



Estimating mineral abundances of clay and gypsum mixtures using radiative transfer models applied to visible-near infrared reflectance spectra



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ABSTRACT

Quantitative mineral abundances of lab derived clay–gypsum mixtures were estimated using a revised Hapke VIS–NIR and Shkuratov radiative transfer model. Montmorillonite–gypsum mixtures were used to test the effectiveness of the model in distinguishing between subtle differences in minor absorption features that are diagnostic of mineralogy in the presence of strong H₂O absorptions that are not always diagnostic of distinct phases or mineral abundance. The optical constants (*k*-values) for both endmembers were determined from bi-directional reflectance spectra measured in RELAB as well as on an ASD FieldSpec3 in a controlled laboratory setting. Multiple size fractions were measured in order to derive a single *k*-value from optimization of the optical path length in the radiative transfer models. It is shown that with careful experimental conditions, optical constants can be accurately determined from powdered samples using a field spectrometer, consistent with previous studies. Variability in the montmorillonite hydration level increased the uncertainties in the derived *k*-values, but estimated modal abundances for the mixtures were still within 5% of the measured values. Results suggest that the Hapke model works well in distinguishing between hydrated phases that have overlapping H₂O absorptions and it is able to detect gypsum and montmorillonite in these simple mixtures where they are present at levels of ~10%. Care must be taken however to derive *k*-values from a sample with appropriate H₂O content relative to the modeled spectra. These initial results are promising for the potential quantitative analysis of orbital remote sensing data of hydrated minerals, including more complex clay and sulfate assemblages such as mudstones examined by the Curiosity rover in Gale crater.

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1. Introduction

Numerous occurrences of a wide variety of hydrated minerals have been identified on the surface of Mars through a combination of orbiter, lander and rover observations. Hydrated sulfates and clay minerals are the two dominant classes of hydrated minerals, both being more common in ancient Noachian and Hesperian terrains than in younger Amazonian terrains (Poulet et al., 2005; Gendrin et al., 2005; Bibring et al., 2006; Murchie et al., 2009; Ehlmann et al., 2011; Carter et al., 2013). These minerals and their host rocks may record global climatic conditions and aqueous processes during the first billion years of Mars' history (Bibring et al., 2005; Chevrier et al., 2007; Murchie et al., 2009; Ehlmann et al., 2011) as well as discrete, localized aqueous conditions during later times (e.g., Mangold et al., 2010). However, in order to relate min-

eralogical observations to potential environmental conditions it is important to identify the specific mineral species as well as their relative, and preferably absolute, abundances.

Initial orbital observations from NASA's Mars Reconnaissance Orbiter CRISM and ESA's Mars Express OMEGA visible–near infrared (VIS–NIR) imaging spectrometers suggested sulfates and clays were largely segregated both temporally and spatially (e.g., Bibring et al., 2006; Poulet et al., 2005). However, subsequent global surveys and detailed local studies suggest there are numerous locations where these minerals coexist (e.g., Wray et al., 2010; Milliken et al., 2010; Roach et al., 2010; Ehlmann et al., 2011; Noe Dobrea et al., 2012; Carter et al., 2013), either in discrete geologic units or possibly mixed below the ~18 m/pixel spatial scale of CRISM. Sulfate and clay assemblages are commonplace in many terrestrial settings (e.g., Baldrige et al., 2009), and it is not unexpected that the same may be true of Mars, particularly for alluvial/fluviol and lacustrine environments or rocks that have been subject to diagenesis.

Indeed, recent results from the Curiosity rover at Gale crater provide excellent examples of strata that host both clay

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minerals and sulfates, where both are believed to have formed in situ (Grotzinger et al., 2014; Vaniman et al., 2014). CheMin X-ray diffraction measurements of rock powders drilled from the Sheepbed mudstone indicate as much as ~22% smectite and ~3.6% Ca-sulfate (bassanite and anhydrite) may be present (Vaniman et al., 2014). However, the mudstone is crosscut by numerous veins and nodules filled with Ca-sulfate (Grotzinger et al., 2014), thus sulfates are likely a much more volumetrically important component of the unit as a whole than indicated solely by the XRD results. Intriguingly, no hydrated minerals were observed in CRISM orbital data for this region, likely due to the thin dust cover on the outcrops, though spectral signatures of both clay and sulfate minerals are present in other lower Mt. Sharp strata in Gale crater (Milliken et al., 2010). In the Sheepbed mudstone, the clays have been interpreted to be authigenic and the crosscutting, sulfate-filled veins are indicative of a later diagenetic event. Therefore, knowledge of the relative abundance of these phases can be used to assess the relative contribution of these two distinct processes, and similar concepts may apply to other clay and sulfate-bearing assemblages on Mars.

Therefore, methods that allow for absolute or relative estimates of clay and sulfate abundance from VIS-NIR reflectance spectra can help to constrain the type and extent of processes that may be responsible for the co-occurrence of these minerals. Assessing how abundances of clay and sulfate vary within a stratigraphic sequence can also provide important insight into temporal changes in local water chemistry, water–rock interaction, and paleoclimate. However, uniquely identifying individual components in mixtures of hydrated minerals using VIS-NIR reflectance spectroscopy can be complicated by overlapping or non-unique absorption features as well as mixing between strong and weakly absorbing (spectrally ‘neutral’) components. Qualitative methods that rely solely on the positions and/or widths of individual absorptions may be prone to missing the presence of volumetrically subordinate (yet geologically important) components, oversimplification of mineral identifications, or misidentification of minerals.

