

**Spectral Characterization of Acid Weathering on Martian Basaltic Glass.** M. H. Yant<sup>1</sup>, A.D. Rogers<sup>1</sup>, H. Nekvasil<sup>1</sup>, and Y.-y. S. Zhao<sup>1</sup>. Stony Brook University, 255 Earth and Space Sciences Building, Stony Brook University, Stony Brook, NY 11794-2100 (marcella.yant@stonybrook.edu).

**Introduction:** Acidic weathering of basalt has received significant attention as a dominant style of weathering on Mars because of the abundance of sulfates present on the surface [e.g. 1]. The presence of ferric sulfates, which form exclusively under low-pH conditions, combined with a lack of Al-phyllsilicates or Al-sulfates in altered materials suggests an acidic, low water-to-rock ratio weathering environment. It is suggested that such altered materials present on the surface of Mars were derived from acid sulfate alteration of an originally basaltic rock under low water to rock ratios and/or nearly isochemical conditions [e.g. 2, 3].

Although the process of acidic weathering of basalt is well understood, it has been difficult to assess this process globally. Remote spectral measurements used for compositional analysis are complicated by non-linear spectral mixing, particularly for altered surfaces where there are a variety of grain sizes, textures and coating geometries [e.g. 4]. Thus, the infrared (IR) spectral character of an acid-weathered basalt or glass is not easily predicted using linear mixing models.

In this study, geochemical experiments are linked with IR spectral measurements to understand basalt weathering and regolith development on Mars. For the first time, direct IR spectral analyses of Martian basaltic materials, altered under controlled conditions, are presented. This will allow for the direct comparison of laboratory spectral data to TES, Mini-TES, and CRISM/OMEGA data, which will expand the assessment of the extent of acidic Martian alteration to include more locations than just landing sites.

This experiment aims to answer two important questions regarding the environmental history of Mars. 1) What was the dominant style of weathering and 2) how did weathering conditions vary spatially and temporally? Understanding the alteration processes that occur on Mars will help unravel the history of the Martian climate and past geologic events.

**Procedures Overview:** The procedural outline of this experiment was (1) synthesize basaltic glass of Irvine composition; (2) react basaltic glass (63µm - 400µm grains) with acidic fluids of variable pH and a constant water-to-rock ratio under ambient temperature and pressure; (3) evaporate the fluids from the basalt after a 14 day reaction period [e.g. 5]; and (4) to perform mineralogical and spectral analyses on the unaltered and altered material. A variety of

analytical methods including Electron Microprobe, SEM, XRD, Raman, VNIR and TIR spectroscopy were used to examine the unaltered and altered samples.

**Starting Material:** Since the alteration assemblage is dependent on the starting composition [e.g. 5], it is preferable to start with a known Martian basalt composition. In-situ chemical data gathered from the Mars Exploration Rovers provides a variety of Martian basalt compositions to choose from. Gusev crater contains several basalts that are considered to be the least altered Martian rocks [e.g. 6]. "Irvine" (**Table 1**), a rock found on the crest of Husband Hill in Gusev Crater, was chosen as the first starting composition because it is a relatively unaltered, aphanitic, rock with a basaltic composition. For simplicity, we begin with a glass starting material. An identical Irvine crystalline starting sample will be synthesized, altered, and analyzed in the near future.

**Table 1.** Target Irvine composition reported in weight percent oxide.

Oxide	Wt. %	Oxide	Wt. %
SiO <sub>2</sub>	47.0	Na <sub>2</sub> O	2.68
TiO <sub>2</sub>	1.06	K <sub>2</sub> O	0.68
Al <sub>2</sub> O <sub>3</sub>	8.29	P <sub>2</sub> O <sub>5</sub>	0.97
Fe <sub>2</sub> O <sub>3</sub> <sup>a</sup>	7.61	Cr <sub>2</sub> O <sub>3</sub>	0.20
FeO <sup>a</sup>	12.20	S <sup>b</sup>	0.30
MnO	0.36	Cl <sup>c</sup>	1.00
MgO	10.60	H <sub>2</sub> O <sup>d</sup>	1.00
CaO	6.03		

Source: McSween *et al.*, 2008.

<sup>a</sup>All Fe<sub>2</sub>O<sub>3</sub> and FeO values have been converted into an 80:20 ratio.

<sup>b</sup>Sulfur values are set at a constant of 0.30 wt. %.

<sup>c</sup>Chlorine values are set at a constant of 1.00 wt. %.

<sup>d</sup>Water values are set at a constant 1.00 wt. %

Since Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios control the redox conditions during the melting experiment, a ratio of 80:20 was used to obtain the desired oxygen fugacity. The volatile components (sulfur, chlorine, and water) all have fixed values of 0.30, 1.00, and 1.00 wt. % respectively.

