

Origin of Acid Sulfate Alteration of the Porphyry Peak Rhyolite, Bonanza Caldera, San Juan Volcanic Field, South Central Colorado

Miranda I. Loflin

Department of Geology, The College of Wooster, Wooster, OH 44691

Faculty Sponsor: Lori Bettison-Varga, The College of Wooster

INTRODUCTION

The focus of this study is to determine the origin of acid sulfate alteration of the Porphyry Peak rhyolite, a hydrothermally altered area on the northern rim of the Bonanza Caldera, south central Colorado. The stable isotope data of sulfur, oxygen, and hydrogen in alunite will determine the fluid source of the acid sulfate alteration. In addition, two other KECK students are conducting fluid inclusion analyses for temperature and depth of alteration, and rare earth element analysis to determine zones of alteration in the Porphyry Peak area. Collectively, the analyses will define a complete picture of the alteration that occurred, and determine whether ore formation is possible beneath the altered Porphyry Peak rhyolite.

GEOLOGIC SETTING

The Bonanza caldera is 36 Ma, located in the far northeast corner of the San Juan volcanic field in south central Colorado. It is one of 18 early Oligocene calderas in the San Juan volcanic field of Colorado, covering 30 to 35 square miles (Burbank, 1932). It was first documented by Burbank (1932) who recognized a collapse structure near the Bonanza mining district, and suggested the depression could have formed from the removal of a magma source beneath the Bonanza area.

The Porphyry Peak rhyolite is an exogenous dome that cuts the volcanic flows on the northern rim of the Bonanza the Caldera. Smith and Varga (1982) dated this intrusion at 33 Ma. The area considered in this study consists of three intrusive domes of the Porphyry Peak rhyolite (see J. Lenz, this volume, fig. 1). The southernmost dome has been affected by acid sulfate alteration. By analyzing stable isotope data obtained on the acid sulfate mineral alunite, temperature and source of hydrothermal fluids can be determined for this site.

METHODS

Three weeks were spent in the Porphyry Peak field area with fellow KECK students Jennifer Lenz, Patrick Roehrdanz and Angela Dudek. Together, we mapped the area of Porphyry Peak, which includes (from south to north) Southwest Dome, (elev.: 11,142), West Porphyry Peak (elev.: 11,680), and East Porphyry Peak (elev.: 11,583) (see J. Lenz, this volume, fig. 1). The area consists of flaggy rhyolite and blocky, siliceous zones concentrated on the top of the Southwest Dome, and in a small confined area in the saddle between the Southwest Dome and West Porphyry Peak. The siliceous rocks define the zone of hydrothermal alteration. Once this area was defined, we collected and tested samples for alunite to obtain a preliminary idea of the zones of alteration.

A simple field test was conducted to determine the presence of alunite in our samples. Alunite is usually clear to chalky white, and occurs with large amounts of fine grained quartz. The field test consists of a series of simple steps, which could be done in the field. The test was helpful in defining an alunitized area on the Southwest Dome and saddle. Our group worked in the field, mapping and collecting samples eight days during the project. We collected a total of 73 samples on which further analyses would be conducted.

Sample preparation for isotopic analyses consisted of NaOH dissolution and HF dissolution of a finely powdered whole rock sample. The purpose of performing NaOH dissolution is to create a barium sulfate precipitate from alunite. The BaSO₄ precipitate is then used for ¹⁸O_{SO4} and ³⁴S analyses. A whole rock sample is dissolved in HF to acquire a pure sample of alunite. This is very important, as the remaining sample is used for oxygen isotope analysis, and the presence other minerals in the sample will yield an inaccurate result. The HF treated samples are used for extracting oxygen with the BrF₅ line. The HF treated samples are used because they are presumably pure alunite. The BrF₅ line extracts all of the oxygen from the OH site of alunite and half from the SO₄ site. The process of extracting hydrogen from a sample is performed using the hydrogen extraction line at the USGS in Denver. This was done by analyzing six whole rock samples that contained only quartz and alunite. Three separate mass spectrometers were used to measure the ³⁴S, ¹⁸O and D isotopes. Lab assistant Cyndi Brock and Dr. Robert Rye at the USGS, Denver ran the analyses. The sulfur isotope analyses were performed using the NaOH treated samples. The completed data set is shown in Table 1.

