REFLECTANCE SPECTROSCOPY OF CLAY-SULFATE MIXTURES: IMPLICATIONS FOR QUANTIFYING HYDRATED MINERALS AND DETERMINING DEPOSITIONAL ENVIRONMENTS ON MARS. K. M. Stack1 and R. E. Milliken2, 1California Institute of Technology, Pasadena, CA 91125, USA 2University of Notre Dame, Notre Dame, IN 46556, USA. (kstack@caltech.edu)

Introduction High-resolution mapping by visible and near-infrared orbital spectrometers (CRISM and OMEGA) has revealed a diversity of hydrated minerals on the surface of Mars [1-6]. While it is generally observed that phyllosilicate- and sulfate-bearing terrains are spatially, stratigraphically, and likely temporally distinct [1], continuing observations from OMEGA and CRISM have revealed a number of locations and possible sedimentary depositional environments where clay and sulfate minerals occur together. Examples include Terby Crater [7], parts of the Valles Marineris canyon system [8], and Gale Crater (Fig. 1), where interbedded Fe/Mg clay, sulfate, and mixed clay and sulfate layers crop out in the walls of the Gale Crater Grand Canyon [9].

To correctly interpret past depositional and diagenetic conditions on Mars, it is essential that we accurately determine the absolute, or at least relative, proportions of hydrated phases in these mixed-composition deposits. For example, the absolute sulfate content of a deposit could be used to distinguish an evaporative playa-lake setting from less-extensive diagenetic precipitation in the pore space of pre-existing sediments. In this context, the abundance and spatial resolution of reflectance spectra of the martian surface and their role in identifying these phases makes visible-near infrared reflectance spectroscopy a potentially powerful tool for distinguishing depositional, diagenetic, and alteration environments. A number of recent studies have addressed the spectral properties of clay-bearing mixtures [10, 11], but fundamental gaps exist in our understanding of how quantitative spectral models deal with fine-grained hydrated sulfate and clay mineral mixtures. To address this issue, we examined the spectral properties of a suite of binary mixtures containing hydrated magnesium sulfate mixed with varying proportions of Fe, Mg, or Al-smectite. In this study we: (1) assess the ability of current spectral models to accurately estimate mineral abundances in these mixtures, (2) use spectral models to establish quantitative detection limits for phases in such mixtures if they exist on Mars, and (3) use the results of these laboratory experiments to analyze the mineralogy of mixed clay/sulfate deposits on Mars.

Methods For direct relevance to minerals identified in CRISM and OMEGA data, we analyzed samples of 2 nontronites, 2 saponites, and 2 montmorillonites (all <25 µm) mixed with 5, 10, 20, 50, 80, 90, and 95 weight % reagent-grade magnesium sulfate powder (labeled as epsomite, MgSO₄•7H₂O) to create six sets of clay-sulfate mixtures (42 total mixtures in addition to the 7 pure endmembers). A Nicolet Fourier transform infrared (FTIR) spectrometer fitted with an Analect biconical accessory utilizing an MCT detector was used to measure the diffuse reflectance of each sample over a wavelength range of 1.25-7.67 µm.

Quantitative mineral abundances were estimated from spectra of powder mixtures using two models of spectral unmixing: a “checkerboard” model in which the mixture reflectance spectrum was assumed to be a linear sum of the endmember reflectance spectra weighted by their fractional volumes (cross-sectional areas), and a model designed for intimate mixtures based on the principles of Hapke theory, in which reflectance spectra are converted to single-scattering albedo (SSA) to minimize nonlinear effects of multiple scattering [12]. In the intimate mixture model, each SSA spectrum is modeled as a linear combination of endmember SSA spectra weighted by their fractional volumes [12]. Each mixture spectrum was modeled via linear least squares inversion in reflectance and SSA space from 1.25-2.6 µm, and as a second test the metal-OH ‘clay’ band was isolated and modeled separately from ~2.1 to 2.4 µm, depending on the clay composition. The modeled mineral percentages were then used to forward calculate the mixture spectra for comparison to the lab spectra to help determine which wavelength regions were most problematic in the model fits.
Results A sample set of mixture spectra and modeling results are presented in Figure 2. We find that modeled estimates of clay content are generally closest to measured values when the clay band (~2.1-2.4 µm) is isolated, as opposed to the full 1.25-2.6 µm wavelength region. This is not unexpected in these well-constrained experiments because the clay component of each binary mixture is the dominant contributor to the depth and shape of this absorption feature. We do note, however, that mixtures of high (80-95%) clay content are commonly best modeled by the full 1.25-2.6 range, whereas mixtures with low clay content are best modeled by isolating the clay band. Converting reflectance spectra to single-scattering albedo also generally improves estimates of clay content, although this improvement is most apparent when modeling mixtures of high (80-95%) clay content and minimal to nonexistent for other mixtures. Clay content is often underestimated (generally <15% but up to 20% for 50-80% clay mixtures), regardless of the model (reflectance or SSA), wavelength region (clay band or 1.25-2.6 µm), or clay composition.

Conclusions Conversion of reflectance spectra to single-scattering albedo yields a slight improvement to estimates of clay abundance in binary particulate clay/Mg-sulfate mixtures, particularly in high clay content mixtures when the clay band is isolated. However, the SSA model results are often not significantly different from those derived from reflectance spectra when the 1.25-2.6 um wavelength range is used. Even for these idealized laboratory mixture experiments in which the mineral endmembers and abundances are known, the modeled clay contents are commonly underestimated and the results are worst for intermediate compositional ranges. This suggests that there are scattering effects in intimate sulfate-clay mixtures that are not properly accounted for even when converting reflectance spectra to SSA, possibly due to sulfate grains coating clays or vice-versa. In addition, ‘clay’ bands are often not readily apparent by visual inspection of spectra of clay-sulfate mixtures for <20% clay, though their presence is often detected in the models. This suggests sulfate deposits on Mars may contain significant amounts of clay that cannot be detected by simple visual inspection of CRISM or OMEGA spectra. Therefore, increased scrutiny of spectra for previously reported martian sulfate deposits, including detailed modeling, is recommended to fully assess the distribution, transport history, and timing of formation of clay minerals on Mars.


Figure 2. Sample set of spectra and modeling results for SWa-1, a ferruginous smectite. A) FTIR reflectance spectra of SWa-1 + Mg-sulfate mixtures. All spectra except the 100% SWa-1 spectrum have been vertically stacked for clarity. B) Results of “checkerboard” and Hapke modeling for SWa-1 + Mg-sulfate mixture spectra. The dashed green line represents a reference where modeled clay fraction equals expected clay fraction.