

MARS ANALOGUE MINERALS' SPECTRAL REFLECTANCE CHARACTERISTICS UNDER MARTIAN SURFACE CONDITIONS. J.T. Poitras¹, E.A. Cloutis¹, and P. Mann¹. ¹Dept. of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, MB, Canada R3B 2E9; poitras-j@webmail.uwinnipeg.ca, e.cloutis@uwinnipeg.ca, p.mann-ra@uwinnipeg.ca

Background: Reflectance spectra of potential Martian hydrated minerals exposed to Mars surface conditions are needed to robustly analyze Martian remote sensing data obtained by orbiters, rovers, and landers. Previous studies have shown that astrobiologically-important hydrated minerals can undergo spectral structural and compositional changes when exposed to Martian surface atmospheric conditions [1].

Of the mineral species identified as being present on Mars, three groups have been chosen for this project: sulfates, silica, and carbonates. A variety of sulfates have been identified from orbital [2,3], rover, and lander missions [4,5,6,7]. Silicas have been identified in numerous places on the surface [8,9], and would therefore be well mixed into atmospheric dust. Carbonates have been identified [10,11], and are of particular interest because the quantity, type and distribution of carbonates are essential to understanding the evolution of Mars' water and atmosphere [12].

In order to better assess the spectral "fingerprints" of various minerals that may be present on Mars, an analogue mineral must be exposed to similar environmental conditions so that its spectral characteristics, relevant to Mars observational data, can be more reliably determined. We know that there are changes in absorption bands associated with H₂O and OH from previous studies [1]; it is, therefore, pertinent to document these changes in a wider range of possible and known Mars surface materials.

Methods: From the three mineral groups described above, a suite of 28 minerals were selected for analysis. Samples were ground by hand in an alumina mortar and pestle, then dry-sieved to a grain size of <45 µm. Fine-grained samples were used in order to better reproduce the fine-grained component of Martian dust and to enable any spectral changes that may accompany exposure to Mars surface conditions to be more rapidly enabled. After sieving, samples were poured into Al sample holders and placed in one of two 20 cm diameter turntables. Each sample holder had a well 22 mm in diameter and 2 mm in depth.

Samples were placed in the Mars Environmental Chamber (ME), as described by [13]. A 150-watt in-house QTH lamp was used with $i=30^\circ$ and an Analytical Spectral Devices (ASD) spectrophotometer was used to collect diffuse reflectance at $e=0^\circ$ over the range of 350 – 2500 nm. All sample spectra were measured relative to a halon 99% diffuse reflectance standard which had been referenced against a NIST-traceable Spectralon puck, and a total 500 individual

spectra were averaged together to obtain high signal-to-noise ratio data.

Reflectance spectra were first measured in air before sealing ME with a 10 mm-thick sapphire window. Spectra were then obtained through the viewing window before subjecting the samples to Martian conditions.

After obtaining pre-Martian spectra, ME was pumped down to ~5 Torr under a CO₂ atmosphere to mimic Mars surface conditions as described by [13]. Reflectance spectra were then measured periodically to monitor short-term and longer-term changes. To date, the samples have been exposed to these conditions for 76 days.

The reflectance spectra were normalized at 1250 nm (Figures 1, 2 and 3) to minimize variations in absolute reflectance associated with "shrinkage" of samples due to dehydration. Results for some representative minerals (Table 1) are presented below.

Table 1: Selected Minerals Included in This Study

Mineral	Lab Code	Formula
Magnesite*	CRB114	MgCO ₃
Fibroferrite	SPT121	Fe ³⁺ (SO ₄)(OH) 5H ₂ O
Botryogen	SPT124	MgFe ³⁺ (SO ₄)(OH) 7H ₂ O

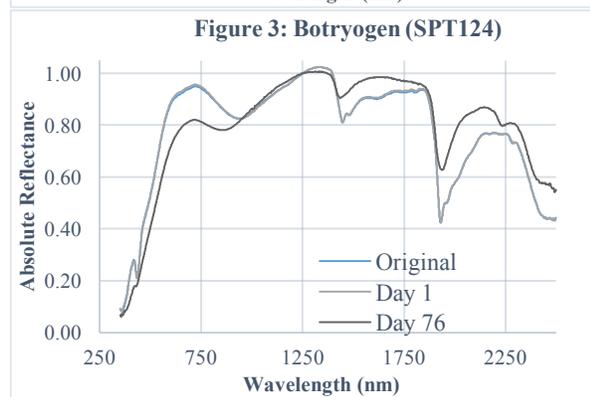
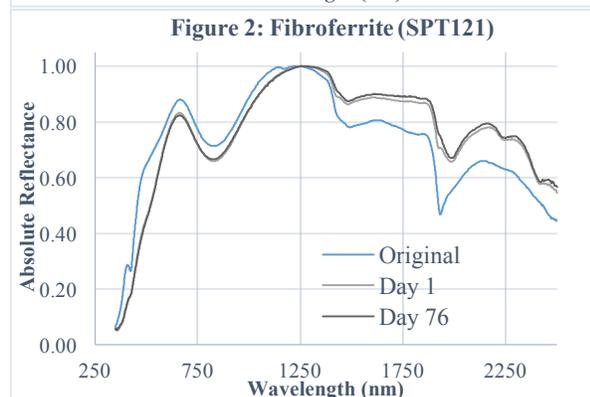
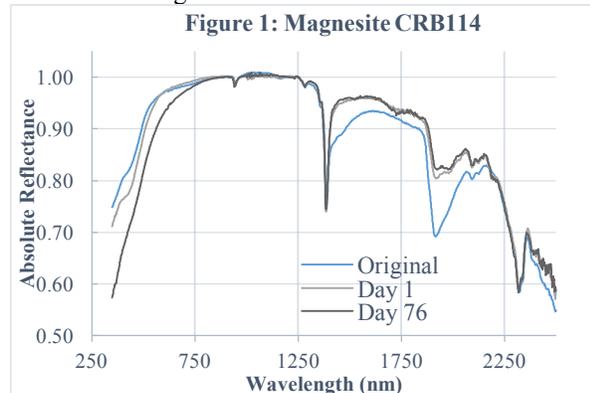
* - sample contains magnesite and huntite by XRD.

