

ACID ALTERATION OF BASALTS, ANDESITES, AND ANORTHOSITES: NEAR-IR SPECTRA AND IMPLICATIONS FOR MARTIAN SOIL FORMATION. B. Horgan¹, P. Mann², J. Stromberg², E. A. Cloutis²,
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Introduction: Acidic and oxidizing conditions have probably persisted on Mars for much of the past several billion years [1,2]. These conditions can cause alteration of mafic rocks and minerals, producing a variety of secondary mineral assemblages, some of which have been observed by surface and orbital investigations at Mars [2-4]. As such, previous laboratory investigations of these alteration processes have focused on the production and spectral character of the secondary minerals [5,6]. In this study, we are investigating the effects of acid alteration on the abundances and spectral characteristics of the primary, mafic minerals. Because mafic minerals have different solubilities (Figure 1) [7], they alter at different rates, so their relative abundances in altered surfaces may help constrain the alteration processes that have occurred.

Spectral observations of Mars suggest that relative abundances of mafic minerals do exhibit variations that are not easily explained by differences in primary lithologies. In the mid-IR, comparing the composition of bedrock to local soils reveals that soils have lower olivine abundances and higher plagioclase:pyroxene ratios, suggesting that aqueous alteration has played a role in soil formation in these regions [8,9]. In the near-IR, broad regions of the northern lowlands are spectrally consistent with high abundances (80-95%) of glass that has undergone acidic leaching [10]. These glass abundances may be too high to be consistent with a primary lithology, and instead may imply that other mafic minerals were dissolved during acidic alteration.

Methods: Six rock samples, consisting of four basalts, one andesite and one anorthosite (Table 1) were selected to recreate an open hydrologic system.

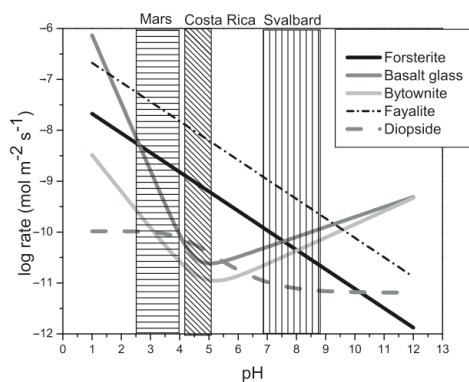


Figure 1: Mafic minerals exhibit large differences in solubility, and these solubilities depend on pH. At moderately low pH, plagioclase is the most stable while olivine is the least, and glass and pyroxene exhibit intermediate solubilities [7].

All six rock samples were crushed and dry sieved to a grain size of 500-1000 μm . Four of the samples exhibited naturally weathered surfaces, and these were also cut with a diamond rock saw to obtain a freshly cut surface for comparison.

Initial reflectance spectra between 0.35 to 2.5 μm were collected as a baseline from all the samples using an ASD FieldSpec Pro HR spectrometer. A 150W QTH light source was used to illuminate the samples and reflectance spectra were measured at $i=30^\circ$, $e=0^\circ$. To reduce the effects of specular reflections, all granular samples were spun during data collection.

Two stock acid solutions were made using concentrated H_2SO_4 and distilled H_2O : Acid A (pH of 1.0) and Acid B (pH of 3.0). The surface samples and approximately 7g of each of the crushed samples were placed in separate Teflon vessels with 30 ml of the stock acid solutions and 10 ml of 30% H_2O_2 (a candidate for the oxidant in Martian surface materials [6,11]), resulting in ten acid baths for both solutions.

The samples were fully immersed in the solutions for several months, and were analyzed for spectral changes daily, initially, and less frequently (up to one week between analyses) as the experiment continued. At each analysis stage, the pH of each solution was recorded and the acid was decanted into an evaporation dish for future analysis. The samples were rinsed with distilled H_2O and dried at 80°C for two hours prior to spectral analysis. Following data collection, a few grains of each sample were also set aside for future mineralogic analysis. To mimic an open hydrologic system [5,6], a fresh solution of acid and H_2O_2 was then prepared, the pH was recorded, and the samples were again placed in the solution.

Preliminary Results: As of day 29, the Icelandic and Kiluaea basalts exhibit the most notable spectral changes, as shown in Figure 2. The near-IR spectra of iron bearing minerals are characterized by broad absorptions near 1 and 2 μm , and the positions and shapes of these absorptions vary with crystal structure and composition. Initially, BAS101 exhibits bands that are consistent with iron-bearing glass. When BAS101 grains are exposed to acid A, the bands rapidly change to positions and shapes that are more consistent with a high-calcium pyroxene (HCP) mixed with glass. However, when BAS101 grains are exposed to acid B, the glass absorptions remain. The initial spectrum of the natural BAS101 surface does not exhibit absorption bands, however, it does have a concave continuum

slope that may be consistent with a leached or oxidized glassy rind [12]. With exposure to acid A, the concave slope deepens, and resembles leached, glassy regions in the northern lowlands [10].

ICE170 is initially spectrally consistent with a high calcium pyroxene mixed with either olivine or glass. With exposure to acid A, the spectrum loses the 2 μm iron band and acquires bands near 1.9 and 2.2 μm (most likely due to a hydrated silica coating). The 1 μm band also changes shape, taking on the asymmetry characteristic of olivine, or possibly a mixture of HCP and glass. Acid B causes different changes. In the natural surface, the 1 and 2 μm absorptions deepen and narrow, becoming consistent with HCP. For the grains, the 1 μm band widens, the 2 μm band becomes more shallow, and the continuum reddens; all of these effects may be consistent with a greater glass influence in the spectrum.

