

SPECTRAL REFLECTANCE PROPERTIES OF COMMON METAL-OXALATES EXPOSED TO SIMULATED MARS SURFACE CONDITIONS: IMPLICATIONS IN THE SEARCH FOR EXTINCT OR EXTANT LIFE ON MARS. D. M. Applin^{1*}, E. A. Cloutis¹, and M. R. M. Izawa¹, ¹Hyperspectral Optical Sensing for Extraterrestrial Reconnaissance Laboratory, Department of Geography, University of Winnipeg, 515 Portage Ave., Winnipeg, MB, Canada R3B 2E9, *daniel.m.applin@gmail.com

Introduction: Metal-oxalates are quite common on or very near the surface of Earth, as has been comprehensively reviewed by [1]. Abiogenic metal-oxalates are found in low-temperature hydrothermal veins and diagenetic deposits, almost always associated with organic-rich sediments. Metal-oxalates have also been found in the Murchison CM2 carbonaceous chondrite [2]. By far the most common occurrences of oxalate minerals on Earth are as biogenic deposits at the near-surface, where oxalate plays an important role in weathering, mineral dissolution, and soil formation [3].

Calcium oxalates are the most common and important oxalate biominerals associated with life on Earth [4], while magnesium oxalates are of secondary importance, but are also formed near-surface [5]. Oxalates are a very common product of primitive organisms (e.g., lichens, cyanobacteria), especially in endolithic communities [6], where they play an important role in regulating H₂O and heavy metals [7]. It is thought that the secretion of oxalic acid aids these organisms in penetrating the host rock by dissolution [8]. If endolithic communities exist or existed on Mars, metal-oxalate minerals may indicate their current or former presence. Additionally, oxalates are the only geologically stable minerals of any organic acid [9], so the likelihood of their presence on Mars, if life exists or existed, is high.

The difference in atmospheric pressure and composition, as well as the additional ultraviolet radiation may lead to molecular instability, and hence the destruction of the biomarker or the inheritance of a different spectral signature from molecular rearrangement.

We have conducted a spectroscopic study of whewellite (CaC₂O₄·H₂O) and glushinskite (MgC₂O₄·H₂O) under simulated Mars surface conditions.

Methods: Synthetic whewellite and glushinskite were acquired from Alfa Aesar (stock numbers 3230 and 43976). Both were verified by X-ray diffraction (XRD). Samples were crushed with an alumina mortar and pestle and dry-sieved to isolate the <45 μm fraction.

Mars surface conditions were simulated using HOSERLab's mini Mars Environment (mini-ME) chamber [10]. Mars atmospheric composition was approximated using commercial grade CO₂ that was passed through Drierite[®]. A pressure of 600 pa was achieved using a continuously running scroll pump.

UV irradiation was provided by a 25 W deuterium lamp. One day of this exposure has been calculated to be equivalent to 5 years on Mars. A cooling system kept the sample surfaces at <10 °C.

Spectral data was collected through a 10 mm thick sapphire window, which provides <1% absorbance from 0.2 to 6 μm.

Reflectance spectra from 0.35-2.5 μm were collected with an ASD FieldSpec Pro HR spectrometer, with a spectral resolution of between 2 and 7 nm. Incident light was provided by an in-house 100 W quartz-tungsten-halogen (QTH) light source. Spectra were acquired at *i*=0° and *e*=0° using a bifurcated reflectance probe. Reflectance spectra were measured relative to a halon standard located in the sample disk. In each case, 1000 spectra of the dark current, standard, and sample were acquired and averaged, to improve SNR.

Reflectance spectra from 2-5.2 μm were collected with a D&P Model 102F FT infrared spectrometer. Sample illumination was again provided by an in-house 100W QTH light source. Samples were measured at *i*≈30° and *e*=0°, with a spot size of ~7 mm. Reflectance spectra were acquired relative to an Infragold[®] diffuse gold-coated standard. Reference spectra were collected through a second sapphire window with the same path length. Viewing geometry and number of averages (100) were maintained for both reference and sample collection.

Due to the light scattering of the sapphire window and the interior of the chamber, the resulting spectra are noisy and absorption bands appear considerably less intense than those measured in air. We are nonetheless able to analyze changes in band position and band shapes.

Results: 0.35-2.4 μm: Whewellite appears to retain water, as there is no decrease in intensity of the OH and H₂O absorption bands at 1.5 and 2 μm. The only observable change is the development of a colour center at 0.58 μm and a slight reddening of the slope into the UV. These account for a visible change from white to yellow (Fig 1A). Glushinskite appears to have partially dehydrated, observed as a decrease in intensity of the OH and H₂O absorption bands near 1.5 and 2 μm. Glushinskite has also developed a sharp reddening into the UV, also turning the mineral yellow (Fig 2A).

2-5.2 μm: It appears that whewellite may have partially dehydrated and has structural changes. The char-

acteristic absorption bands between 2.4 and 2.5 μm (C-O overtone and possible water combination) are subdued, but nevertheless observable. The probable C-O overtones/combinations between 3 and 4 μm , and the O-C=O bending overtone near 4.4 μm is very subdued (Fig 1B). We can observe that glushinkite lost H_2O and has had significant structural alteration, as the spectrum appears radically different from day zero. The characteristic absorption band at $\sim 2.42 \mu\text{m}$, a C-O stretch overtone, has lost most of its intensity and has slightly shifted to a longer wavelength. The 3-4 μm bands are again unrecognizable. The O-C=O bending overtone near 4.4 μm has either disappeared or shifted to a longer wavelength, and there appears to be new absorption bands at $\sim 4.6 \mu\text{m}$ (Fig 2B).

