

Spectral Characterization of Acid Weathering on Martian Basaltic Glass and Rock. M. H. Yant¹, A.D. Rogers¹, H. Nekvasil¹, and Y.-y. S. Zhao¹. 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 [1, 2]. A previous study by Tosca et al. [3] focused primarily on the solution chemistry and secondary mineralogy of these acid alterations with Pathfinder basalt and glass. 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 [4]. These coatings can induce non-linear mixing because they cause scattering, which can decrease the spectral contrast of the features. Scattering occurs when the surface is rough or the radius of the grain is smaller than the wavelength of the energy source. In addition to surface scattering, there can also be changes in spectral shape due to increased transmission through grains with a smaller particle size. 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. 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. It was postulated that Mars underwent global acidification, resulting in the sulfates that exist on the current surface [5].

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 to (1) synthesize basaltic glass and rock of Irvine composition [6]; (2) react samples (63 μ m - 400 μ m grains) with acidic fluids (0-4 pH) and a constant water-to-rock ratio of 1, under ambient temperature and pressure; (3) evaporate the fluids from the basalt after a 14 day reaction period [3]; and

(4) 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. TIR emission spectra were acquired between approximately 350-2000 cm^{-1} . VNIR (350-2500nm) bidirectional reflectance spectra were acquired with incidence and emergence angles of 30° and 0°, respectively.

Starting Material: Because the alteration assemblage is dependent on the starting composition [3], 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 [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.

Table 1. Target Irvine composition [9] reported in weight percent oxide.

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

^aAll Fe₂O₃ and FeO values have been converted into an 80:20 ratio.

^bSulfur values are set at a constant of 0.30 wt.%.

^cChlorine values are set at a constant of 1.00 wt.%.

^dWater values are set at a constant 1.00 wt. %

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. A stepwise cooling method is programmed for the crystalline sample. The glass was analyzed by microprobe and compared to target composition. Transmission micro-FTIR indicated water contents of approximately 3.0 wt. %.

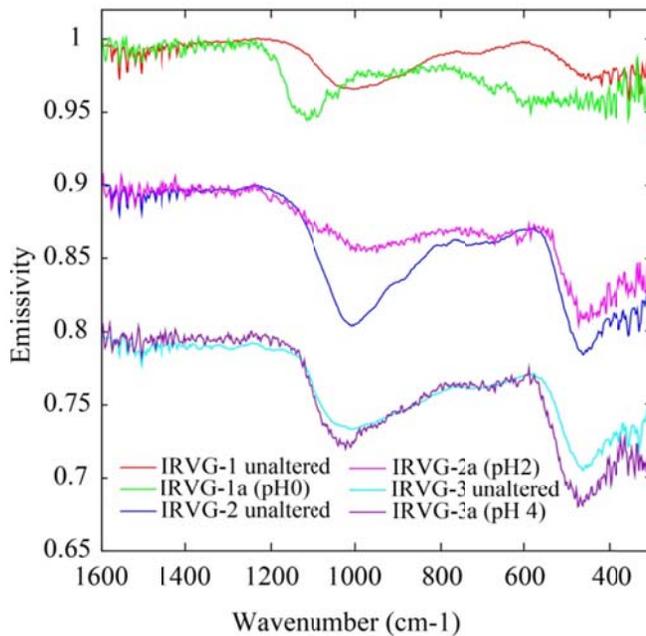


Fig. 1: Emissivity spectra of unaltered and altered glass samples (each pair is offset for clarity). The unaltered material was measured hot (80°C) [7], and the altered material was measured cold (-15°C) [8] to avoid phase changes with heating.

Glass Results: Only the sample altered in the most acidic environment had TIR spectral features that were considerably different from the unaltered sample spectrum (**Fig. 1**). The TIR absorptions in the IRVG-1a (pH 0) spectrum are most consistent with pickeringite, but are also similar to apjohnite and rozenite. The VNIR spectrum for IRVG-1a is most consistent with pickeringite, which agrees with the TIR. SEM indicated an assemblage including pickeringite, halotrichite, epsomite, and jarosite. Micro-Raman analyses for this sample indicate the presence of three groups of spectral features (not shown). The first feature is most consistent with apjohnite, dietrichite, halotrichite, and/or pickeringite which all have similar Raman features. Based on a combination of the other analyses, this feature is most likely due to halotrichite and pickeringite. The second spectral feature displays evidence of a combination of epsomite and hexahydrate. A magnesium sulfate is confirmed by SEM/EDS, but based on morphology, epsomite was the only phase present at the time of SEM. It is likely that the hydration changed based on fluctuations in the ambient atmosphere. The third spectral feature is consistent with gypsum.

