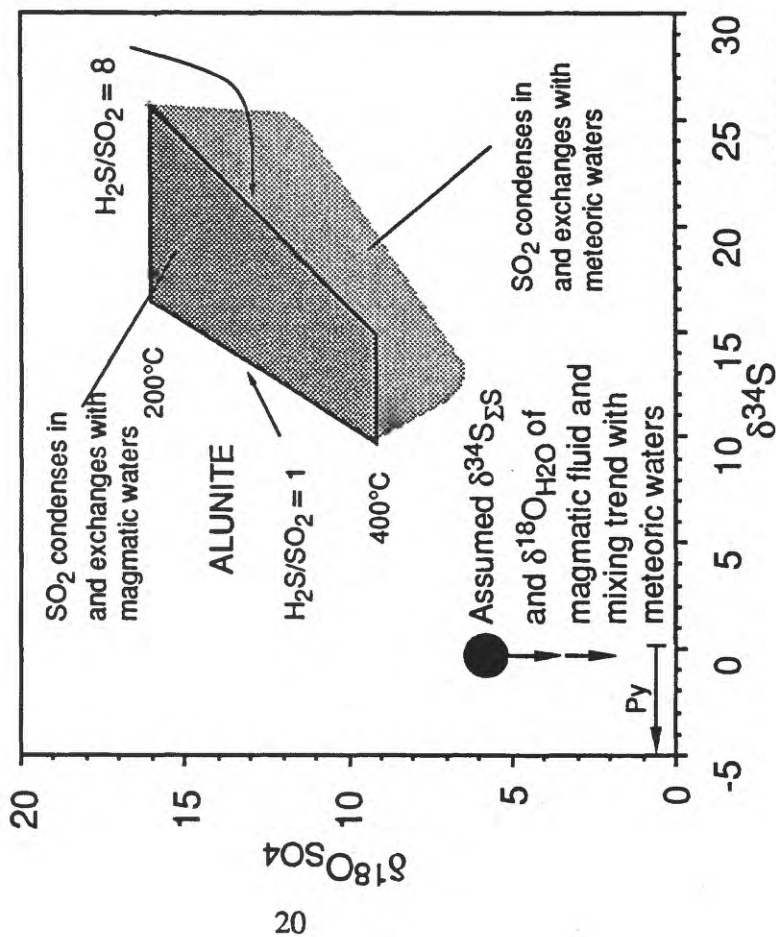


FIGURE 5a

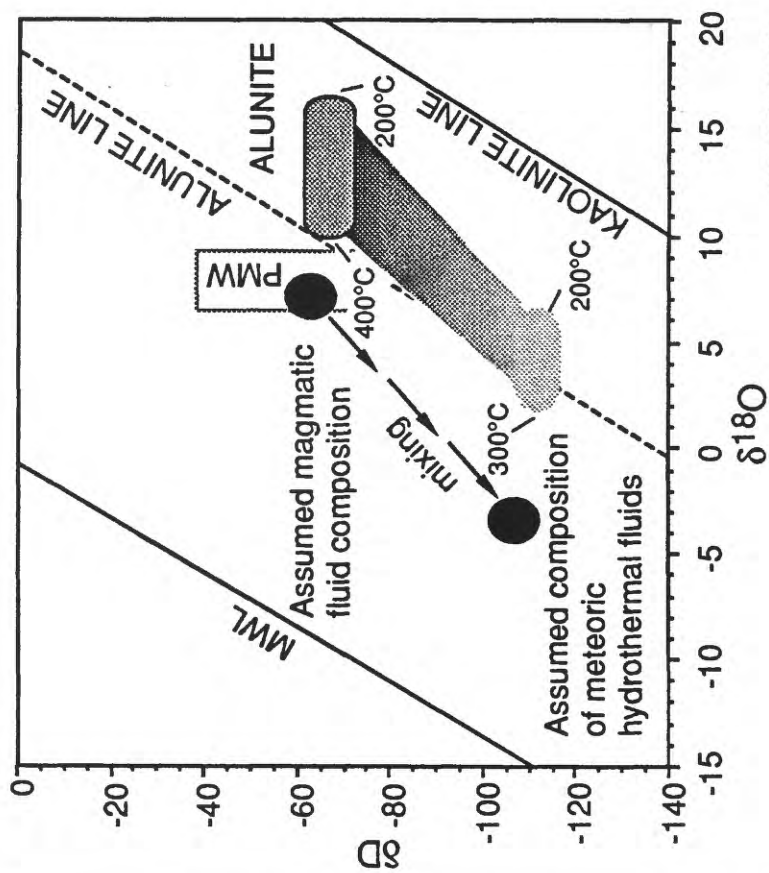
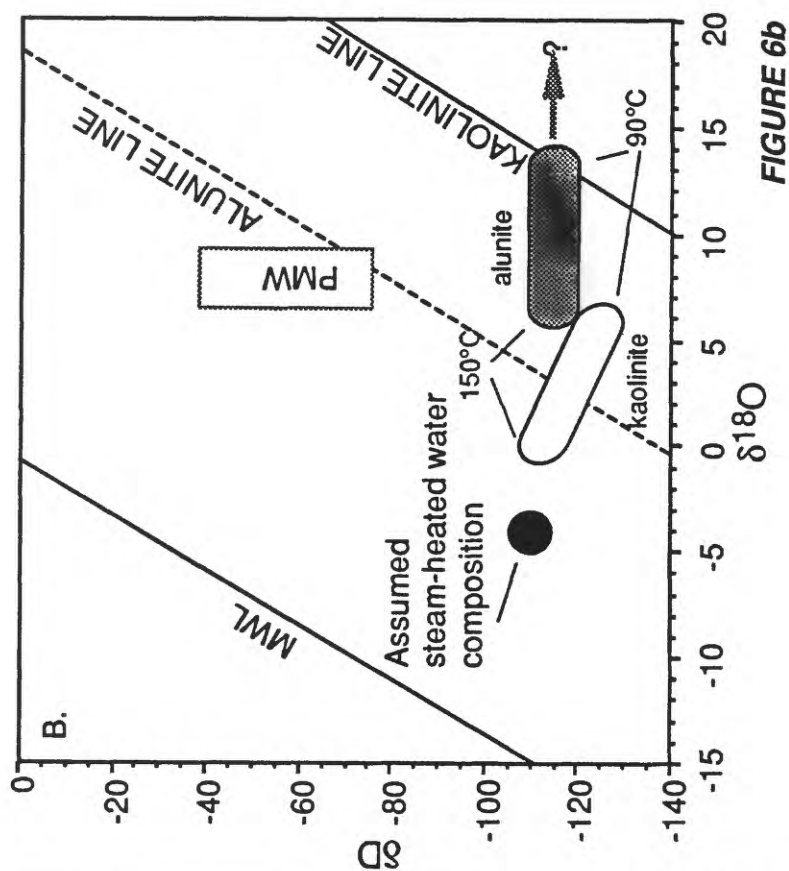
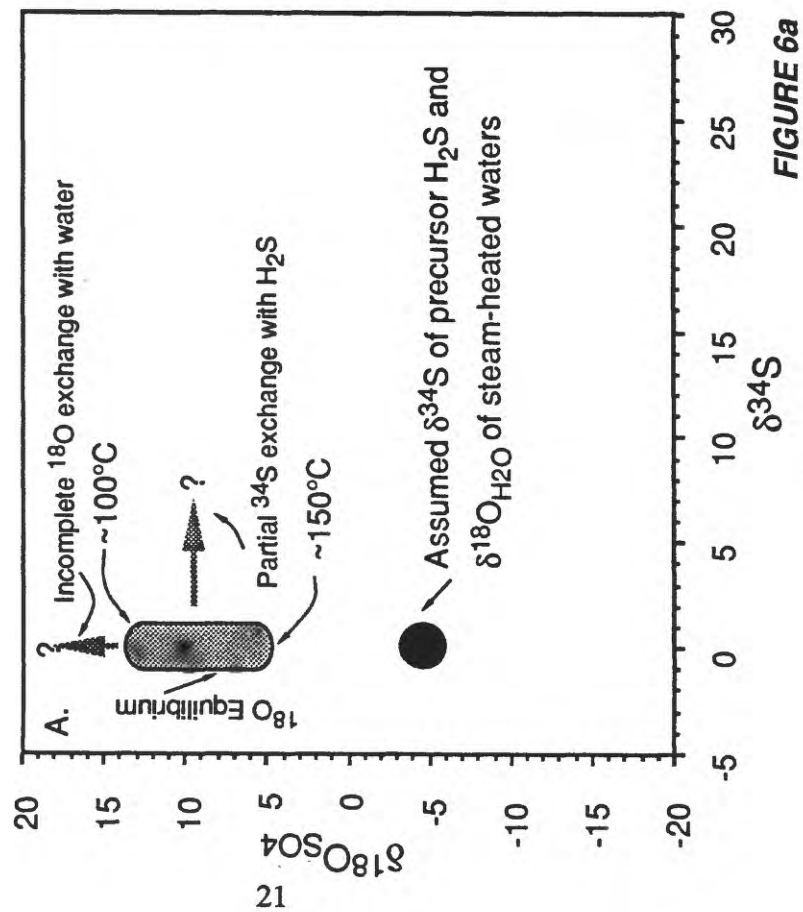


