LABORATORY STUDIES OF SMECTITE CHLORITIZATION: APPLICATIONS TO THE CLAY MINERALOGY OF GALE CRATER, MARS

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Introduction

The CheMin X-ray diffraction (XRD) instrument on the Mars Science Laboratory (MSL) rover, Curiosity, analyzed two mudstones, John Klein and Cumberland, at Yellowknife Bay, Gale Crater, Mars [1]. The XRD data revealed the presence of clay minerals, based on the presence of broad 10Å and ~14Å peaks (Fig. 1). The position and breadth of the 10Å peak suggests a collapsed 2:1 phyllosilicate. The specific identity of the ~14Å phase is unknown, although two explanations have been proposed, namely a smectite with hydrated Mg^{2+} or Ca^{2+} interlayer cations or a partially chloritized smectite (Fig. 2) [1-2].

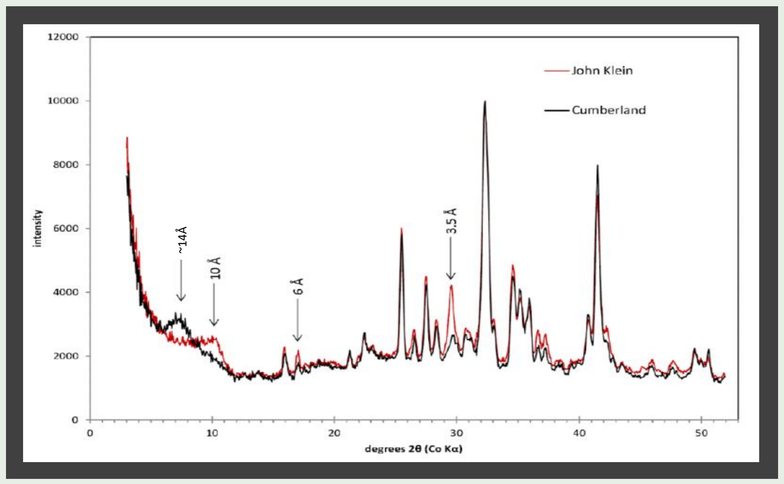

Figure 1. Comparison of XRD patterns from John Kline (red) and Cumberland (black) with the positions of major phyllosilicate peaks labeled. CheMin uses Co-Kα radiation to perform analyses (after [1]).

Methods

This study focused on synthesis and XRD analyses of Mg-exchanged and chloritized smectites to clarify the nature of the ~14Å phyllosilicate from Cumberland.

Pillared smectites were synthesized using methods closely based on Slaughter and Milne (1960) [3]. $Mg(OH)_2$ and $Al(OH)_3$ pillaring experiments were conducted for each clay mineral at three different Mg:Al ratios, 1:0, 2:1, and 3:1, and Mg and Ca cation-exchange experiments were also conducted. In all, seven products (four cation-exchanged, three pillared) were synthesized for each clay mineral.

In order to assess the effectiveness of the pillaring and cation-exchange experiments, XRD was used to measure the 001 peak positions of the clay samples. Samples were subjected to a vacuum environment and analyzed on an Anton Paar TTK450 heating stage from 22°C to 250°C in order to evaluate samples under low-pressure/low relative humidity (RH) conditions comparable to those in the CheMin instrument on Mars.

Table 1. Structural Formulae of Smectites Used

	SWy-1[1]	Cheto (SAz-1)[2]	H-33b[3]	Burro Creek
Si	3.83	3.93	3.500	3.84
Al	0.17	0.07	0.500	0.16
∑ Tet	4.00	4.00	4.000	4.00
Al	1.54	1.48	0.142	0.05
Fe	0.22	0.09	1.821	0.06
Mg	0.27	0.66	0.049	2.88
Mn	-	-	0.004	-
Ti	-	0.01	-	-
∑ Oct	2.03	2.24	2.016	2.99
Ca	-	0.44	0.250	0.11
Na	-	0.01	-	0.01
K	-	0.03	-	-
Mg	-	-	-	0.05
∑ Int	0.37	0.47	0.250	0.12