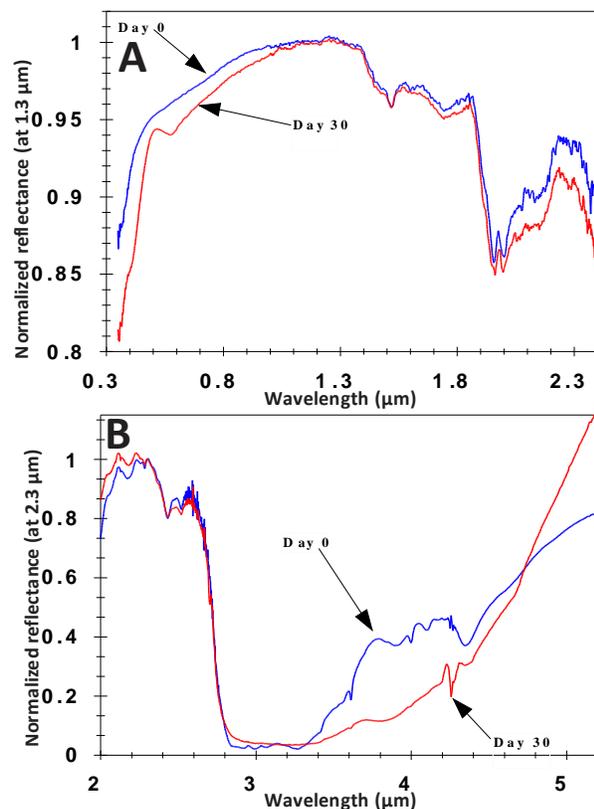


Figure 1: Spectra before and after exposure to simulated Mars surface conditions **A)** VIS-NIR reflectance spectra of whewellite. **B)** NIR-MIR reflectance spectra of whewellite.

Discussion and conclusion: Both glushinkite and whewellite undergo dehydration when exposed to simulated Mars surface conditions. Glushinkite has lost much water, whewellite less so. The spectral changes associated with the oxalate anion are interesting, and planned additional spectral measurements will clarify these changes.

Our results suggest that Ca and Mg oxalate minerals become damaged by martian surface conditions.

We do, however, still observe C-O bonds, so the oxalate has not decomposed. This raises the possibility that carbon could be present in the martian regolith as dehydrogenated oxalate.

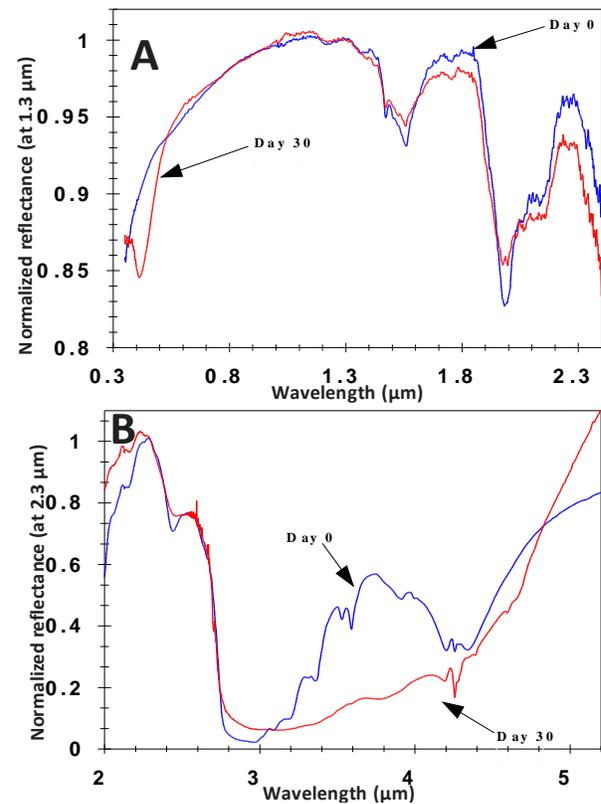


Figure 2: **A)** Spectra before and after exposure to simulated Mars surface conditions **A)** VIS-NIR reflectance spectra of glushinkite. **B)** NIR-MIR reflectance spectra of glushinkite.

References: [1] Hoffman B. A. and Bernaxoni S. M. (1998) *Chem. Geo.*, 149, 127-147. [2] Fuchs L. H. et al. (1973) *Smith. Contr. Earth Sci.*, 10, 39p. [3] Graustein W. C. et al. (1977) *Science* 198,, 1252-1254 [4] Baron E. G. and P. V. Monje. (2008) *Met. Ions Life Sci.*, 219-254. [5] Wilson M. J., et al. (1980) *Min. Mag.* 43, 837-840. [6] Johnston C. G. and Vestal R. (1993) *Microb. Eco.* 25, 305-319. [7] Miralles I., et al. (2012) *Astrobiology* 12, 743-753. [8] Sun H.J. and Friedmann E.I. (1999) *Geomicrobiol. J.*, 16, 193-202 [9] Hoffman B. A. (2004) In Ehrenfreund P., *Astrobiology: Future Perspectives*, 317-331. [10] Craig M., et al. (2001) LPSC XXXII, Abstract #1368.

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