FIGURE 5b

# PREDICTED $\delta D$ - $\delta^{34}S$ - $\delta^{18}O_{SO_4}$ OF STEAM-HEATED ALUNITE



# PREDICTED $\delta D$ - $\delta^{34}S$ - $\delta^{18}O_{SO_4}$ OF MAGMATIC-STEAM ALUNITE

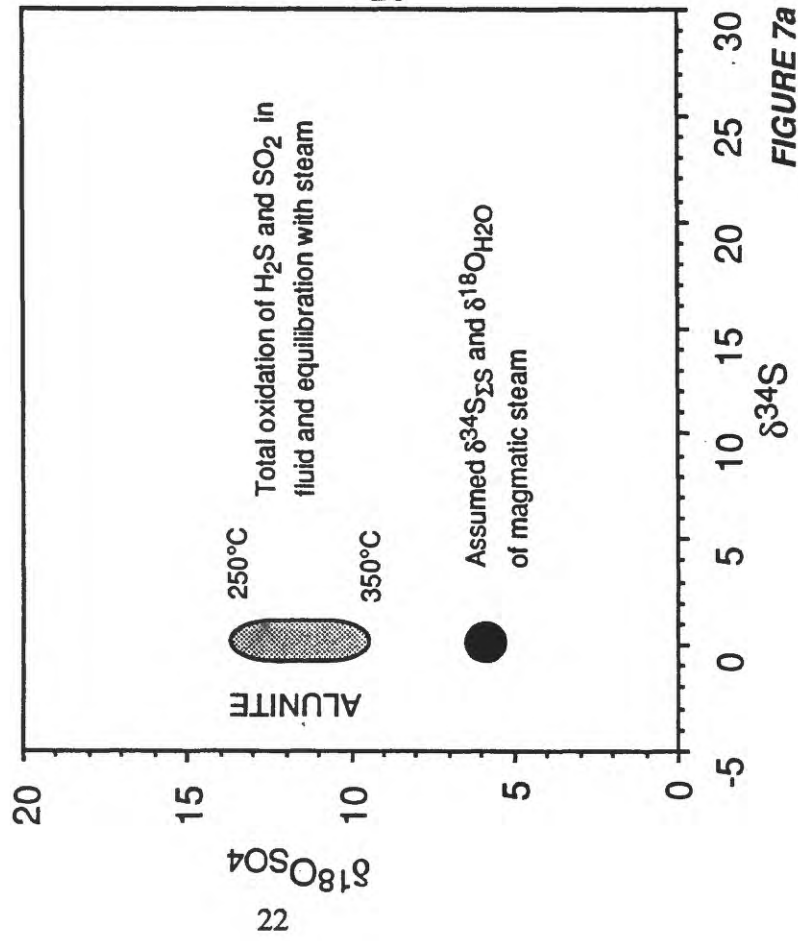


FIGURE 7a

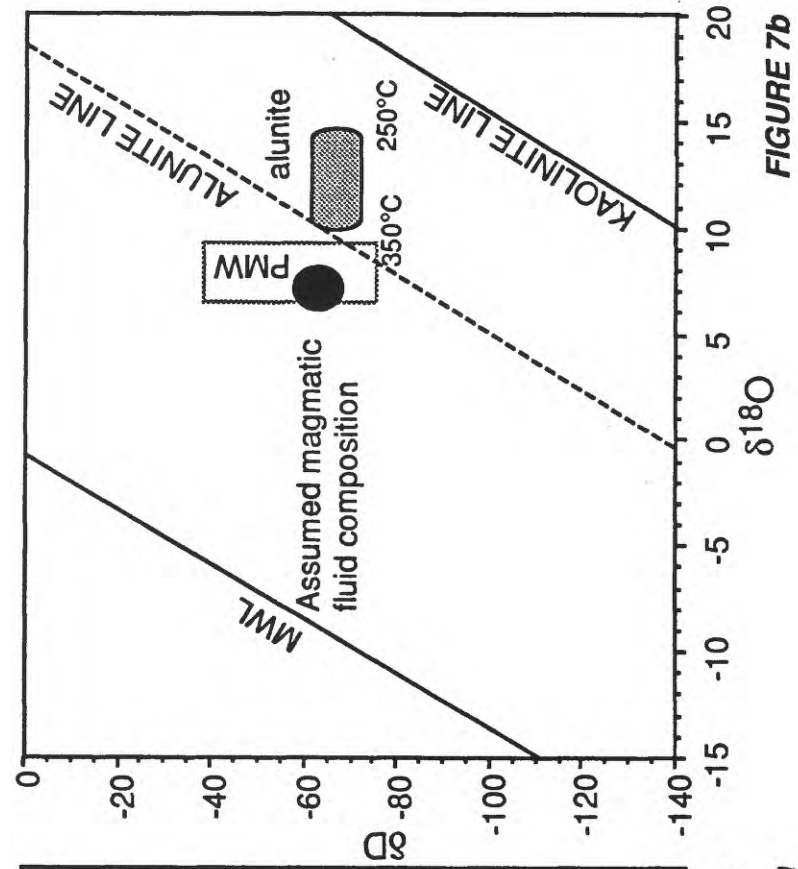


FIGURE 7b

# $\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$ OF SUPERGENE ALUNITE: CREEDE, CO

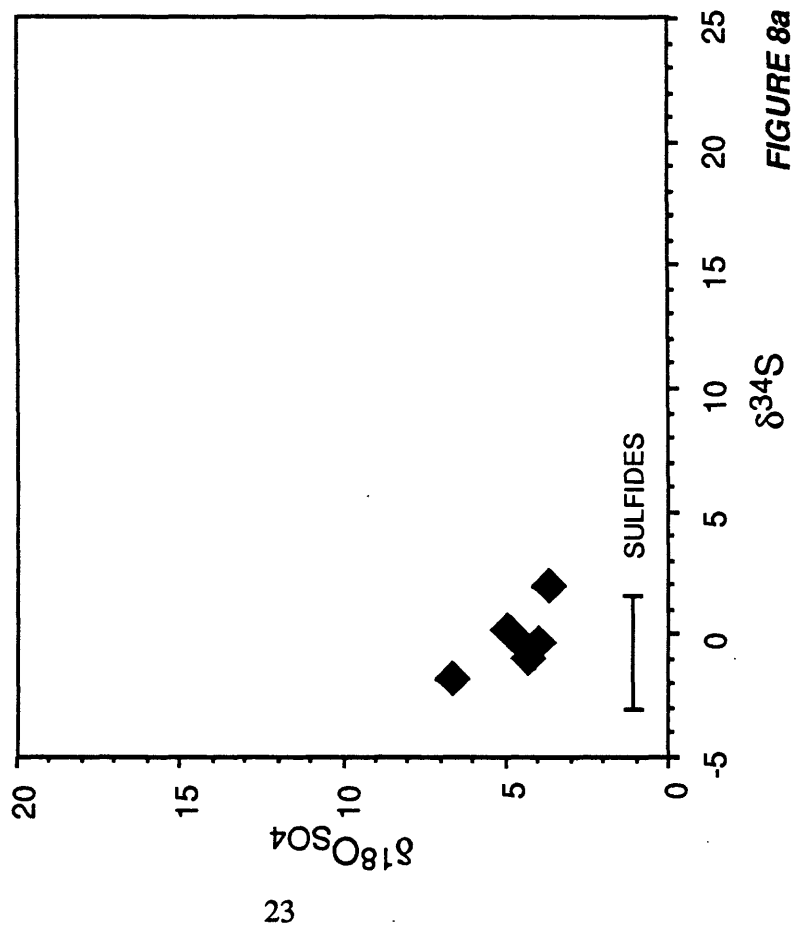