Tet = tetrahedral cations, Oct = octahedral cations, Int = interlayer cations

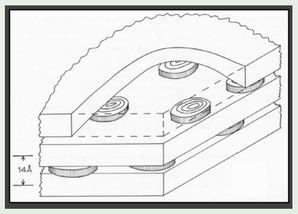

Table 1. Structural formulae from: [1]Madejová et al. (1994, after Kelley, 1955), [2]Mermut and Faz Cano (2001), [3]Cardile and Johnston (1985).

Figure 2. Schematic diagram of a pillared smectite. Smectite layers are represented by rectangular blocks, and pillars are represented by cylindrical blocks [3].

Results

Sixteen cation-exchanged smectites and 12 pillared smectites were produced. Five of these experiments produced smectites with 001 d values similar to those found for Cumberland. Cation-exchanged smectites (Fig. 3) did not show basal peaks near 14Å. The experiments producing 001 d values close to Cumberland are discussed below.

Experiment #1

SWy-1, Mg:Al 1:0. XRD analyses showed a d value of ~13.2Å under vacuum, and this 13.2Å peak was retained when heated to 250°C (Fig. 2). The 1:0 data indicate that SWy-1 was modified from its initial montmorillonite structure (~10Å 001), but the basal spacing was not consistent with a completely pillared smectite (~14Å). The pillars may have precipitated between some layers of smectite resulting in partial interstratification as indicated by the 13.2Å peak after heating.

Experiment #2

SWy-1, Mg:Al 3:1. The 001 reflection for the 3:1 Mg:Al SWy-1 mixture had an initial d value of 15.0Å, which decreased to ~13.0Å under vacuum. The 001 reflection increased slightly to 13.2Å upon heating to 250°C (Fig. 4). These data suggest that experiments with a 3:1 ratio mixture were partially successful in creating a pillared smectite, providing results similar to those obtained with the 1:0 mixtures.

Experiment #3

Cheto, Mg:Al 2:1. XRD analyses showed an initial 001 d value of 15.0Å, which decreased to ~13.7Å in vacuum and to 13.5Å when heated to 250°C (Fig. 4). These data indicate that this smectite was modified from its initial structure, consistent with formation of a pillared smectite, as indicated by the 13.5Å spacing for the sample after heating.

Experiment #4

H-33b, Mg:Al 3:1. XRD analyses showed an initial 001 d value of ~16.4Å for the air-dried clay, which decreased to 14.3Å under vacuum and to 13.8Å after heating to 250°C under vacuum (Fig. 4). The data for this 3:1 mixture suggest that the smectite was modified from its original nontronite structure to produce a pillared smectite (~14Å).

Experiment #5

Burro Creek, Mg:Al 3:1. XRD analyses showed an initial, air-dried 001 d value of 15.0Å, which decreased to 12.7Å under vacuum. Upon heating to 250°C, the peak decreased and broadened to two lower-intensity peaks centered at ~13.2Å (Fig. 4) and ~10.7Å. The XRD data for this 3:1 mixture show that the clay was modified from the original saponite.

