

**CHARACTERIZING THE PHYLLOSILICATE COMPONENT OF THE SHEEPBED MUDSTONE IN GALE CRATER, MARS USING LABORATORY XRD AND EGA.** E. B. Rampe<sup>1</sup>, R. V. Morris<sup>1</sup>, D. W. Ming<sup>1</sup>, P. D. Archer<sup>1</sup>, D. L. Bish<sup>2</sup>, S. J. Chipera<sup>3</sup>, D. T. Vaniman<sup>4</sup>, D. F. Blake<sup>5</sup>, T. F. Bristow<sup>5</sup>, B. Sutter<sup>1</sup>, J. D. Farmer<sup>6</sup>, R. T. Downs<sup>7</sup>, R. Leveille<sup>8</sup>, C. A. Achilles<sup>2</sup>, J. A. Crisp<sup>9</sup>, D. J. Des Marais<sup>5</sup>, J. M. Morookian<sup>9</sup>, S. M. Morrison<sup>7</sup>, P. C. Sarrazin<sup>10</sup>, N. Spanovich<sup>9</sup>, A. H. Treiman<sup>11</sup>, A. S. Yen<sup>9</sup>, and the MSL Science Team. <sup>1</sup>NASA JSC (Houston, TX, elizabeth.b.rampe@nasa.gov), <sup>2</sup>Indiana Univ., <sup>3</sup>CHK Energy, <sup>4</sup>PSI, <sup>5</sup>NASA ARC, <sup>6</sup>Arizona State Univ., <sup>7</sup>Univ. Arizona, <sup>8</sup>McGill Univ., <sup>9</sup>JPL-Caltech, <sup>10</sup>In-Xitu, <sup>11</sup>LPI.

**Introduction:** The Curiosity rover investigated the mineralogy of the Sheepbed mudstone member of the Yellowknife Bay formation in Gale crater. Data from the Chemistry and Mineralogy (CheMin) X-ray diffractometer (XRD) helped identify phyllosilicates in the two drilled samples, John Klein and Cumberland. These patterns showed peaks at low angles, consistent with (001) peaks in 2:1 swelling phyllosilicates [1]. Evolved gas analyses (EGA) by the Sample Analysis at Mars (SAM) instrument of these samples confirmed the presence of phyllosilicates through the release of H<sub>2</sub>O at high temperatures, consistent with dehydroxylation of octahedral OH in phyllosilicates [2].

CheMin data for the phyllosilicates at John Klein and Cumberland show that they are structurally similar in that their (02*l*) peaks are near 22.5 °2θ, suggesting both samples contain trioctahedral 2:1 phyllosilicates [1]. However, the positions of the (001) peaks differ: the phyllosilicate at John Klein has its (001) peak at 10 Å, whereas the phyllosilicate at Cumberland has an (001) peak at 14 Å. Such differences in (001) d-spacings can be ascribed to the type of cation in the interlayer site [3]. For example, large monovalent cations (e.g., K<sup>+</sup>) have low hydration energies and readily lose their H<sub>2</sub>O of hydration, whereas small divalent cations (e.g., Mg<sup>2+</sup>) have high energies of hydration and retain H<sub>2</sub>O in the phyllosilicate interlayers [3,4]. The goal of this study is to determine whether differences in the interlayer cation composition can explain the CheMin data from John Klein and Cumberland and to use this knowledge to better understand phyllosilicate formation mechanisms.

**Methods:** We performed Mg- and Ca-saturations and Mg-pillaring procedures on four 2:1 swelling phyllosilicates [5]: three smectites (montmorillonite, nontronite, and saponite) and a trioctahedral vermiculite. We chose Ca- and Mg-saturations because CheMin XRD patterns and bulk chemical data from APXS suggest that the phyllosilicate at John Klein is Ca-enriched and the phyllosilicate at Cumberland is Mg-enriched [1]. Treated and untreated materials were analyzed in the laboratory version of CheMin at the Johnson Space Center (JSC). All samples were dehydrated under flowing N<sub>2(g)</sub> (~100 ppm H<sub>2</sub>O) for up to seven

days in order to mimic the dry environment on the martian surface. Evolved gas analyses of the phyllosilicates were done at JSC using a Netzsch STA 449 F1 Jupiter coupled to a Pfeiffer ThermoStar GSD 320 quadrupole mass spectrometer under conditions similar to the SAM instrument. H<sub>2</sub>O (m/z = 18) release was measured by the mass spectrometer and recorded as a function of temperature.