PETROGRAPHY

Petrographic analysis was completed on twenty-seven thin sections. Analyses showed fifteen samples containing an abundant amount of alunite, nine with an intermediate amount of alunite, and three relatively unaltered rhyolite samples, consisting of alkali feldspar, quartz, and biotite. The fifteen samples containing abundant alunite were the same samples thought to contain alunite after conducting the field test. This confirmed that the field test was an accurate way of preliminarily deciphering which samples contained alunite. The composition of the altered rhyolite is quartz + alunite \pm kaolinite.

Alunite [$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$] is a sulfate mineral that is usually associated with the hydrothermal alteration of volcanic rocks. It typically occurs as bladed crystals with distinct (0001) cleavage. The interference colors in thin section can reach first order blue, but are usually seen as first order yellow to red.

Alunite in the Porphyry Peak rhyolite forms in a distinctive pattern. The bulk of the alunite is found growing into voids left by alkali feldspar. The alkali feldspar was dissolved by rapid, extreme base leaching (Stoffregen, 1987). Alunite also grows in the fine-grained groundmass with quartz. The alunite is mainly confined to the voids left by alkali feldspars, indicating that there cannot be a significantly larger amount of alunite in the rock than the original amount of alkali feldspar. Mineral percentages were obtained by using the area calculation program in NIH Image. The program works much like a point count. The average percentage of alunite found in the quartz-alunite zone is ~30%.

DISCUSSION

The acid sulfate alteration in the Porphyry Peak area consists of three alteration zones: a sugary silica core, quartz-alunite zone, and slightly altered porphyry Peak rhyolite. The sugary silica and quartz-alunite zones are typically found in magmatic hydrothermal areas, as described by Rye et al. (1992). The magmatic hydrothermal environment is the only one that describes the zones of alteration as grading into propylitized wall rock. This is seen at Porphyry Peak with the relationship between the altered zones and the Porphyry Peak rhyolite. The altered rocks at Porphyry Peak contain a trace amount of pyrite. The sulfuric acid in the supergene environment uses the oxidation of pyrite for the main source of H_2S in the system. Thus, the Porphyry Peak rhyolite could not have been altered by a supergene environment.

The formation of alunite in the Porphyry Peak area occurs in bladed crystals growing into the voids of dissolved alkali feldspar. It is also seen intergrown with quartz in the groundmass. This type of growth is indicative of magmatic hydrothermal acid sulfate alteration. The unique growth of alunite in the various acid sulfate alteration environments gives an initial interpretation of the type of acid sulfate environment present at a particular location.

Stable isotope data is the most conclusive evidence for determining the specific hydrothermal environment. The given data set can be very helpful in calculating the temperature of the acid sulfate fluids. The calculated temperatures are slightly lower than expected for a magmatic hydrothermal system (200°C to 400°C). The absence of ^{34}S pyrite data account for some of the discrepancies in the values.

When $^{34}\text{S}/^{18}\text{O}$ and $^{18}\text{O}/\text{D}$ are plotted against each other, particular patterns form that indicate the type of acid sulfate environment altering the Porphyry Peak area (figs. 1 & 2). When compared to the $^{34}\text{S}/^{18}\text{O}$ and $^{18}\text{O}/\text{D}$ magmatic hydrothermal plots determined by Rye et al (1992), it is evident that the system was altered by magmatic hydrothermal fluids. For instance, the offset between the SO_4 and OH values on figure 1 reflect the difference in fractionation factors for the oxygen in each sample. The Porphyry Peak values coincide with the darkest shaded values on the Rye et al. (1992) magmatic hydrothermal plot, which indicate that the composition of the alunite was deposited from a pure magmatic source over a temperature range typical for magmatic fluids.

The $^{18}\text{O}/\text{D}$ systematics of alunite are plotted on figure 2. When compared to the $^{18}\text{O}/\text{D}$ plot for magmatic hydrothermal systems (Rye et al., 1992), the Porphyry Peak data plots in the same field. The D and ^{18}O fractionations are such that the D data of the alunite closely reflect the values of the water in the fluid. The ^{18}O values are all in the magmatic hydrothermal range except for two samples. The two analyses that plot in the meteoric water field are questionable. Since the $^{18}\text{O}_{\text{OH}}$ on the two samples plot directly below the $^{18}\text{O}_{\text{SO}_4}$ field and do follow the mixing trend of the fluid, there is reason to believe the data is incorrect. Also, one of the samples was re-tested, and the second result showed a magmatic hydrothermal fluid signature.

