

## T37. Sulfate Minerals: Hydrothermal Systems, SESSION 19

### 9:45 AM Fifarek, Richard H.

#### STABLE ISOTOPES SYSTEMATICS OF THE PIERINA AU-AG DEPOSIT, PERU: IMPLICATIONS FOR MAGMATIC-HYDROTHERMAL PROCESSES IN THE EPIHERMAL ACID-SULFATE ENVIRONMENT

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The Pierina Au-Ag deposit consists of alteration and fracture or vug filling assemblages characteristic of the epithermal acid-sulfate environment. Alunite of an alunite-quartz-kaolinite-pyrite alteration assemblage has variable  $\delta^{34}\text{S}$  (17.6–31.7 ‰),  $\delta^{18}\text{O}_{\text{SO}_4}$  (4.9–16.5 ‰),  $\delta^{18}\text{O}_{\text{OH}}$  (2.2–13.9 ‰) and  $\delta\text{D}$  (-97 to -39 ‰) values, whereas pyrite, enargite, covellite and sulfur have relatively uniform  $\delta^{34}\text{S}$  values (0±3 ‰). Alunite-pyrite sulfur isotope fractionations yield temperatures of 165 to 353 °C. These data imply a magmatic vapor plume with  $\delta^{34}\text{S}_{\text{S}_2}=3$  ‰ and  $\Sigma\text{H}_2\text{S}/\Sigma\text{SO}_4=5$  condensed and mixed with meteoric water to form alunite-stable fluids (pH=2). The acidity was largely a product of the disproportionation of magmatic  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4+\text{H}_2\text{S}$  below ~400 °C. Two samples of relatively late coarsely plumose vein alunite of magmatic steam origin have  $\delta^{34}\text{S}$  values (8.5, 21.1 ‰) that reflect sulfate-sulfide disequilibrium and  $\delta\text{D}$  values (-83, -95 ‰) that suggest either the  $\delta\text{D}$  evolution of water in the underlying magma or the incorporation of meteoric water into rapidly rising columns of steam. Near equilibrium  $\delta^{18}\text{O}_{\text{SO}_4-\text{OH}}$  values of most alunites indicate minimal retrograde isotopic exchange in the OH site.

Alteration and vein kaolinite, dickite, pyrophyllite, and illite have similar  $\delta^{34}\text{S}$  values (3.2–10.1 ‰) but lower  $\delta\text{D}$  values (-126 to -94 ‰) than alunite. Calculated clay fluid compositions vary in  $\delta\text{D}_{\text{H}_2\text{O}}$  values without a complementary change in  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values, suggesting either the involvement of  $^{18}\text{O}$ -shifted meteoric water in wallrocks adjacent to veins or retrograde H isotope exchange.

Finally, two steam-heated alunites have  $\delta^{34}\text{S}$  (12.3, 14.2 ‰),  $\delta^{18}\text{O}$  (11.3, 11.7 ‰) and  $\delta\text{D}$  (-62 ‰) values that suggest magmatic steam reached shallow levels and that aqueous sulfate formed by  $\text{H}_2\text{S}$  oxidation in the vadose zone partially equilibrated with streaming  $\text{H}_2\text{S}$ . Similarly, late barite  $\delta^{34}\text{S}$  (7.4–29.0 ‰) and  $\delta^{18}\text{O}$  (-0.4 to 15.1 ‰) values imply magmatic-hydrothermal sulfate mixed with sulfate formed in shallow steam-heated meteoric water.

### 10:15 AM Juliani, C.

#### EARLY PROTEROZOIC VOLCANIC-HOSTED QUARTZ-ALUNITE EPIHERMAL DEPOSITS IN THE TAPAJÓS GOLD PROVINCE, AMAZONIAN CRATON, BRAZIL

