

REFLECTANCE MEASUREMENTS OF CLAYS AND SULFATES UNDER MARS-LIKE TEMPERATURE AND RELATIVE HUMIDITY CYCLES AND IMPLICATIONS FOR CLAY-SULFATE ASSEMBLAGES IN GALE CRATER. R. Y. Sheppard^{1*}, R. E. Milliken¹, K. M. Robertson¹. ¹Dept. Earth, Environmental, and Planetary Sciences, Brown University.

Introduction: Mt. Sharp in Gale crater contains ~5 km of strata that may span the transition in Mars' climate from conditions favoring clay formation to those favoring sulfate formation [1-4]. As NASA's Curiosity rover approaches sulfate-rich strata in the coming years, variations in sulfate cation, abundance, hydration state, and crystallinity will be closely tracked as indicators of lacustrine and/or diagenetic conditions. Recent orbiter-based mineral mapping of strata around the entirety of Mt. Sharp reveals complex relationships between clays and sulfates (Fig. 1) [5]. This includes clays and sulfates in a range of stratigraphic positions, sometimes transitioning laterally into each other, and areas where sulfate co-exists in multiple hydration states at the modern surface. Consistent with these orbital results, recent *in situ* chemical observations suggest the presence of Mg sulfate (MGS) along the rover traverse [6], but crystalline forms of MGS have not yet been identified in CheMin XRD data. Curiosity's REMS instrument has measured a range of relative humidities (%RH) at Gale crater, varying on daily and seasonal cycles [7]. Past experimental work has shown the MGS system to be strongly dependent on both temperature (T) and %RH, characterized by metastability, sluggish kinetics, and path dependence (e.g., [8]). It is likely therefore that some sulfate outcrops at Gale crater could record multiple fluid alteration and de/hydration events at the surface and/or subsurface. Therefore, we seek to constrain the reaction pathways that sulfates and clays can follow to change phase and hydration state under a range of T and %RH condi-

tions, determine when these changes are spectrally distinguishable at martian surface conditions, and whether they are likely to adsorb/desorb water on diurnal and/or seasonal timescales.

We present results from *in situ* measurements of the changes to visible-near infrared (VNIR) reflectance spectra during Mars-like changes in T and %RH. We seek to constrain the stability of clay and sulfate hydration states and lay out testable hypotheses the rover can address as it approaches relevant strata. We also consider which of the observed spectral changes, if occurring on the martian surface, could be observed in our current generation of orbital reflectance data.

Methods: We analyzed powdered hydrous minerals with interlayer and structurally adsorbed water, focusing on Al- and Fe-smectites (e.g., montmorillonite and nontronite), Mg sulfates, and physical mixtures thereof. Powdered samples were loaded into copper sample holders adjacent to Halon as a white reference. The copper plate was placed in a Linkam environmental chamber with a CaF₂ window. To lower %RH, the chamber could be exposed to vacuum, elevated temperatures, or 'dry' air. The 'dry' air has a dewpoint of -70°C at ambient P and T, equivalent to ~0.016%RH. To raise %RH, the chamber could be cooled to a desired temperature via automated pumping of liquid nitrogen through the stage.

VNIR spectra (0.35-2.5 μm) were collected throughout the experiments using a using an ASD FieldSpec3 spectroradiometer; band depths, position, and shapes were assessed using continuum-removed data and compared with previous studies [9]. To the

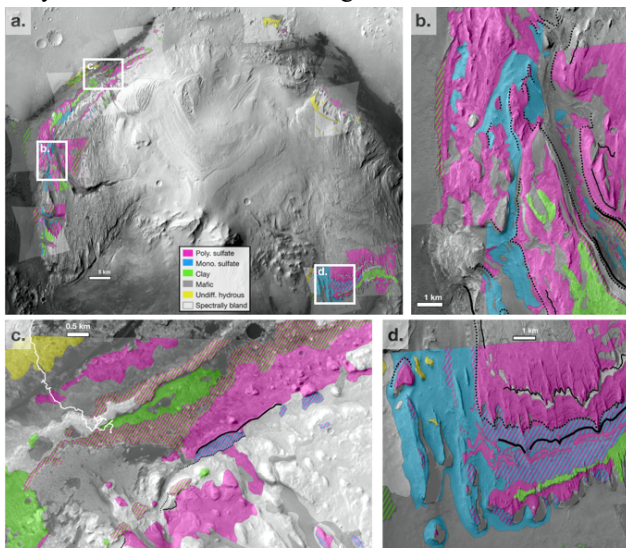


Fig. 1: a. Complete mineral map of Gale crater from [5]. b-d. Examples of exposures in Gale crater with clays in multiple stratigraphic positions and closely co-existing polyhydrated (magenta) and monohydrated (cyan) Mg sulfates.

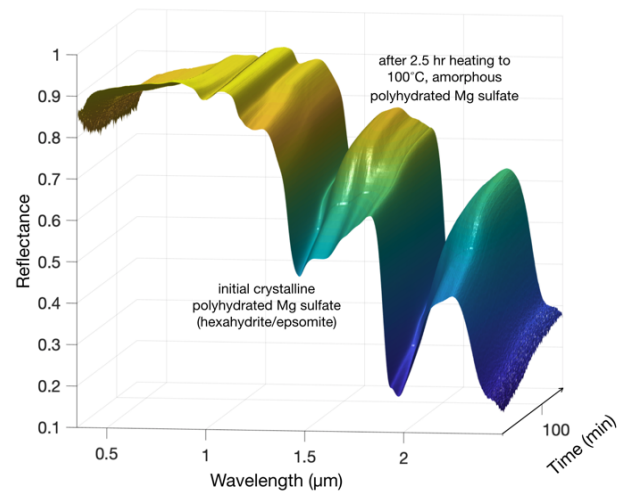


Fig. 2: Dehydration of MGS causes distinct changes in reflectance spectra. Frontmost spectrum is initial crystalline MGS, backmost spectrum is amorphous but still polyhydrated MGS after heating.

extent possible, mineralogy was validated before and after each run using rapid, limited-range scans on a Bruker D2 Phaser X-ray diffractometer.

