

ACID-SULFATE WEATHERING EXPERIMENTS AND THE EFFECTS OF FLUID:ROCK RATIO: AN EARLY MARS ANALOG. E. C. Marcucci^{1,2}, B. M. Hynek^{1,2}, and T. M. McCollom², ¹Department of Geological Sciences, UCB 399, University of Colorado, Boulder, CO 80309, ²Laboratory for Atmospheric and Space Physics, UCB 392, University of Colorado, Boulder, CO 80309.

Introduction and Motivation: Observations of the Martian surface by the Mars Express OMEGA and the Mars Reconnaissance Orbiter CRISM instruments, and the Mars Exploration Rovers Spirit and Opportunity have identified numerous deposits of sulfate-rich bedrock in diverse geological settings [1-3]. The specific formation mechanisms of such deposits are currently not well-constrained and probably vary geographically, but many of these deposits may have formed through some mechanism of acid-sulfate weathering of basalt-like mineralogy. One proposed mechanism for the sulfate-rich deposits is the high temperature alteration of Martian basalt by sulfur-rich vapors [1, 4]. Due to high initial heat flux and transient heating from impactors early in Mars' history, it is likely that hydrothermal alteration was widespread. Cerro Negro, Nicaragua represents such an analogous terrestrial system with high temperature, low pH, and parent rock lithology closely matching that of unweathered Martian basalt and SNC meteorites [5]. In order to fully characterize this system, we are conducting a suite of experiments investigating the affect of temperature and fluid:rock ratio on formation of secondary minerals, as well as, the contributions deriving from the primary minerals. The experiments seek to understand the geochemical weathering pathways of this terrestrial system, which will in turn provide insight into the geological evolution and astrobiological potential of early Mars.

Methodology: In the experiments, we broke Cerro Negro basalt into its component minerals and weathered each one individually. Cerro Negro composition was taken from [6] and [7]. We ran experiments in which bytownite, augite, olivine ($Fe_{0.88}$), quartz, and glass were reacted with 1 M H_2SO_4 at 65°C in Teflon acid digestion vessels. Minerals were prepared by grinding and sieving to a grain size of 212-106 microns, then rinsing and sonicating in ethanol to remove excess small pieces. The experiments were run in a time series ranging from 3-60 days and with varying fluid:rock ratios—1:1, 4:1, and 10:1.

At the termination of each experiment a fluid sample was taken and diluted with deionized water for analysis with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Solid products were analyzed with x-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) to characterize the chemical and mineralogical composition of the alteration. Geochemical modeling with Geochemist's Workbench (GWB)

is being used to help interpret the laboratory experiments [8].

Results: Visible and/or microscopic alteration is immediately evident in all samples. Visible alteration includes elongated crystals forming on top of augite grains, a gel layer over bytownite, and a gel layer and color change from light green to orange in forsterite. Analysis with XRD and SEM/EDS show sulfate minerals are present even in the shortest timestep.

In the 4:1 fluid:rock ratio experiments (Fig. 1), the same suite of minerals is present in the shortest and longest timesteps. Alteration of augite results in abundant anhydrite and Mg-sulfate minerals (in several crystalline forms); whereas, bytownite alteration produces gypsum and an Al-SO₄-Si phase (likely from the dried gel). The Ca-sulfate in each experiment was a single form, anhydrite or gypsum, identified by XRD. All forsterite experiments performed thus far exhibit extensive surface alteration, which EDS identifies as Mg-sulfate. Although no crystalline forms are evident in SEM. XRD identified the presence of hydrated sulfates, possibly starkeyite and hexahydrate. Very little alteration is seen in experiments with obsidian, but there are sporadic microcrystals of Ca- and Fe-sulfate. No alteration products are seen in quartz experiments.

The complete time series of experiments for the 10:1 and 1:1 are still in progress; however, analysis of timesteps completed thus far show the same type of secondary minerals but new crystalline forms are present in augite and bytownite. The minerals formed in the 1:1 experiments are extensive (Fig. 2A, C), but those in the 10:1 experiments (Fig. 2B, D) are smaller in size and abundance than the ones in other fluid:rock ratios, as characterized in the SEM images. Additionally, visible changes in the 10:1 experiments are less. Elongated crystals are not observed in augite experiments and minimal gel forms on bytownite. The forsterite sample in the three day experiment had white precipitates in the higher fluid:rock ratio set; whereas, they were orange in the lower fluid:rock ratio sets and longer timesteps for 10:1.

Geochemical models representing these experiments are in early stages but preliminary results, and those from [10], indicate general agreement with experimental products (Table 1). Using the React program within GWB, reactions are set up with experiment parameters of temperature and relative amounts of solids and water. To most accurately represent the composition of minerals, reactants were entered as oxides. The

first predicted alteration minerals for augite and bytownite are silica and anhydrite (e.g. Fig. 3). In the augite model, as the reaction progresses silicates precipitate; however, this is at higher pH than the experiment described above. Comparing experimental sulfate concentration with the model shows that only the first twenty percent of the reaction progress is representative of the augite experiment. Notably missing from the model are Mg-sulfates. This could be a function of saturation with silica and hydroxides as the system evolves, kinetics not yet been introduced into the model, or accuracy of thermodynamic data. The bytownite experiments are represented by about thirty percent of the reaction progress (Fig. 3). The model also predicts the formation of natroalunite, which has been seen in the experiments and field.