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The Tapajós Gold Province is in a metamorphic sequence that includes greenstones (~ 2.1 Ga), the Cuiú-Cuiú Metamorphic Suite (2.06 Ga), the Parauru intrusive granodiorites (1.90 Ga), the Ingarana mafic-ultramafic intrusive rocks (~ 1.88 Ga), rhyolitic to andesitic volcanic-volcaniclastic rocks of the Iriri Group (1.88–1.89 Ga), the Maloquinha (1.88–1.89 Ga) and Teles Pires granitoid suites, rhyolitic to dacitic porphyries, and Middle Proterozoic very low-grade metasedimentary sequences. High-sulfidation gold mineral assemblages alunite+natrolalunite+pyrophyllite + andalusite + quartz + rutile + diasporite ± woodhouseite ± kaolinite ± pyrite ± enargite occur mainly in volcanic breccias in the Iriri volcanics. These volcanics have undergone potassio, propylitic, sericitic, argillic and advanced argillic alterations mainly associated with satellite volcanic structures at the rim of probable calderas related to the underlying Maloquinha intrusions, the presumed source of crosscutting dacitic to rhyolitic porphyries. Alunite occurs disseminated in the advanced argillic haloes or fills branching veins, partially replaced by a second generation of fine-grained alunite. Strong silicification commonly occurs with alunite. An extensive silica cap, sometimes brecciated and usually showing hematitization, is found on top of the breccias. Basal dacitic flows are propylitized. Stable isotope studies support a magmatic-hydrothermal origin for the alunite.  $\delta^{34}\text{S}$  values of alunite range from 18.1 to 36.9‰; sulfur isotope alunite-pyrite and oxygen isotope alunite-sulfate-OH temperatures range from 150 to 320°C;  $\delta^{18}\text{O}$  values for hydrothermal fluids also suggest the predominance of magmatic water, with a small meteoric contribution. This province contains the first high-sulfidation gold deposits found in the Amazonian Craton and since such deposits form at relatively shallow levels their discovery provides new perspectives for mineral explorations for the Tapajós Province and perhaps other Precambrian cratons. The results of argon age dating of the alunite will be presented.

### 10:30 AM Truesdell, Alfred H.

#### SULFATE IN ACTIVE GEOTHERMAL SYSTEMS FROM SOURCE TO SURFACE

TRUESDELL, Alfred H., 700 Hermosa Way, Menlo Park, CA 94025, [ahtruesdell@lbl.gov](mailto:ahtruesdell@lbl.gov) The conversion of magmatic (fluids (and heat) into geothermal fluids is now generally accepted; with  $\text{SO}_2$  and  $\text{HCl}$  key to the process. Geothermal wells drilled near andesitic volcanoes provide samples intermediate between acid, oxidizing magmatic gases and neutral, reduced geothermal fluids. At sub-critical temperatures  $\text{HCl}$  and  $\text{SO}_2$  dissolve in water (part magmatic and part surface in origin), ionize, disproportionate and react with feldspars to form geothermal fluid with Na, K, Ca, Cl,  $\text{SO}_4$ ,  $\text{H}_2\text{S}$  and  $\text{SiO}_2$ , accompanied by  $\text{CO}_2$  and some  $\text{H}_2\text{S}$  from magmatic gases. Much of the Ca and  $\text{SO}_4$  are removed by deposition of anhydrite at high temperatures or if seawater infiltration occurs. Some geothermal reservoirs retain acid waters if reservoir rock lacks feldspars (e.g., Tatum, Taiwan) or if drillholes are located too close to volcanic edifices (e.g., Japan, Philippines). During upflow and boiling,  $\text{H}_2\text{S}$  and  $\text{CO}_2$  partition into steam and react with rock and air-saturated water to form dilute Na ( $\text{SO}_4$ ,  $\text{HCO}_3$ ) solutions that may corrode well casings.  $\text{H}_2\text{S}$  that reaches the surface may be oxidized (catalyzed in part by sulfur-oxidizing bacteria) by  $\text{O}_2$  in air to form concentrated acid sulfate waters, partially oxidized to sulfur, or react with  $\text{Fe}^{++}$  to form pyrite in yellow or gray mudpots. Much of the  $\text{H}_2\text{S}$  enters the atmosphere where it is more or less slowly oxidized to  $\text{H}_2\text{SO}_4$  aerosols, contributing to acid rain. Some acid reservoir waters consist in part of infiltrated acid sulfate waters formed at the surface. In areas of steaming ground, efflorescences of alum and other sulfate minerals are common. Because of its decreasing solubility with temperature, anhydrite may seal the margins of geothermal reservoirs and limit cold water inflow. Because of this property, high  $\text{CaSO}_4$  surface water and particularly seawater has not been used to recharge geothermal reservoirs, although recently an inhibitor has been tested successfully. Geothermal  $\text{H}_2\text{S}$  and  $\text{SO}_4$  have been traced by isotopic studies with the fractionation of O-18 between  $\text{SO}_4$  and  $\text{H}_2\text{O}$  used extensively as a geothermometer. Fractionation of S-34 between  $\text{SO}_4$  and  $\text{H}_2\text{O}$  occurs only above 300°C, but distinguishes  $\text{SO}_4$  of deep and shallow origins.

