TOWARD UNDERSTANDING FERRUGINOUS SMECTITE MG-FOR-CA INTERLAYER CATION EXCHANGE, CRYSTALLINE CA-SULFATES, AND AMORPHOUS MG-SULFATES ON MARS.
R.V. Morris1, D.T. Vaniman2, J.V. Clark3, E.B. Rampe1, D.W. Ming1, C.N. Achilles4, D.P. Archer1. 1NASA JSC, Houston, TX, 2PSI, Tucson, AZ, 3Jacobs, NASA JSC, Houston, TX, 4NASA GSFC, Greenbelt, MD.

Introduction. Crystalline Ca-sulfate minerals (gypsum CaSO4·2H2O; bassanite CaSO4·0.5H2O; and anhydrite CaSO4) were detected in most X-ray diffraction patterns acquired to date by the CheMin transmission XRD instrument [1] onboard the Mars Science Laboratory (MSL) rover Curiosity during its ongoing mission at Gale crater [e.g., 2-10]. Relative proportions of Ca-sulfate minerals vary from sample-to-sample and, in some case, vary during multi-sol CheMin analyses in response to different environmental conditions in situ and within the CheMin instrument [11]. Chemical associations of Ca and S are prevalent at Gale crater, particularly in Ca-sulfate-rich veins that penetrate local sedimentary rock [e.g., 12-14]. No other crystalline monocation sulfates or their hydrated equivalents (e.g., MgSO4·nH2O) have yet been detected by CheMin though chemical associations (e.g., Mg and S) are present [e.g., 12-14].

No detection of crystalline monocation sulfates by CheMin, excepting Ca-sulfates, implies other monocation sulfates (e.g., MgSO4, MnSO4, FeSO4, and Fe2(SO4) and hydrated equivalents) are present below CheMin detection limits, are XRD amorphous [e.g., 15-18], or were not sampled. We advance here a pathway for precipitation of crystalline Ca-sulfates and amorphous Mg-sulfate based on experimental evidence for replacement of Ca interlayer cations in smectite SWa-1 by Mg sourced from Mg sulfate solutions.

Samples and Methods. Clay Mineral Society smectite SWa-1 was purified as a <0.5 µm size fraction by grinding, sonic probe disaggregation, Stokes-Law settling in deionized water, and centrifuging and washing multiple times with deionized water. Air dried purified powder is referred to here as SWa1_ORIG. A 1.0g portion was combined with 10 g of Ca-free, 0.05 M MgSO4 reagent solution, and resulting the suspension was agitated on a shaker arm at ~25 °C for 21 d. After agitation, a split was air dried (SWa1_EVAP), and remaining sample subjected to two centrifuge (8000 rpm for ~40 min), decant, and wash cycles with deionized water (no intervening drying) before air-drying (SWa1_WASH). Samples were analyzed by XRD (Siemens D500 at LANL and CheMin-4 (CM4) at JSC), VNIR reflectance spectroscopy (ASD FieldSpec3 at JSC) in air or N2 purged glove box (25°C; RH~0.4%), thermogravimetric (TG) analysis (Netzsch STA F1 Jupiter coupled to Pfeiffer QMS at JSC; He/1000mbar/3sccm), and XRF (Rigaku ZSX at LANL). VNIR peak positions were determined from continuum-removed spectra.

Results and Discussion. The SWa1_ORIG XRD pattern (Fig. 1) is typical for ferric dioctahedral smectites with 001 reflections at 15.2 Å in air and 13.6 Å in dry N2 and at 02L reflections at 4.50 Å for both atmospheres. The smectite pattern is invariant across all three samples, and gypsum peaks are present only for SWa1_EVAP.