CONCLUSION

Stable isotope analyses of alunite in the Porphyry Peak area provide evidence that the origin of acid sulfate alteration is pure magmatic hydrothermal fluids. Location, petrographic analysis, alteration patterns, and stable isotope analyses are the main indications that the Porphyry Peak rhyolite is altered by magmatic hydrothermal fluids.

The Porphyry Peak area consists of three exogenous domes, which is an environment conducive to magmatic hydrothermal acid sulfate alteration. Other areas that are similar in topography and hydrothermal alteration are Summitville, CO (Stoffregen, 1987), and Marysvale volcanic field, UT (Cunningham et al., 1984).

Petrographic evidence for magmatic hydrothermal alteration is the type of alunite growth seen in thin section. The alunite typically grows in voids of alkali feldspar that have dissolved due to rapid, intense base leaching (Stoffregen, 1987). The voids are filled with bladed crystals of alunite, the typical type of alunite growth seen in a magmatic hydrothermal environment. Alunite also grows in the groundmass with quartz, another feature unique to magmatic hydrothermal systems. The alunite growth seen in the Porphyry Peak area is indicative of magmatic hydrothermal alteration.

The δD values for alunite clearly indicate that the fluids are magmatic hydrothermal, ranging from 57‰ to 84‰. The two values that plotted in the meteoric water range (-162‰ and -165‰) are most likely incorrect data, being contaminated during sample preparation. Also, the calculated temperature data is within the proposed temperature range at which magmatic hydrothermal fluids alter a particular area. When the stable isotope data is plotted on isotope graphs and compared to those of Rye et al. (1992), the acid sulfate environment at Porphyry Peak is clearly magmatic hydrothermal.

REFERENCES CITED

- Burbank, W. S., 1932, *Geology and Ore Deposits of the Bonanza Mining District, Colorado*: US Department of the Interior, Geological Survey, professional paper 169.
- Cunningham, et al., 1984, *Origins and Exploration Significance of Replacement and Vein-Type Alunite Deposits in the Marysvale Volcanic Field, West Central Utah*: *Economic Geology*, v. 79, p. 50 - 71.
- Rye, et al. 1992, *The Stable Isotope Geochemistry of Acid Sulfate Alteration*: *Economic Geology*, v. 87, No. 2, Mar- Apr p. 225 - 262.
- Smith & Varga, 1982, *Petrology and Geochemistry of alunite at Bonanza, Colorado: A Potential Alumina Resource and an Indicator of Possible Sulfide Mineralization at Depth*: Union Science and Technology Division, Union Oil Company of California Research Center, Brea, CA. E&P GEOL 82-8M.
- Stoffregen, R. 1987, *Genesis of Acid Sulfate Alteration and Au-Cu-Ag Mineralization at Summitville, Colorado*: *Economic Geology*, v. 82, p. 1575-1591.

Table 1. Data from ^{34}S , δD , $^{18}\text{O}_{\text{SO}_4}$, and $^{18}\text{O}_{\text{OH}}$ isotope analyses, performed at the USGS in Denver, CO.

Sample	^{34}S	δD	$^{18}\text{O}_{\text{SO}_4}$	$^{18}\text{O}_{\text{OH}}$
20-8	16.7	-72	13	8
20-10	21.5	-70	10.6	6.7
27-2.4	19.9	-162	11.7	6.3
27-2.4	19.9	-57	11.7	6.3
27-2.5	18.7	-84	-84	8.3
27-2.7	10.7	-72	-72	4.7
27-2.9	19.1	-165	12.3	7.1
19-1	20.9			
19-2	17.4			
20-7	17.8			
20-9	19.7			
22-1	15.7			
22-2	16.9			
27-2.3	17.5			
29-3	15.8			

Figure 1. $^{34}\text{S}/^{18}\text{O}$ alunite plot. Note the displacement between ^{18}O and $^{18}\text{O}_{\text{OH}}$, showing fractionation.