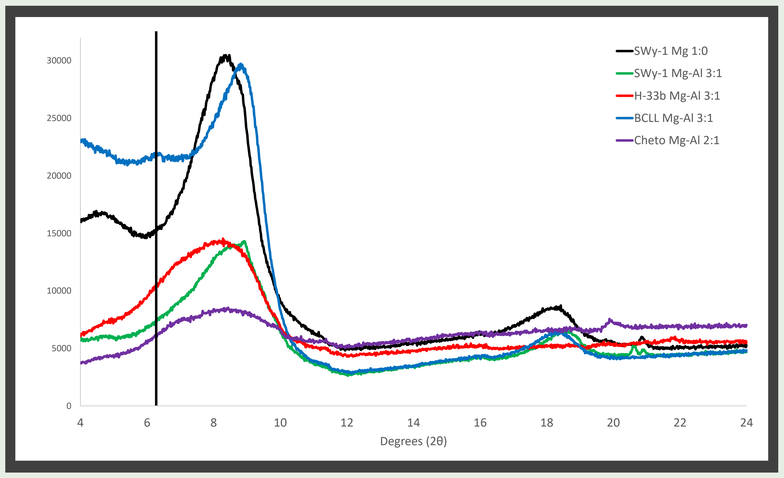

Figure 3. 001 peaks of cation-exchanged smectites from the same Mg:Al mixtures that produced pillared smectites. Vertical line represents the position of the ~14Å peak in the Cumberland XRD pattern.

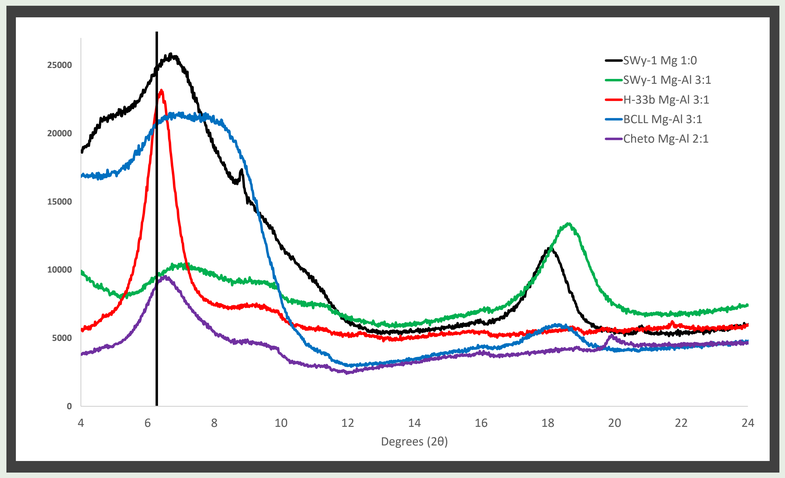

Figure 4. 001 peaks of pillared smectites measured at 250°C under vacuum. Vertical line represents the position of the ~14Å peak in the Cumberland XRD pattern.

Implications for CheMin XRD Data

Several experiments produced pillared smectites, and these measurements provide insight into how pillared smectites may behave on Mars and in the CheMin instrument environment. Analyses under conditions relevant to those in the CheMin XRD instrument show that a few of these experimentally pillared samples may be good analogs to the ~14Å phyllosilicate detected in the Cumberland mudstone. The H-33b nontronite 3:1 Mg:Al mixture experiments produced results that most closely resemble the ~14Å phyllosilicate detected with CheMin.

Mg-exchanged smectites are not likely candidates for the Cumberland clay mineral based on the experimentally observed behaviors under vacuum, where all samples collapsed to <~12Å (Fig. 3). XRD data for these exchanged and pillared smectites reveal restricted collapse under vacuum and elevated-temperature conditions, and suggest that partially chloritized smectites are a viable explanation for the expanded material seen by CheMin at Cumberland. If both John Klein and Cumberland clay minerals formed authigenically, these data suggest that the Cumberland clay was likely further altered/modified during diagenesis. This suggestion is supported by the presence of Mg-Fe-Cl-rich raised ridges and other diagenetic features observed at Yellowknife Bay [4]. As Curiosity continues to explore Gale Crater, laboratory-based XRD characterization of smectites will be important to interpreting CheMin XRD data and of understanding the geologic history of the region.

References

[1] Vaniman, D. T. et al. (2014) Science, 343, 1243480. [2] Bristow, T. F. et al. (2015) Am. Mineral. 100, 824-836.
[3] Slaughter and Milne (1960) 7th Nat. Conf. on Clays & Clay Minerals 114-124. [4] McLennan, S. M. et al. (2014) Science, 343, 1244734.