

OBSERVATIONS AND MODELING OF THE ADSORBED WATER IN MONTMORILLONITE WITH REFLECTANCE SPECTROSCOPY. R. E. Milliken and J. F. Mustard, Brown University, Dept. Geological Sciences, Box 1846, Providence, RI 02912, USA. Ralph_Milliken@brown.edu

Introduction: Understanding the role of water in surface and atmospheric processes is a focus of future Mars missions. NASA's Mars Reconnaissance Orbiter and ESA's Mars Express will carry VIS-NIR spectrometers (CRISM and OMEGA, respectively) capable of retrieving spectral data at wavelengths of 0.4-4.0 μm [1]. Characteristic water and hydroxyl absorptions at ≈ 1.4 , 1.9, 2.2, and 3 μm provide the opportunity for these instruments to detect aqueous or hydrothermally altered surface materials. It is anticipated that seasonal variations in the amount of adsorbed H_2O [2] might be detected as well.

Though Mars is known to have a strong 3 μm absorption band due to water [3], the different forms of water (adsorbed, structural, bound) and the structure of the host mineral (clays, hydroxides, etc.) affect the shape and strength of the absorption, making a quantitative assessment of this water difficult. Previous work has focused on the strength of water absorptions as a function of particle size [4] and inter-layer cations [5]. Bishop et al. [5] were able to show the different forms of water (adsorbed and bound) are observed in reflectance spectra of clays, but did not try to quantify the amount of water present. Yen et al. [6] modeled the percentage of water in materials as a function of apparent absorbance. Their results showed a correlation between percent water and apparent absorbance, but the uncertainties in estimating the percent water were $\pm 2\%$. Given that the water content of the Martian soil is < 2 wt. % [7], this method of apparent absorbance may not be sensitive enough to quantify small amounts (or changes in) adsorbed water. Here we model the loss of adsorbed water in reflectance spectra of montmorillonite (SWy-1) as a function of the scattering efficiency (Q_s) and absorption efficiency (Q_A) of water. This method is capable of detecting and modeling changes in reflectance spectra due to small changes (< 0.1 wt. %) of adsorbed water.

Procedure: All samples were measured over the range of 1.5 - 25 μm using a Nicolet FTIR spectrometer in RELAB at Brown University. Multiple samples of SWy-1 montmorillonite were measured for each time-series to test the precision and reproducibility of the results. All samples were first measured under ambient conditions; the sample chamber was then closed and purged by passing dry air (CO_2 and H_2O filtered) across the samples. The samples were then measured at time-steps of 1, 2, 3, 4, 6, 9, and 12 hours while under purged conditions to track spectral changes due to loss of adsorbed water. Samples were weighed immediately

before the first measurement (ambient) and after the last measurement (purged 12 hours) to determine the weight loss due to adsorbed water. A gold reference standard was measured at the beginning of each time-step measurement.

Four replicates of SWy-1 were measured and showed similar spectral changes and weight losses. The reproducibility of the observations indicates the loss of adsorbed water in SWy-1 samples should be equivalent at any given time within the same time-series. Six SWy-1 samples were then placed in the chamber, where two samples were for spectral measurements while the other four were removed after 1, 2, 3, and 4 hours of purging to determine the weight loss at that time-step. The results are several series of spectra of SWy-1 measured under ambient ("0 hours,") and purged (1, 2, 3, 4, 6, 9, and 12 hours) conditions with known weight losses corresponding to the 1, 2, 3, 4, 6, and 12 hour spectra. One of these series is presented in Fig. 1 from 1.8-5.0 μm (a region covered by CRISM and OMEGA) and the weight loss for each time-step is listed in Table 1.

Table 1. Average wt. loss corresponding to reflectance spectra at each purged time-step.

| time-step(h) | 1 | 2 | 3 | 4 | 6 | 12 |
|------------------|-----|------|------|------|------|------|
| Δ wt.(mg) | 5.4 | 8.4 | 9.3 | 10.3 | 10.4 | 12.0 |
| Δ wt. (%) | .18 | .272 | .303 | .333 | .338 | .391 |

Model: Consistent with previous studies [4], the strength of the 1.9 and 3.0 μm H_2O absorptions decrease due to the loss of adsorbed water in a desiccating environment (Fig. 1). No other absorptions change during the measurements, suggesting that all changes in the spectra are due to the loss of adsorbed water. This is shown more clearly in the ratio spectra shown in Fig. 2, where the only features present are found at the wavelengths expected for water. To model these spectra, we first convert all reflectance spectra to single-scattering albedo (w) using the simplification of Mustard and Pieters [8]. Hapke [9] shows that for a size parameter (X) $\gg 1$ and a monominerallic substance, the scattering efficiency (Q_s) is equivalent to w and the scattering and absorption efficiencies sum to unity. If the montmorillonite is considered a two component system (water and "dry," montmorillonite), then the single scattering albedo at a time t (w_t) may simply be the combination of the scattering efficiencies of the two components, such that

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$$w_t = Q_{S,t} = Q_{S,H_2O} \cdot Q_{S,montmorillonite} \quad (1).$$

