

ESTIMATING MINERAL ABUNDANCES OF CLAY-GYPSUM MIXTURES USING VISIBLE-NEAR INFRARED RADIATIVE TRANSFER MODELS. K.M. Robertson¹, S. Li¹, and R.E. Milliken¹. Dept. of Geological Sciences, Brown University, Providence, RI, 02912. kevin_robertson@brown.edu

Introduction: Diverse sulfate and phyllosilicate assemblages have been identified on Mars from CRISM and OMEGA visible near infrared (VNIR) spectra [1,2]. The data returned from these instruments may be indicative of both global aqueous processes [3] on ancient Mars (Noachian/Hesperian) as well as discrete, localized aqueous processes during the Amazonian [4]. Sulfates and phyllosilicates have commonly been identified in distinct lithologies and locations, but certain deposits allude to more complex mineral assemblages [5].

The identification and mapping of these hydrated phases from orbital data has been successful at distinguishing between the likely different aqueous environments, but a more quantitative approach will help to constrain the conditions of formation where phyllosilicates and sulfates appear to be in close proximity, as in Gale Crater. The identification of spectrally ambiguous hydrated salts further complicates possible interpretations. These ambiguous hydrated phases are commonly identified as 'polyhydrated sulfates' and could result from 1) complex mixtures of various sulfates resulting in an ambiguous spectral signature, 2) a single sulfate phase that is being masked/muted by other phases, or 3) scattering effects that weaken or mask diagnostic absorption features.

'Unmixing' of VNIR spectra using radiative transfer modeling will help us to better understand complex mineral assemblages and the conditions at the time of their formation. Previous studies have tested the Hapke radiative transfer model (RTM) for igneous materials with application to the Moon and asteroids [6]. Recently, mixtures of nontronite and various igneous materials were analyzed using both Hapke [7] and Shkuratov [8] models [9]. Results from the application of such models to OMEGA data of clay-bearing deposits are promising [10], but RTMs have not yet been fully tested for fine-grained clay and sulfate mixtures. In this study, we assess the efficacy of both the Hapke and Shkuratov models in estimating modal mineralogy of montmorillonite-gypsum mixtures in the VNIR wavelength range. We determine the effectiveness of the model in distinguishing between subtle differences in minor absorption features that are diagnostic of mineralogy when large H₂O absorptions, which are not diagnostic of distinct phases, are also present.

Methods: Gypsum sand and small chunks of montmorillonite were ground in a mortar and pestle and wet sieved to make four particle size ranges (25-32 μ m, 38-45 μ m, 63-75 μ m and 125-150 μ m). The two end-

members were combined to produce binary mixtures with 0, 10, 25, 50, 75, 90, and 100 wt. % gypsum.

The reflectance spectra for all mixtures were measured in RELAB at Brown University with the bi-directional spectrometer (BDR) and a viewing geometry of: $i = 30^\circ$, $e = 0^\circ$, $g = 30^\circ$. Reflectance spectra were also measured four times using an ASD field spectrometer configured with the same geometry as the BDR. The ASD spectra were linearly scaled to match the absolute reflectance data of the BDR data for a direct comparison. The four series of ASD measurements allow for estimating uncertainties associated with sample heterogeneity, packing, particle orientation, and scattering effects.

The Hapke RTM is designed for intimate mixtures of particulates, whereas Shkuratov RTM treats particles as one-dimensional layers. The details for the parameterization of Hapke and Shkuratov models used in this study can be found in Li and Li [11] and Li and Milliken [12] respectively. The models are first solved for the imaginary part of the index of refraction (k) by using the reflectance spectra, particle size, porosity, and viewing geometry (for Hapke RTM) as input. The value of k for each endmember is then used as the input to the model and the mineral abundance and particle size of each component is solved for by minimizing the difference between the predicted and observed reflectance spectrum for each mixture.

Results: The absolute reflectance spectra for the mixtures are shown in Fig. 1 and are consistent for all particle sizes. The k values were determined from the

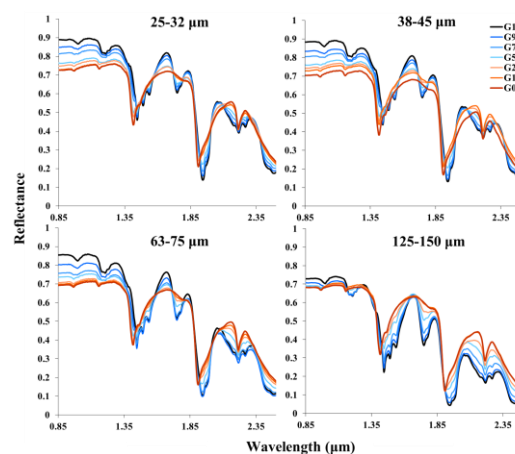


Figure 1. Absolute reflectance of the binary mixtures for the four particle size fractions as measured in the RELAB bi-directional spectrometer. G100=100 wt% gypsum, G50=50 wt% gypsum, G0=0 wt% gypsum.

