

**COMBINED EXPERIMENTAL AND THEORETICAL STUDY OF ACID-SULFATE ALTERATION OF BASALT FOR INTERPRETATION OF SULFATE-RICH DEPOSITS ON MARS.** T. M. McCollom<sup>1</sup>, E. Marcucci<sup>2</sup>, and B. M. Hynek<sup>1,2</sup>, <sup>1</sup>Laboratory for Atmospheric and Space Physics, CB 392, University of Colorado, Boulder 80309, mcollom@lasp.colorado.edu, <sup>2</sup>Department of Geologic Sciences, University of Colorado, Boulder 80309.

**Introduction:** Orbiters and landers on Mars have documented widespread occurrences of sulfate-rich rocks that have apparently been formed under acidic conditions [1-3]. One possible mechanism for formation of these deposits is acid-sulfate alteration of basalt in a volcanic hydrothermal setting [e.g., 3, 4]. We are investigating acid-sulfate alteration at Cerro Negro volcano, Nicaragua, as a terrestrial analog of processes that may have occurred on Mars (for a full description of this location, see presentation by Marcucci et al., this meeting). As part of this investigation, we are conducting laboratory experiments to study reaction pathways during acid-sulfate alteration of pristine Cerro Negro basalt. In parallel, we are constructing numerical geochemical models to aid in interpretation of the experiments as well as samples collected in the field at Cerro Negro. A primary goal of these combined studies is to place constraints on the factors controlling the chemistry and mineralogy of alteration products during acid-sulfate alteration that can be used to help interpret conditions present during formation of sulfate-rich deposits on Mars.

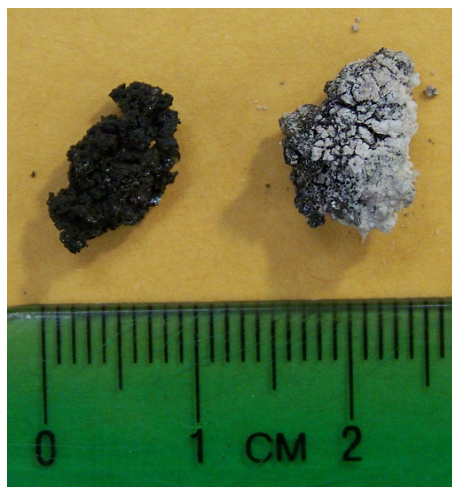
**Experimental studies:** Initial experiments were conducted by reacting cm-size basalt cinders (Fig. 1) with 1 M H<sub>2</sub>SO<sub>4</sub> at ~145°C in stainless steel reactors with Teflon inserts (Parr® acid-digestion vessels) for

periods of up to 90 days. The basalt was obtained from a recent eruption (1999) at Cerro Negro, and consists of larger crystals of plagioclase and smaller crystals of olivine and augite embedded within a glassy matrix (approx. 26% plag., 9% augite, 5% olivine, 59% glass/microcrystals; La Femina et al., 2004). After reaction, the minerals were examined by SEM/EDS and fluids analyzed by ICP.

Following reaction, the altered basalt cinders were typically surrounded by an opaque, light gray gel, that dried to a white solid (Fig. 1). Examination of the solids revealed that, even after reaction of only a few weeks, no remnants remained of the original plagioclase phenocrysts, while the glass showed little evidence of alteration. Major reaction products included gypsum, alunite, and amorphous silica (Fig. 2). The alunite contained small amounts of Na and Fe. Fe-oxides were very rare. No evidence of phyllosilicates was found.

**Geochemical models:** Numerical geochemical models of basalt alteration are being conducted in parallel with the experiments in order to help interpret the results and to allow extrapolation to martian rock compositions. The models are performed with the computer programs EQ3/6 and Geochemist's Workbench (GWB). Calculations performed with GWB with the thermo.com.V8.r6+.dat database indicate that complete equilibration of the experiments should result in solids composed of quartz, anhydrite, alunite, and diaspore, with most of the Al, Mg, and Fe from the rocks remaining in solution. If the glass component is prevented from reacting in the models, the models predict that complete reaction would result in solids composed of quartz, anhydrite, and trace hematite, while all Al remains in solution. The models show fairly good agreement with the experiments, with the proviso that gypsum forms in lieu of anhydrite. The lack of predicted formation of alunite in the models suggests that either some Al may have dissolved from the glass, or that the thermodynamic data for dissolved Al species are inaccurate. We are working to improve the model fits to experimental results with addition of kinetic data and inclusion of solid solutions.