Results and discussion: Dehydration experiments show that, when exposed to elevated T, low P, or dry air, H₂O bands decrease in both depth and band position as the sample dehydrates. This is observed for both smectites (not shown) and MGS (Fig. 2). Previous work has shown that dehydration of polyhydrated MGS does not form kieserite, but rather an amorphous phase with ~2 structural waters [10,11]. Our results are in accordance with this: the final dehydrated MGS is spectrally similar to amorphous MGS with ~2 waters [9] rather than a kieserite or anhydrite, and we find it to be X-ray amorphous. We also observe that rehydration of this amorphous MGS by increasing %RH at low temperature (-65°C) is possible, albeit slow.

Dehydration of the mixture of powdered MGS and smectite (Fig. 3) produced a similar decrease in H₂O band depth and shift to shorter wavelengths. Interestingly, the final mixture after dehydration (Fig. 3, red line) is almost indistinguishable from a spectrum of pure montmorillonite (green line); there is little spectral evidence for sulfate in the dehydrated mixture.

Implications and Conclusions: We find that even minor changes in hydration state and phase (for MGS) cause perceptible changes in the VNIR spectra. These include shifts in water band position, decreasing water band depth, and subtle changes in band shape in the case of MGS. However, many of these changes may be too subtle to be observed in current orbital data, making *in situ* observations an important step in understanding Mars' hydrous mineral budget.

In investigating the relationship between crystallinity and reflectance spectra, we find the amorphous polyhydrated MGS is spectrally similar to some forms of

crystalline polyhydrated MGS, especially when considering the orbital spectral resolution currently available. Based on experiments and REMS data, we expect some polyhydrated Mg-sulfate in Mt. Sharp to be X-ray amorphous, though such phases would be apparent in orbital VNIR data if they are hydrous.

Related to this, clay spectral features appear to obscure spectral evidence of amorphous MGS in physical mixtures. The presence of unusually strong H₂O bands in clay-bearing strata might suggest another hydrous phase is present (such as amorphous polyhydrated MGS), but this will require further validation. Consequently, the presence of MGS may be underestimated in the clay-bearing units of Gale and similar regions observed from orbit. Furthermore, it has been theorized that the extra availability of exchangeable water in smectite-sulfate mixtures may obscure the link between atmospheric conditions and preserved hydration state, with sulfate hydration state depending more on local water exchange within the rock/regolith than on atmospheric %RH [12].

Based on these results, smectites and certain sulfates exposed at the surface are likely to still be able to exchange water with the martian atmosphere under certain conditions, making them part of the present-day hydrological cycle of Mars. Examining the contacts between clay- and sulfate-rich strata *in situ* with the Curiosity rover may resolve the conditions that have led to multiple hydration states of MgSO₄ being present at the optical surface in Gale. Constraining the conditions under which these sulfates can be formed and maintained will help reveal the complex story of authigenesis and diagenesis in Gale crater, including which phases were driven by primary lacustrine conditions versus sediment/rock porosity and permeability.

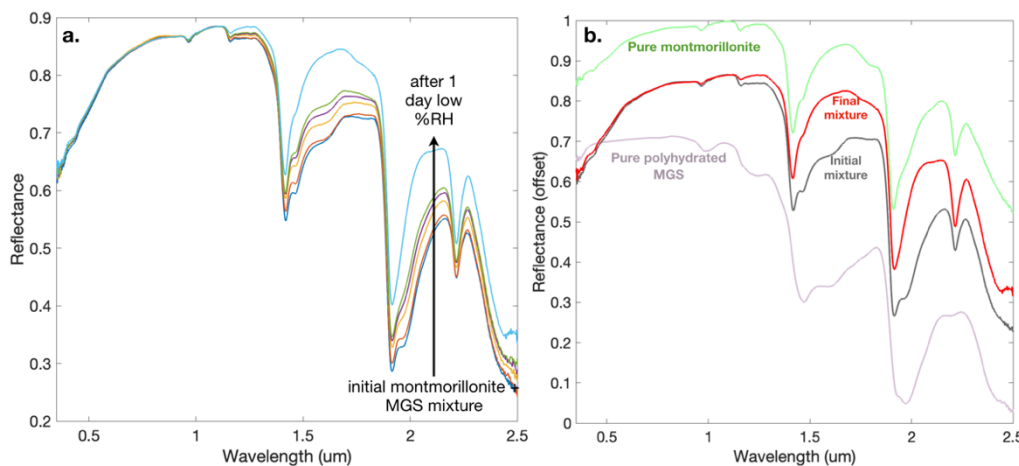


Fig. 3: a. Changes in reflectance spectra during dehydration of a physical mixture of polyhydrated MGS + montmorillonite. b. Spectra at start and end of dehydration experiment, compared to spectra of pure MGS and montmorillonite. Final spectrum of amorphous MGS + montmorillonite (red) looks spectrally very similar to pure montmorillonite (green).

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