Results: SPT121 has a symmetrical Fe³⁺ absorption band at 830 nm that subtly shifts within the first day of Martian conditions from 830 nm to 825 nm by day 76. SPT124 displays a much more apparent shift of the Fe³⁺ absorption band from ~940 nm to ~860 nm and a decrease in normalized peak reflectance at ~720 nm from 95% to 82%. The lower reflectance downturn also shows a loss of the 430 nm ferric iron band in both SPT121 and SPT124.

The water/hydroxyl bands are apparent in all three mineral spectra, all of which show changes. In the 1400-1600 nm region, the H₂O in SPT124 is likely lost to some extent, resulting in a narrowing of the 1400 nm OH band by day 76. There is a slight shift to lower wavelength, from ~1450 nm to ~1430 nm, consistent with a loss of the adjacent H₂O band. SPT121 shows similar spectral behavior: the longer wavelength side of the 1400 nm feature shows the most shallowing, consistent with a loss of H₂O. CRB114 loses the adsorbed water as evidenced by the narrowing of the composite OH/H₂O combined absorption band in the 1400 nm region on its long wavelength side: it becomes more symmetrical without the adsorbed H₂O.

The region of water absorption between 1880 nm and 2050 nm shows similar changes for all three minerals. SPT124 maintains a shallowed 1400 nm OH absorption band while the H₂O side band is lost and the 1900 nm band becomes shallower; this region is more reflective by approximately 20%. SPT121 shows decreases in both the 1400 and 1900 nm band depths and a flatter spectrum beyond 1300 nm. CRB114 shows rapid loss of adsorbed water with greatly decreased 1900 nm band depth.

Between 2200 nm and 2450 nm, we find a region of SO₄-associated absorption bands. Both the SPT121 and SPT124 spectra show more discernible S-O absorption bands in this region after initial exposure. CRB114 is composed of carbonate anion clusters and has a stable absorption feature at 2310 nm. This feature has not changed for the duration of the trial.



Discussion: Our results clearly indicate that even short duration exposure of these minerals to the Mars surface environment has measurable effects on their spectra. Iron oxidation state, and possibly site coordination, can change over time, adsorbed water is rapidly lost, while structural water, at least in these samples, is more easily lost than structural hydroxyl.

The iron band shifting in the SPT121 is minimal but could be indicative of a change in the oxidation state of Fe³⁺ towards Fe²⁺. The loss of the ferric iron band at 430 nm could also be related to a loss of Fe³⁺-bridging OH, and this loss of detail is clearly visible in their spectra.

The spectra for SPT124 display a more prominent shift of the ~900 nm Fe absorption band than those of SPT121. It is possible that this change is also due to change in the oxidation state of the Fe³⁺ to Fe²⁺ and/or loss of bridging OH

CRB114 demonstrates the weakly held nature of H₂O that is not incorporated into the mineral system, but the potential for OH to persist in carbonates and sulfates in a Martian environment.

The results for the full sample suite will provide additional insights into how Mars surface conditions affect mineral stability and their reflectance spectra.

References: [1] Cloutis E. A. et al. (2008) *Icarus*, 195(1), 140-168. [2] Arvidson R. E. et al (2005) *LPSC*, XXXVI, 1934. [3] Bibring J. P. et al. (2005) *Science* 307.5715: 1576-1581. [4] Arvidson R.E et al. (2007). *LPSC XXXVIII*, 1122. [5] Bell J.F. et al. (2000) *JGR*, 105(E1), 1721-1755. *Science*, 307(5715), 1576-1581. [6] Burns R.G. (1987) *LPSC*, XVIII. 141-142. [7] Bandfield J. L. (2002) *JGR*, 107(E6), 9-1 [8] Smith M.R. and Bandfield, J.L. (2012) *JGR*, 117(E6). [9] Ruff S.W. et al. (2011) *JGR*, 116(E7). [10] Christensen P.R. et al. (2004) *Science*, 306(5702), 1733-1739. [11] Ehlmann B.L. et al. (2009) *JGR*, 114. E00D08. [12] Bandfield, J.L. (2003). *Science*, 301. 1084-1087. [13] Craig M. et al. *LPSC*, XXXII 1368 (2001).

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