

**WATER CYCLING IN CLAY MINERALS UNDER MARS-RELEVANT CONDITIONS: A NEAR-IR & MID-IR REFLECTANCE SPECTROSCOPY STUDY.** M. M. Wilson<sup>1</sup>, R. E. Milliken<sup>1</sup>, R. V. Gough<sup>2</sup>, <sup>1</sup>Brown University, Box 1846, Providence, RI 02912, <sup>2</sup>University of Colorado Boulder, Boulder, CO 80309.

**Introduction:** Orbital and *in situ* observations have confirmed that hydrous minerals are widespread on Mars and thus should be considered when assessing the planet's total water budget and hydrological cycle [1-3]. Orbital detections of these phases are based primarily on near-infrared (NIR) reflectance data that are typically cross-referenced with laboratory spectra of pure minerals, where the latter are most commonly acquired under ambient terrestrial conditions. However, the martian atmosphere is significantly drier than that of Earth, and near-surface relative humidity (RH) values can remain low even at very low surface temperatures [4-5].

This combination of factors gives rise to several important questions about the role of hydrous minerals on Mars: what is the expected hydration state of hydrous minerals under modern martian surface conditions? What do the near-IR spectra of hydrous minerals actually look like when acquired under Mars-like temperature, pressure, and %RH conditions? Do hydrous minerals actively cycle H<sub>2</sub>O with the martian atmosphere on diurnal or seasonal cycles and, if so, could changes in reflectance spectra associated with such cycling be observed in orbital data?

The purpose of this study is to begin to address these and related questions by measuring the reflectance spectra of hydrated minerals under static and dynamic Mars-like conditions. Building and expanding on previous work [5-6], our experimental approach focuses on the ~1.6 - 7  $\mu$ m wavelength region that is host to both fundamental and overtone/combination OH/H<sub>2</sub>O absorptions, with an emphasis on controlling %RH at cold, Mars-like conditions.

**Methods:** We ultimately seek to determine which hydrous minerals are likely to act as H<sub>2</sub>O sinks versus those which may play a more active role in the modern hydrological cycle (e.g., participate in regolith-atmosphere exchange over diurnal and/or seasonal cycles). The stability and content of H<sub>2</sub>O in expandable clay minerals, zeolites, and sulfate salts is strongly influenced by %RH [3], yet there exists a paucity of experimental NIR-MIR reflectance data for which temperature is low (<0°C) and for which %RH is known, monitored or controlled. Here we present initial results from experiments that attempt to fill this gap.

Initial samples include SWy-1 montmorillonite (Al<sup>3+</sup>-rich) and nontronite (Fe<sup>3+</sup>-rich) dioctahedral clays, as well as Ca/Na zeolite (clinoptilolite). These minerals are either hypothesized or confirmed to exist

on Mars, and they contain H<sub>2</sub>O that should be readily exchangeable under varying T and %RH conditions [1-2,8-10]. All samples were prepared as <45  $\mu$ m powders and mounted in a Linkam environment stage alongside a diffuse gold reflectance standard. The stage was then mounted on a Bruker LUMOS FTIR microscope for acquisition of spectral data over a wavelength range of ~1.5 - 16  $\mu$ m using a KBr beamsplitter and MCT detector. Reflectance spectra were continuously acquired every 1-3 minutes during the course of each experimental run.

We have so far conducted two sets of experiments: conditions in which the sample was initially 'wet' (i.e., highly hydrated) and ones in which the sample was initially 'dry' (low starting water content). For 'wet' experiments, minerals were exposed to high RH by being placed over a water bath under ambient T & P for 1 week. Samples for the 'dry' experiments were purged under very dry air (dewpoint of -70°C) for 1 week.

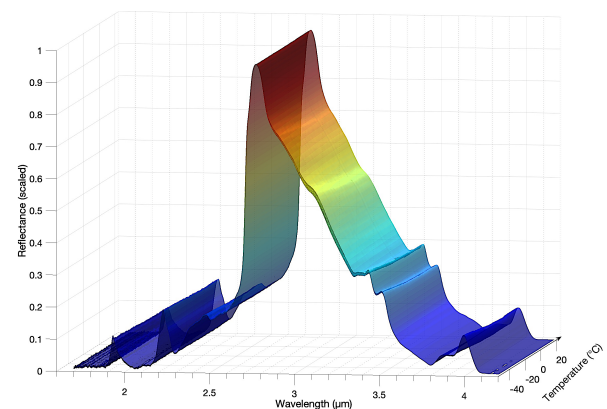


Fig. 1 Band depth spectra for montmorillonite at low and ambient T over the course of an experimental run. Changes in strength of H<sub>2</sub>O features (e.g., at ~1.9 and ~3  $\mu$ m) are relatively small but clearly present, as shown in data in Fig. 2.

The dry purge gas is also allowed to continuously flow through the chamber during the experiments, and as temperature is lowered the %RH increases (until reaching the frost point at -65°C). At the start of each experimental run, the chamber was cooled to -50°C over the course of 72 minutes (1 °C per minute) by pumping liquid nitrogen through the Linkam stage. The sample was then held at -50°C for 3 hours. The purpose of these experiments was to observe how the 3  $\mu$ m region, which includes fundamental H<sub>2</sub>O stretching modes and the first overtone of the H<sub>2</sub>O bending mode, responds to

changing temperature and increased %RH. Because the 3  $\mu\text{m}$  region is measured by the Mars CRISM and OMEGA orbital spectrometers, these lab data have the potential to be compared with existing data of hydrous minerals on Mars acquired that have been acquired under different atmospheric and seasonal conditions.

