

ACID-SULFATE ALTERATION OF BASALT IN FUMAROLIC ENVIRONMENTS ON EARTH AND MARS. T. McCollom¹, B. Moskowicz², T. Berquó³, and B. Hynek¹, ¹Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder CO 80309, mcollom@lasp.colorado.edu, ²Institute for Rock Magnetism, University of Minnesota, Minneapolis, MN 55455, ³Department of Physics, Concordia College, Moorhead, MN 56562.

Introduction: Numerous observations made at Mars over the last couple of decades by orbiting spacecraft and landers have documented the widespread occurrence of sulfate-rich rocks across the planet. While a number of scenarios have been proposed to explain the origin of these deposits, it appears likely that at least some formed by acid-sulfate alteration of martian basalt in volcanic settings [e.g., 1, 2]. In an effort to place constraints on chemical and mineralogical processes that might have given rise to sulfate-rich rocks in volcanic environments on Mars, we are conducting a study of acid-sulfate alteration of basalt at terrestrial fumaroles, using a combination of field work, laboratory experiments, and numerical modeling.

Cerro Negro, a terrestrial analog for acid-sulfate alteration on Mars: As part of our study, we examined the mineral and chemical evolution of basalt during acid-sulfate alteration at Cerro Negro volcano, Nicaragua (CN) [3]. At this site, basaltic tephra, composed of phenocrysts of plagioclase, augite, and olivine embedded within a glassy matrix, are actively undergoing acid-sulfate alteration by SO₂-bearing steam around fumaroles. Examination of altered basalt cinders shows that igneous phenocrysts rapidly decompose during the initial stage of alteration, while the glass remains structurally intact. Primary alteration products are limited to amorphous silica, gypsum, and natroalunite/natrojarosite, with minor amounts of iron oxides or oxyhydroxides (Fig. 1). Crystalline silicate phases, including phyllosilicates, are rarely observed. During alteration, Na, Mg, Ca, Fe, and Al are progressively leached, resulting in deposits that become almost entirely SiO₂. Some deposits then undergo a secondary enrichment in Ca and S in the form of gypsum.

The natroalunites/natrojarosites observed at CN are particularly noteworthy for both their morphology and chemical composition. The minerals are fine-grained (<20 μm) with a pseudocubic habit. Although members of the jarosite subgroup with similar morphology have been identified in a few volcanic settings [4-6], minerals of this group with pseudocubic habit are more commonly associated with low-temperature environments (<50 °C) [7]. Their chemical compositions are highly variable, indicating local control on composition, with Fe and Al contents spanning a range of values intermediate between natroalunite and natrojarosite (Fig. 2). Such intermediate compositions have only rarely been reported from natural systems [8].

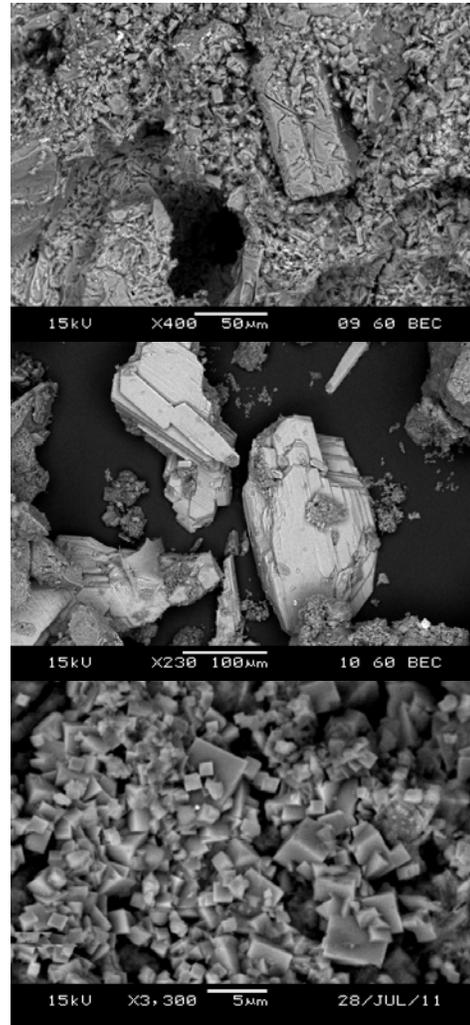


Figure 1. Predominant alteration phases generated during acid-sulfate of CN basalt, including amorphous SiO₂ (top; everything in field of view is composed predominantly of Si & O), prismatic gypsum (middle), and pseudocubic Fe-bearing natroalunite (bottom).

