

**EXPLORING THE UTILITY OF THE WATER ABSORPTION FEATURE AT 6.1 MICRONS.** K. A. Wilk<sup>1</sup>, J. F. Mustard<sup>1</sup>, C. H. Kremer<sup>1</sup>, R. E. Milliken<sup>1</sup> <sup>1</sup>Department of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI, 02912; (kierra\_wilk@brown.edu)

**Introduction:** One of the major challenges of prospecting for water on the Moon and asteroids is distinguishing between the remote signatures of water (H<sub>2</sub>O) and hydroxyl (OH). Among the most useful spectral signatures of hydration at near/mid-infrared wavelengths are features in the  $\sim 2.7 - 4 \mu\text{m}$  range [e.g. 1-4], which may be caused by either H<sub>2</sub>O or OH. Confidently detecting H<sub>2</sub>O on the daylit portions of the Moon with existing remote datasets remains a considerable challenge [1,4]. More recently, telescopic observations from SOFIA identified a  $6.1 \mu\text{m}$  feature, interpreted as the fundamental bending mode of H<sub>2</sub>O [5], demonstrating that measurements in the previously underutilized  $4 - 8 \mu\text{m}$  wavelength range may have strong potential for the remote sensing of volatiles.

Despite these promising measurements, laboratory investigations of the spectral characteristics of water associated with minerals in this range remains sparse [e.g. 6,7]. Robust interpretations of future remote measurements in this wavelength range requires systematic investigation of the influence of H<sub>2</sub>O abundance on the  $6.1 \mu\text{m}$  band, the effect of H<sub>2</sub>O bonding environment on the band, and relationships between H<sub>2</sub>O and silicate related absorptions in this same region [e.g. 8]. We have analyzed laboratory spectra of hydrated minerals, as well as artificial particulate mixtures of hydrated and anhydrous minerals, to explore the utility of the  $6.1 \mu\text{m}$  H<sub>2</sub>O feature.

**Background:** The fundamental and overtone vibrations of water have been used to detect hydration in the laboratory [e.g. 3,6] and the surfaces of solar system objects [e.g. 1,2]. Commonly measured spectral features associated with H<sub>2</sub>O include the  $1.91 \mu\text{m}$  combination bend+stretch mode, as well as the  $\sim 2.9 - 3.1 \mu\text{m}$  asymmetric and symmetric stretching vibrations of water.

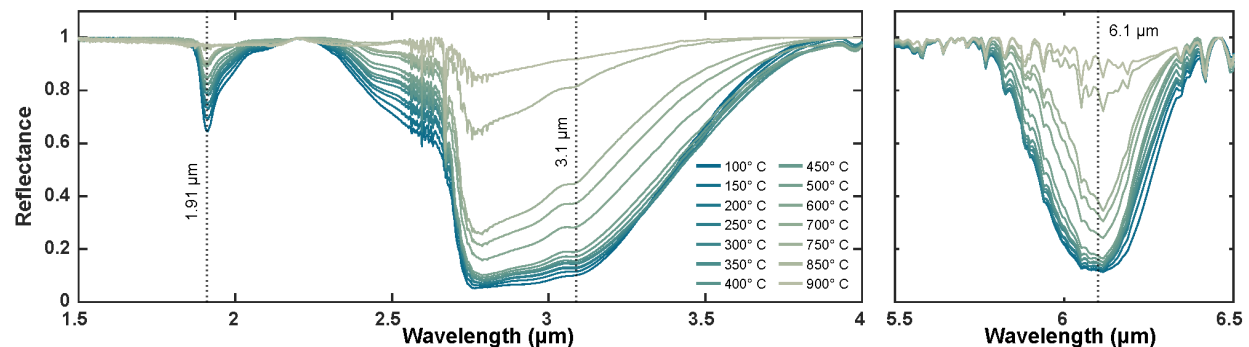
The fundamental bending vibration of water appears at  $6.1 \mu\text{m}$ , without overlapping OH bands, making this feature well suited for the detection and determination of H<sub>2</sub>O abundance. Recent work, however, has shown that this band coincides with several strong bands in common anhydrous silicates such as olivine, pyroxene, and plagioclase [9], and the interactions between these spectral features have yet to be assessed.