Crystalline Results: The samples altered in pH 0 and pH 1 had TIR spectral features that were considerably different from the unaltered sample spectrum (**Fig. 2**). In the TIR spectrum of IRVC-1a (pH 0), most of the features are shallow, producing an almost linear spectrum. The weak absorptions are attributed to the fine grained (<63 μm) alteration surface material. The absorptions in the IRVC-2a (pH 1) spectrum are most consistent with alunogen, but are also similar to melanterite, pickeringite, and

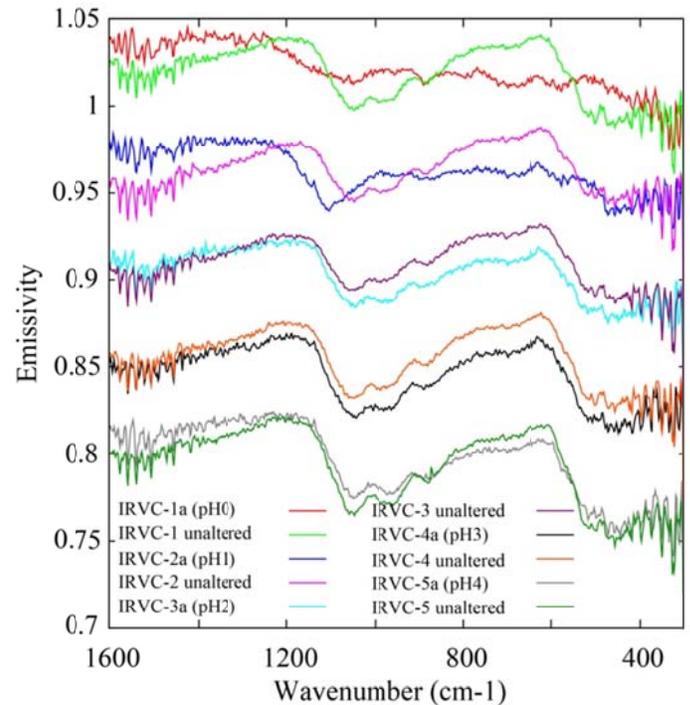


Fig. 2: Emissivity spectra of unaltered and altered Irvine crystalline samples (offset for clarity). Emission spectra were measured from cooled samples (-15°C) [8] to avoid phase changes that can occur with heating.

rozenite. The VNIR spectra for IRVC-1a and IRVC-2a have similar spectral features to each other and to halotrichite and pickeringite. SEM indicated an assemblage including iron sulfate, anhydrite, and halotrichite for IRVC-1a. The secondary mineral phases observed for IRVC-2a included alunogen, gypsum, and Fe, Mg sulfate. Micro-Raman analyses for IRVC-1a indicate the presence of two groups of spectral features. The first feature is most consistent with apjohnite, dietrichite, halotrichite, and pickeringite. Based on SEM analyses, this feature is most likely due to halotrichite. The second spectral feature is consistent with gypsum. Three secondary mineral phases were observed using Micro-Raman for IRVC-2a including, gypsum, ilesite, and alunogen.

Discussions/Future Work: Differences between the spectral and chemical data sets for the altered Irvine glass and crystalline samples provides evidence for non-linear mixing in the TIR. Also, differences in the weathering between the glass and crystalline samples displays how weathering varies with changes in crystallinity for a Martian basalt. Future analyses include XRD. Future work will be expanded to include a Backstay composition. More results will be posted at the conference.

References: [1] Burns, R.D., and D.S. Fisher (1990), *JGR*, 95, pp. 14415–14421. [2] Bell, J.F., (2000), *JGR*, 105, pp. 1721–1755. [3] Tosca, N.J., *et al.* (2004) *Am. Mineral.* 94, 1629–1637. [4] Michalski, J.R., (2006), *Earth and Planetary Science Letters*, v.248, p. 822–829. [5] Bibring, J.P., (2006), *Science*, v.312, no.5772, pp. 400–404. [6] McSween, H.Y., *et al.*, (2006), *JGR*, 111 (E9), E09S91. [7] Ruff, S. W., P. R. Christensen *et al.* (1997), *JGR*, 102(B7), p. 14,899–14,913. [8] Baldrige, A.M., P.R. Christensen (2009), *Applied Spectroscopy*, v. 63, p. 678–688. [9] McSween, H.Y., *et al.*, (2008), *JGR*, 113 (E6), E06S04.