Equation (1) assumes the absorption coefficient of the system is an additive relationship between the absorption coefficients of the two components. Furthermore, since we can determine water losses relative to the final weight, we can consider our driest spectrum (12 hour purge) to represent the “dry,, montmorillonite. Substituting w_{12} for $Q_{S, mont.}$ and dividing both sides of (1) by w_{12} gives

$$\frac{w_t}{w_{12}} = \frac{Q_{S,H_2O,t} \cdot Q_{S,mont.}}{Q_{S,mont.}} = \frac{Q_{S,H_2O,t} \cdot w_{12}}{w_{12}} = Q_{S,H_2O,t} \quad (2).$$

Equation (2) allows us to determine the scattering efficiency due to adsorbed water (relative to the driest sample measured) at any other time-step. Values of Q_{S,H_2O} for the spectra in Fig. 1 are plotted in Fig. 2. Using theories outlined by Hapke [9], we can model Q_{S,H_2O} using the optical constants of water and an internal-transmission factor (θ). Though several models for determining θ exist, we find that the internal-scattering model described by Hapke [9] provides the best fits to our values of Q_{S,H_2O} . An example of a fit for Q_{S,H_2O} at 2 hours purged is plotted in Fig. 2. The two variables in this model are the optical path length (d) and the near-surface scattering coefficient (s). The value of d decreases over time as adsorbed water is lost (Fig. 3) and the value of s increases (removing water increases scattering).

Conclusions: Modeling Q_S of water in montmorillonite relative to a “dry,, sample allows us to isolate spectral changes due solely to the loss of adsorbed water. These early results suggest the approach has high sensitivity to changes in the amount of water of <0.1 wt. % and perhaps as low as 0.01 wt. %. This sensitivity makes it a potential model for examining surface-atmosphere interactions on Mars, which may involve very small amounts of water. Future work will concentrate on a variety of hydrated minerals to examine effects of mineral structure on adsorbed and structural water loss, and on refining the modeling and quantification of water abundance.

References: [1] Murchie, S. et al. (2002) LPSC 33, #1697; [2] Zent, A. and R. Quinn (1997) *JGR*, 102, 9085-9095; [3] Sinton, W. (1967) *Icarus*, 6, 222-228; [4] Cooper, C. and J. Mustard (1999) *Icarus*, 142, 557-570; [5] Bishop, J. et al. (1994) *Clay and Clay Min.*, 42, 702-716; [6] Yen, A. et al. (1998) *JGR*, 103, 11125-11133; [7] Kieffer, H. et al. (1992) *Mars*, 1498pp., University of Arizona Press; [8] Mustard, J. and C. Pieters (1989) *JGR*, 94, 13619-13634; [9] Hapke, B. (1993) *Theory of reflectance and emittance spectroscopy*, 455pp., Cambridge Press.

Fig. 3 Values of d from modeled best-fit curves vs. measured wt. % loss relative to the driest sample in the corresponding time-series. The data show a power law relationship.

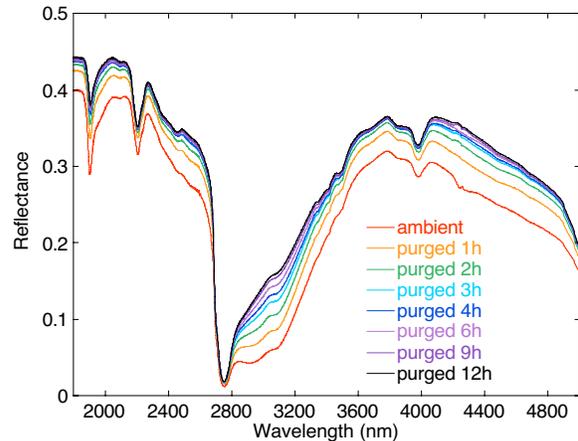


Fig. 1 Time-series of SWy-1 montmorillonite. The 2.2 μm metal-OH absorption does not change, whereas the 1.9 and $\sim 3 \mu\text{m}$ absorptions do. This shows that only adsorbed H₂O is being lost during the purging process.

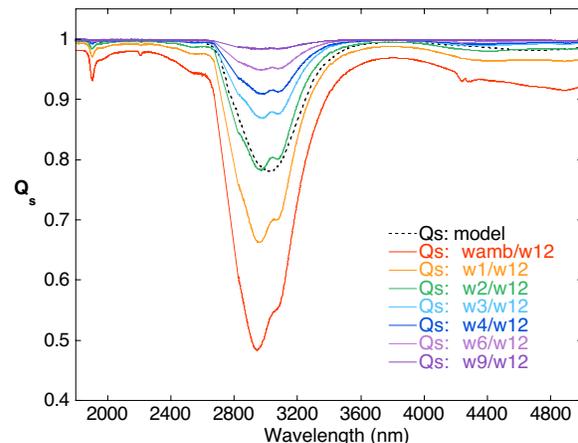


Fig. 2 Estimates of Q_{S,H_2O} at each time-step relative to the driest (12 hour) time step. These values of Q_S can be modeled using the optical constants of water and varying the optical path length and near-surface scattering coefficient.

