

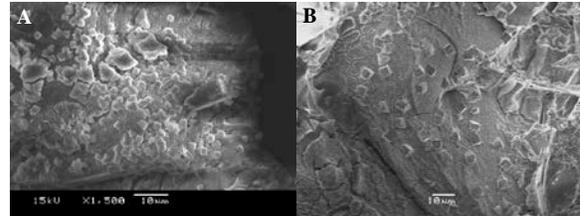
**ACID-SULFATE WEATHERING OF CERRO NEGRO BASALT: AN EARLY MARS ANALOG.** E. C. Marcucci<sup>1,2</sup>, B. M. Hynek<sup>1,2</sup> and T. M. McCollom<sup>2</sup>, <sup>1</sup>Department of Geological Sciences, UCB 399, University of Colorado, Boulder, CO 80309 (emma.marcucci@colorado.edu), <sup>2</sup>Laboratory for Atmospheric and Space Physics, 3665 Discovery Drive, University of Colorado, Boulder, CO 80303.

**Introduction:** Understanding the acid-sulfate weathering reactions at Cerro Negro, Nicaragua gives insights into the formation of sulfates found on Mars by orbiting and landed missions [1, 2, 3]. These sulfate deposits are widespread and occur in diverse geological settings. It is generally understood that the sulfates are forming through acid-sulfate weathering; however, the specific environments may vary with location. Here we discuss alteration in a hydrothermal, volcanic environment, using the early Mars analog, Cerro Negro, Nicaragua.

Cerro Negro (CN) is a young volcanic system in Nicaragua, which is an ideal early Mars analog for two reasons: its young, recorded history allows for realtime observation of alteration and the basalt chemistry closely matches that of unaltered Martian bedrock [4] and secondary products [1, 4]. CN also hosts a complex photosynthetic endolithic community and microorganisms subsisting on S-redox reactions, making it relevant to habitability of acid-sulfate volcanic systems on early Mars [5].

**Mineral and CN Basalt Experiments:** To more completely understand the reaction pathways occurring at the field site, we designed a series of experiments, which broke the basalt into component minerals—plagioclase, pyroxene, olivine, and obsidian—and reacted each with 1M sulfuric acid over varying durations, fluid:rock ratios, and temperatures. Solid and fluid products were analyzed with x-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The experiments were accompanied by corollary thermodynamic models. Dominant alteration and evaporitic secondary minerals for each mineral type are: anhydrite and Mg-sulfate for pyroxene; natroalunite, gypsum, and Al-Si-SO<sub>4</sub> gel for plagioclase; Mg-sulfate surface coatings and Fe-O spheres for olivine; obsidian has little to no alteration. The results of these individual mineral experiments and models demonstrated that secondary mineralogy was controlled by primary mineralogy and not parameter variations. The changes due to duration, fluid:rock ratio, and even temperature, manifested in microscopic changes, including crystal size, shape, and fluid:rock ratio (Figs. 1, 2) [6].

To synthesis a story of whole rocks and compare it to individual minerals, we are now in the process of running experiments on basalt cinders from the 1999



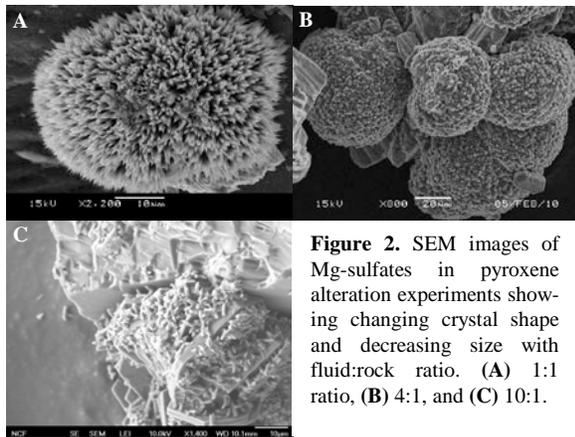
**Figure 1.** SEM images of plagioclase alteration experiments demonstrating change in natroalunite abundance. (A) 1:1 experiments have more than (B) 4:1 set ups. No natroalunite has been observed in 10:1 experiments.

