

Geochemistry and alunite mineral chemistry of the acid-sulfate alteration in the Porphyry Peak rhyolites, Bonanza Caldera, central Colorado

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INTRODUCTION

The Porphyry Peak rhyolites are a series of silicic bodies found on the northern rim of the Bonanza Caldera that have been emplaced as exogenous domes late in the life of the volcanic center (Varga and Smith, 1984). Areas of the Porphyry Peak rhyolite (PPR) have undergone extreme leaching and replacement of minerals through acid-sulfate alteration. Acid-sulfate wall-rock alteration typically occurs when magmatic steam, including SO₂, is introduced into the system, and the steam then condenses creating an acid environment enriched with sulfur (Rye et al., 1992). Acid-sulfate alteration is seen as two distinct alteration zones in the PPR. The most highly altered zone, the silica zone, is characterized by the leaching of all minerals except quartz. The quartz-alunite alteration zone is characterized by the mineral alunite [KAl₃(SO₄)₂(OH)₆] replacing all alkali feldspars, and all other rock-forming minerals having been leached out except quartz and minor amounts of kaolinite. The mineral assemblage of the quartz-alunite zone and the appearance of the silica zone are characteristic of an acid-sulfate alteration due to magmatic vapors (Rye et al., 1992). Acid-sulfate alteration can be produced in three different environments; a steam-heated environment, which occurs in the upper portions of hydrothermal systems, a magmatic hydrothermal environment, which is driven by magmatic heat and has significant magmatic components in the hydrothermal fluids, and a magmatic steam environment which is dominated by a vapor phase of magmatic origin (Rye et al., 1992). Each of these environments has a specific petrological and geochemical thumbprint.

METHODS

Seventy-six samples were collected from the PPR over a large area with varying degrees of alteration (see figure 1). Thin sections were prepared for petrographic analysis from twenty-eight of the samples. Twenty of these were analyzed for major, minor and trace element data; seven from the relatively unaltered PPR, ten from the quartz-alunite zone, and three from the silica zone. Major, minor, and many trace elements were determined by x-ray fluorescence (XRF). Ten samples were further analyzed for rare earth elements (REE) by inductively coupled plasma mass spectrometry (ICP-MS). All geochemical work was performed in the labs at Michigan State by Thomas A. Vogel. Nine samples were also chemically analyzed using a JEOL JSM 6400 Digital Scanning Electron Microscope with an Oxford ISIS Energy Dispersive Spectrometer.

PETROGRAPHY

The mineral assemblage of the relatively unaltered PPR includes quartz, sanidine, and biotite with some areas of plagioclase. Groundmass makes up about 50% of the PPR and is mainly composed of quartz and alkali feldspar. The PPR also contains many quartz veins that occur along the folds with no alteration halos around the veins. Accessory minerals are hematite, rutile, and zircon. The quartz-alunite zone assemblage includes quartz, alunite, and major or minor amounts of kaolinite. Accessory minerals are rutile, zircon, pyrite and other sulfides. The alunite has variable morphologies including euhedral bladed crystals up to 1mm long (see figure 2) and extremely fine-grained laths of alunite that are intergrown with quartz in the groundmass. The euhedral bladed alunite crystals are only found replacing alkali feldspar phenocrysts. In these cases, the shape of the feldspar phenocryst is still obvious. The silica zone assemblage is comprised of fine-grained, intergrown, anhedral quartz grains with few quartz phenocrysts and contains many small voids. The only accessory minerals found are zircon, and rutile which is primarily in the form of rutilated quartz where the rutile crystals are hair-like in shape and form a crosshatched pattern (see figure 3). Rutilated quartz is the dominant form of quartz in the silica zone, but it is also found in areas of high acid-sulfate alteration in the center of the quartz-alunite zone. Based on this information it is reasonable to believe that the environments for the quartz-alunite and silica zones are similar. It has been discussed by Stoffregen (1987) that the silica zone is produced by further leaching of the quartz-alunite zone of all primary rock-forming minerals except quartz. This complete leaching of phenocrysts produces the voids found in the silica zone (Rye et al., 1992). The silica zone, therefore, generally occurs at the center and grades outward into the quartz-alunite zone (Hayba et al., 1985). The reason this is not seen in the PPR most likely due to fracture controlled preferential movement of the acid-sulfate waters. The hydrothermal fluids would be more concentrated in these

areas so extreme leaching of the wall rock in the silica zone could have been produced very locally with little quartz-alunite surrounding it.

