**A LABORATORY-BASED MODEL FOR ESTIMATING ABSOLUTE $H_2O$ CONTENT OF MINERALS USING VIS-NIR SPECTROSCOPY.** R. E. Milliken[1] and J. F. Mustard[1], [1]Dept. Geological Sciences, Brown University, Providence RI 02912 USA. Email: ralph_milliken@brown.edu

**Introduction:** The OMEGA and CRISM VIS-NIR spectrometers (on ESA's Mars Express and NASA'a MRO, respectively) will provide high-resolution data that covers both the 3.0 and 1.9 μm water absorptions [1,2]. The 3.0 μm band is present in all spectra acquired by OMEGA thus far, and a 1.9 μm band is visible in localized regions [3]. Our goal is to use this data to estimate the absolute and/or relative $H_2O$ content of the martian surface both spatially and temporally [4]. Previous studies have used laboratory data to find relationships between water content, mineralogy, and various spectral parameters [5,6,7,8,9]. Building on our previous work [10,11], we use laboratory-derived spectra to calculate and compare several absorption band parameters to total $H_2O$ content in an attempt to find a relationship between water absorption strength and water content. Our proposed model is applicable to laboratory data as well as spectra of Mars, lunar deposits, asteroids, or other hydrated planetary surfaces.

**Methods:** We chose a suite of hydrated samples that cover several mineral classes (sulfates, zeolites, clays, alteration products) and range in crystallinity from well-ordered to amorphous. Samples include SWy-1 (montmorillonite), Mg-exchanged SWy-1 (provided by Janice Bishop), $MgSO_4$ (chemical grade powder), HWMK101 (palagonite, provided by Dick Morris), and clinoptilolite (a zeolite, provided by Dave Bish). The montmorillonite and sulfate samples were bulk powders, the rest were sieved to <45 μm. All spectra were acquired in RELAB at Brown University using a Nicolet FTIR spectrometer. Samples were measured from ~1 - 4.5 μm in order to capture the 1.4 μm (overtone), 1.9 μm (combination overtone), and 3.0 μm (fundamental stretch) water absorptions. Spectra are acquired under $H_2O$ and $CO_2$ purged conditions at intervals of 5 minutes for the first half hour (see [10,11] for description) and then at 1 h. Samples were also incrementally heated in a furnace (typically 50°C increments, 15 minutes each), with spectra taken after each heating step. Samples were immediately removed from the spectrometer and weighed to determine the wt.% loss. Only 20 scans are averaged to produce the final spectrum in order to avoid effects of sample rehydration (adsorbed water). Approximately 30 seconds elapse between removal of the sample from the furnace, spectra acquisition, and weighing. Each sample was also measured using the bi-directional spectrometer to determine the wavelength and value of the maximum reflectance point. All FTIR spectra for a given sample were scaled to their corresponding maximum reflectance. Two examples of heated samples, $MgSO_4$ and clinoptilolite, are shown in Figs. 1 and 2.

Three parameters were calculated to find a relationship between water content and absorption strength. First, the 1.9 μm and 3.0 μm absorptions were converted to band depths (BD) by dividing each point within the band by its corresponding continuum value (a linear fit defined by the maximum reflectance values on either side of the absorption). These band depths were then integrated and normalized by their wavelength region to produce integrated band depths (IBD). These parameters have been used previously to characterize the hydration state of the martian surface [12,13]. A third parameter, the normalized path length ($d_{NORM}$), was calculated by solving Beer's Law, $R = e^{-\alpha d}$ (1), where R is reflectance, α is the absorption coefficient of the material, and *d* is the optical path length, for *d* at the maximum absorption point. The absorption coefficient of bulk water at 1.9 and 3.0 μm was used for α and the continuum value at the wavelength corresponding to the maximum absorption was used as a baseline for starting the exponential fit. The resulting *d* values were then normalized by the maximum possible value of *d* for each spectrum (determined by solving (1) again using R = 0) to produce $d_{NORM}$. The reflectance spectra were then converted to single scattering albedo, *w* [14], and the 3 parameters were calculated again. An additional parameter, *Hapke's espat* function [14], was also calculated at the maximum absorption point for the single scattering albedo spectra.