FIGURE 8a

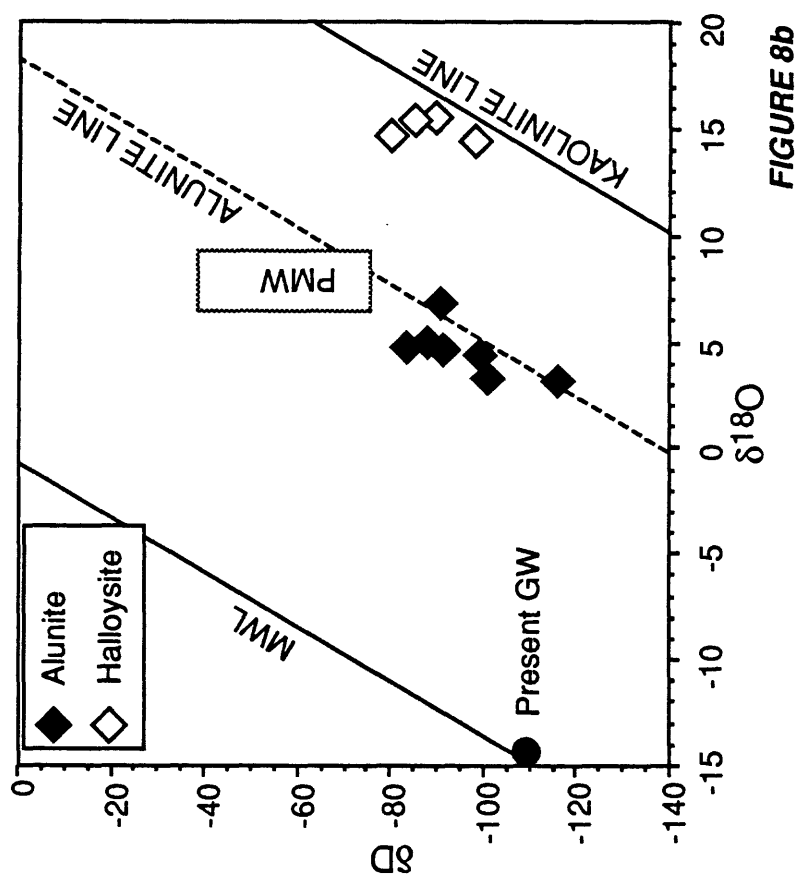


FIGURE 8b

$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF STEAM-HEATED ALUNITE:  
 BUCKSKIN MTN., NATIONAL DISTRICT, NV

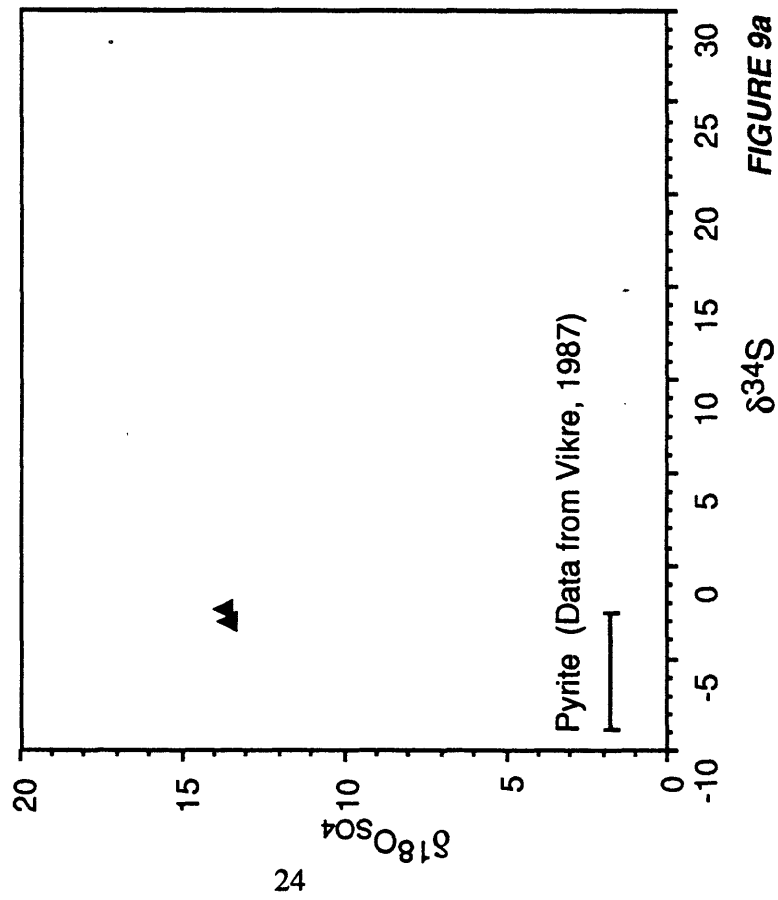


FIGURE 9a

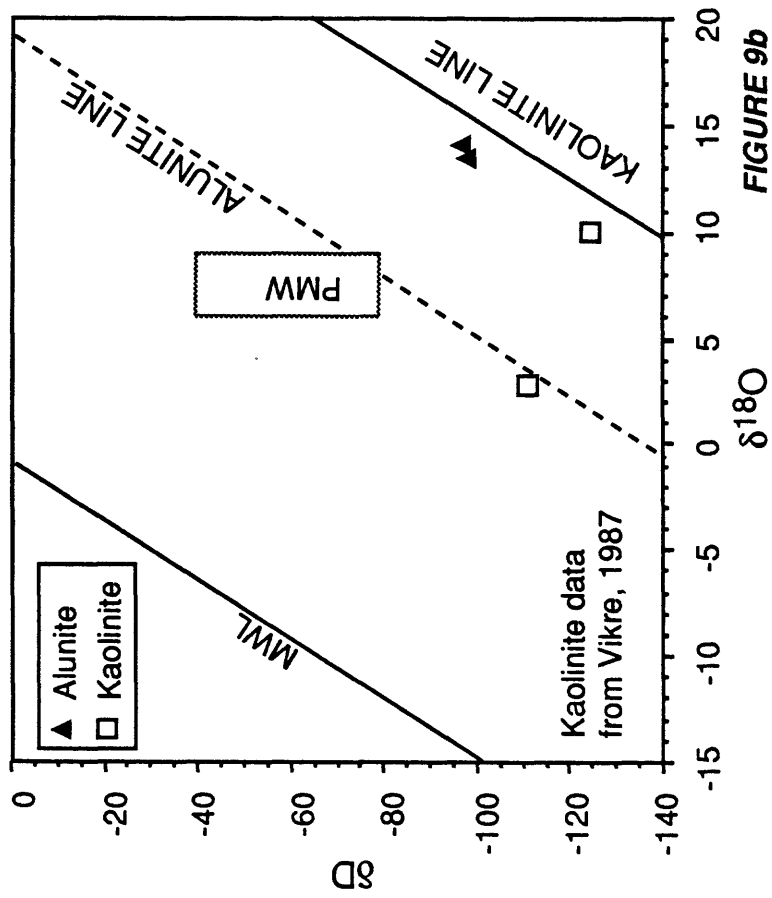


FIGURE 9b



$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF STEAM-HEATED ALUNITE:  
REPLACEMENT DEPOSITS, **MARYSVALE, UT**

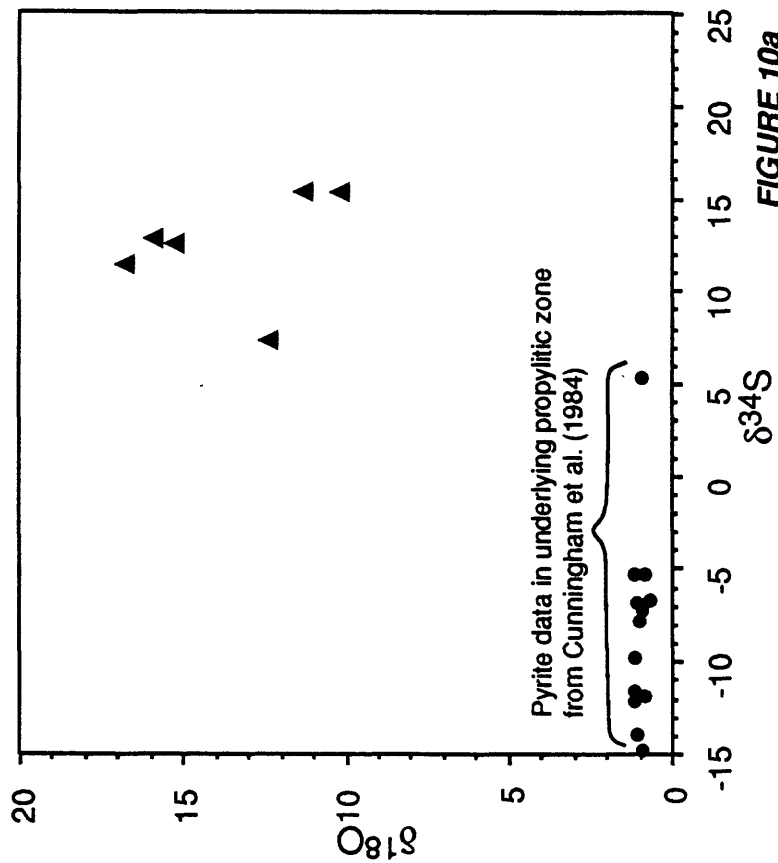


