

EFFECT OF SURFACE ADSORBED H₂O/OH ON LUNAR RELEVANT MINERALS AT 3 AND 6 MICRONS. K. A. Wilk¹, J. F. Mustard¹, R. E. Milliken¹, C. M. Pieters¹, ¹Department of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI, 02912; (kierra_wilk@brown.edu)

Introduction: Three independent spacecraft have detected the widespread presence of an absorption feature at $\sim 3\ \mu\text{m}$ that is indicative of hydration on the lunar surface [1–3]. However, the $3\ \mu\text{m}$ feature can consist of several overlapping absorptions caused by H₂O and/or OH, thus resolving the speciation of this lunar ‘water’ with existing remote datasets has proven difficult. Unlike the $3\ \mu\text{m}$ region, molecular H₂O exhibits a fundamental bending mode absorption at $6\ \mu\text{m}$ that does not coincide with OH bands. Evidence for such a feature on sunlit portions of the lunar surface were recently identified in telescopic SOFIA observations, interpreted as clear evidence for H₂O at the lunar surface [4,5]. Future space-based measurements in the $4 - 8\ \mu\text{m}$ wavelength range thus have strong potential for identifying and quantifying volatiles, and water speciation in particular, for the Moon.

Diurnal variability and latitudinal dependence in the strength of the $3\ \mu\text{m}$ hydration feature has been observed in multiple datasets, suggesting changes in surface temperature are likely associated with the accumulation and migration of H₂O/OH on the lunar surface [3,6,7]. The temperature dependence indicates at least some of the lunar water must be weakly bound, whereas other portions may be trapped in agglutinitic glass and remain stable over diurnal cycles [6,8]. These interpretations are consistent with the SOFIA data, for which H₂O contents estimated from the $6\ \mu\text{m}$ feature were calculated to be too high for solely surficial water [5]. However, additional laboratory studies are needed to better understand how observed water absorptions at 3 and $6\ \mu\text{m}$ relate to H₂O abundance for lunar-relevant (i.e., H₂O-poor) materials.

We acquired reflectance spectra of olivine, pyroxene, and plagioclase in situ to investigate how features at ~ 3 and $\sim 6\ \mu\text{m}$, caused in part by surface-adsorbed H₂O, changed during heating experiments. We also explored the degree to which surface adsorbed H₂O can give rise to a discernable $6\ \mu\text{m}$ feature in these nominally anhydrous minerals.

Methods: Anorthite (Miyake-Jima; An>90), enstatite, and olivine (San Carlos) (Figure 1) were prepared as powders for reflectance measurements (<25, 25-45, 45-75 μm for anorthite and enstatite; <20, 20-45, 45-75 μm for olivine). Samples were mounted in a Linkam THMS600 environmental stage fixed to a Bruker LUMOS Microscope FTIR (μFTIR). Each sample was measured at ambient conditions (23.1 – 23.9°C, <10% relative humidity, RH) and then dry air

(RH<0.1%) was continuously passed through the environmental chamber for 25 minutes while being held at 25°C to purge the system. The sample stage was then heated to 200°C at a rate of 3°C/min and held at 200°C for 1 hour. Reflectance spectra (1.6 – 16 μm) were acquired every 5 minutes. Reflectance measurements of the smallest particle size fractions were also taken after the sample had cooled back down to 25°C and been exposed to ambient air for 20 minutes. All reflectance measurements were taken at 125x125 μm spot sizes.

Spectra were normalized to 1 using the average reflectance value between 2.2056 – 2.2096 μm . We performed a straight line continuum removal between 2.2076 μm and 4.0020 μm to further analyze changes in the $3\ \mu\text{m}$ feature.

Results: Olivine, enstatite, and anorthite all exhibit a broad $3\ \mu\text{m}$ feature indicative of H₂O under ambient conditions (Figure 2). For olivine and enstatite, as surface-adsorbed H₂O is removed via heating, the $3\ \mu\text{m}$ feature decreases in strength and becomes narrower and more asymmetric, with a band minimum centered near $\sim 2.8\ \mu\text{m}$. In contrast, the $3\ \mu\text{m}$ feature in anorthite decreases in strength but remains broad in nature. The incomplete removal of the $3\ \mu\text{m}$ feature suggests there is either residual H₂O adsorbed on the surface or there exists H₂O within the anorthite (e.g., inclusions) that could not be removed in this temperature range. For each mineral, when the fine size fraction was re-exposed to ambient conditions the strength of the $3\ \mu\text{m}$ feature reapproached that of the initial spectra (Figure 3). This indicates changes in the $3\ \mu\text{m}$ region were reversible and consistent with surface-adsorbed H₂O.

In contrast, we observed no clear spectral changes in the $4-8\ \mu\text{m}$ region that can be associated with the loss/gain of H₂O. The dominant features observed in this spectral region are associated with vibrational modes of the silicates themselves. The identification of

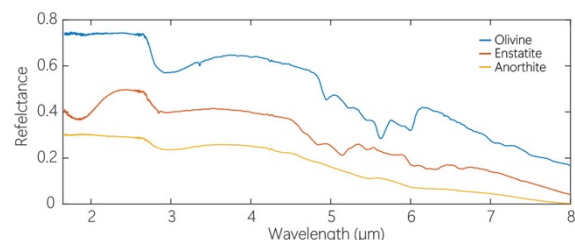


Figure 1: Reflectance spectra (1.6 – 8 μm) of olivine (<20 μm), enstatite (<25 μm), and anorthite (<25 μm) at ambient room temperature.

H₂O stretching modes in the $\sim 3 \mu\text{m}$ region indicates molecular H₂O was lost and re-gained. The lack of complementary features/changes in the $\sim 6 \mu\text{m}$ region that are unambiguously attributable to H₂O may indicate there is not sufficient molecular water present to give rise to this feature.