### 10:45 AM Shanks, W. C. III

#### STABLE ISOTOPES STUDY OF ALUNITE FROM YELLOWSTONE NATIONAL PARK

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Mapping in Yellowstone National Park using AVIRIS (Airborne Visible and Infra-Red Imaging Spectrometer) delineates significant zones of surficial, vapor-dominated geothermal alunite deposits at Roaring Mountain and in the Ragged Hills area of Norris Geyser Basin. This discovery prompted a detailed stable isotope study of modern geothermal alunite deposits. Stable isotopic studies of alunite are a remarkably powerful tool because 4 isotopic species can be analyzed in a single mineral:  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in hydroxyl, and  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  in sulfate. These data allow evaluation of waters that formed the alunite, sulfur sources, isotopic geothermometry, and methods for estimating rates and relative residence times of sulfates formed by  $\text{H}_2\text{S}$  oxidation.

Sulfur isotope values for Norris alunites are similar to local geothermal  $\text{H}_2\text{S}$  (1.9–2.9 permil), as expected for derivation of sulfate from surficial oxidation of  $\text{H}_2\text{S}$  in steam. At Roaring Mountain alunite  $\delta^{34}\text{S}$  values (5.0–6.3) are significantly different than those for  $\text{H}_2\text{S}$  (0.7). This may indicate exchange between aqueous sulfate and  $\text{H}_2\text{S}$  or, more likely, that the alunites formed some time ago when  $\delta^{34}\text{S}$  of  $\text{H}_2\text{S}$  at Roaring Mountain was substantially different.

The isotopic composition of waters in equilibrium with alunite at boiling temperatures (93°C in Yellowstone) can be estimated using  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of hydroxyl and sulfate in the alunite structure. These calculations predict waters with  $\delta\text{D} = -105$  to -126 and  $\delta^{18}\text{O} = -11.7$  to -19.7. Present-day local meteoric water has  $\delta\text{D} \sim -140$  and  $\delta^{18}\text{O} \sim -20$ , so these alunites cannot be used to directly calculate the isotopic value of contemporaneous meteoric water. However, studies of boiling surface pools in Yellowstone indicate that residual waters evolve along a  $\delta\text{D}$ - $\delta^{18}\text{O}$  trajectory with a slope of 2.0 to 2.5. Steam in equilibrium with such waters has  $\delta\text{D}$  values that are lower by 27.8 permil and  $\delta^{18}\text{O}$  values lower by 5.2 permil. In general, only the calculated isotopic values for waters in equilibrium with alunite hydroxyl fit this array of possible waters. Many of the  $\delta^{18}\text{O}$  values of waters predicted using sulfate oxygen isotope data plot well to the left of the global meteoric water line, indicating that aqueous sulfate in these systems did not achieve oxygen isotope equilibrium with water in the fluids due to a relatively short residence time between formation of sulfate in the oxidizing geothermal system and precipitation of alunite.

### 11:00 AM Zimbelman, D. R.

#### SULFATE MINERALS IN ACTIVE ANDESITIC STRATOVOLCANOES

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Active andesitic stratovolcanoes contain a diverse suite of sulfates, often accompanied by native sulfur and generally lack sulfides. The sulfates are a product of reactions between volcanic gases and acid hydrothermal solutions with the volcanic rock. At most volcanoes the sulfates are intimately intergrown with clays and vary on a micron scale in crystal form, anion and cation chemistry, and isotopic composition. These characteristics result from variable exposure to acid fluids and changes in fluid composition. Sulfate alteration is an indicator of structural weakening of a volcanic edifice; many active volcanoes have weakened to the point of collapse, with associated loss in human life and property.