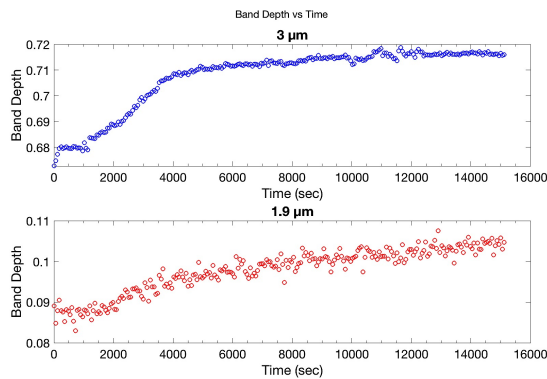


Fig. 2: Band depth values for montmorillonite for distinct  $\text{H}_2\text{O}$  absorptions. At time 0, the sample is relatively dry at ambient temperature. The sample reaches  $-50^\circ\text{C}$  at 4320 seconds and is held at that temperature for the remainder of the experiment. Absorption strengths increase with increasing RH.

Spectral data were processed by scaling all spectra to a common value at a wavelength outside of the absorptions of interest. Band depth spectra were then derived by dividing each spectrum by its spectral continuum, which was defined by a piecewise linear fit. Band depth values for absorptions of interest were then evaluated as a function of experimental conditions (e.g., time, temperature, and %RH; see Fig. 2).

**Results:** Experiments show that montmorillonite will rapidly gain  $\text{H}_2\text{O}$  at lower temperatures as %RH increases. The 3  $\mu\text{m}$  feature weakens after initial drying the sample, as expected, and then quickly rehydrates when exposed to low T, high %RH conditions. The rehydration appears to stabilize or complete within several hours (Fig. 2). Spectral changes due to  $\text{H}_2\text{O}$  gain/loss are most noticeable in the  $\sim 2.9 - 3.5 \mu\text{m}$  region, and though similar changes are observed for the combination mode at  $\sim 1.9 \mu\text{m}$ , changes in the latter are much weaker in terms of absolute values (Fig. 3). Absorptions associated with OH ( $\sim 2.2 \mu\text{m}$ ,  $2.7 \mu\text{m}$ ) do not change during the experiments, consistent with expectations for these conditions. We note that the sample never fully rehydrates to its initial 'wet' condition.

These results suggest that changes in spectral features due to loss/gain of  $\text{H}_2\text{O}$  in clay minerals may be detectable in orbital NIR-MIR datasets (e.g., CRISM and OMEGA), but these changes may be difficult to

discern if focused on the weaker 1.9  $\mu\text{m}$ , particularly if noise levels are high. Water cycling by clay minerals on Mars is likely easier to detect using the stronger fundamental vibrations in the  $\sim 3 \mu\text{m}$  region.

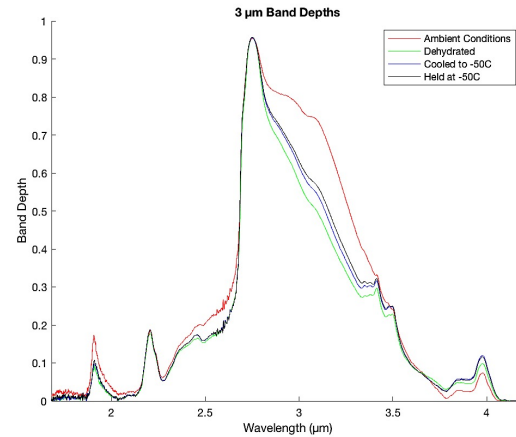


Fig. 3: Changes in band depth spectra for the 3  $\mu\text{m}$  absorption in montmorillonite. Initial spectrum is under ambient (red), 'dry' spectrum (green) was collected a week later after the sample was flushed with dry purge air. Other spectra were taken when the sample first reached  $-50^\circ\text{C}$  (blue) and after the sample was held at this temperature for 3 hours (black). Sample gained  $\text{H}_2\text{O}$  (increased band depth) when RH was increased by lowering temperature.

**Future Work:** Ongoing experiments are planned in which the samples will be held at lower temperatures for increasingly longer periods of time to observe how the sample spectra change over longer duration at cold conditions. In addition, we plan to build on the work of [3] to cycle temperature (and thus %RH) in the sample chamber to mimic diurnal cycling expected for some locations on Mars. These experiments will reveal whether or not the fundamental  $\text{H}_2\text{O}$  stretching modes may be expected to exhibit detectable variations in existing orbital data due to water cycling between hydrous minerals in the regolith and the atmosphere, particularly for locations with in situ geological context such as Gale and Jezero craters.

**References:** [1] Birbring J. P. et al. (2006) *Science*, 312, 400-404. [2] Ehlmann B. L. et al. (2009) *JGR*, 114, E00D08. [3] Fialips C. L. et al. (2001) *Amer. Min.*, 86(3), 304-311. [4] Yen A. et al. (1998) *JGR*, 103(E5), 11125-11133. [5] Feldman W. C. et al. (2004) *JGR*, 109, E09006. [6] Sheppard R. Y. (2020) *Dissertation, Brown University*, Providence, RI. [7] Cloutis E. A. et al. (2000) *JGR*, 105, 7053-7070. [8] Rampe E. et al. (2017) *E&P Sci. Letters*, 471, 172-185. [9] Squyres S. W. et al. (2006) *JGR*, 111, E12S12. [10] Arvidson R. E. et al. (2006) *JGR*, 111, E02S01.