Despite the apparent value of the  $6.1 \mu\text{m}$  water absorption feature, little work has been done to characterize the nature of this absorption feature. In addition, detailed study is warranted to understand how to estimate the abundance of water from reflectance spectra in the  $6 \mu\text{m}$  region.

**Methods:** We examined previously acquired [10] laboratory FTIR reflectance spectra of Na-Ca montmorillonite (SWy), Mg-exchanged montmorillonite (Mg-SWy), clinoptilolite, and palagonite to compare the strength and evolution of the  $6.1 \mu\text{m}$  feature as H<sub>2</sub>O is removed from the host phase. The samples were purged under dry air conditions for upwards of three hours to remove loosely bound H<sub>2</sub>O and subsequently heated stepwise for 15 – 20 minutes at each temperature, ranging from 100 – 800 °C, to remove the remaining H<sub>2</sub>O. Samples were heated longer at the last temperature step to ensure that all the water had been removed. Each sample was measured before and after the ambient measurements, as well as after each heating step to determine weight loss. Detailed methods are described in [3].

We also examined olivine – nontronite mixtures to compare the strength and evolution of the  $6.1 \mu\text{m}$  water feature as the spectral signature is diluted due to mineral mixing [11].

We performed a continuum removal on the spectra in order to calculate band depths associated with water



**Figure 1** Continuum removed spectra of dehydrated clinoptilolite. As the temperature increases, more water is removed from the sample, as indicated by a decrease in the  $1.91$ ,  $\sim 3.1$ , and  $6.1 \mu\text{m}$  band depth.

at 1.91, 3.1, and 6.1  $\mu\text{m}$  (Fig.1). All spectral measurements were made in the Reflectance Experiment Laboratory (RELAB) at Brown University using a Thermo Nexus 870 FTIR.

**Results:** The minimum position of the 6.1  $\mu\text{m}$  fundamental bending vibration was virtually the same throughout the 4 mineral samples examined. We compared the strength of the 6.1  $\mu\text{m}$  absorption band depth to the percent weight change of the sample. Weight loss within the sample is assumed to be from the removal of water, with the purging experiments removing loosely bound water and the heating experiments removing the more strongly bound water molecules [3].

Band depth and weight loss of the mineral samples are correlated, with increasing weight loss resulting in a decrease in band depth. When comparing the percent weight loss to the 6.1  $\mu\text{m}$  band depths, the samples exhibit a change in slope (Fig. 2a). In clinoptilolite, for example, minimal change in the 6.1  $\mu\text{m}$  band depth occurs despite a 11% weight loss, until the sample exhibits an abrupt 0.62 decrease in band depth over a 5% weight loss. This could be due to the 6.1  $\mu\text{m}$   $\text{H}_2\text{O}$  feature initially being saturated and subsequently weakening as water is removed and the feature is no longer saturated.

