

REFLECTANCE SPECTROSCOPY OF MARS ASTROBIOLOGY- AND HABITABILITY-RELEVANT MINERALS EXPOSED TO MARS-LIKE SURFACE CONDITIONS.

N. N. Turenne¹, E. A. Cloutis¹, and D. M. Applin¹, ¹Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9; nat.turenne@hotmail.com.

Introduction: The possibility of life on Mars has been investigated for many decades, and the search for life will continue with missions geared towards exploring new regions of the planet for habitability and biosignatures (e.g., Mars2020, ExoMars) [1]. An essential ingredient for life as we know it is water, and there is compelling evidence for its presence on Mars in the past [2, 3, 4, 5, 6]. These missions will be equipped with optical spectrometers of various kinds that can detect spectral evidence of OH/H₂O [1].

Reflectance spectroscopy has helped transform our understanding of Mars geology and its past climatic history via identification of minerals such as phyllosilicates, and hydrated sulfates that form in the presence of liquid water [3, 5, 6, 7, 8, 9, 10].

Our current study focused on the spectral changes accompanying long-duration (~26 months) exposure of a suite of nine hydrated minerals, including zeolites, sulfates, and hydrated silica-rich materials, to Mars-like surface conditions in the laboratory: a longer duration than previously studied [6, 11].

We had several objectives: (a) assess spectral and structural changes associated with exposure to Mars surface conditions (including effects of UV irradiation); (b) relate these spectral changes to compositional or structural changes; and (c) determine which changes are reversible by re-exposing the samples to Earth's environment. Here we focus on the results for sulfates.

Sulfates were included to better understand how their spectral characteristics change under the Mars-like surface conditions. This is significant because most sulfates having very restricted conditions in which they form and/or only remain stable in a narrow range of environmental conditions [6, 12, 13].

The selection of the samples was based on their known or suspected presence on Mars, and their utility for constraining past surface conditions that may have been prevalent when they formed. The sample suite included two zeolites (ZEO201: chabazite; ZEO200: heulandite), five hydrated sulfates (SPT120: hydronium jarosite; SPT121: fibroferite; SPT125: copiapite; SPT126: coquimbite; SPT139: rhomboclase), a hydrated silicate (PIG205: sodium silicate decahydrate), and a silica sinter (SIL203: opal-A). The samples were subjected to 763 days of simulated daytime Mars surface condition and included two periods of ultraviolet (UV) light irradiation. Throughout this period, diffuse reflectance spectra were acquired 33 times. The samples used were <45 μm powders. For a more detailed description of the methodology refer to [12]. After the experimental run, the samples were taken out of the chamber and put into storage for a period of six weeks before being re-exposed to ambient conditions to observe any rehydration.

Results: Spectral changes were assessed in terms of any significant changes in band depths, shapes, position, and overall spectral slope. It should be noted that some of these changes may be due to the choice of continuum for isolating absorption features.

1. SPT139 Rhomboclase: this mineral experienced the most spectral changes (Figure 1). One of the most interesting was that of its color, also observed by [11, 12] in shorter duration runs. The sample started white-light gray and turned black, while the other sulfates showed only slight color changes: darkening or reddening.

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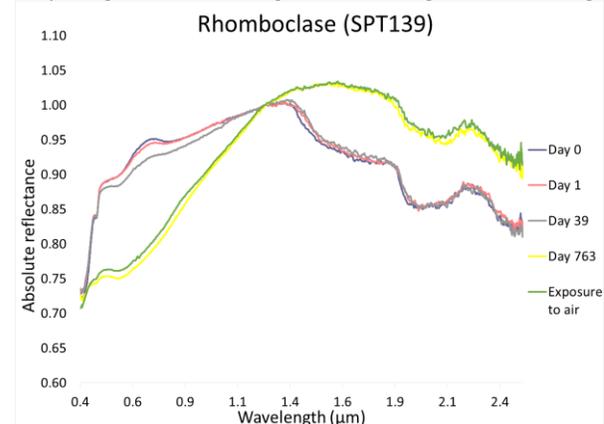


Figure 1: Rhomboclase (SPT139) reflectance spectra (with sapphire window)

With exposure, the 0.43 μm band was reduced in depth from day 1 to ~day 147, and then stabilized (Figure 1). The 0.53 μm Fe³⁺ band decreased in depth over time in association with the color change; it became narrower and deeper until day 237, after which it stayed constant. The 0.79 μm band disappeared completely around day 92 and did not return with re-exposure to ambient terrestrial conditions.

The loss and reduced depths of these Fe³⁺ bands was accompanied by a steeper spectral slope below ~1.4 μm. Accompanying the change in slope, the peak reflectance shifted from ~1.4 to ~1.7 μm. The H₂O band at 1.9-2.1 μm exhibited a change in shape (widened) and a gradual reduction in depth. This suggests

that the H₂O was lost and/or rearranged causing the band minimum to shift to longer wavelengths, similar to previous results [11, 12].

The final spectrum bears little spectral resemblance to the initial one, but still retains some evidence of being a ferric iron and water-bearing material.