The normalized path length for the 1.9 μm band was plotted against measured wt.% loss for each sample to determine the total $H_2O$ content. A line is fit to the data and the x-intercept is assumed to represent the total $H_2O$ content (Fig. 3). The 3.0 μm band was not used because it is affected by the presence of $OH^-$, and absorptions are still present even when all $H_2O$ has been removed. The 1.9 μm band, however, is only affected by $H_2O$. The samples examined here are highly hydrated and all weight loss is assumed to be due to $H_2O$ ($OH^-$, organics, and other impurities are assumed to be minor components of the total wt. loss). For some minerals, such as palagonite, the 1.9 μm band disappears before all $H_2O$ has been removed (Fig. 3). The 3.0 μm band was used for these samples and values were compared against weight loss values obtained from thermogravimetric analysis (TGA) [10] (found to agree within <0.5 wt.%). All seven parameters were plotted against the estimated total $H_2O$ content to search for a relationship that is independent of composition.

**Results:** *1.9 μm*: Of the seven parameters, none seem to provide a strong relationship to $H_2O$ content for the samples as a group. The *espat* function and $d_{NORM}$ (R and *w* spectra) parameters show linear correlations to total $H_2O$ content for individual samples, which may be useful for Mars if the surface composition is known. The IBD parameter showed a weak exponential trend for some samples, but not all.

*3.0 μm*: The BD and *espat* parameters showed no strong correlation to $H_2O$ for the samples as a group. Though the *espat* function worked well for each sample at 1.9 μm, small changes in very low R values for the fully hydrated samples (saturated at 3.0 μm) resulted in large differences when converted to *w*. This is a result of the strongly non-linear conversion of R to *w* [14]. The 1.9 μm bands have higher reflectance values and are not affected as strongly. For this reason, parameters using *w* spectra are not useful in the 3 μm region when the absorption is saturated. The IBD and $d_{NORM}$ parameters (using R spectra) both show exponential

relationships when plotted against $H_2O$ content. If $d_{NORM}$ is plotted on the y-axis, the resulting curve is similar to a plot of apparent absorbance [8] or mean optical path length [14], both of which are non-linear. *Hapke* [14] suggests using the *espat* function to create a linear relationship, but it is not suitable here for the reasons mentioned above. Either IBD or $d_{NORM}$ could be used to predict $H_2O$ content, but the $d_{NORM}$ parameter gives a better fit (Fig. 4). These are the only two parameters that show unique correlations to absolute water content across a range of sample compositions and structures. The relationship between $d_{NORM}$ and $H_2O$ is described exponentially by: $H_2O = 0.0253\ e^{7.08\ d}$ (Fig. 4). Several data points for clinoptilolite, corresponding to temperatures of 400-500°C, lie outside of the main group. The spectra for these points showed a sudden decrease in reflectance at wavelengths >3.5 μm, possibly caused by a temperature-induced change in crystal structure. This changes the linear continuum fit, which causes an increase in the value of $d_{NORM}$. No other sample showed a similar effect. If these points are removed from the group, the $R^2$ value improves to ~0.98 and $H_2O$ estimates have an error of ~±1 wt.%. We believe the absence of a similar unifying parameter for the 1.9 μm band is because the absorption is a combination bend-stretch overtone, which is strongly dependent on the sample's crystal structure. The wide 3.0 μm band is formed by several fundamental O-H-O stretching absorptions (~2.8 –3.0 μm) and an overtone of the $H_2O$ bend (~3.0-3.2 μm) [6], none of which are combination overtones and whose strength and shape do not seem to be as strongly affected by the crystal structure.

**Conclusions:** We have found a relationship between a VIS-NIR spectral parameter (3.0 μm $d_{NORM}$) and absolute $H_2O$ content that appears to be independent of composition and has an error of ~±1 wt.% $H_2O$. This relationship can be applied to current OMEGA [4] or upcoming CRISM data to estimate the water content of the martian surface as well as estimate the $H_2O$ content of laboratory samples. Future work will include expanding the suite of mineral compositions, determining effects of grain size, and testing the model with low-albedo samples.