Conclusions: The suite of experiments being used to characterize the Cerro Negro system shows that type and crystalline form of secondary minerals precipitated is affected by the primary mineral and the fluid:rock ratio. Extensive alteration occurs even in the shortest experiments and the secondary mineralogy generally agrees with field samples, computer models, and Mars observations. While the types of secondary minerals produced for each primary mineral is the same in the different fluid:rock ratio experiments, there are differences in the crystalline form, size, and abundance of each mineral.

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] McCollom T. M. and Hynke B.M. (2005) *Nature*, 438, 1129-1131. [5] Hynke, B. M. et al. (2010) *GSA Spec. Pub.: Planetary Analogs* (in review). [6] Walker J. A. and Carr, M. J. (1986) *GSA Bulletin*, 97, 1156-1162. [7] Roggensack K. et al. (1997) *Science*, 277, 1639-1642. [8] Bethke, C.M. and Yeakel, S. (2009) *GWB*, Ver. 8. [9] Marcucci E. M. et al. (2010) LPSC XXXXI, Abstract #2167. [10] McCollom T. M. et al. (2010) LPSC XXXXI, Abstract #1380. [11] Bibring, J.P. et al. (2006) *Science*, 312, 400-404. [12] Ehlmann, B.L. (2009) *JGR*, 114, E00D08.

Table 1: Acid-sulfate mineralogy of experimental secondary products, theoretical geochemical models, Cerro Negro alteration products, and materials from Mars lander and orbiter observations.

	Experiments	Cerro Negro [5, 9]	Theoretical models [10]	Mars (i.e. [1], [3], [11], [12])
Sulfates/salts	Gypsum, anhydrite, Mg-sulfate, Al-sulfate, natroalunite	Anhydrite, gypsum, Mg-sulfates, natroalunite	Alunite, anhydrite, Mg-sulfates, natroalunite	Gypsum, kieserite, polyhydrated sulfates, halite
Fe minerals	Possible iron oxide spherule	Bernalite, jarosite	Hematite	Hematite, jarosite, unidentified Fe3D3
Clay minerals	None observed	Amorphous clays, smectites	Kaolinite	Ntrontrite, montorillonite
Silica	Amorphous silica	Opaline, amorphous silica	Quartz	Opaline, amorphous and hydrated silica

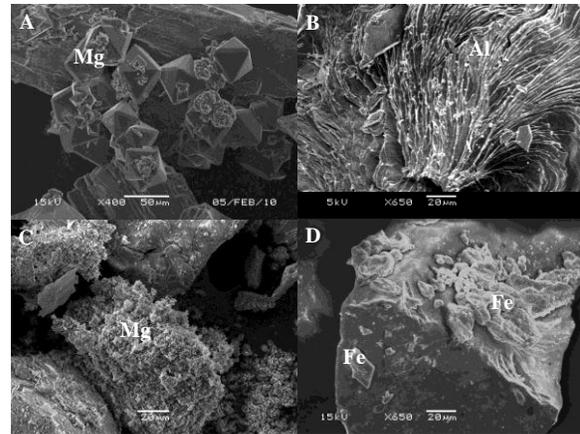


Figure 1: SEM images of alteration products for experiments with fluid:rock ratio of 4:1. (A) Forms of Mg-sulfate (Mg) from primary mineral augite. (B) Layers of Al and SO₄ from bytownite (Al), mostly likely an amorphous phase from drying of gel. (C) Surface alteration of forsterite (Mg), possibly starkeyite and hexahydrite. (D) Small quantities of Fe-sulfate (Fe) on obsidian.

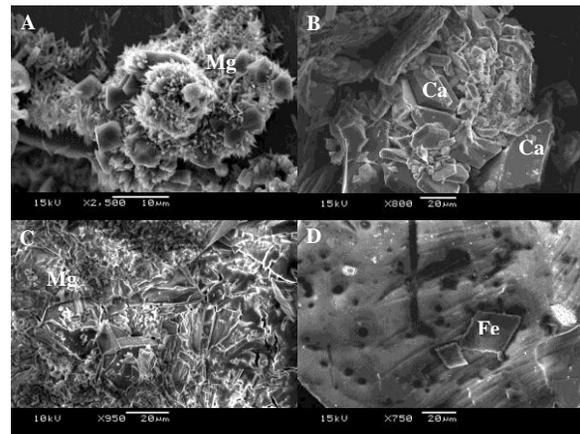


Figure 2: SEM images of alteration products for experiments with fluid:rock ratio of 1:1 (A and C) and 10:1 (B and D). (A) Mg-sulfate (Mg) from augite alteration. (B) Ca-sulfate (Ca) crystals on bytownite. (C) Surface alteration of forsterite, Mg-sulfate (Mg). (D) Fe-sulfate (Fe) on obsidian.

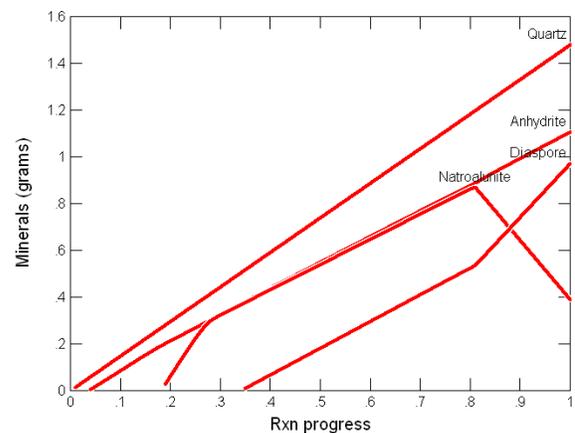


Figure 3: Example plot of secondary minerals produced during the reaction of bytownite and 1 M H₂SO₄ in Geochemist's Workbench-React.