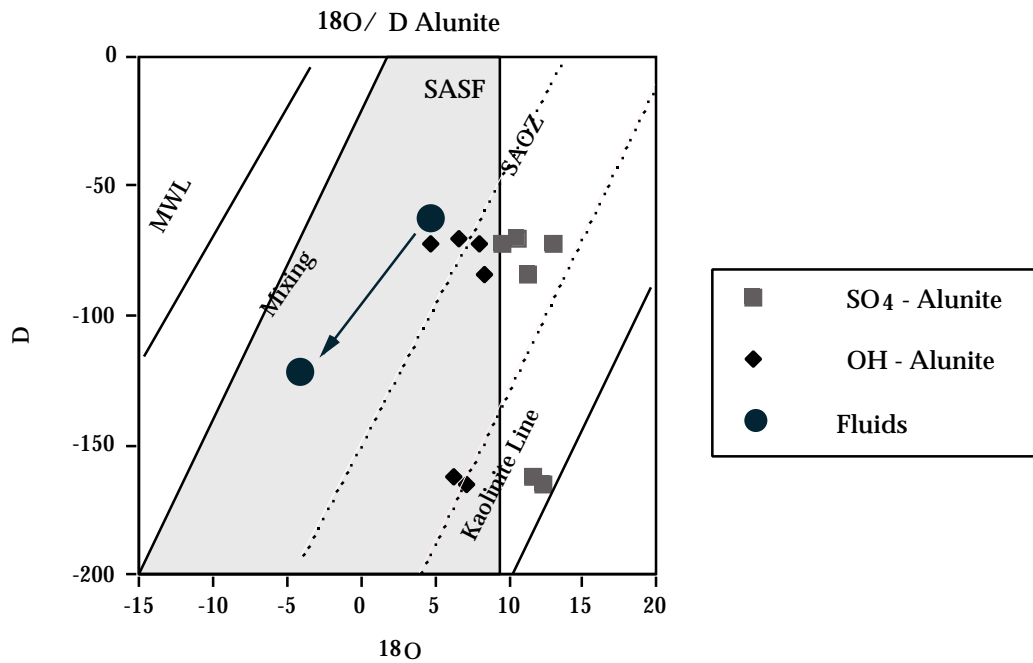
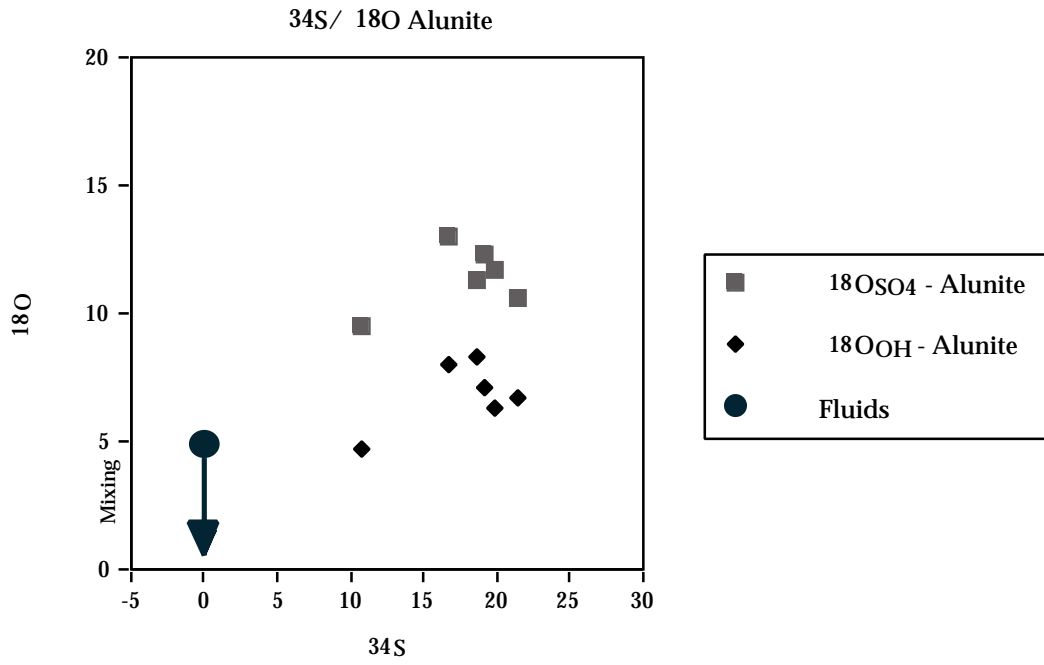


Figure 2. $^{18}\text{O}/\text{D}$ alunite plot. Note the horizontal displacement between SO_4 and OH isotopes, indicative of magmatic hydrothermal fluids. Modified from Rye et al, 1992.