FIGURE 10a

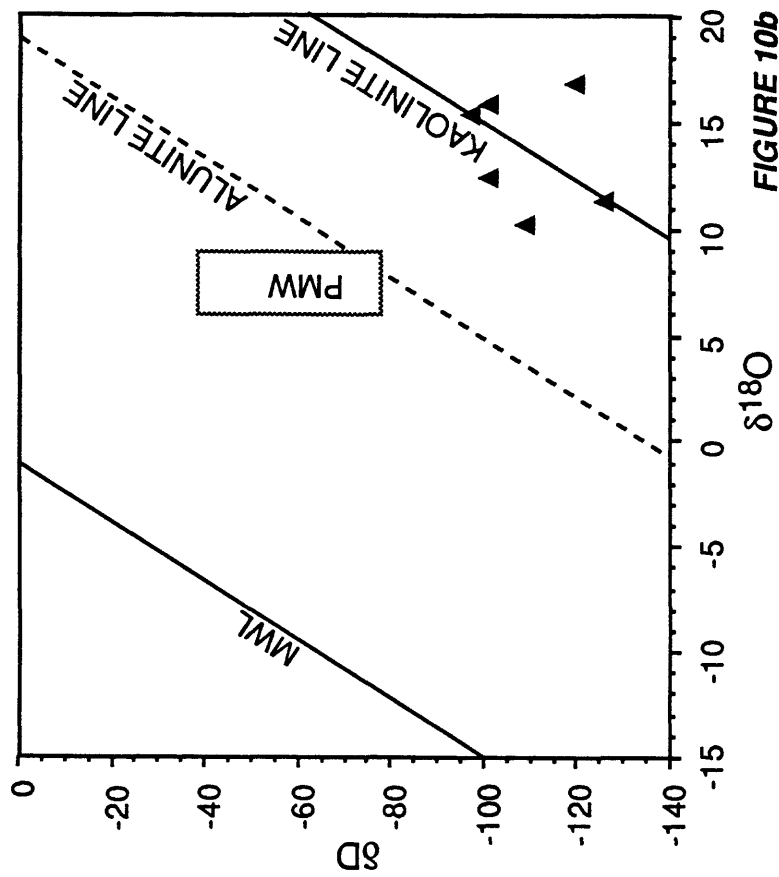


FIGURE 10b

$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF ALUNITE IN A PURE  
MAGMATIC SYSTEM: JULCANI DISTRICT, PERU

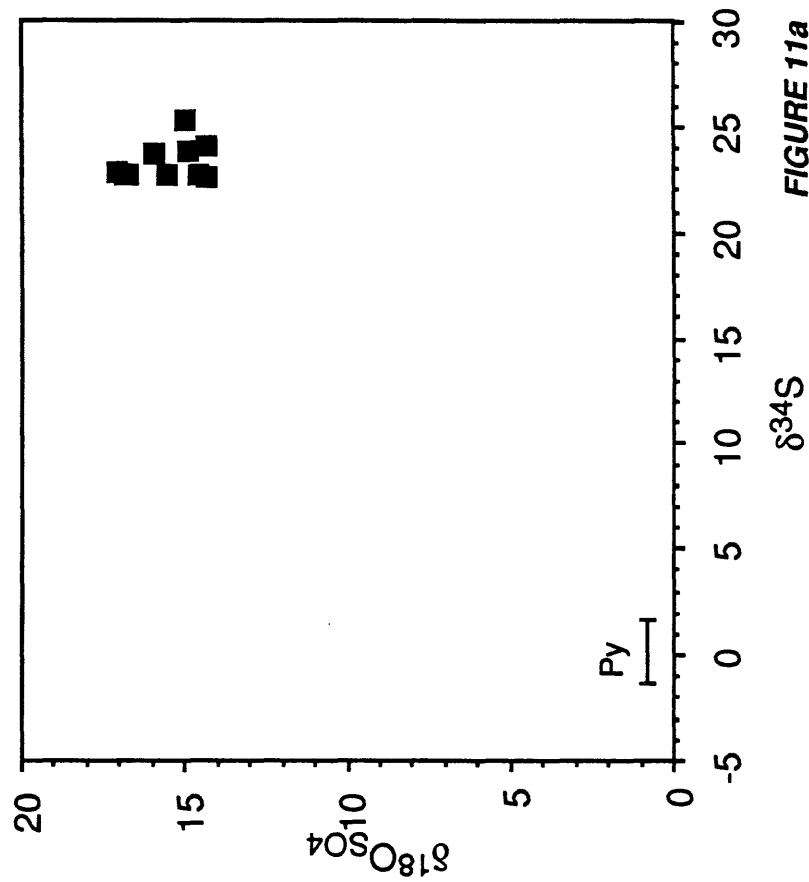


FIGURE 11a

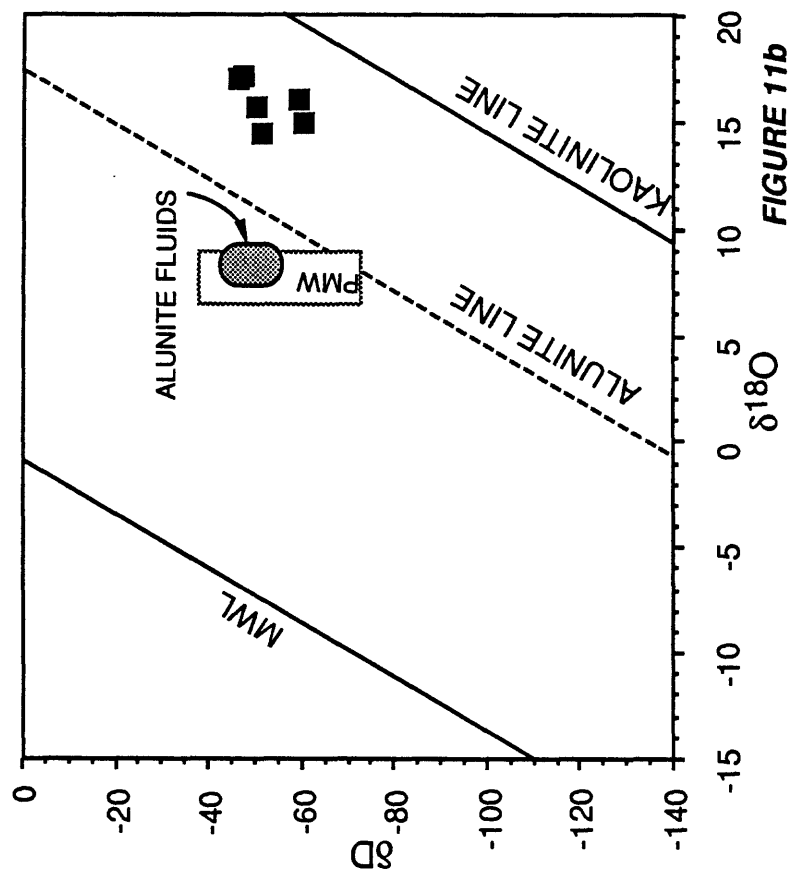


FIGURE 11b

$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF ALUNITE IN A MAGMATIC-METEORIC  
HYROTHERMAL SYSTEM: SUMMITVILLE, CO