For a given amount of an absorbing species, the absorption strength will be governed by the absorption coefficient, which is proportional to the imaginary component of the complex index of refraction (k) and inversely proportional to wavelength. In the case of bulk liquid H₂O, the absorption coefficient at $\sim 2.9 \mu\text{m}$ is nearly 4.5 times stronger than the value at $6.1 \mu\text{m}$. It may be possible that thin layers of H₂O adsorbed onto the mineral surface are insufficient to produce an absorption feature at $6 \mu\text{m}$ but sufficient to produce a feature at $3 \mu\text{m}$. If correct, it remains unclear as to how much surficial H₂O is required to produce a distinct $6 \mu\text{m}$ feature, but the amount of adsorbed water in the experiments presented here was clearly insufficient.

Discussion: Our results illustrate changes in the $3 \mu\text{m}$ region attributable to weakly held H₂O on nominally anhydrous minerals as a function of temperature. Better understanding how the full $3 \mu\text{m}$ feature changes, both in strength and overall shape, throughout the lunar day may provide additional insights into the speciation of lunar water and any potential differences in

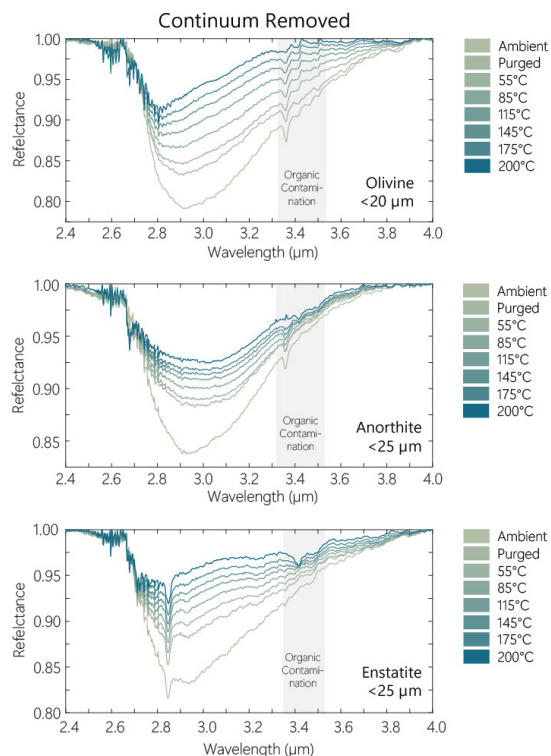


Figure 2: Continuum removed spectra of olivine, anorthite, and enstatite between $2.2076 - 4.0020 \mu\text{m}$. As the samples are heated, the strength of the $3 \mu\text{m}$ feature decreases.

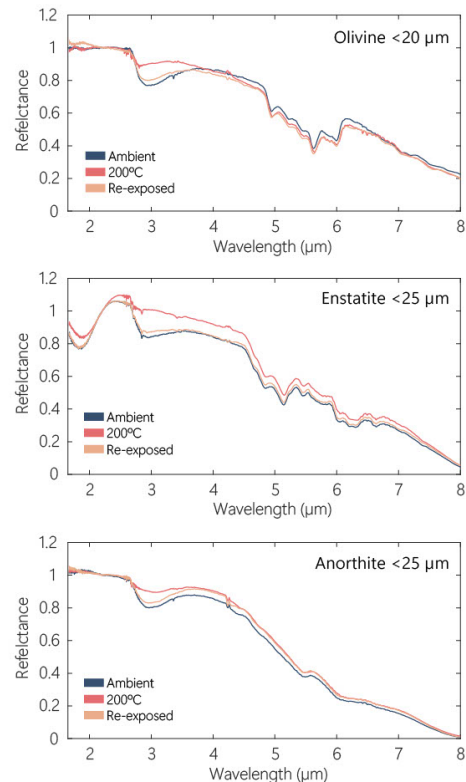


Figure 3: Reflectance spectra ($1.6 - 8 \mu\text{m}$) of olivine, enstatite, and anorthite at ambient conditions, after having been gradually heated to 200°C for 60 minutes, and then re-exposed to ambient air conditions for 20 minutes.

hydration due to surface composition. Future Lunar Trailblazer measurements should contribute insight to this effort.

We were unable to identify a $6 \mu\text{m}$ feature due to H₂O in the samples evaluated here, despite evidence for H₂O in the $3 \mu\text{m}$ region. Ongoing work will focus on quantifying how much H₂O is needed to observe features/changes in the $6 \mu\text{m}$ region. Future work into the effect of surface H₂O/OH on space weathered materials and lunar soils, which are more direct analogs to lunar observations, are also warranted. Repeat measurements throughout the lunar day in the $4 - 8 \mu\text{m}$ region will be critical in determining if the $6 \mu\text{m}$ feature also exhibits diurnal variations, which in turn can be compared with the $3 \mu\text{m}$ region to help understand the mechanism(s) by which lunar water varies over the course of a lunar day.

References: [1] Pieters, C. M. et al. (2009) *Science*, 326, 568–572. [2] Clark, R. N. (2009) *Science*, 326, 562–564. [3] Sunshine, J. M. et al. (2009) *Science*, 326, 565–568. [4] Honniball, C. I. et al. (2020) *Nat Astron*, 5, 121–127. [5] Honniball, C. I. et al. (2022) *Geophysical Research Letters*, 49. [6] Li, S. and Milliken, R. E. (2017) *Sci. Adv.*, 3, e1701471. [7] Wöhler, C. et al. (2017) *Sci. Adv.*, 3, e1701286. [8] Liu, Y. et al. (2012) *Nature Geosci*, 5, 779–782.