The derived Irvine composition (**Table 1**) was converted into an equivalent mixture of oxide, silicate, phosphate, chloride, and sulfide components that represent the bulk chemical composition. The components were homogenized by grinding in an automatic agate mortar/pestle in 35 minute intervals for a total of approximately 3 hours. The mixture was then added to a large volume graphite capsule and melted at 1400°C (176 bars, overpressurized to 212

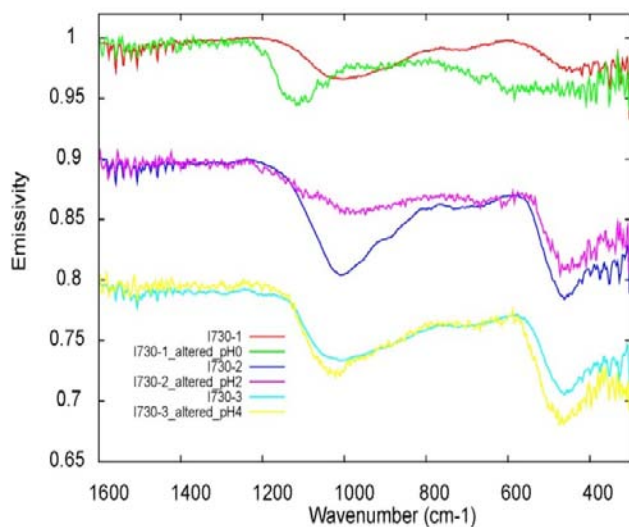
bars). After 3 hours at 1400°C the assemblage is quenched resulting in a glass. The glass was analyzed by electron microprobe and compared to the target composition. Transmission micro FTIR indicated water contents of approximately 3.0 wt. % H<sub>2</sub>O.

**Experimental Alteration Procedure and Spectral Acquisition:** The Irvine glass was crushed into 63µm - 400µm size particles and then reacted with acidic fluids in batch experiments. For each of the three reactions, approximately 150 milligrams of basaltic glass was added to a Savillex™ Teflon® beaker. Diluted mixtures of sulfuric acid and hydrochloric acid with a 5:1 molar ratio were used to react with the samples at room temperature and pressure. A pH range of 0-4 was used, with pH's of 0 (I730-1), 2 (I730-2), and 4 (I730-3). A water- to-rock ratio of 1 was used for each solution. The duration of each experiment was 14 days.

The beakers were opened three times per week, for a few seconds, in order to equilibrate the mixture to the atmosphere [e.g. 7]. This process was done under a fume hood to prevent contamination. Following the reaction period, the samples were air dried at room temperature for 4 days.

TIR emission spectra were acquired between approximately 350-2000cm<sup>-1</sup> using procedures described by [e.g. 8] and [e.g. 9]. VNIR (350-2500cm<sup>-1</sup>) bidirectional reflectance spectra were acquired with incidence and emergence angles of 30° and 0°, respectively.

**Results:** After the reaction period visible alteration could be seen on I730-1a with the naked eye, but magnification was needed to view the alteration on I730-2a and I730-3a. On the surface of I730-1a there is a white crystalline coating overlain in part by white powder. I730-1a has both crystalline and poorly crystalline materials on its surface. The alteration on **Figure 1:** Emissivity spectra of unaltered and altered Irvine samples.



the surface of I730-2a and I730-3a is poorly crystalline. Hot (80°C) emissivity measurements were done on the unaltered Irvine samples, as there are no phases that would be changed with this extent of heating (**Fig 1**). The unaltered glass samples all have distinct absorptions at approximately 1000 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, 600 cm<sup>-1</sup>, and 500 cm<sup>-1</sup>.

The altered glasses show variation in their cold (approximately -10°C) emissivity measurements, with respect to each other and also with respect to the unaltered sample. In the spectrum from the most acidic environment (**Fig. 1**), pH 0 (I730-1a), the original unaltered glass absorptions are lost and the spectrum now has an absorption at approximately 1100cm<sup>-1</sup>. This absorption indicates that the spectrum of the sample surface is now dominated by sulfate(s). The glass subjected to the intermediate acidic environment, pH 2, has retained the original glass absorptions at around 1000 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, 600 cm<sup>-1</sup>, and 500 cm<sup>-1</sup>, but the absorption at 1000 cm<sup>-1</sup> is broadened from the addition of the sulfate absorption at 1100 cm<sup>-1</sup>. This indicates some sulfate alteration, but there is still a large enough amount of glass on the surface to keep sulfate from dominating the spectrum. The spectrum of the glass subjected to the least acidic environment, pH 4, still retains all of the original glass absorptions and does not show any indication of secondary mineral formation.

**Discussions/Future Work:** The differences in the altered sample spectra follow a trend that we would expect in acidic conditions; the extent of alteration lessens as the pH increases. Some alteration in an environment with a pH of 4 is expected, though not seen in this set of analyses. The sulfate phase present in I730-1a and I730-2a has not been analyzed at this time. Further analyses will be done in order to assess the secondary mineral assemblages of all three samples. These future analyses include Raman spectroscopy, Electron Microprobe, Scanning Electron Microscope, and X-ray Diffraction. More results will be posted at the conference.

#### References:

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