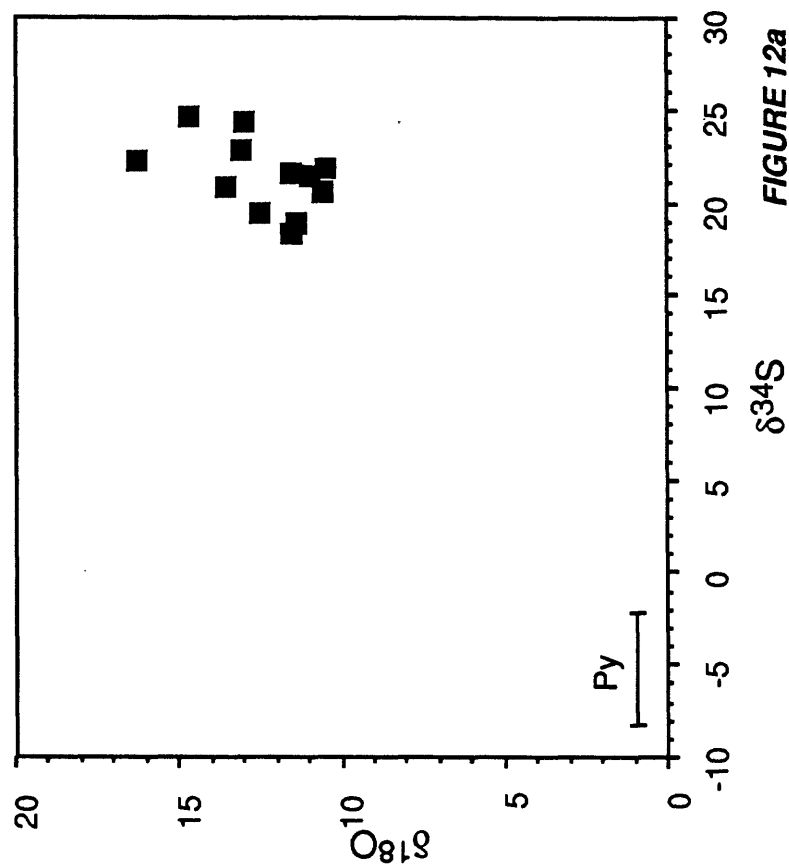


FIGURE 12a

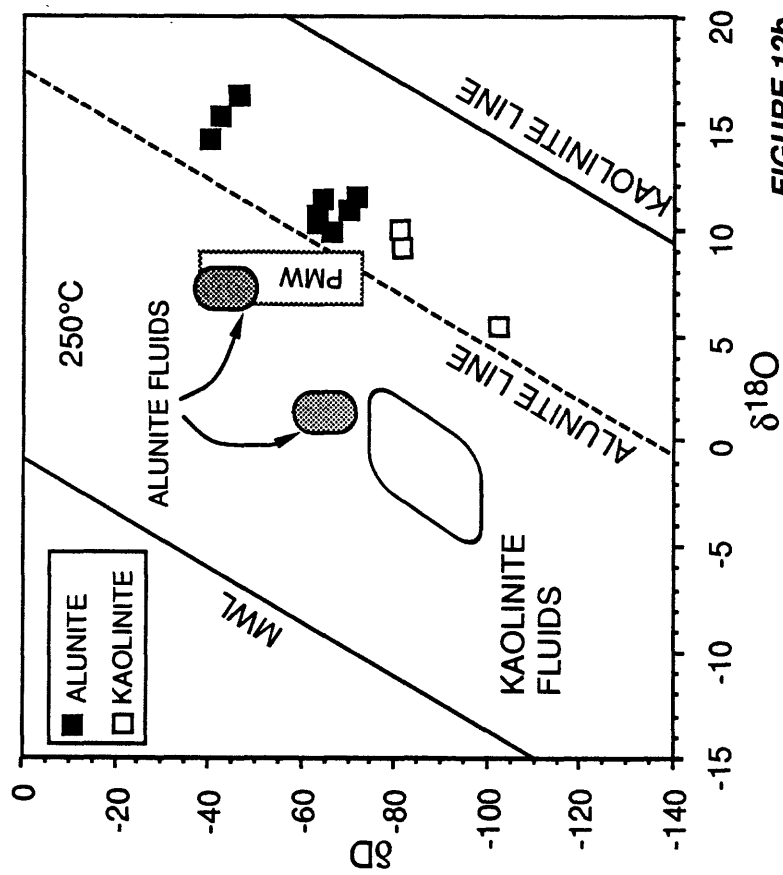
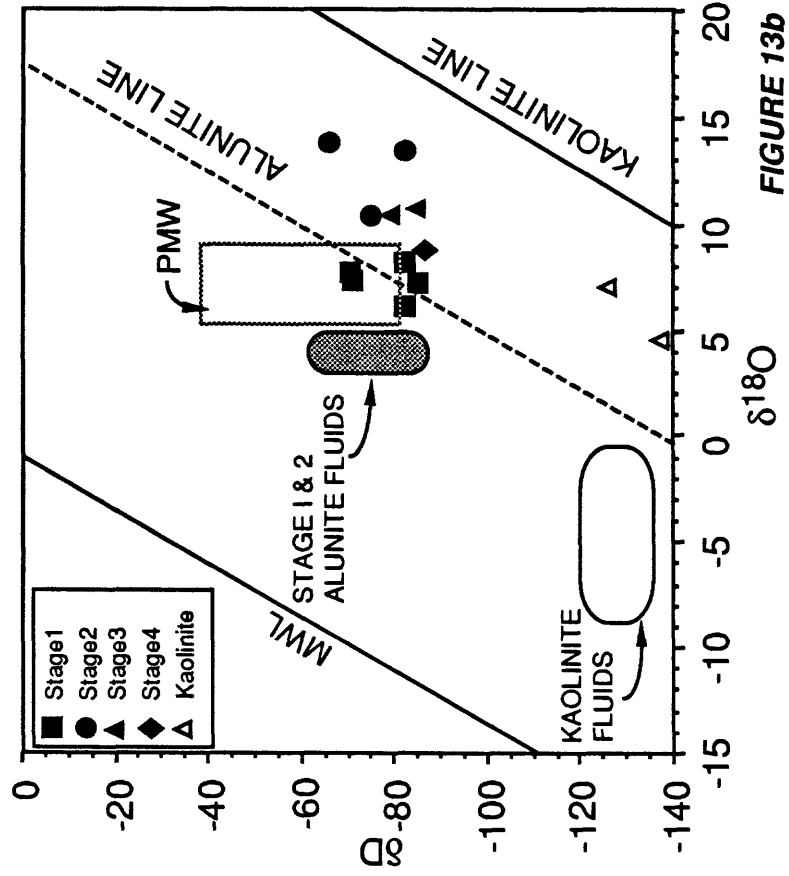
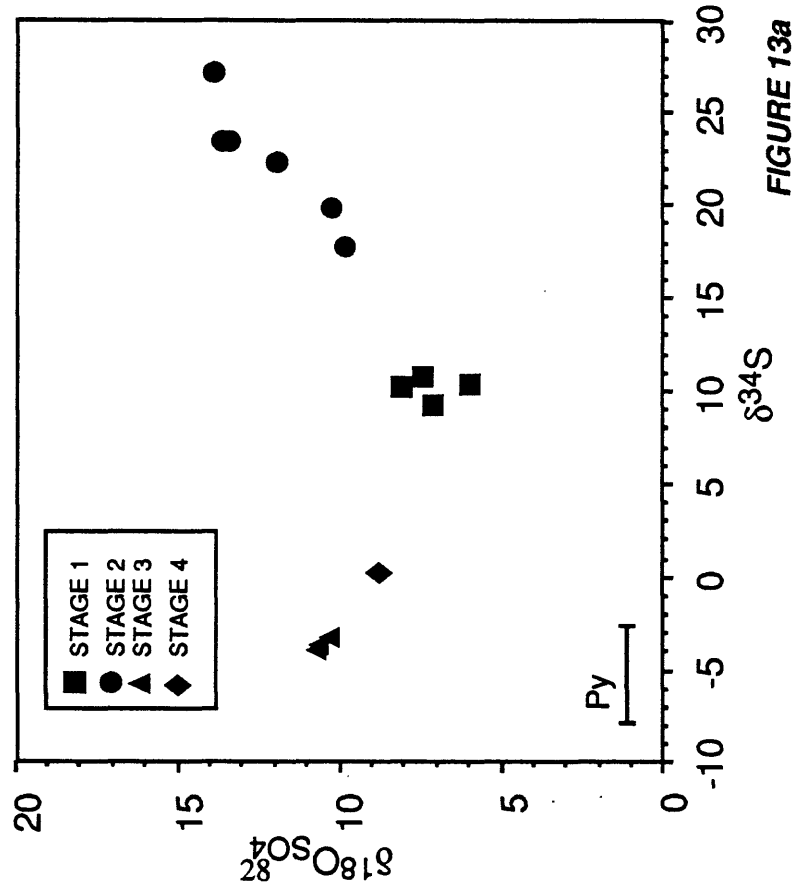