GEOCHEMISTRY

All geochemical data for the hydrothermally altered samples were normalized to the average geochemical data from the seven relatively unaltered PPR. This allows us to analyze the deviations in the whole rock data for altered rock in the alunite and silica zones from their possible original values (see figures 4-6). The whole rock and REE geochemical data display the mobility of the elements in the quartz-alunite zone and the silica zone. The major, minor, and trace element data show extreme leaching of sodium, calcium, and rubidium in the quartz-alunite zone, while strontium is enriched. The strontium enrichment is because alunite can take strontium into its crystal structure making the strontium endmember of alunite Svanbergite $[(\text{SrAl}_3(\text{SO}_4)(\text{PO}_4)(\text{OH})_6)]$ (Getahun, 1994). The silica zone shows leaching of all elements except for SiO_2 , titanium, and zirconium, which corresponds to the assemblage of the silica zone. In the REE data the quartz-alunite zone shows minimal, yet variable, leaching of both heavy and light REEs. In contrast, the one silica zone sample shows that light REEs were clearly mobile in the system, but heavy REEs were less mobile and had similar mobilities compared to the quartz-alunite zone.

ALUNITE MINERAL CHEMISTRY

The composition of the alunite is variable because there is a solid solution between alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$ and natroalunite $[\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6]$. The euhedral alunite crystals have relatively pure alunite with up to 10% sodium replacement. The fine grained alunite crystals have up to 17% sodium replacement, but there is also a 10% substitution of phosphate for sulfur. The alunite found in sample 29-3, which is located adjacent to the silica zone, has much more natroalunite with up to 65% of the potassium replaced by sodium. The highest-temperature occurrences of natural alunite are also usually high in sodium (Stoffregen and Cygan, 1990). Therefore, the alunite in sample 29-3 was produced in a hotter environment, which coincides with the alteration being fracture controlled. These fluids confined in fractures would be able to reach a higher temperature. The slightly higher sodium replacement in the fine-grained alunite may also be due to hotter temperatures. The occurrence of phosphate in the fine-grained alunite is a unique attribute of acid-sulfate alteration assemblages produced in a magmatic hydrothermal environment (Rye et al., 1992).

CONCLUSIONS

The petrology and geochemistry of this suite of altered rocks is characteristic of hydrothermal alteration due to magmatic vapors. The magmatic hydrothermal environment includes all hydrothermal systems that are driven by magmatic heat and have a significant amount of magmatic vapors in the hydrothermal fluids (Rye et al., 1992). In this environment sulfuric acid is produced by the disproportionation of SO_2 according to the reaction $4\text{SO}_2 + 4\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + \text{H}_2\text{S}$ (Rye et al., 1992). This creates an acidic vapor plume enriched with sulfur that alters the wall-rock when it condenses (Rye et al., 1992). For the silica zone to form, which is a unique characteristic found in magmatic hydrothermal environments, the leaching of aluminum must occur, which requires a pH of 2 or below at a temperature of 250°C (Stoffregen, 1987). There is evidence using petrography, mineral chemistry, and whole rock geochemistry that the PPR has been submitted to a magmatic hydrothermal environment in the past.

