

SPECTRA OF MARTIAN ANDESITIC MATERIALS. M. E. Minitti¹, M. J. Rutherford² and C.M. Weitz³.
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Introduction: The results from the Thermal Emission Spectrometer (TES) on the Mars Global Surveyor mission suggest that a compositional dichotomy exists between the southern and northern hemispheres on Mars [1,2]. Spectra of southern hemisphere are best fit by plagioclase-rich basalt [1] while spectra of the northern hemisphere are best fit by plagioclase- and glass-rich andesite [2]. Rocks of andesitic composition were also detected by the Mars Pathfinder mission, typified by the “sulfur-free” rock composition [3]. While the mineralogies determined for the TES andesite and the sulfur-free rock differ, it may be possible to link the two detected andesites through the effects of crystallinity, SNC-like glass compositions and oxidation on andesitic sample spectra. We have synthesized and initiated spectral studies of Mars andesite compositions in order to understand the influences of glass, glass composition and oxidation on Martian andesites.

Experimental: Two Mars andesite compositions were synthesized from oxide and carbonate powders for use in this study. The first composition, SFA2, is based upon the original sulfur-free rock identified at the Mars Pathfinder landing site by the APXS instrument [3] (Table 1). Recently, [4] established a mechanism of formation for the sulfur-free rock involving equilibrium crystallization of a SNC parent basalt containing ~1-1.5 wt.% dissolved water. The second andesite composition, SFA3, is based on the sulfur-free rock composition determined from the recalibrated APXS data [N. Foley, pers. comm.] and is intermediate between SNC basaltic melts and the original sulfur-free rock (Table 1).

Table 1: Starting andesite compositions

Oxide	SFA2	SFA3
SiO ₂	62.0	57.7
Al ₂ O ₃	10.6	11.5
FeO	12.0	16.6
MgO	2.1	1.8
CaO	7.3	6.9
Na ₂ O	2.6	2.5
K ₂ O	0.7	1.2
TiO ₂	0.7	0.6
P ₂ O ₅	0.5	0.5
MnO	0.5	0.5

The two andesitic compositions were first fused in TZM pressure vessels at $P_{\text{total}} = P_{\text{H}_2\text{O}} = 200$ bars (1.5 wt % H₂O), 1060 °C and $f_{\text{O}_2} = \text{QFM}$ to create glassy starting materials. The glassy starting materials were then run at temperatures between 875-1050 °C to cre-

ate samples of varying crystallinities (10-70%). A similar set of fusion and crystallization experiments was run without water ($P = 1$ atm) for both starting materials. Glassy starting material was fused in either Fe-saturated Pt or AgPd tubes (depending on temperature) sealed within evacuated silica glass containers. A QFM oxygen buffer was placed in the silica tube external to the sample container in order to monitor the oxygen fugacity of the sample during the experiment.

In order to conduct spectral analyses on the samples, the experimental products were ground and sieved to obtain samples with particle sizes between 100 and 500 μm . For the initial portion of the study, only the water-bearing SFA3 samples were analyzed. At the RELAB facility at Brown University, biconical reflectance spectra between 1.8 μm and 26 μm were obtained on the FTIR spectrometer with a 30° incidence angle and a 30° emergence angle. Reflectance spectra between 0.32 μm and 2.55 μm were obtained by the bi-directional spectrometer with a 30° incidence angle and a 0° emergence angle; however, the coarse particle size of the sample led to complicating particle size effects in the visible and near-infrared (VISNIR) spectral data.

Once the spectra of the unoxidized water-bearing SFA3 samples were obtained, the samples were oxidized at 700 °C in air for a period of seven days. This procedure follows that of [5] and in SNC basaltic samples leads to microcrystallization of glass, oxidation of pigeonite and augite in the samples and the formation of a hematite coating on exposed glass surfaces. While this exact oxidation mechanism is likely not active on Mars, the oxidation process primarily produces hematite, an oxidation product known to be present on Mars [6,7].

Results and Discussion: The results of the experiments using a water-bearing SFA3 composition summarized in Table 2.

Table 2: Optically estimated modes (vol.%) for hydrous SFA3 experiments

Sample	Glass	Pyroxene*	Plagioclase	Oxide
SFA3-2	100%	-	-	-
SFA3-1	90%	8%	-	2%
SFA3-3	60%	25%	10%	5%

*Relative distribution of pigeonite vs. augite not determined

The glasses in the SFA3 samples became increasingly SiO₂-rich with increasing crystallization because the phases that crystallized in the experiments are SiO₂-

poor relative to the starting andesite composition. The optically estimated average grain size of the samples is 20-40 μm .