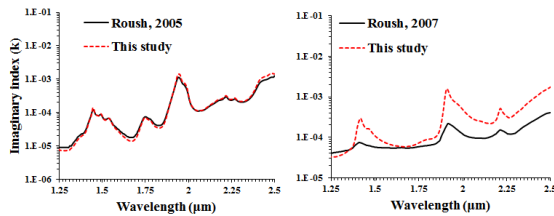


Figure 2. The optimized optical constant (k) for a) gypsum and b) montmorillonite. Results are compared to the optical constants

end-member spectra of the four particle size ranges by optimizing the particle size input to the model in order to obtain a single, consistent k -value. While the optimized particle sizes for gypsum were similar to those determined from optical microscopy, the phyllosilicate particle sizes were significantly lower. The phyllosilicate particles are actually aggregates of much smaller crystallites. The 'effective' particle size modeled here can be considered an empirical estimate of the shorter optical path length in the aggregates.

The k -values for gypsum determined from the Hapke model in this study are very similar to those of Roush et al., 2007 [13], whereas the k -values for montmorillonite are not as well constrained [14] (Fig. 2). Minor differences in the slope and H₂O absorption band depths are observed between the two results, which are consistent with variations in hydration levels. This result highlights the difficulties associated with using optical constants for phyllosilicates and other minerals that are sensitive to relative humidity in a laboratory setting. Minor differences in hydration level can result in significant differences in k -values and thus estimated mineral abundances.

The Hapke un-mixing results of the BDR data for all size fractions are presented in Figure 3. Weight fraction estimates are all within 5% of actual values, with the greatest error observed in the 0-50% gypsum mixtures. An example of a modeled and measured spectrum is presented in Figure 4. The spectral fit resulted in an $\text{RMS} = 5 \times 10^{-6}$ with the largest variations at short wavelengths near the $\sim 1.4 \mu\text{m}$ H₂O absorption feature, and overall excellent spectral fit.

Un-mixing results for the ASD data produced similar results as those shown in Figs. 3 and 4, though minor variations between ASD and BDR data were observed, resulting in slightly larger errors in the mineral abundances. Hapke and Shkuratov methods both produced similar results for the BDR and ASD data, though the Shkuratov method was not as accurate for some of the 50:50 mixtures.

Conclusions: The results shown here are promising for the application of both Hapke and Shkuratov RTMs to mixtures of hydrated phases. Here, gypsum is well constrained, but small variations in montmorillonite spectra for the different particle sizes

can increase uncertainties in k , which increases uncertainties in derived mineral abundance. Even so, results are within 5% of actual values for both Hapke and Shkuratov methods. Future work will test the model with more complex mixtures, rocks, and ultimately apply the model to orbital VNIR data.

References: [1] Murchie, S.L. et al., (2009) *JGR*, E00D07. [2] Poulet F. et al., (2005) *Nature*, 438, 623-627. [3] Bibring et al., (2005) *Science*, 307, 1576-1581. [4] Mangold et al., (2010) *Icarus*, 207, 265-276. [5] Wray et al., (2010) *Icarus*, 209, 416-42. [6] Mustard, J.F. and C.M. Pieters, *JGR* 94, 13,619-13,634. [7] Hapke, B., (2005) Cambridge university press. [8] Shkuratov et al., (1999). *Icarus* 137, 235-246. [9] Ehlman et al., (2011) LPSC abstract #1704 [10] Poulet et al., 2008 *A&A*, 487, L41-L44. [11] Li, S. and Li, L. (2011), *JGR*, E09001. [12] Li, S. and Milliken, R. E., (2013) 44th LPSC. [13] Roush et al. (2007) *JGR*, E10003. [14] Roush (2005), *Icarus*, 179, 259-264.

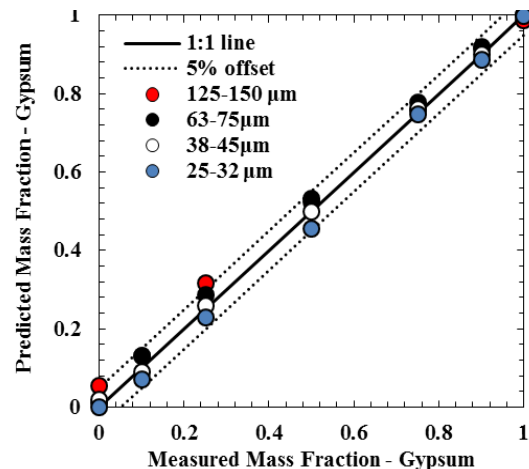


Figure 3. Hapke unmixing results for spectra of four size fractions using optical constants for gypsum and montmorillonite. All results are within $\sim 5\%$ of actual values.

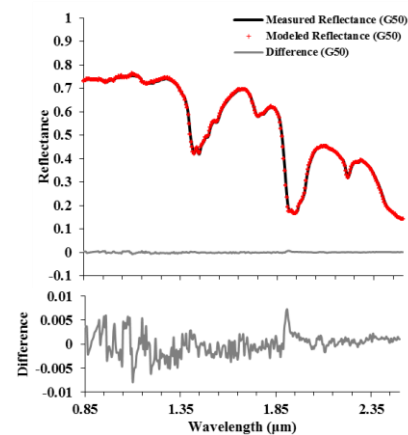


Figure 4. Modeled and measured spectra and difference for the 50:50 mixture in the 63-75 μm fraction using Hapke RTM.