WATER CYCLING OF HYDROUS MINERALS UNDER MARS-RELEVANT CONDITIONS AND IMPLICATIONS FOR INTERPRETING NEAR-IR SPECTRA OF MARS.

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Introduction: Hydrous minerals such as phyllosilicates, zeolites, hydrated silica, and sulfate salts are found in numerous locations on Mars [1-7]. Previous work suggests some of these minerals may exchange water with the near-surface atmosphere on diurnal or seasonal cycles [e.g., 8], and changes in mineral hydration state of these minerals or mixtures may be apparent in near- and mid-infrared (NIR-MIR) reflectance spectra [9]. However, the rates of such hydration changes under modern Mars-like surface conditions and whether or not potentially subtle changes could be observed in orbital reflectance data warrants additional study [9].

Relative humidity (RH) is a main driver for changes in the hydration state of many hydrous minerals, and the surface of Mars experiences significant changes in RH over diurnal, seasonal, and obliquity cycles [10]. As temperature decreases into the night or with the onset of winter, RH increases, and certain hydrous minerals may uptake H_2O. Conversely, some minerals may readily lose H_2O as RH decreases due to a temperature increase [10-12]. Smectites, for example, have readily exchangeable H_2O in their interlayers, whereas zeolites can host H_2O in a variety of channel structures [13], and both may respond quickly to changes in RH [8].

NIR-MIR reflectance spectroscopy should detect subtle changes in hydration state given the strong absorption coefficient of water. Most previous Mars NIR studies have relied on the 1.9 µm combination bend+stretch vibration mode of H_2O to identify H_2O-bearing minerals and possible hydration changes over time on Mars [e.g., 14], but stronger fundamental
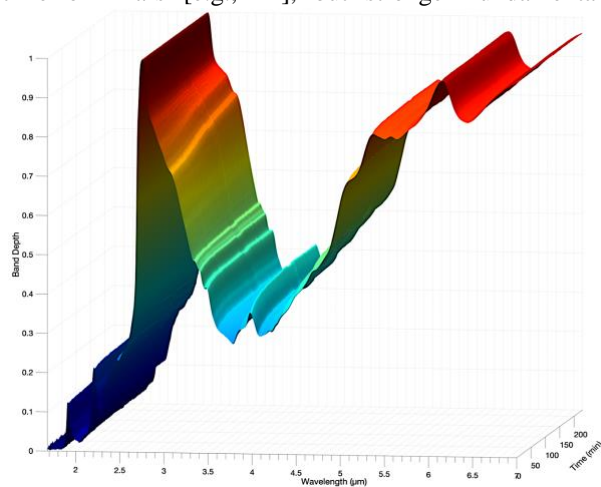

Fig. 1: 3D band depth plot for initially 'dry' montmorillonite. Wavelength (µm) is on the x-axis, band depth value on y-axis, and time (experimental minutes) is on the z-axis. The 3.1 µm feature strengthens over time, expanding into longer wavelengths as band depth increases in value.

vibration modes (v_1, v_3) and the $2v_2$ bend overtone of H_2O are also detectable in existing datasets in the ~2.7-4 µm wavelength region. It is possible that subtle changes in hydration state are more visible in this region than in the 1.9 µm region. Still, an important first step is to construct an experimental basis for how best to evaluate this hypothesis in orbital data.

In this study, we seek to conduct systematic, *in-situ* VIS-NIR reflectance measurements for a wide range of hydrous minerals under Mars-relevant low T and variable RH conditions, focusing on the 1.9 µm and 3.1 µm H_2O features. Our work aims to answer the following research questions: 1) Which hydrous minerals are likely to act as long-term H_2O sinks or be active participants in the modern Martian hydrological cycle? 2) How sensitive are NIR-MIR reflectance data to hydration state changes, and could these be observed in orbital reflectance data?

Methods: Our present study is focused on minerals that do not experience reconstructive phase transitions with the loss or addition of H_2O. We have examined the dioctahedral phyllosilicates montmorillonite and nontronite, the zeolites clinoptilolite and chabazite, and a clay-poor palagonite from altered volcanic materials on Hawaii. The latter is similar to material described by [15] and is of particular interest given the strong water adsorption properties found in that study.

Each sample was mounted in a Linkam environmental stage fixed to a Bruker LUMOS FTIR microscope. Dry purge gas (dewpoint of -70°C) was continuously and slowly passed through the chamber during the experimental run. The sample stage was cooled to -50 or -90°C at a rate of 1°C/minute then held until the sample reached equilibrium, producing a strong increase in RH. Reflectance spectra (1.5 to 16 µm) were acquired every minute during each experimental run.

All samples were prepared (dry sieved) as <45 µm powders and measured two different ways, under initially 'wet' or 'dry' starting conditions. Initially, 'wet' samples were placed over a water bath in a sealed container under ambient T and P for one week. 'Dry' samples were either exposed to the dry purge gas air for one week or heated to low temperatures in the environmental chamber to remove H_2O. All reflectance spectra were scaled over the ~1.7 – 8 µm range to maximize spectral contrast to evaluate subtle changes in absorption strength during each experiment.