**References:** [1] Bibring, J-P et al., (2004) *ESA SP* 1240; [2] Murchie, S. et al. (2002) *LPSC 33*, #1697; [3] Bibring, J-P et al., *submitted*; [4] Milliken, R. et al. (2005) *this conference*; [5] Cooper, C. and J. Mustard (1999) *Icarus*, 142, 557-570; [6] Bishop, J. et al. (1994) *Clays Clay Min.*, 42, 702-716; [7] Bishop, J. et al. (1995) *Icarus*, 117, 101-119; [8] Yen, A. et al. (1998) *JGR*, 103, 11125-11133; [9] Bish, D. et al. (2003) *Icarus* 164, 96-103; [10] Milliken, R. and Mustard, J. (2004) LPSC 34 #1620; [11] Milliken, R. and Mustard, J. (2003) LPSC 33 #1345; [12] Murchie, S. et al. (2000) *Icarus* 147, 444-471; [13] Calvin, W. (1997) *JGR* 102, 9097-9107; [14] Hapke, B. (1993) *Thry of ref. and em.. spec.*, 455pp., Cambridge Press.

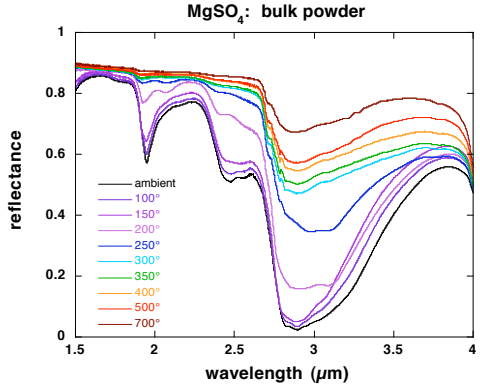


**Figure 1**. Scaled reflectance spectra of $MgSO_4$ (chemical grade powder). Near T = 200°C, the sample approaches mono-hydration and an additional water absorption is visible at 2.1 μm.

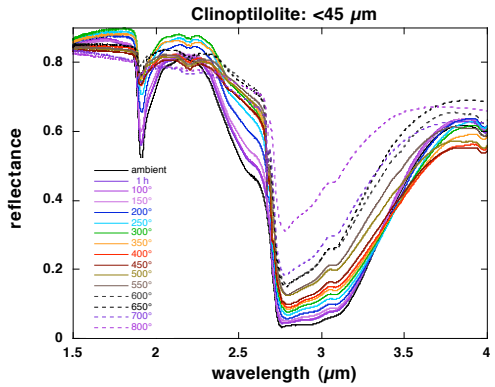


**Figure 2.** Scaled reflectance spectra of clinoptilolite. Water is still present at very high temperatures, as noted by the presence of the 1.9 and 3.0 μm band at T = 800°.

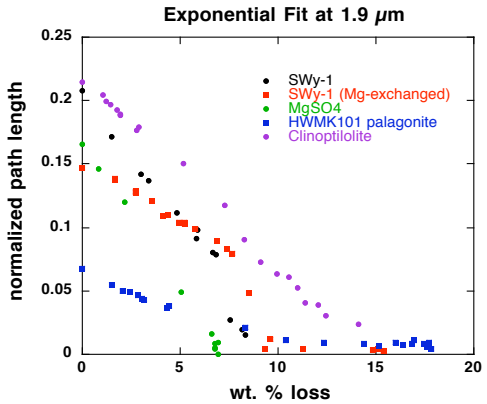


**Figure 3**. Plot of $d_{NORM}$ vs. wt.% loss. For most samples, the x-intercept represents the total $H_2O$ content (see text for description).

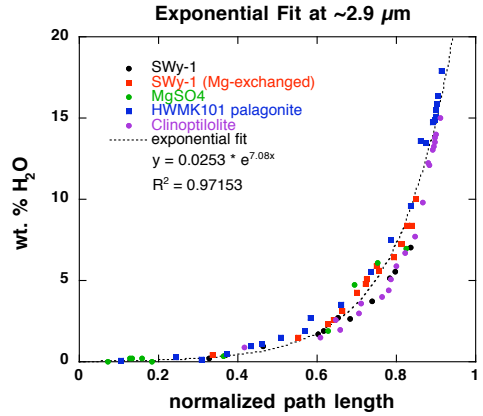


**Figure 4.** Plot of $d_{NORM}$ vs. total $H_2O$ content. The data are best fit by an exponential curve. Error bars are smaller than the marker size.