2. *SPT126: Coquimbite*: This sulfate also exhibited spectral changes over time (Figure 2). Its spectrum has a number of characteristic absorption bands, three of which are Fe³⁺ bands (near 0.43, 0.55, and 0.8 μm). These all exhibited a decrease in depth with time, and were very subdued by the end of the run (Figure 2). The loss or reduced depths of these bands was accompanied by a steeper spectral slope below ~1.4 μm. The 0.43 and 0.80 μm bands had the same gradual decrease in depth, while the 0.55 μm band showed a similar trend but may have increased slightly after day 517.

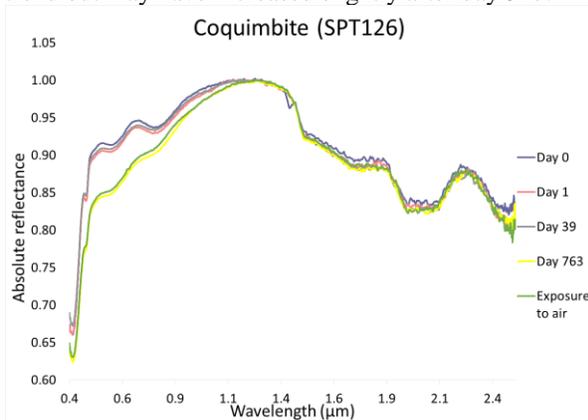


Figure 2: Coquimbite (SPT126) reflectance spectra (with sapphire window)

Coquimbite has a very similar spectrum to SPT139 (rhomboclase) beyond 1.4 μm, however, unlike rhomboclase it did not exhibit a change in shape or slope, staying relatively the same as day 1. No changes occurred to the 1.9-2.1 μm absorption feature. A weak OH/H₂O band near 1.4 μm disappeared rapidly, from day 0 to day 1, and did not come back with re-exposure to terrestrial conditions. This mineral appears to be stable on the Martian surface.

3. *SPT121: Fibroferrite*: This mineral experienced some changes in regards to band depths as well as band minima shifts (Figure 3). Fibroferrite is characterized by five absorption bands, with three Fe³⁺ bands at 0.43, 0.55 and 0.85 μm that all gradually reduced in depth and did not return with re-exposure to terrestrial conditions. They also all experienced shifts in their minima to shorter wavelengths, likely due to the slope change occurring below ~1.1 μm.

The 0.55 μm band progressively became shallower throughout the run and almost disappeared by day 237. The OH/H₂O band at 1.4 μm initially decreased in

depth until around day 92, it then showed increases and decreases until the end of the run with no obvious trend. The H₂O band near 1.9 μm did not seem to have any definitive depth decrease over time, however it did change shape, but this did not affect the band minimum position.

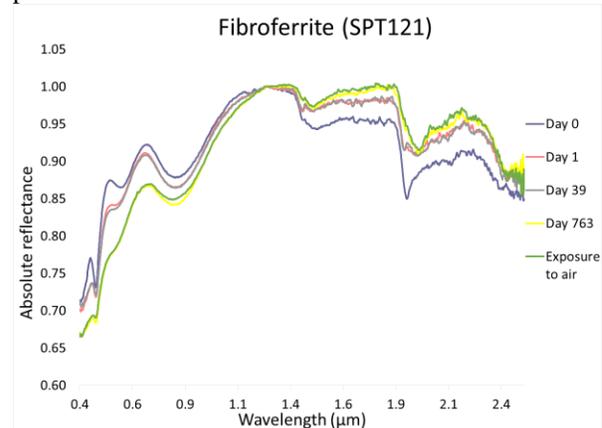


Figure 3: Fibroferrite (SPT121) reflectance spectra (with sapphire window)

From day 0 to day 1 the spectra exhibited a change in shape, associated with H₂O being rapidly pulled out of the sample, causing changes in the ~1.4 μm band, as well as a change below ~1.1 μm to a steeper slope, likely due to changes in Fe oxidation state or Fe-O/OH binding. The spectra did not appreciably change after re-exposure to terrestrial ambient conditions.

The final spectrum suggest that SPT121 is stable on the Martian surface and the decomposition product still retains some evidence of being a ferric iron and water-bearing spectra.

Summary: Not all sulfates behave in the same way; some are more robust and resemble their initial spectra throughout the entire course of the run while others do not. Fe³⁺ bands can all change in depth and minima positions due to the slope that affects all three of these bands. As well, some spectra did not change once re-exposed to terrestrial conditions.

References: [1] Ehrenfreund et al. (2011) *IJA*, 10(3), 239-253. [2] Grotzinger et al. (2014) *Sci.*, 343 (6169). [3] Ehlmann B. L., and Edwards, C. S. (2014) *AREP Sci.*, 42(1), 291-315. [4] Carr, M. H., and Head, J. W. (2010) *EPSL*, 294(3), 185-203. [5] Fairén et al. (2010) *Astrobiology*, 10(8), 821-843. [6] Cloutis et al. (2007) *GRL*, 34 (20), L20202. [7] Bibring et al. (2006) *Sci.*, 312 (5772), 400-404. [8] Gendrin et al. (2005) *Sci.*, 307 (5715), 1587-1591. [9] Langevin et al. (2005) *Sci.*, 307 (5715), 1584-1586. [10] Poulet et al. (2005) *Nature*, 438 (7068), 623-627. [11] Poitras et al. (2018) *Icarus*, 306, 50-73. [12] Cloutis et al. (2008) *Icarus*, 195 (1), 140-168. [13] Hawthorne et al. (2000) *RMG*, 40 (1), 1-112.