Hydrated salts (e.g., hydrated sulfates and chlorides) are an excellent example of the difficulties associated with qualitative spectral analyses, as VIS-NIR reflectance spectra for some of these minerals lack unique diagnostic absorptions. Examples of ‘polyhydrated’ sulfates on Mars (e.g., Gendrin et al., 2005; Bibring et al., 2006; Murchie et al., 2009; Carter et al., 2013) could represent complex mixtures of various sulfates/hydrated phases (e.g., Cloutis et al., 2006) or they could represent a single sulfate phase for which weaker diagnostic absorptions are masked or muted.

Spectral ‘unmixing’ of VIS-NIR reflectance spectra using radiative transfer models (RTMs) can help to constrain the mineralogy of complex assemblages through the simultaneous fitting of reflectance values at many wavelengths. RTMs are also advantageous in that they can provide estimates of the abundance and particle size of each component in a mixture. However, as noted in previous studies (e.g., Sklute et al., 2015), widespread application of these models to spectra of planetary surfaces has been somewhat limited, primarily due to the lack of accurate optical constants (real, n , and imaginary, k , components of the complex index of refraction) for appropriate minerals, which are required inputs to the models. This is particularly true for clay and sulfate minerals, and though optical constants at VIS-NIR wavelengths have been reported for montmorillonite (Roush, 2005), gypsum (Roush et al., 2007), bloedite, epsomite, hexahydrite (Dalton and Pitman, 2012), and select Fe-sulfates (Pitman et al., 2014; Sklute et al., 2015), they are not readily available for many other hydrated minerals that are of importance to Mars (e.g., nontronite, saponite, chlorite, bassanite, kieserite, etc.) or for phases with variable H₂O content. In addition, the application of these optical constants in radiative transfer models for well-controlled mineral mixtures has been very limited,

particularly for minerals relevant to sedimentary environments and compositions (e.g., clays, sulfates, and other hydrated phases).

Two commonly used models in remote sensing applications for planetary bodies are those of Hapke (2005) and Shkuratov et al. (1999), both of which are considered in this study. Previous laboratory studies have tested the Hapke RTM for igneous materials with applications to the Moon and asteroids (Mustard and Pieters, 1987, 1989; Li and Milliken, 2015). Of relevance to Mars, laboratory mixtures of nontronite and various igneous materials (Ehlmann et al., 2011) were recently analyzed using both Hapke (2005) and Shkuratov et al. (1999) models, and Stack and Milliken (2015) also used the Hapke model for a suite of clay and Mg-sulfate (epsomite) mixtures. In addition, Poulet et al. (2009) applied the Shkuratov model directly to OMEGA spectra of clay-bearing regions on Mars. This study yielded promising results, but a detailed and well-controlled laboratory study of how the Hapke and Shkuratov models perform for clay and sulfate mixtures when starting with optical constants is currently lacking. Although optical constants for montmorillonite and gypsum are available in the literature and both phases have been observed on Mars, to our knowledge these optical constants have not yet been tested in RTMs for laboratory mixtures of clay and sulfate. This is of course a necessary first step in order to understand and quantify potential uncertainties in modal mineralogy derived from such models when applied to actual reflectance spectra of Mars.

In this study we assess the efficacy of the Hapke model in estimating modal mineralogy of montmorillonite–gypsum mixtures at VIS-NIR wavelengths. We examine the effectiveness of the model in distinguishing subtle differences in moderate or weak absorption features that are diagnostic of mineralogy when they are in the presence of stronger, non-unique H₂O absorptions, as typify many CRISM spectra of Mars. In addition, we derive independent estimates of the optical constants for montmorillonite and gypsum using two different spectrometers and compare our results to previously published values. The effectiveness of the ASD Fieldspec3 spectroradiometer is evaluated as a tool for performing Hapke modeling and is directly compared to the bidirectional reflectance spectrometer. We present estimates of modal mineralogy derived from the Hapke RTM for a suite of binary mixtures that encompass a range in gypsum-to-montmorillonite ratios and particle sizes, and as a final step we compare these results to those derived from an implementation of the Shkuratov model. Though sedimentary rocks on Mars are likely composed of more than two mineral phases it is important to begin validation of RTMs with simple, well-controlled cases where variables can be minimized and/or isolated. The results presented here for binary sulfate–clay mixtures can provide a foundation for future application of Hapke and Shkuratov models to more complex lab mixtures, and ultimately to reflectance spectra of sedimentary deposits on Mars.

2. Methods

2.1. Sample preparation

The gypsum used in this study was coarse and poorly sorted gypsum sand collected near White Sands, NM, and the montmorillonite was sample SAz-2 obtained from the Clay Minerals Society (CMS). Though the CMS offers several different montmorillonite samples, the SAz-2 variety was chosen for this work because the bulk material arrived as large pieces, which allowed us to easily grind, sieve, and control the particle size of this component.

The gypsum sand and montmorillonite chips were ground in an agate mortar and pestle, wet sieved with H₂O to remove clinging fines, and dried in air to make two separate groups of particle size fractions (Table 1). Group 1 consisted of four particle size ranges (25–32 μm , 38–45 μm , 63–75 μm and 125–150 μm) and each

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