FIGURE 12b

$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF ALUNITES IN A MULTI-STAGE MAGMATIC-HYDROTHERMAL SYSTEM: **RED MOUNTAIN, LAKE CITY, CO**



$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF ALUNITE IN A MAGMATIC  
STEAM SYSTEM: VEIN DEPOSITS **MARYSVALE, UT**

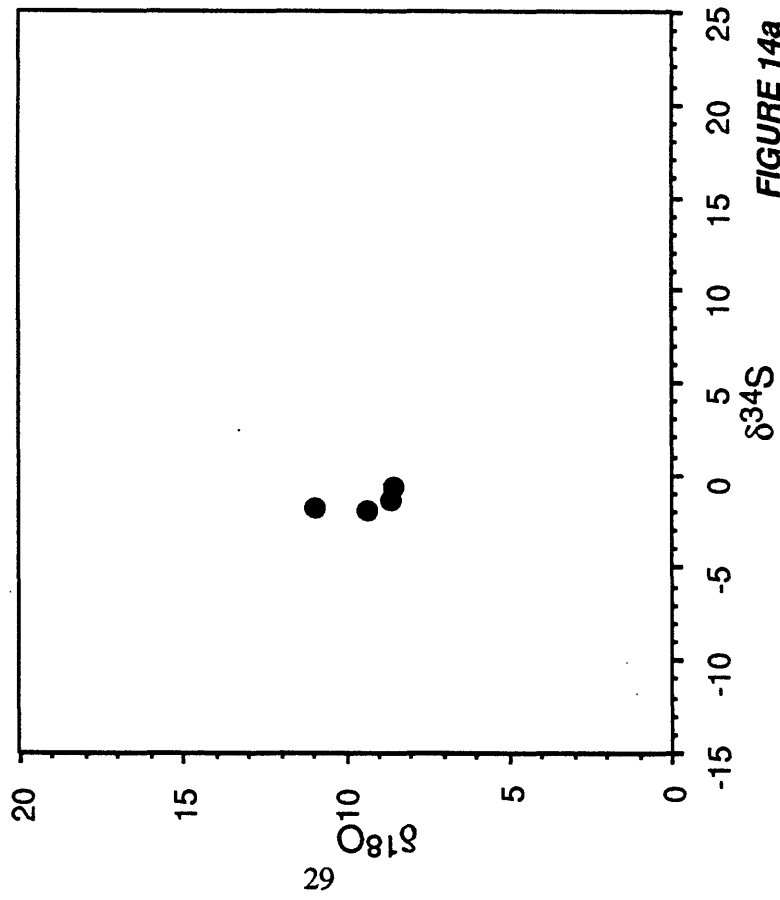


FIGURE 14a

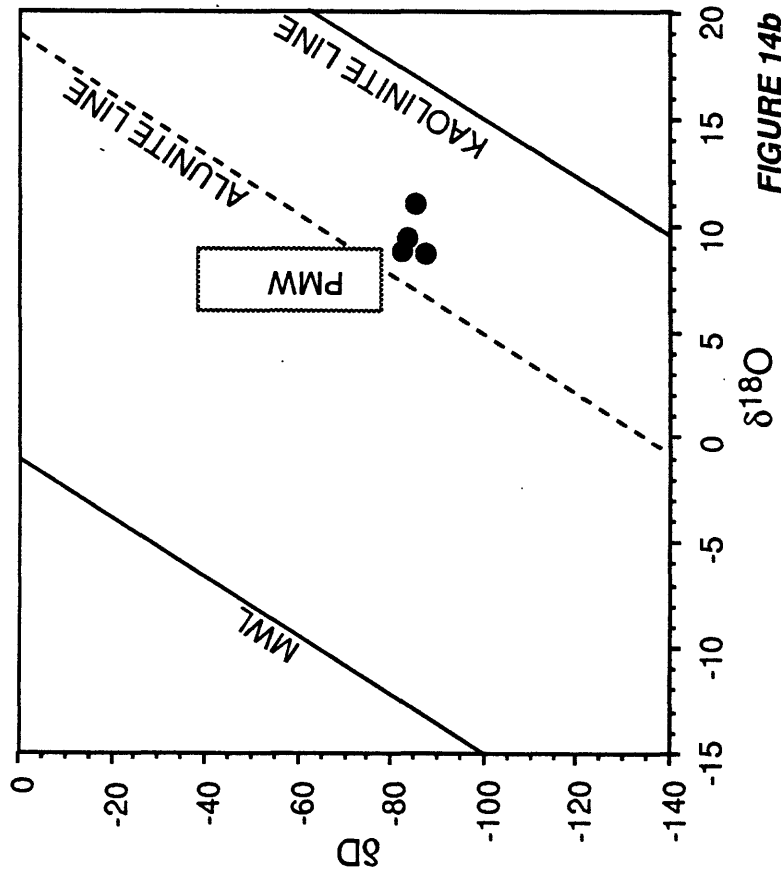


FIGURE 14b

$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF ALUNITE IN MULTIPLE  
TYPE SYSTEM: RODALQUILAR, ALMERIA, SPAIN

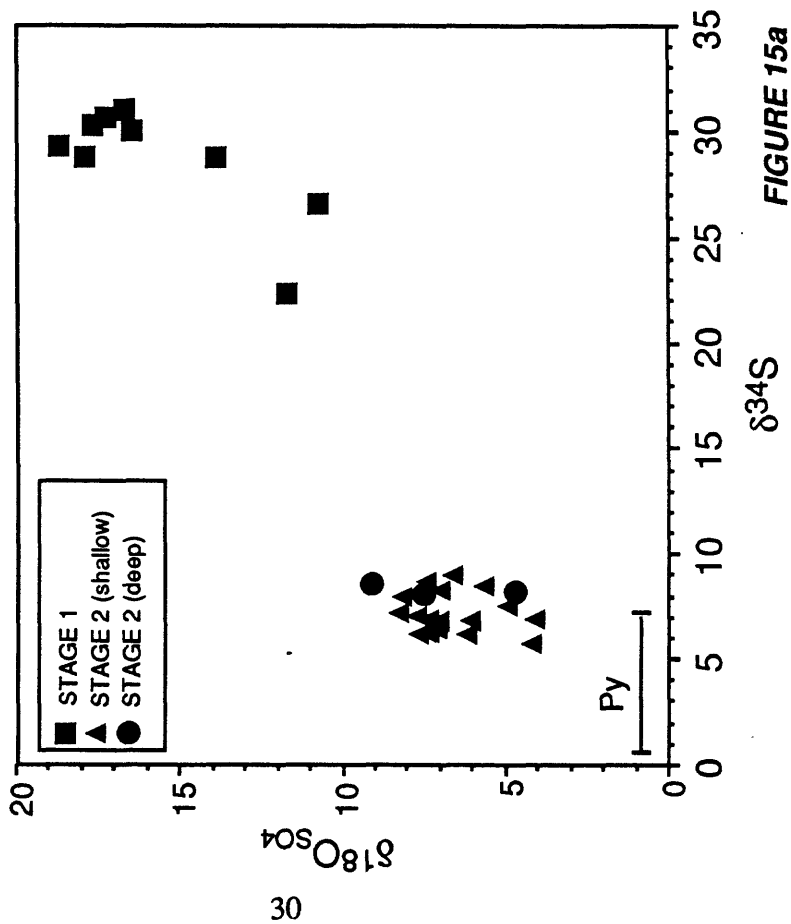


FIGURE 15a

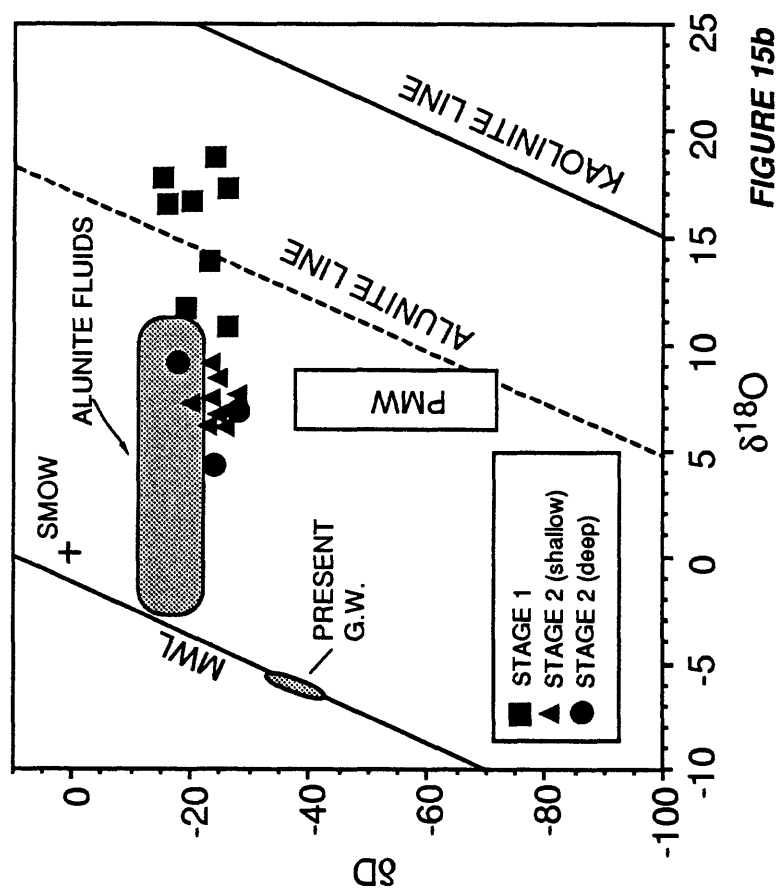


FIGURE 15b

$\delta D - \delta^{18}O_{SO_4} - \delta^{34}S$  OF ALUNITE IN DIVERSE  
SYSTEMS: NEVADA TERTIARY DEPOSITS