Cerro Negro eruption, following the same experimental set up for duration and fluid:rock ratios that we used for the mineral experiments, and run at 65°C. The 3 and 12 day experiments, for fluid:rock ratios of 1:1, 4:1 and 10:1, have recently finished and the 30 and 60 day experiments will be completed in the next month.

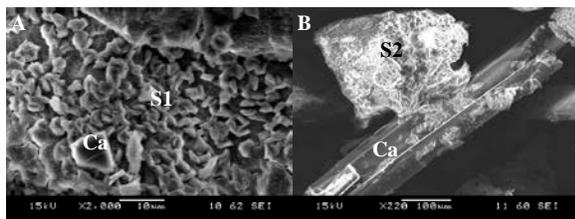
Overall the alteration of the CN 1999 basalt, closely matched that of the plagioclase experiments, including a prominent Si gel layer, Ca-sulfate, and complex sulfates. For the 4:1 and 10:1 ratios, the dominant peaks in the XRD spectra were identified as primary basalt material, with additional peaks identified as gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). This is consistent with Ca-sulfate crystals observed with SEM/EDS. In 1:1 experiments, gypsum XRD peaks were not present, but crystals were seen in SEM/EDS (Fig. 3). This discrepancy is likely due to smaller quantities of precipitated Ca-sulfate in the 1:1 set ups, below the XRD detection limit. The fact that XRD detected gypsum, and not anhydrite as would be expected from Geochemist's Workbench (GWB) models, may be due to conversion as products cool or to remnant evaporitic deposits from incomplete rinsing. Additional secondary products were observed in SEM, which have yet to be identified by name. The composition, as indicated by EDS, includes more complex sulfates with Mg-Al and Al-Fe-Na (Fig. 3). These could be analogous to the natroalunite that we observed in individual plagioclase experiments [6]. These minerals are consistent with GWB models, which indicate anhydrite, natroalunite/alunite/jarosite, hematite, and amorphous SiO<sub>2</sub>, as primary minerals-specific quantities and combinations vary with fluid:rock ratio. The models also indicated phyllosilicates. It is difficult to identify phyllosilicates in XRD, which could be why we do not see them in our experimental products. Alternatively, they may be kinetically inhibited, which the models do not take into account.

**Conclusion:** Acid-sulfate alteration is a rapid and extensive process throughout all parameter variations. In mineral experiments, the primary mineral is the dominant influence dictating the secondary mineralogy that forms, while variation in duration, fluid:rock ratio, and temperature affect microscopic features, such as, the size, shape, and abundance of crystals. When evaporation is included in the alteration process, the experiments, GWB models, and Martian observations are in good agreement.

Experiments with whole rock CN basalt continue the trend of only microscopic changes due to duration and fluid:rock ratio variations. The secondary products of these experiments seem to indicate that plagioclase weathering is the dominant process, producing similar gels, Ca-sulfate (gypsum), and complex sulfates.



**Figure 2.** SEM images of Mg-sulfates in pyroxene alteration experiments showing changing crystal shape and decreasing size with fluid:rock ratio. (A) 1:1 ratio, (B) 4:1, and (C) 10:1.



**Figure 3.** SEM images of CN 1999 basalt alteration experiments. (A) From the 4:1 12 day experiment, with Ca-sulfate (Ca) and an Fe-Al-Na sulfate (S1). (B) From the 4:1 1 day experiment, containing Ca-sulfate and Mg-Al sulfate (S2).

Widespread sulfate deposits observed on Mars suggest a variety of formation environments. Understanding the formation environment proves information on regional evolution and habitability. Our experiments on volcanic, hydrothermal alteration indicate that change due to different paleoconditions is likely seen on the microscopic level, and that plagioclase weathering is kinetically the fastest. This information will provide a framework for the interpretation of Mars data from past missions and the upcoming mineralogical and microscopic work from the Mars Science Laboratory.

**References:** [1] Gendrin A. et al. (2005) *Science*, 307, 1587-1591. [2] Murchie S. et al. (2009) *JGR*, 114, E00D07. [3] Squyres S. W. et al. (2007) *Science*, 316, 738-742. [4] Hynek B. et al. (2011) *GSA Spec. Pub.: Planetary Analogs* 483. [5] Hynek B. et al. this conference. [6] Marcucci E. et al. (2011) LPSC XXXXII, Abstract # 1521.