**Results:** The (001) peaks of the XRD patterns of the untreated phyllosilicates measured under dry N<sub>2(g)</sub> show that the presence of a monovalent cation in the interlayer site allows the structure to fully collapse to 10 Å (Fig. 1). The untreated phyllosilicates had a mixture of different cations in the interlayer site, and montmorillonite was the only phyllosilicate with a monovalent cation (Na<sup>+</sup>) as the dominant interlayer cation. XRD patterns of the Mg-saturated phyllosilicates measured under dry N<sub>2(g)</sub> display (001) peaks at larger d-spacings than the untreated phyllosilicates (Fig. 2). The (001) peaks in XRD patterns of the Ca-saturated phyllosilicates measured under dry N<sub>2(g)</sub> show that the phyllosilicate structures remain open; however, the d-spacings are smaller than the Mg-saturated phyllosilicates because Ca<sup>2+</sup> has a lower hydration energy than Mg<sup>2+</sup>. XRD patterns of the Mg-pillared phyllosilicates (i.e., interlayer cations are replaced with hydroxylated Mg) all have (001) peaks ~14.3 Å and small peaks ~7 Å, indicating partial chloritization.

The different cation saturation treatments had subtle effects on the EGA measurements of H<sub>2</sub>O release. In general, all phyllosilicates display low-T H<sub>2</sub>O releases from dehydration of interlayer H<sub>2</sub>O and high-T H<sub>2</sub>O releases from dehydroxylation of OH groups in the octahedral layers (Fig. 3). The dehydration reaction occurs at slightly higher temperatures for the Mg-saturated phyllosilicates than for the untreated and Ca-saturated phyllosilicates. Dehydroxylation of Mg- and Ca-saturated phyllosilicates occurs at slightly lower temperatures than the untreated phyllosilicates. EGA data of Mg-pillared phyllosilicates display sharp H<sub>2</sub>O releases from dehydroxylation near 300 °C that are not seen in the other measurements.

**Discussion:** The laboratory XRD measurements under dry N<sub>2(g)</sub> shown here indicate that the type of cation in the interlayer site can explain the differences

in (001) peak positions of the phyllosilicates in John Klein and Cumberland. A large monovalent cation in the interlayer site allows for complete collapse of the phyllosilicate structure to the 10 Å d-spacing seen in the John Klein CheMin data. A divalent cation with a high hydration energy (i.e.,  $Mg^{2+}$ ) in the interlayer site retains  $H_2O$  and keeps the structure expanded even under very dry conditions. Saponite has been suggested as the phyllosilicate in the Sheepbed mudstone, and laboratory XRD patterns of a Mg-Fe-saponite with a relatively high layer charge (“griffithite”) support this [6]. However, for the suite of phyllosilicates studied here, Mg-saturated trioctahedral vermiculite best fits the (001) peak position seen in CheMin data of Cumberland and the (02 $l$ ) peak positions in both John Klein and Cumberland. If vermiculite, rather than smectite, is present in the Sheepbed mudstone, the most likely formation mechanism would be through alteration of a chlorite parent material, rather than through saponitization of olivine [1,7]. Hydroxylated Mg in the interlayer site of the phyllosilicate at Cumberland has been proposed as an explanation for the expanded structure [1,2,7]. However, XRD and EGA data from Mg-pillared phyllosilicates do not fit CheMin and SAM data from Cumberland (i.e., there is no 7 Å peak in CheMin data and no sharp dehydroxylation peak near 300 °C in SAM data).

Our data suggest that the same trioctahedral 2:1 swelling phyllosilicate is present at John Klein and Cumberland, but they were exposed to fluids of different compositions. We propose either: 1) the phyllosilicate at Cumberland formed in Mg-rich fluids, then localized later-stage fluids containing monovalent cations caused Na- and/or K-saturation of the phyllosilicate at John Klein; or 2) the phyllosilicate at John Klein formed in Na- and/or K-bearing fluids, then localized later-stage Mg-rich fluids caused Mg-saturation of the phyllosilicate at Cumberland. Abundant Mg-rich raised ridges in the Sheepbed mudstone support the presence of Mg-rich fluids [8], and veins in the John Klein drill hole indicate late-stage fluids, but the sequence of diagenetic events that affected the phyllosilicates at John Klein and Cumberland remains enigmatic.