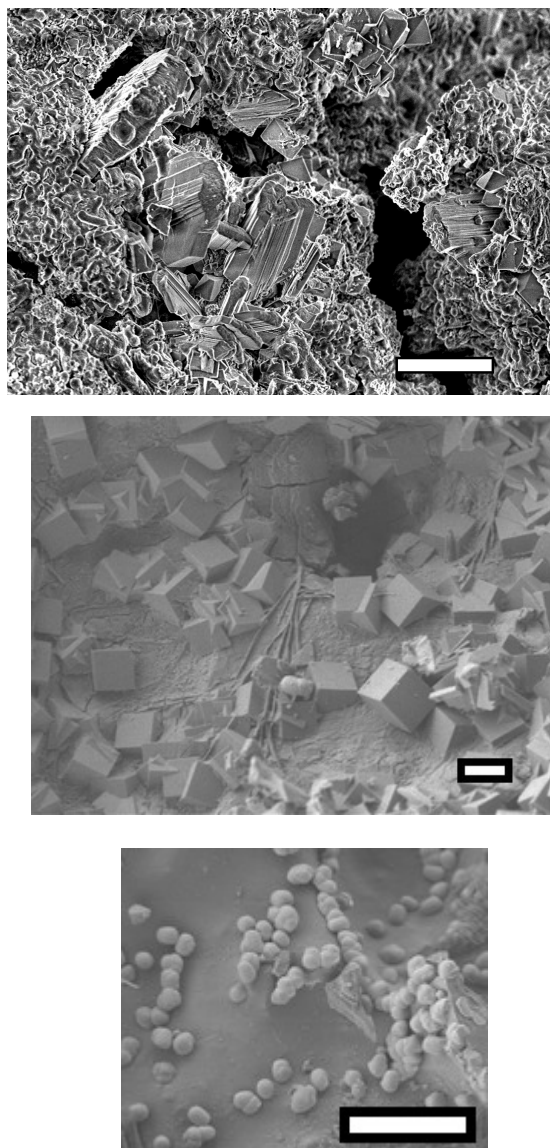
An initial model to investigate how martian basalt would alter under the same conditions (temperature, fluid:rock ratio, and total H<sub>2</sub>SO<sub>4</sub> in the system) using



**Figure 1.** Cerro Negro basalt cinders before (left) and after (right) reaction with sulfuric acid at 147°C for 28 days.

the composition of the rock “McKittrick” measured by the Opportunity rover [5] to represent martian basalt, predicts solid products would include quartz, hematite, anhydrite, alunite, kaolinite and kieserite, with a fluid containing substantial dissolved Mg, Na, and Al in addition to sulfate. Evaporation of the fluid results in precipitation of additional kieserite, thenardite, and hydrated Al-sulfate. These predictions exhibit fair agreement with the inferred mineralogy of martian sulfate deposits [e.g., 3, 6]. Using the experimental studies to calibrate the models, we should be able to make increasingly accurate predictions and use the models to constrain conditions present in sulfate-forming environments on early Mars.

**References:** [1] Gendrin A. et al. (2005) *Science*, 307, 1587-1591. [2] Murchie, S et al. (2007) *JGR*, 112, E05S03. [3] Squyres S. W. et al. (2007) *Science*, 316, 738-742. [4] McCollom T. M. and Hynek B.M. (2005) *Nature*, 438, 1129-1131. [5] Rieder R. et al. (2004) *Science*, 306, 1746-1749. [6] Glotch T. et al. (2006) *JGR*, 111, doi:10.1029/2005JE002672.



**Figure 2.** Examples of mineral products generated during experimental acid-sulfate alteration of Cerro Negro basalt. (top) Calcium sulfate minerals, probably gypsum. (middle) Alunite. (bottom) Iron oxide. Scale bars are 50  $\mu\text{m}$  in top image and 10  $\mu\text{m}$  in other images.