Conclusions: Our preliminary results indicate that acid alteration does cause spectrally observable changes to mafic minerals in basaltic surfaces and soils. In addition, the nature of the spectral change is different for low vs. moderately low pH in every case where changes are observed. With careful analysis, we may be able to shed some light on which conditions promote enrichment in various minerals.

We will continue to acquire spectra until no further

changes are observed in the samples. To further explore the mineralogic changes that have occurred in the samples, we will use the reserved samples from each stage for XRD analysis. Evaporation and analysis of reserved solutions may also help to constrain which phases were leached or dissolved.

References: [1] Hurowitz J. *et al.* (2010) *NGeo*, 3, 323-326. [2] Bibring J.-P. *et al.* (2005) *Science*, 307, 1576. [3] Squyres S.W. *et al.* (2004) *Science*, 306, 1709. [4] Murchie S.L. *et al.* (2009) *JGR*, 114, E00D06. [5] Tosca N.J. *et al.* (2004) *JGR*, 109, E05003. [6] Golden D.C. *et al.* (2005) *JGR*, 110, E12S07. [7] Hausrath E. *et al.* (2008) *Geology*, 36, 67. [8] Rogers A.D. *et al.* (2009) *Icarus*, 200, 446. [9] Bandfield J.L. *et al.* (2010) *Icarus*, doi:10.1016/j.icarus.2010.08.028. [10] Horgan B.H. *et al.* (2010) *AGUFM*, #P52B-06. [11] Zent, A.P., and McKay C.P. (1994), *Icarus*, 108, 146–157. [12] Minitti M.E. *et al.* (2007) *JGR*, 112, E05015.

Sample	Source	Grains	Cut Surface	Nat. Surface
BSB101	Black Sand Beach, HI	A, B		
MAI221	Ivory Pit Anorthosite, QC	A, B		
HAY012	Hayden Andesite, AZ	A, B	A, B	A, B
ICE170	Basalt, Iceland	A, B	A, B	A, B
BAS101	Kilauea Basalt, HI	A, B	A	A
BAS205	Columbia River Basalt	A, B	A, B	A, B

Table 1: Sample information. A,B indicate acid solutions used.

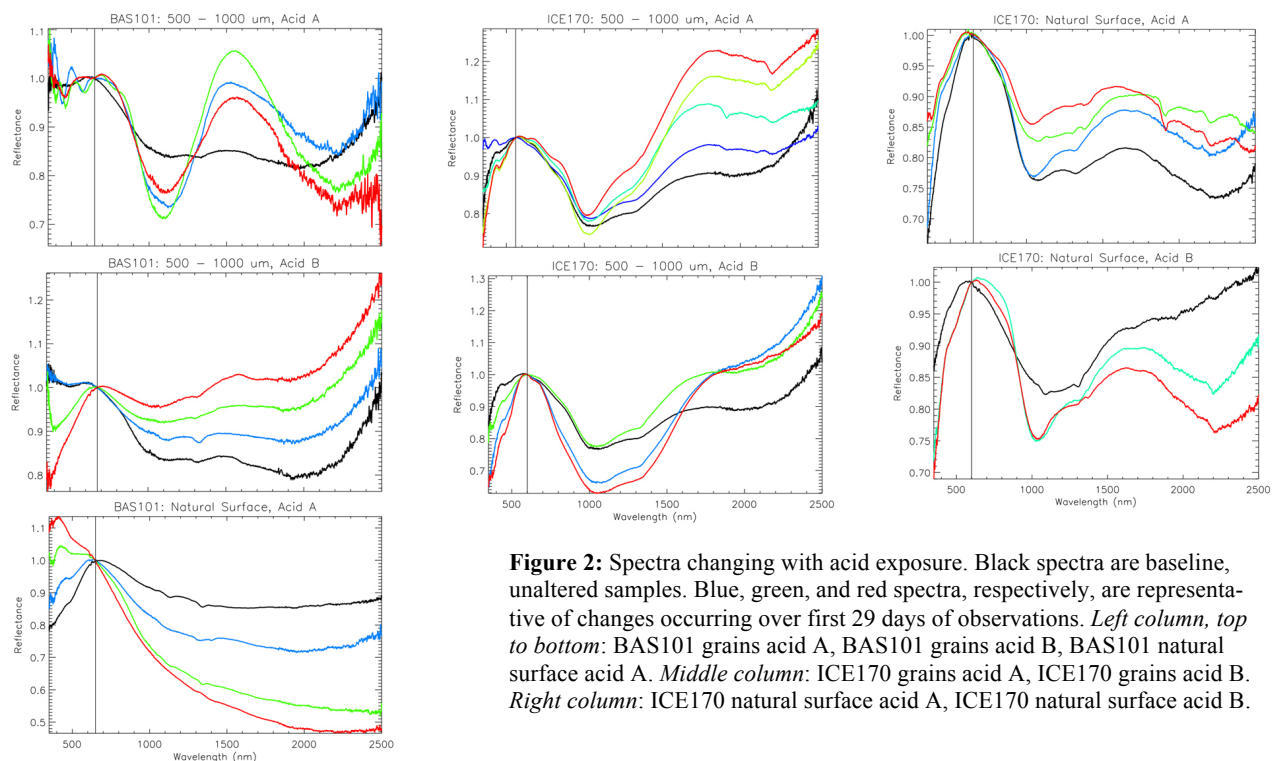


Figure 2: Spectra changing with acid exposure. Black spectra are baseline, unaltered samples. Blue, green, and red spectra, respectively, are representative of changes occurring over first 29 days of observations. *Left column, top to bottom:* BAS101 grains acid A, BAS101 grains acid B, BAS101 natural surface acid A. *Middle column:* ICE170 grains acid A, ICE170 grains acid B. *Right column:* ICE170 natural surface acid A, ICE170 natural surface acid B.