**References:** [1] Vaniman D. T. et al. (2013) *Science*, doi:10.1126/science.1243480. [2] Ming D. W. et al. (2013) *Science*, doi:10.1126/science.1245267. [3] Sawhney B. L. (1972) *Clays and Clay Mins.*, 20, 93-100. [4] Ferrage et al. (2005) *Am. Mineral.*, 1358–1374. [5] Moore D. M. and Reynolds R. C. (1997) Oxford Univ. Press. [6] Treiman A. H. et al. (in review) *Am. Mineral.* [7] McLennan S. M. et al. (2013) *Science*, doi:10.1126/science.1244734. [8] Leveille R. (in prep) *JGR*.

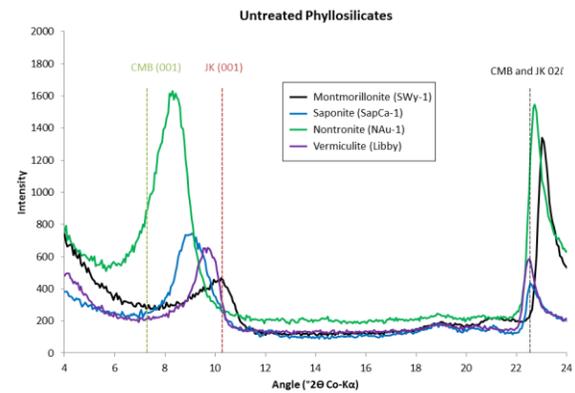


Figure 1. Lab CheMin XRD patterns of untreated swelling 2:1 phyllosilicates measured under dry  $N_{2(g)}$ . (001) peak positions for the phyllosilicates in Cumberland and John Klein samples are denoted by the green and red dashed lines, respectively. The position of the Cumberland and John Klein (02 $l$ ) phyllosilicate peak is denoted by the grey dashed line.

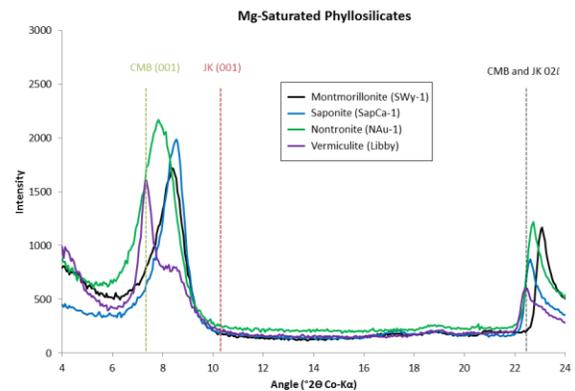


Figure 2. Lab CheMin XRD patterns of Mg-saturated swelling phyllosilicates measured under dry  $N_{2(g)}$ . Dashed lines are the same as in Fig. 1.

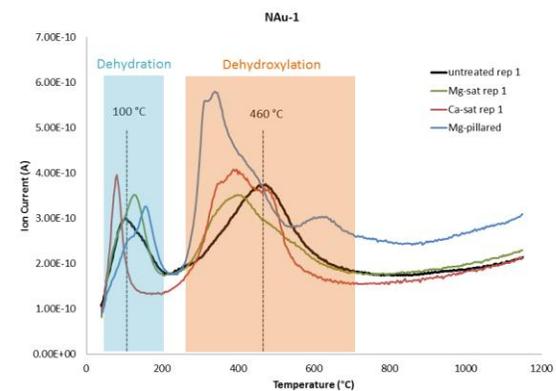


Figure 3. Evolved gas analysis curves for nontronite m/z 18 (i.e.,  $H_2O$ ). Dehydration and dehydroxylation temperatures for the untreated material are denoted by the vertical dashed lines.  $H_2O$  evolutions from dehydration and dehydroxylation temperatures are shaded in blue and orange, respectively.