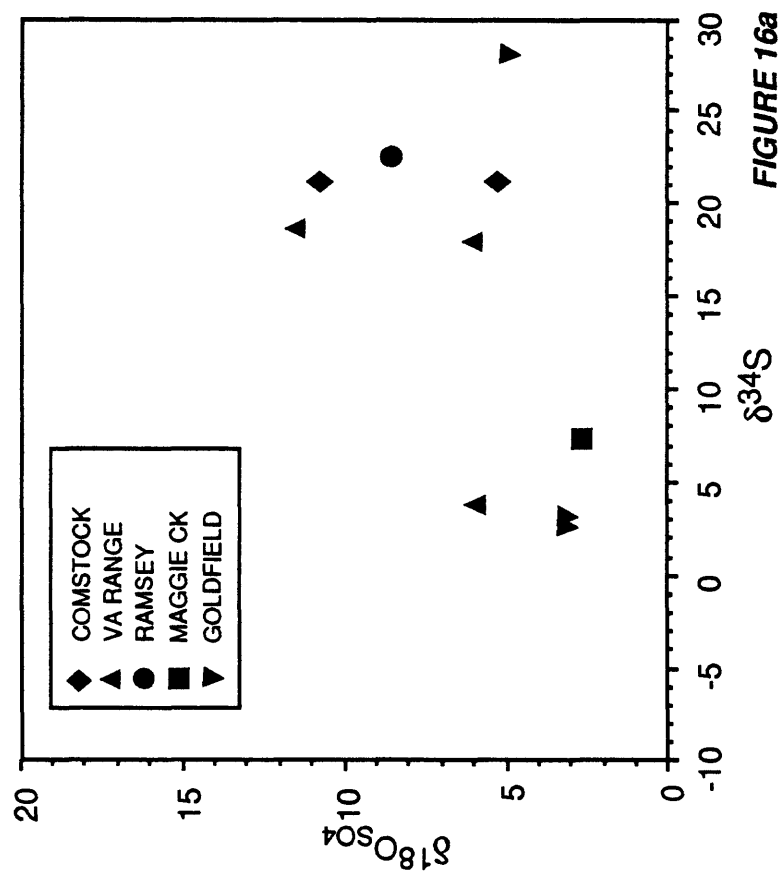


FIGURE 16a

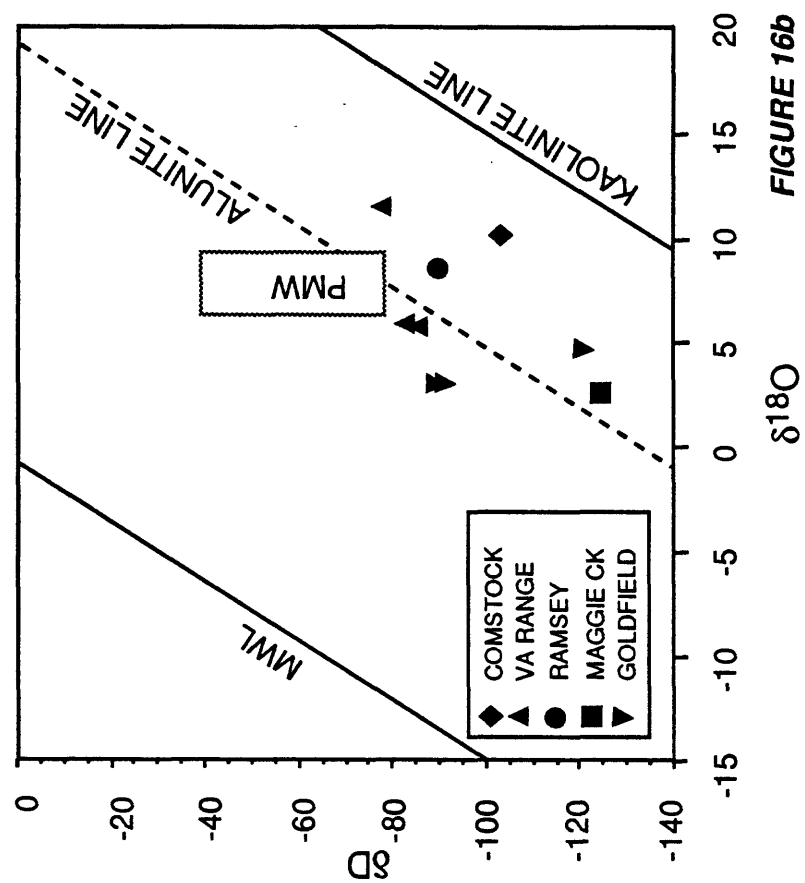


FIGURE 16b

# SUMMARY OF PREDICTED $\delta D - \delta^{34}S - \delta^{18}O_{SO_4}$ OF ALUNITE IN ACID-SULFATE ENVIRONMENTS

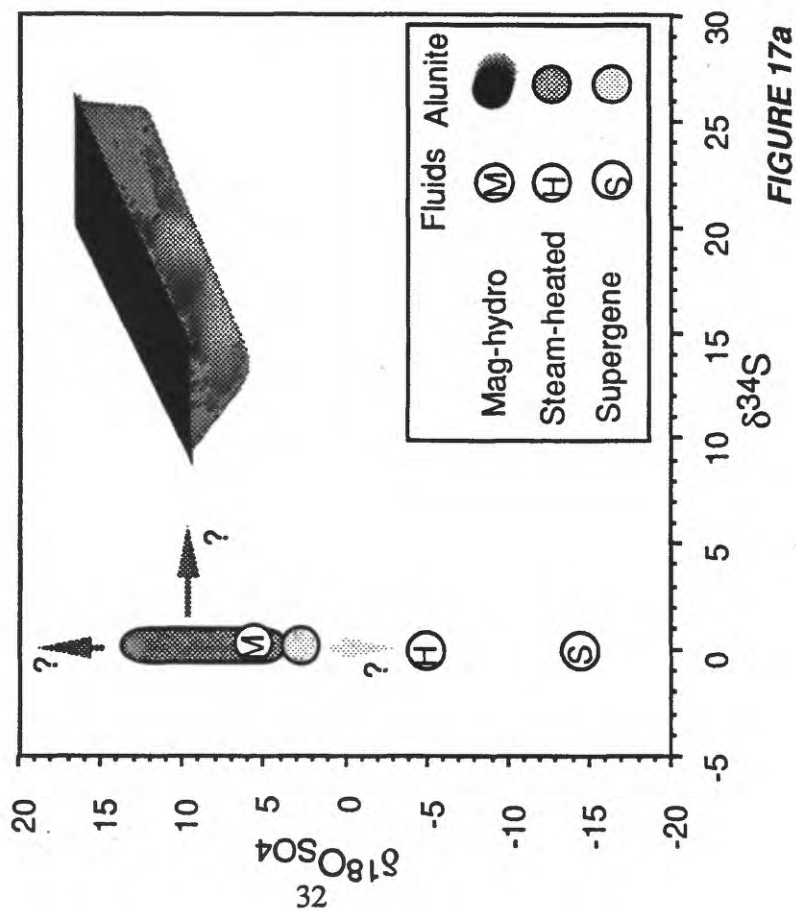


FIGURE 17a

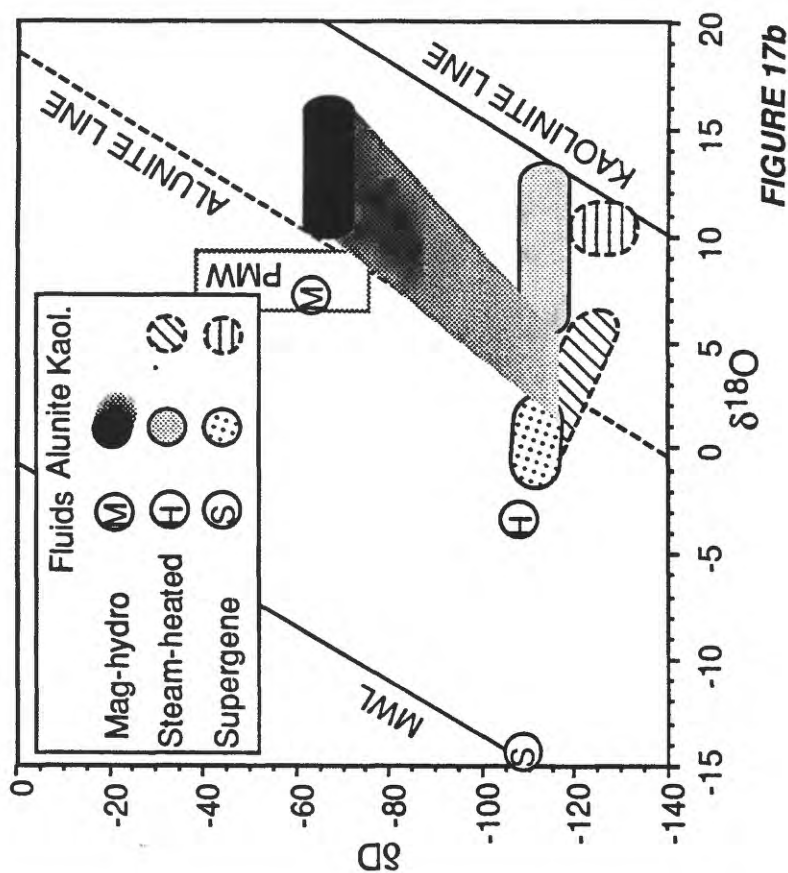