Citlaltepetl volcano, Mexico, has experienced three distinct growth stages separated by two large edifice collapse events. The current summit contains historic flows, active fumaroles, and altered rock with alunite, sodium alum, minamite, gypsum, arhydrite, and alunogen/metaalunogen accompanied by native sulfur, kaolin, and various forms of silica. Rocks from an intermediate stage represent deeper alteration zones and contain alunite, minamite, letovite, sodium alum, and phillipsite, accompanied by kaolin and various forms of silica. The oldest parts of the edifice are more deeply incised and alteration consists of minor occurrences of minamite and alunite accompanied by various forms of silica, halloysite, and iron-oxides and hydroxides. Active stratovolcanoes in the Cascade Range contain a range of alteration minerals, including sulfates. For example, Mount Shasta contains altered zones similar to those at Citlaltepetl's summit, consisting of kaolin, gypsum/arhydrite, alunite, and cristobalite. In contrast, Mount Adams, Hood, and Rainier contain more smectite than kaolin, jarosites, and widespread occurrences of various soluble sulfate minerals. In active andesitic environments, alteration mineral assemblages, crystal forms, chemical zonings, and isotopic characteristics suggest deposition in rapidly changing conditions, including swift cooling of hydrothermal systems by predominantly meteoric waters, and in association with fluids of very low pH and high  $\text{FO}_2$ .

### 11:15 AM Lueth, Virgil W.

#### HYDROTHERMAL "SOUR GAS" JAROSITE: ANCIENT AND MODERN ACID SULFATE MINERALIZATION EVENTS IN THE RIO GRANDE RIFT

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Fluorite-barite-jarosite deposits occur along the Rio Grande rift from central New Mexico to near Chihuahua, Mexico. Jarosite occurs as a late stage hydrothermal mineral co-precipitated with fluorite following gypsum-hematite mineralization. These deposits range in age from 10 to 0.4 Ma based on  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of jarosite. The duration of hydrothermal jarosite mineralization in one of the deposits is approximately 1 Ma. The mineralizing fluids had calculated isotopic signatures and high trace element concentrations (notably As and F) similar to modern geothermal waters.  $\delta^{34}\text{S}$  values of < -15‰ imply an organic or "sour gas" origin for precursor  $\text{H}_2\text{S}$  that exchanged with  $\text{SO}_4^{2-}$ . Calculated  $\delta\text{D}_{\text{H}_2\text{O}}$ ,  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$ , and  $\delta^{18}\text{O}_{\text{SO}_4}$  of parent fluids for these sour gas jarosites (SGJ) reveal a spectrum of values ranging from values typical of meteoric water to deep basin brine.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values are typical of steam heated jarosites. Mixing of acidic geothermal water with oxidized groundwater containing dissolved Permian sulfate appears responsible for SGJ mineralization. The low pH necessary for the precipitation of jarosite resulted from the oxidation of  $\text{H}_2\text{S}$  derived from the thermochemical reduction of  $\text{SO}_4^{2-}$  and/or the thermal degradation of organic matter in the Paleozoic rocks during renewed rifting accompanied by the introduction of deep-seated HF. Jarosite formed after the pH buffering capacity of the host rock (usually limestone) was neutralized by precipitation of earlier minerals.  $\Delta^{18}\text{O}_{\text{SO}_4-\text{OH}}$  temperatures of jarosite formation range from 80 to 200 °C similar to homogenization temperatures in late stage fluorite. A homogenization temperature of 180°C was determined from fluid inclusions in jarosites from Mexico. Sour gas jarosites encode a record of tectonic, hydrologic, and geomorphic processes that have operated in the rift over the last 10 Ma years. Models for sour gas jarosite mineralization have immediate application to the understanding of geologic controls on water resources, water quality, mineral exploration, paleoclimate, uplift rates and public health issues in this rapidly growing population corridor.

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