Results: The initially dry swelling clays were responsive to increased RH at Mars-like temperature and continued to show increasing band depths for H_2O features well after the start of the final temperature hold

at ~110 minutes (Figs. 1-2). The 3.1µm region exhibits a wider range in band depth values than the 1.9 µm region. In contrast, the initially wet clay samples show a more significant change in the 1.9 µm region (Fig. 2).

Wet zeolites (chabazite and clinoptilolite) did not exhibit a significant increase or decrease in H_2O absorption features throughout the experiment (Fig. 3). Zeolites dried under purge gas also showed little detectable change, and absorptions in the 3 µm region appeared to be at saturation from the start. However, zeolites heated to >150˚C prior to the temperature drop lost H_2O and then regained H_2O at low T (increased RH).

Palagonite behaved similarly to the zeolites in that it required higher temperatures to produce an initially 'drier' state; low RH alone was insufficient to promote water loss. Initially 'wet' palagonite showed no appreciable change over time. In contrast, drier palagonite exhibited increased absorption in both the 1.9 µm and 3.1 µm features.
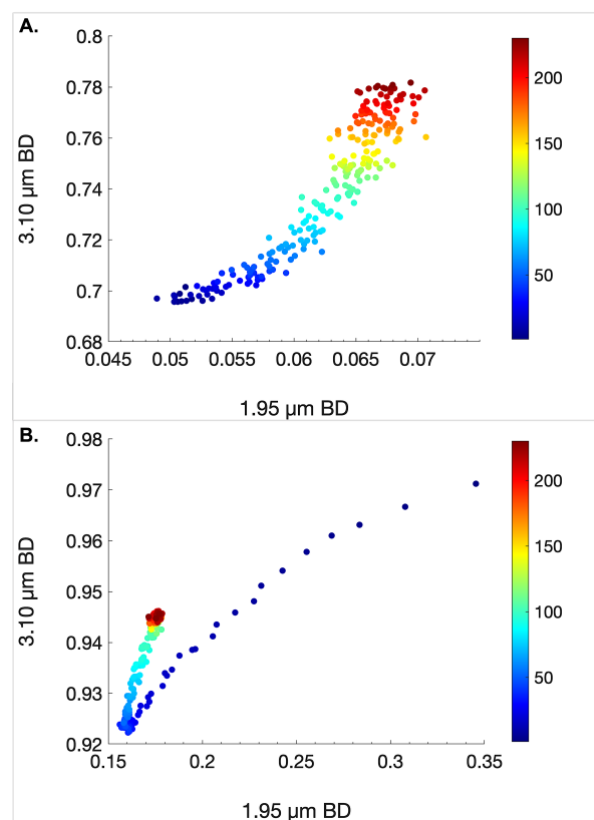

Fig. 2: Two plots comparing the band depth of the 3.1 µm absorption against the 1.95 µm absorption for dry montmorillonite (A) and wet montmorillonite (B). The color bars on the righthand side represent experimental time in minutes, moving from the start (dark blue) through to the end of the experiment (dark red).

Conclusion: Our zeolites and palagonite demonstrate an affinity for quickly adsorbing water under high RH conditions at low Mars-like temperatures, but they likely will retain that water when re-exposed to low RH conditions (in the absence of heating). On Mars, these phases may act as H_2O sinks. In contrast, the swelling clays readily exchanged water with the air as RH changed, though the process was somewhat sluggish compared with previous experiments at ambient temperature. The spectral changes associated with this water gain/loss can be subtle and are most noticeable in the ~3 µm region. It remains unclear if such changes could be distinguishable in lower spectral resolution/lower signal orbital datasets [e.g., 9].

Future Work: Next steps involve exposing samples to low T and variable %RH in a way that mimics diurnal cycling on Mars. We also anticipate resampling these data to CRISM bandpasses by adding various levels of random noise. By doing this, we will see whether the finer scale changes in hydration state (seen in low-noise and high-resolution laboratory spectra) are resolvable in orbital datasets for direct comparison with similar results at NIR wavelengths presented by [9].
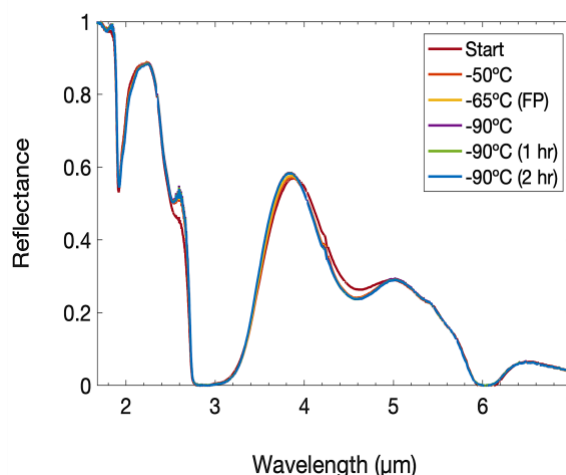

Fig. 3: Scaled reflectance spectra for wet chabazite at different timesteps. FP = frost point. Changes are minimal, with the most obvious change at ~2.6 µm, a region obscured by atmospheric CO_2 on Mars.

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