

Spectral Characterization and Effects of Volatiles on Synthetic Irvine Basalt and Glass. M. H. Yant¹, A.D. Rogers¹, and H. Nekvasil¹. Stony Brook University, 255 Earth and Space Sciences Building, Stony Brook University, Stony Brook, NY 11794-2100 (marcella.yant@stonybrook.edu).

Introduction: GRS global mapping, rover rock analysis, and SNC meteorites provide evidence for a high abundance of chlorine [1, 2, 3] and water [4, 5, 6] in various locations on Mars. It is important to understand how volatiles affect surface mineralogy because they play a crucial role in the surface alteration of Mars as well as during magmatic and degassing processes. Previous studies have examined the effect of chlorine and water on the primary mineralogy of Martian and terrestrial rocks [3, 7, 8, 9, 10, 11]. However, this study is unique in that it examines (1) how chlorine and water influence the primary mineralogy of Martian basalt and (2) the effects on the secondary mineralogy both chemically and spectrally. It is vital to add a spectral analysis component because it can be applied to the entirety of Mars instead of being limited to rover sites.

Procedures Overview: The procedural outline of this experiment was to (1) synthesize basaltic glass and rock of Irvine composition [e.g. 12] with no volatiles added; (2) react samples (63 μ m - 300 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 [e.g. 13]; (4) perform mineralogical and spectral analyses on the unaltered and altered material, and (5) compare the spectral and chemical characteristics of the volatile free samples with volatile containing samples. A variety of analytical methods including Raman, VNIR, and TIR spectroscopy as well as electron microprobe, SEM, and XRD were used to examine the unaltered and altered samples. TIR emission spectra were acquired between approximately 350-2000 cm^{-1} using procedures described by [14] and [15]. VNIR (350-2500 cm^{-1}) bidirectional reflectance spectra were acquired with incidence and emergence angles of 30° and 0°, respectively.

Starting Material: Irvine (**Table 1**) was chosen for the analog composition in order for comparison with the volatile containing Irvine composition from a previous study [16]. This composition was originally used because it is a relatively unaltered, aphanitic, Martian basalt. The volatile containing composition had 1 wt. % Cl and H₂O added and the volatile free composition had no Cl or H₂O added.

Results: Based on the chemical analyses, the volatile free and volatile containing glass compositions both have a secondary mineralogy including Ca, Fe, Al, and Mg-sulfates. The main

Table 1: Target Irvine volatile free composition reported in weight percent oxide.

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

Source: [12]

^aFe₂O₃ and FeO values have been converted into an 80:20 ratio.

difference is the presence of Na-Mg-sulfate in the volatile free samples and Mg-Al and Fe-Al-sulfates in the volatile containing samples. The TIR and VNIR spectra for both unaltered glass compositions have very similar features; however the absorptions for the altered material vary significantly (**Fig. 1 A,B**). The thermal emission spectral features for the volatile free Irvine glass are most consistent with Fe⁺³-sulfate (with influences from Ca, Mg, (Zn,Fe,Mn)Al-sulfate, silica, and Fe-oxides), whereas the volatile containing glass has features most consistent with (Mg,Mn)-Al-sulfate (with influences from Fe-Al, Al, Ca, Fe⁺², Fe⁺³, and Mg-sulfate and Fe-oxides). Due to a lack of fully glass material for the volatile containing composition, a sample was not altered in pH1. However, a volatile free sample was subjected to pH1 conditions and had a TIR signature most consistent with Fe⁺³-sulfate (with influences from Al, Fe⁺², Ca, Mg-sulfate, Fe-oxide, and silica). The TIR spectrum for the volatile free sample altered in pH2 suggests little alteration material, which is consistent with the chemical analyses. This varies from the volatile containing sample altered under identical conditions, which had shallowed features as well as additional features near 1150, 665, and 605 cm^{-1} . These features are likely due to the presence of Ca-sulfate. In the VNIR range both glass compositions altered in pH0 exhibit features consistent with Mg-Al-sulfate, but the additional feature near 2.1 μ m for the volatile free material suggests influences from Na-Mg-sulfate and/or Fe⁺²-sulfate. The spectral signature in the VNIR for the volatile free glass altered in pH1 was most consistent with Fe⁺²-sulfate. The TIR and VNIR features for samples from both compositions subjected to the weaker acids (pH2-4), are most consistent with unaltered material.