The XRD patterns are interpreted as follows: (1) Ca is initially present only as an interlayer cation (ORIG); (2) Mg partially replaced Ca as the smectite interlayer cation, and gypsum precipitated from the suspartially pension during air drying (EVAP); and (3) gypsum and (if present) XRD amorphous Mg-sulfate were removed by dissolution during washing, leaving only smectite with enhanced Mg/Ca ratio (WASH). Crystalline Mg-sulfate phases were not detected in EVAP. Confirming XRD interpretations, XRF analyses show Ca concentrations decrease (0.33 to 0.18 cations/22O) and Mg concentratins increase (0.40 to 0.57 cations/22O) in WASH relative to ORIG. We cannot exclude, with XRD data alone, either low concentrations of amorphous Mg-sulfate in EVAP or minor incorporation Mg into smectite octahedral sites. Both are unsupported by other data as discussed next.

XRD patterns (dry N2 instrument purge) for amorphous Mg-sulfate from solid-state desiccation of epsom salts (dry N2 glove-box purge) are charaterized by two broad humps centered near 18 and 31 deg. 2θ by two broad humps centered near 18 and 31 deg. 2θ (Fig. 2a), similar to amorphous Mg-sulfates from vacuum desiccation and cryo-precipitation [e.g., 15-19]. TG data (Fig. 2b) for one sample represent it as a dihydrate (similar to [15,16]) with dehydration and
desulfurization near 200°C and 1100°C, respectively.

VNIR spectra for amorphous Mg-sulfates from solid-state desiccation of epsom salt (Fig 3a; spectra acquired under desiccating conditions) are characterized entirely by OH and HOH vibrational features. The spectra are distinct from kieserite (crystalline MgSO₄·H₂O) with its 2.10 µm spectral feature and similar to other crystalline and hydrated Mg-sulfates (esp. starkeyite and pentahydrate [e.g., 20]), terrestrial materials including smectites that are associated with the H₂O molecule, and martian surface spectra typically interpreted as representing “polyhydrated sulfate” [21].

VNIR spectra for untreated (ORIG) and treated (EVAP and WASH) (Fig. 3b; spectra acquired in air) are characterized by Fe³⁺ electronic spectral features near 0.42, 0.66, and 0.97 µm and OH/H₂O vibrational features near 1.4 and 1.9 µm and between ~2.2 and ~2.5 µm. The Fe³⁺ and OH/H₂O 1.4 and 1.9 µm features are attributed to SWA-1 with interlayer sites occupied by Ca (ORIG) and Mg (EVAP and WASH) with possible contributions from amorphous Mg-Sulfate to EVAP with weakest OH/H₂O features (0.98 and 1.17 µm) being masked by more intense smectite Fe³⁺ features.

Smectite cation-hydroxyl vibrational spectral features occur between ~2.1 and ~2.5 µm, and their positions and intensities are equivalent for our three samples (Fig. 3b; inset). Assignments are (Fe,Fe)-OH (2.29 µm), (Al,Fe)-OH (2.24 µm), and (Al,Al)-OH (shoulder below ~2.24 µm). A 2.31 µm spectral feature for (Mg,Mg)-OH was not detected for EVAP and WASH, confirming XRD data that Mg is present as an interlayer and not an octahedral cation. If amorphous Mg-SO₄ is not present in EVAP, the smectite incorporated all aqueous Mg as interlayer cations.

Applications to Mars. (1) Formation pathways for locally-sourced crystalline Ca-sulfate minerals and concomitant Mg-enriched smectite include Mg for Ca exchange of smectite interlayer cations from percolating Mg-bearing solutions and local precipitation of Ca-sulfates. (2) Interlayer cation exchange and aqueous Ca transport can result in sulfate diagenetic features with Ca in-part to wholly sourced from smectite interlayer Ca. (3) Orbital spectral signatures of martian optical surfaces interpreted as consistent with Mg polyhydrated sulfate [21] are consistent the signature of amorphous Mg-sulfate. (4) This study corroborates results of [22] showing that smectite, zeolites, and palagonite can all produce gypsum from pure Mg-sulfate solution by cation exchange, but of these smectite is most effective.