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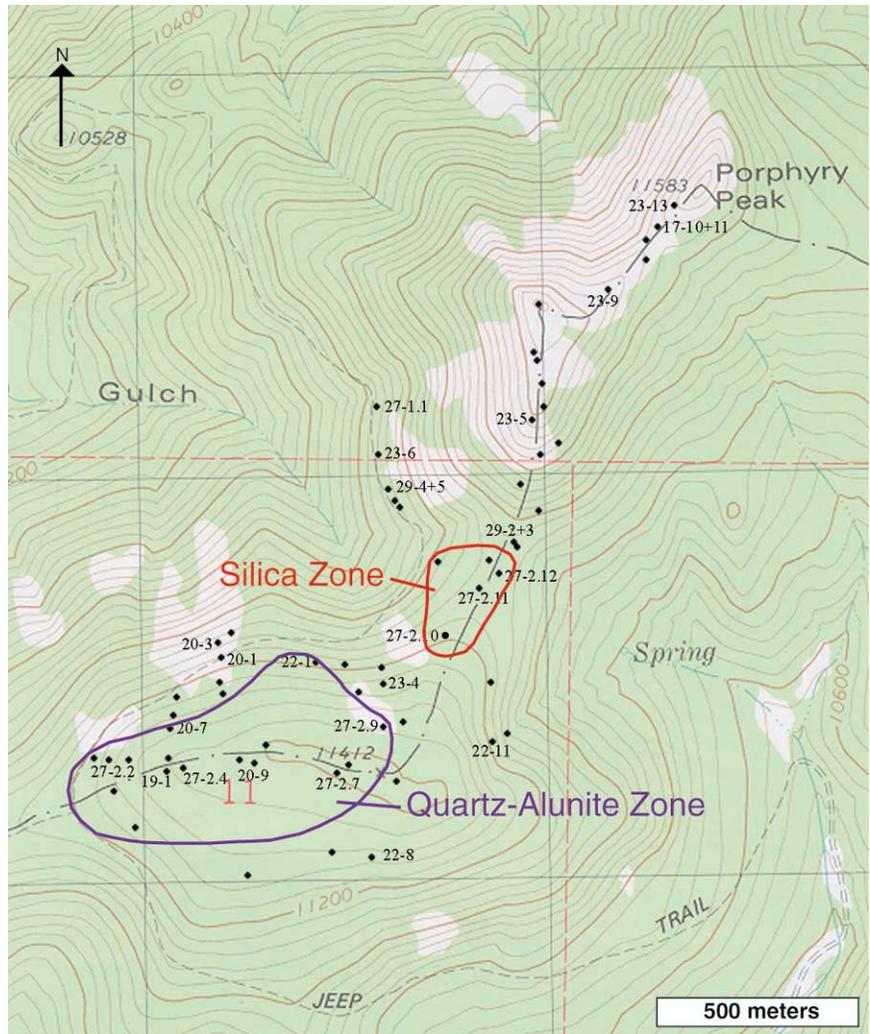


Figure 1. Map of sample locations, quartz-alunite zone, and silica zone in the Porphyry Peak area. From the Bonanza quadrangle in central Colorado.

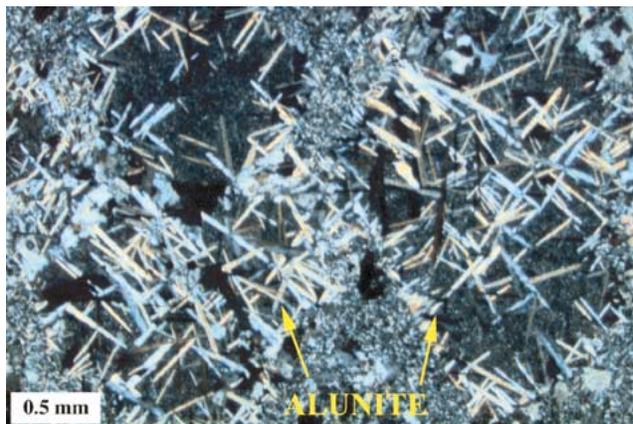


Figure 2. Photomicrograph of euhedral blade-like alunite crystals replacing sanidine phenocrysts from sample 20-7.

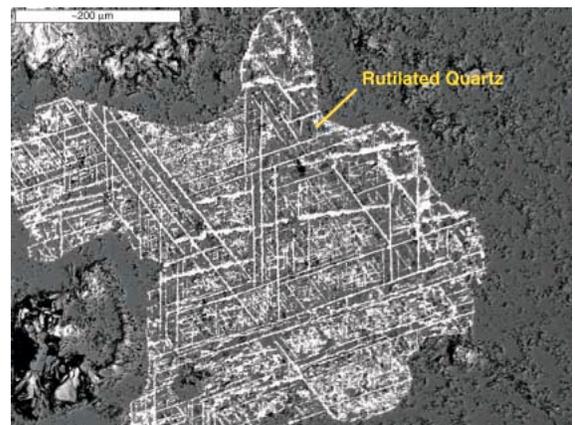


Figure 3. SEM image showing rutiled quartz from sample 27-2.4. Image taken at a working distance of 15mm, an accelerating voltage of 20kv, and a magnification of 180x.