FIGURE 17b



# STEAM-HEATED ACID SULFATE AND MAGMATIC-STEAM ENVIRONMENTS OVER MAGMATIC-HYDROTHERMAL ENVIRONMENTS

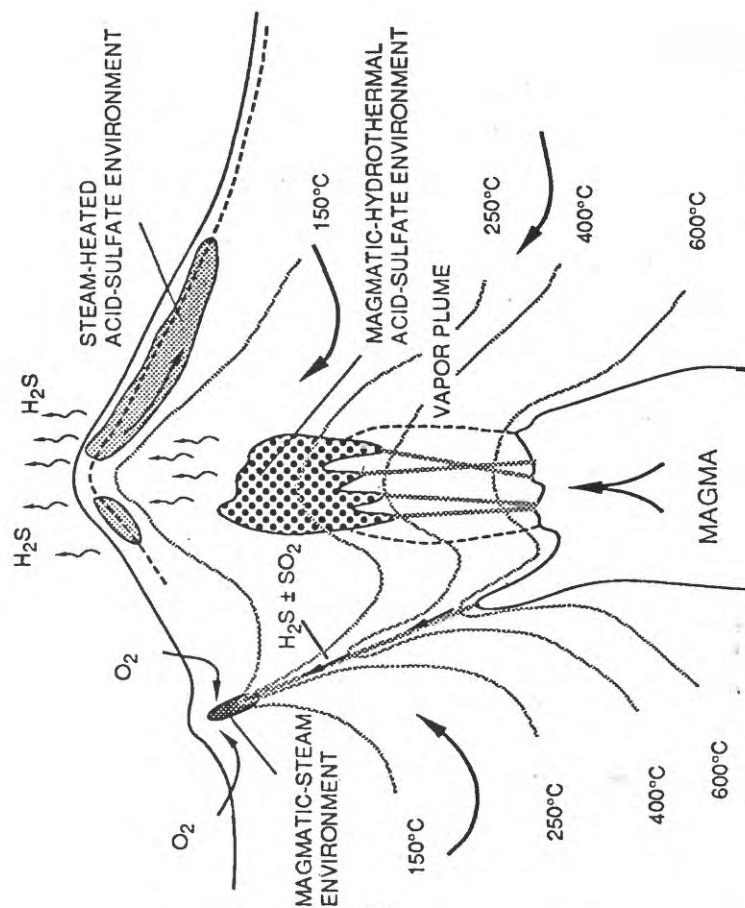


FIGURE 18

# STEAM-HEATED ACID-SULFATE ENVIRONMENT ABOVE ADULARIA-SERICITE EPITHERMAL SYSTEM

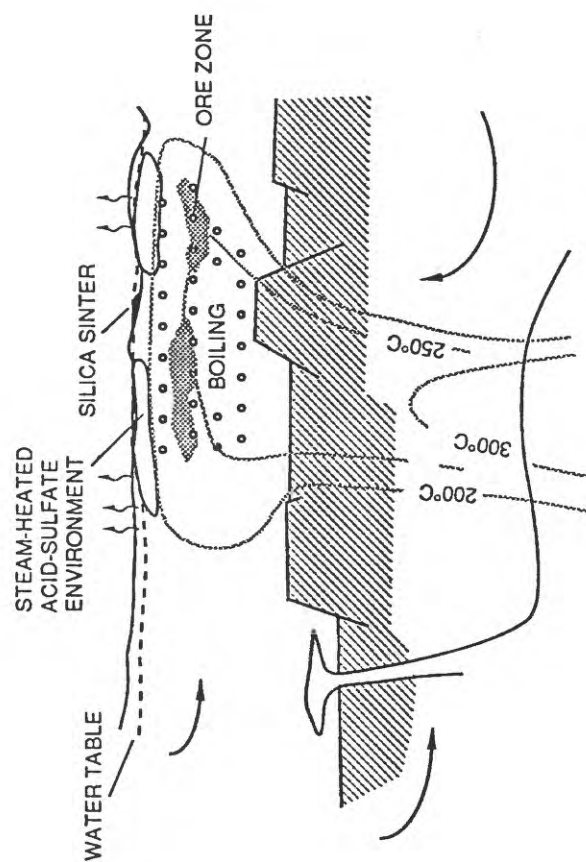


FIGURE 19