Although the spectral characteristics are similar for the unaltered crystalline volatile free and volatile containing samples, differences are expected in the XRD data due to the variations in the alteration

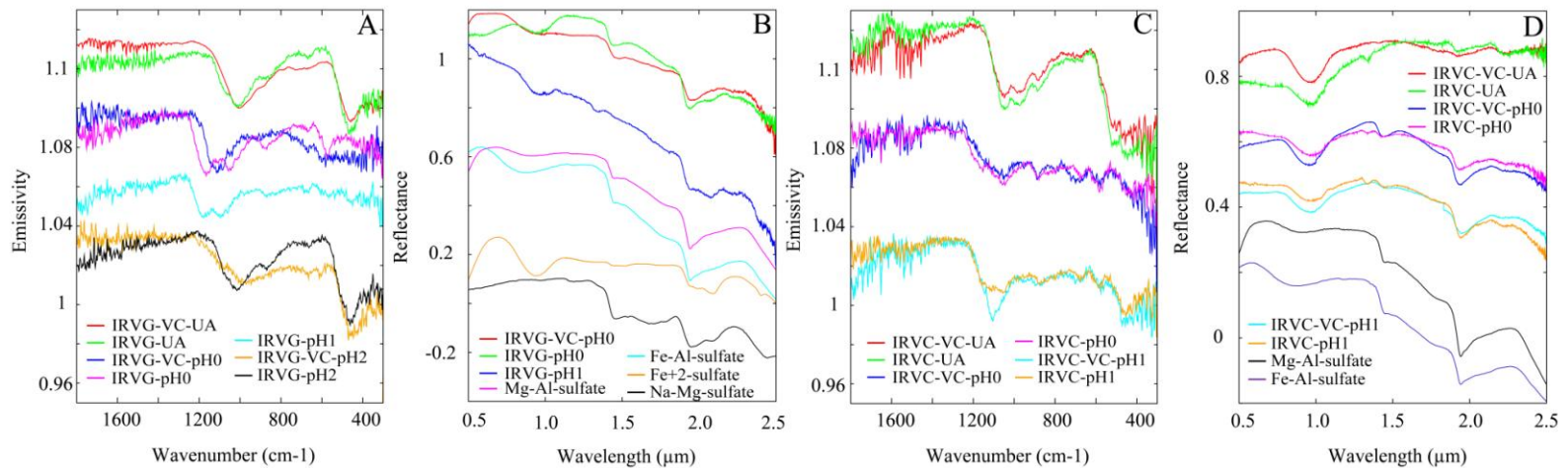


Figure 1: TIR spectra of unaltered (UA) and altered volatile free and volatile containing (VC) Irvine glass (A) and crystalline (C) material and VNIR spectra of altered volatile free and volatile containing glass (B) and crystalline (D) material. Y-axis is offset for clarity.

assemblages. The compositions both have a secondary mineralogy including Ca, Fe, and Fe-Al-sulfates, according to the chemical analyses. The presence of Na-Mg, Mg, and Mg-Al-sulfates in the volatile free material and Al, Na-Al, and Mn-sulfates in the volatile containing material distinguishes the two alteration assemblages. The thermal emission (**Fig. 1C**) and reflectance (**Fig. 1D**) spectral features for the volatile free and volatile containing crystalline Irvine samples are similar for both the unaltered and altered samples. The TIR spectra for both samples altered in pH0 conditions are shallow, suggesting finer grain sizes, and have similar features. The volatile free sample is most consistent with Fe⁺³-sulfate (with influence from Al-sulfate and Fe-oxide), whereas the best match for the volatile containing sample is (Zn,Fe,Mn)Al-sulfate (with influence from Fe⁺³, Ca, Al, Mg-sulfate, and silica). Both of the samples altered in pH1 have comparable spectral absorptions that are consistent with Al-sulfate, although Fe⁺³-sulfate contributes considerably to the volatile free spectrum. The shape of the feature at 1110cm⁻¹ distinguishes these two samples; the volatile free absorption at this wavenumber is a relatively broad and shallow absorption, whereas the volatile containing sample has a narrow and deeper absorption. The reflectance features for the samples altered in pH0 and pH1 from both compositions are most consistent with Fe-Al-sulfate. However, a distinction between the two compositions can be made by the presence of an additional feature near 1.4 microns for all of the volatile free samples, including the unaltered material. The crystalline samples subjected to the weaker acids, pH 2-4, do not display significant differences from the unaltered material in the TIR or VNIR.

Discussions/Future Work: The IR spectral characteristics of glass and crystalline volatile free and volatile containing Irvine samples are similar for the unaltered material, however differences can be observed in the altered spectral signatures. Differences are also displayed in the alteration assemblages as determined by Raman, SEM/EDS, and XRD. Alteration phases dominated the TIR spectral signatures in pH0-1 conditions for both compositions and crystallinities. Another trend observed for both compositions was a variety of sulfates in the lower pH conditions (pH≤1) and a limited amount of phases in the less acidic conditions. These results provide evidence for how IR spectral characteristics are influenced by the presence of volatiles as well as place constraints on the alteration assemblages for Martian surface material. Future analyses include XRD. More results will be posted at the conference.

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