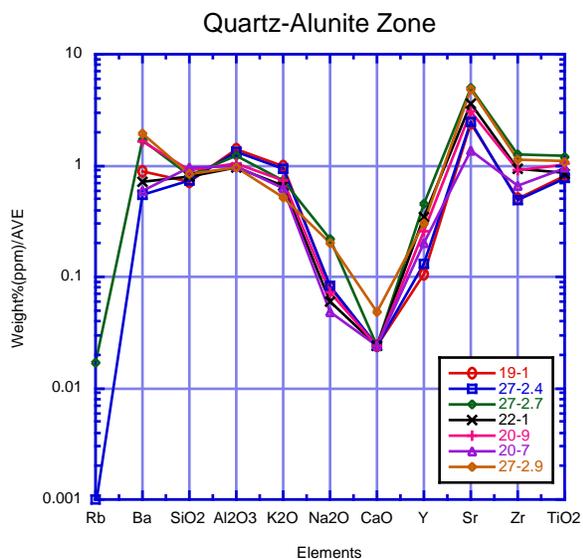


Figure 4. Whole rock geochemistry of major and trace elements in the quartz-alunite zone normalized to (or divided by) the average relatively unaltered PPR geochemistry (AVE). This shows what elements have been depleted or enriched with alteration.

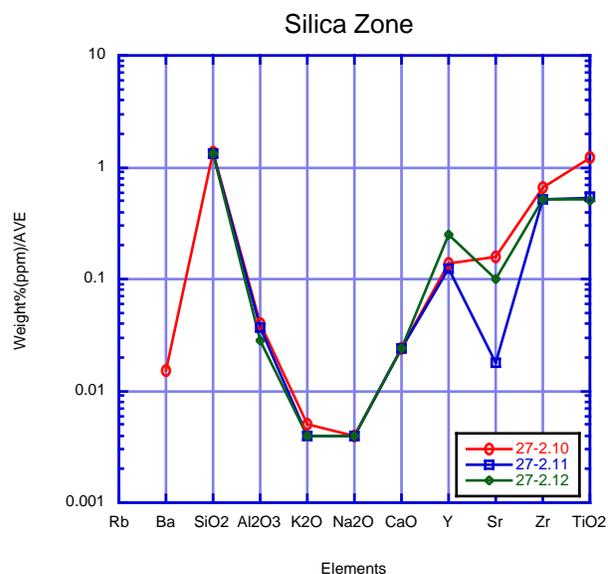


Figure 5. Whole rock geochemistry of major and trace elements in the silica zone normalized to the average relatively unaltered PPR geochemistry.

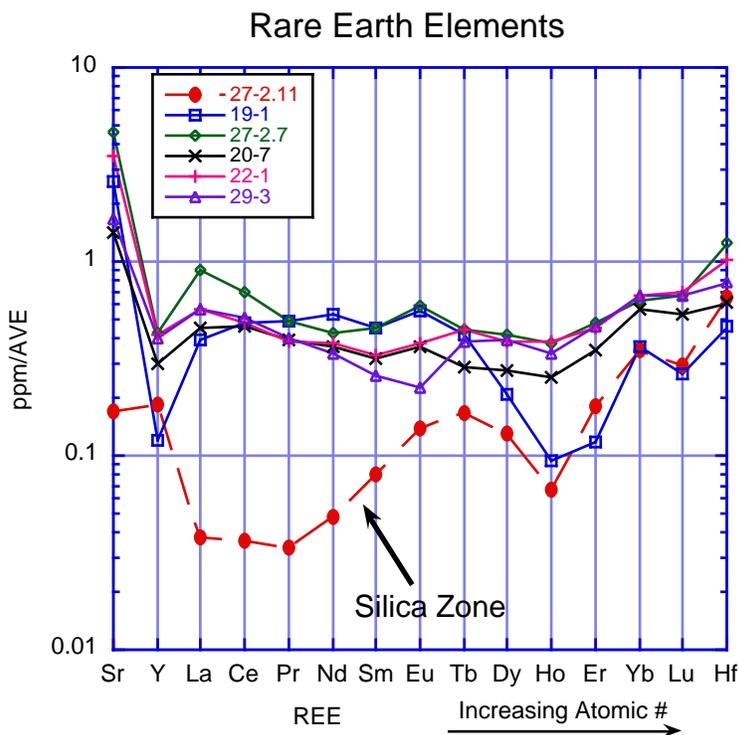


Figure 6. Whole rock geochemistry of REEs normalized to the average relatively unaltered PPR geochemistry. This graph shows the data for the quartz-alunite zone and one sample from the silica zone.