Laboratory study of acid-sulfate alteration: To further examine mineral and chemical alteration pathways at Cerro Negro, we conducted laboratory experimental studies of basalt alteration in parallel with the field work. In these experiments, fresh CN basalt cinders were heated with 1 M sulfuric acid at 145 °C for 7 to 56 days at a fluid:rock ratio of ~4. The experiments produced a suite of minerals similar to those observed at the field site, with amorphous Si-rich gel, anhydrite,

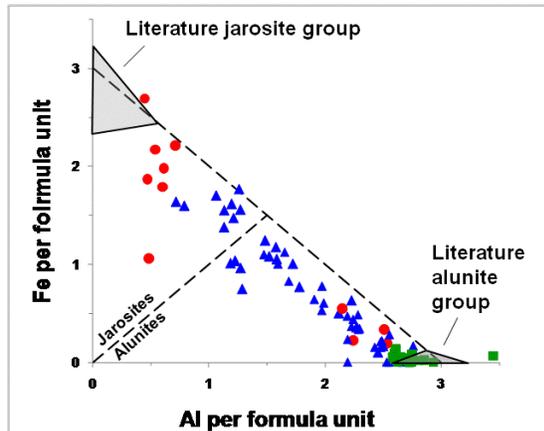


Figure 2. Relative molar proportions of Fe and Al in alunite-jarosite group minerals from three acid-sulfate altered deposits from Cerro Negro.

and Fe-bearing natroalunite as the primary products, along with small amounts of Fe oxides/oxyhydroxides and Mg-sulfates. As in the field samples, crystalline silicates, including clay minerals, were not observed.

Mössbauer analysis: Analysis of field and experimental samples by Mössbauer (MB) spectroscopy revealed a component of the alteration assemblages with a signature that closely resembles jarosite, even for samples containing only Fe-bearing natroalunite with a small amount of Fe, suggesting that Fe-bearing natroalunite produces a MB signal similar to jarosite (Table 1). To confirm this possibility, we synthesized pure Fe-bearing natroalunites and found that substitution of only a few mole % of Fe for Al in the structure produced a MB signal very similar to jarosite.

Table 1. Mössbauer parameters for the alunite-jarosite group component of field and natural samples. Shown for comparison are range of values for natural jarosites and a component from the Burns Formation on Mars inferred to be jarosite [data from 9 and refs. therein].

	IS (mm/s)	QS (mm/s)
Natural jarosites [9]	0.33- 0.40	1.01- 1.25
Altered CN basalt	0.38	1.06
Experimental acid-sulfate	0.40	1.14
Synthetic Fe-bearing natroalunite (mole% Fe = 20)	0.38	1.23
Burns Formation, Mars [9]	0.37	1.21

Numerical models of acid-sulfate alteration: To aid in interpretation of the field and laboratory results, we also developed numerical geochemical models of acid-sulfate basalt alteration. The models are designed to monitor the changing mineral composition of CN basalt during reaction with sulfuric acid as a function of the extent of reaction. The models are performed

using the EQ3/6 software package with a database customized to expand coverage of sulfate minerals, including a solid-solution model for the alunite-jarosite mineral group. Models that are allowed to reach complete thermodynamic equilibrium result in a predicted alteration mineralogy that differs substantially from the field and laboratory samples, consisting of phyllosilicates, anhydrite, and end-member natroalunite. However, disequilibrium models performed with the assumptions that: (a) igneous silicate phenocrysts (plagioclase, augite, olivine) react much faster than basaltic glass, and (b) there are kinetic inhibitions to the precipitation of Si- and Al-bearing phyllosilicates, as well as hematite and goethite, result in predicted alteration assemblages composed of amorphous silica, anhydrite (or gypsum at lower temperatures), and Fe-rich natroalunite that closely resemble mineral assemblages found in the field samples and laboratory experiments.

Implications for Mars: The results of our study indicate that the initial stages of acid-sulfate alteration of martian basalt in fumarolic environments should result in rapid reaction of crystalline igneous phases while the glass remains largely intact, and should result in an alteration mineral assemblage dominated by amorphous silica, sulfate minerals, and remnant glass. Numerical models based on the same constraints used to model the terrestrial system but substituting a martian basalt composition predict an alteration assemblage consisting of amorphous silica, anhydrite or gypsum (depending on temperature), Fe-bearing natroalunite, and kieserite. If Fe-oxides/oxyhydroxides are allowed to precipitate, hematite joins the predicted alteration assemblage, and the natroalunite becomes depleted in Fe. In addition, the MB analyses indicate that Fe-bearing alunite group minerals should be considered as a possible alternative for the MB component in rocks from Meridiani Planum previously ascribed to jarosite.

References: [1] Squyres S. W. et al. (2007) *Science*, 316, 738–742. [2] Yen A. S. et al. (2008) *JGR* 113, doi:10.1029/2007JE002978. [3] Hynek B. M. et al. (2011) *Geol. Soc. Amer. Spec. Paper* 483, 279–285, doi:10.1130/2011.2483. [4] Morris R.V. et al. (1996) in *Mineral Spectroscopy: A Tribute to Roger G. Burns*, 327-336. [5] Zimbelman D. R. et al. (2005) *Chem. Geol.* 215, 37-60. [6] Deyell C. L. et al. (2005) *Chem. Geol.* 215, 185-218. [7] Stoffregen R. E. and Alpers C. N. (1992) *Am. Min.* 77, 1092-1098. [8] Stoffregen R. E. et al. (2000) in *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance*, 453-479. [9] Morris R. et al. (2006) *JGR*, 111, doi:10.1029/2006JE002682 (2006).