The unoxidized sample spectra of the hydrous SFA3 compositions all exhibit absorptions of varying strengths at $\sim 1200\text{ cm}^{-1}$, $\sim 1100\text{ cm}^{-1}$ and $\sim 950\text{ cm}^{-1}$ and the nature of these features change with crystallinity. In addition to the changes observed in the absorption features, the Christiansen frequency of the spectra shifts to shorter wavelengths with increasing crystallization. The shift of the Christiansen frequency is likely due to the increasing SiO_2 content of the dominant phase in the samples, glass, with increasing crystallization. The strong absorption near 1100 cm^{-1} in the spectra resembles an absorption at $\sim 1100\text{ cm}^{-1}$ seen in both basaltic and rhyolitic glasses studied by [8]. The absorption is believed to be caused by Si-O or Al-O vibrations that occur in sheet-like silicate structures within the glasses [8], but the absorption could also be influenced by Si-OH and Al-OH bonds in the water-bearing glasses of this study [9]. The shift of the 1100 cm^{-1} absorption to shorter wavelengths with increasing crystallization is also observed in the basaltic glasses studied by [8]. Increasing polymerization of glass, which alters the population of Si-O and Al-O structures in the glass, leads to the movement of the 1100 cm^{-1} feature to shorter wavelengths [8]. Increasing polymerization of the glasses in this study is expected with the increasing SiO_2 content of the glasses with crystallization.

The 1200 cm^{-1} feature likely has source similar to that of the 1100 cm^{-1} feature. In the spectra of the glasses of [8], the $\sim 1200\text{ cm}^{-1}$ feature is attributed to Si-O bonds involved with chain-like silicate structures. A contribution to the feature from metal-OH bonds in the glass is also possible [9]. As is observed with the 1100 cm^{-1} feature, the proposed cause of the movement of the $\sim 1200\text{ cm}^{-1}$ absorption to shorter wavelengths with increasing crystallization is increasing polymerization of the glass.

The shoulder present at longer wavelengths relative to the absorption at $\sim 1100\text{ cm}^{-1}$ also shifts with increasing crystallization from $\sim 950\text{ cm}^{-1}$ to 1000 cm^{-1} . The cause of this feature is less well understood. A similar feature is present in the rhyolitic glass studied by [8] which suggests it is due to Si-O bonds in the structure of the glasses; however, contribution from water in the glasses must be considered as a potential contributor to this feature.

Finally, the feature at $\sim 460\text{ cm}^{-1}$ sharpens with increasing crystallization. The feature is likely primarily due to bonding in the glass and may sharpen with increasing crystallization due to the increasing influence of pyroxene on the spectra.

Overall, the spectra of the hydrous Martian andesitic samples do not resemble the TES spectra, indicat-

ing that similar samples do not exist at the Martian surface. This result is not surprising, especially because samples of water-bearing igneous rocks are not expected on the Martian surface due to the low atmospheric pressure of Mars and the low viscosity of Fe-O-rich Martian melts.

Spectra of the oxidized samples have not yet been obtained but the oxidation step led to unusual behavior in the glass-rich, water-bearing andesites. The SFA3-3 sample (40% crystalline) looked macroscopically similar before and after the oxidative heating with the exception of a red sheen developed on the surface of the samples. The more glass-rich samples (SFA3-1 and SFA3-2), however, softened and expanded from originally angular, shard-like fragments to brown, crystal-rich and red, glass-rich spherules. The result of oxidizing the water-bearing samples likely represents an extreme response of a Mars-based igneous rock to an oxidizing environment. In turn, the spectra of these samples will serve as potential extreme endmembers of water-bearing andesites that erupt to the Martian surface without degassing. As implied above, the spectra of the dry andesitic compositions, and their oxidized counterparts, are expected to represent andesitic materials more likely to exist on Mars. Spectra of unoxidized and oxidized dry andesites will be obtained in addition to VISNIR spectra of both wet and dry andesites of appropriate particle size.

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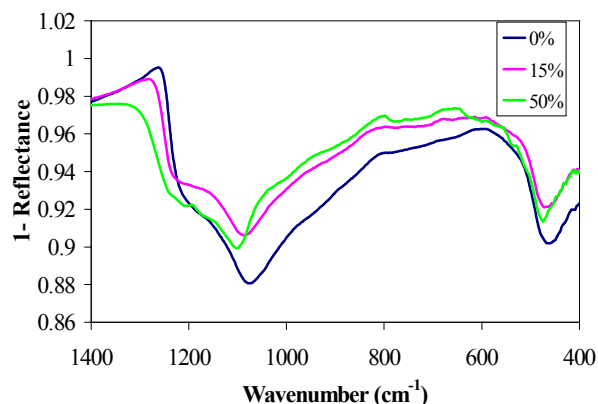


Figure 1: Emissivity (1 – reflectance) vs. wavenumber for the unoxidized, water-bearing SFA3 andesite composition. Position of the features and their movement with crystallization are addressed in the text.