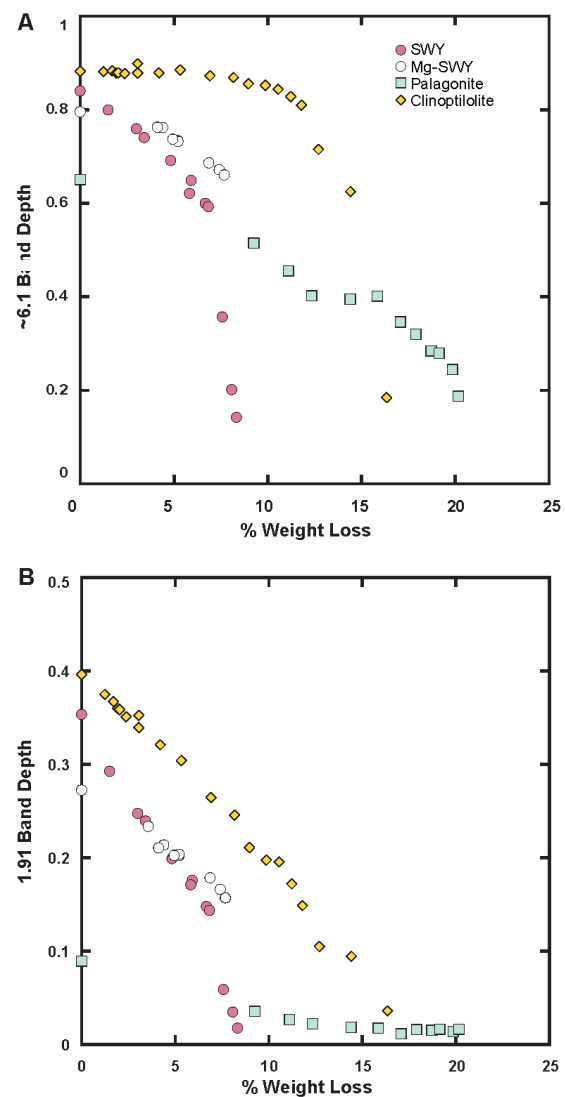
When looking at the 1.91  $\mu\text{m}$  feature, we do not find a similar change in slope (Fig. 2b). Rather, the 1.91  $\mu\text{m}$  band depth changes are linear with weight loss, indicating the continuous removal of  $\text{H}_2\text{O}$ . Disparities between the 1.91  $\mu\text{m}$  and 6.1  $\mu\text{m}$  features could be due to differences in band saturation or that the bending mode of  $\text{H}_2\text{O}$  represented in the 1.91  $\mu\text{m}$  feature is not a major contributor to the overall bending mode represented at 6.1  $\mu\text{m}$ . This could be influenced by the type and degree of hydrogen bonding.

Spectra of the olivine – nontronite mixtures exhibit a distinct 6.0  $\mu\text{m}$  silicate band and a 6.1  $\mu\text{m}$   $\text{H}_2\text{O}$  absorption band. The 6.0  $\mu\text{m}$  silicate band is present when the mixture contains at least 50% olivine, whereas the 6.1  $\mu\text{m}$   $\text{H}_2\text{O}$  feature is present when the mixture contains at least 50% nontronite. No spectral water signature was observed in the 6  $\mu\text{m}$  region at less than 5% nontronite, despite the presence of the 1.91  $\mu\text{m}$  and 3.1  $\mu\text{m}$   $\text{H}_2\text{O}$  absorption features.

**Future Work:** Future work will include additional experiments to fully discern the relationship between the 6.1  $\mu\text{m}$  and the 1.91  $\mu\text{m}$  and 3.1  $\mu\text{m}$  water absorption features. Continued analysis of  $\text{H}_2\text{O}$  and spectral silicate bands in the 6.0  $\mu\text{m}$  region is also required to understand their relationship and potential ambiguity in distinguishing these two spectral features in remotely sensed data.

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**References:** [1] Li and Milliken (2017) *Science Advances*, 3, 9. [2] Milliken et al. (2007) *JGR*, 112, E08S07 [3] Milliken and Mustard (2005) *JGR*, 110, E12001. [4] Pieters et al. (2009) *Science*, 326, 568-572. [5] Honniball et al. (2021) *Nature Astronomy*, 5, 121-127 [6] Bishop et al., (1994) *Clays and Clay Minerals*, 42, 6, 702-716. [7] Hibbitts et al. (2020), *51<sup>st</sup> LPSC Abstract #2526* [8] Kremer et al., (2020) *Geophysical Research Letters*, 47 [9] Kremer et al. (2021) *52<sup>nd</sup> LPSC Abstract #2196* [10] Milliken, R.E (2006) *PhD Thesis*, Brown University, Providence, RI [11] Lapotre and Ehlmann (2017) *JGR*, 122, 983-1009



**Figure 2** Band depth of the A) 6.1  $\mu\text{m}$  fundamental bending vibration of water and B) the 1.91  $\mu\text{m}$  overtone vs. the percent weight loss of the sample which is the result of water removal.