

EFFECTS OF KAPTON SAMPLE CELL WINDOWS ON THE DETECTION LIMIT OF SMECTITE: IMPLICATIONS FOR CHEMIN ON THE MARS SCIENCE LABORATORY MISSION. C. N. Achilles¹, D. W. Ming², R. V. Morris², and D. F. Blake³, ¹ESCG/Hamilton Sundstrand, Houston, TX 77058, cherie.n.achilles@nasa.gov, ²NASA Johnson Space Center, Houston, TX 77058, ³NASA Ames Research Center, Moffett Field, CA 94035.

Introduction: The CheMin instrument on the Mars Science Laboratory (MSL) rover Curiosity is an X-ray diffraction (XRD) and X-ray fluorescence (XRF) instrument capable of providing the mineralogical and chemical compositions of rocks and soils on the surface of Mars. CheMin uses a microfocus X-ray tube with a Co target, transmission geometry, and an energy-discriminating X-ray sensitive CCD to produce simultaneous 2-D XRD patterns and energy-dispersive X-ray histograms from powdered samples. CheMin has two different window materials used for sample cells – Mylar and Kapton. Instrument details are provided in [1, 2, 3].

Fe/Mg-smectite (e.g., nontronite) has been identified in Gale Crater, the MSL future landing site, by CRISM spectra [4]. While large quantities of phyllosilicate minerals will be easily detected by CheMin, it is important to establish detection limits of such phases to understand capabilities and limitations of the instrument. A previous study [5] indicated that the (001) peak of smectite at 15\AA was detectable in a mixture of 1 wt.% smectite with olivine when Mylar is the window material for the sample cell. Complications arise when Kapton is the window material because Kapton itself also has a diffraction peak near 15\AA ($6.8^\circ 2\theta$). This study presents results of mineral mixtures of smectite and olivine to determine smectite detection limits for Kapton sample cells. Because the intensity and position of the smectite (001) peak depends on the hydration state, we also analyzed mixtures with “hydrated” and “dehydrated” smectite to examine the effects of hydration state on detection limits.

Materials and Methods: A two mineral system composed of smectite from Cheto Mine, AZ (predominantly montmorillonite) and olivine from Twin Sisters Mine, OR, were mixed in varying proportions. The montmorillonite was sized to $<2\text{ }\mu\text{m}$ and olivine was ground and sieved to $45\text{--}90\text{ }\mu\text{m}$ then manually mixed in different proportions by gently grinding to produce four mixtures with 10, 3, 2, and 1 wt% smectite. A sample with no smectite was analyzed to provide a baseline comparison.

CheMin IV instruments are laboratory versions of the CheMin flight unit and are used to baseline the capabilities of the flight instrument. To provide XRD measurements under arid conditions that more closely resemble a contemporary Mars, the CheMin IV at the

NASA Johnson Space Center was configured to provide a constant flow of N_2 gas to the sample chamber during analysis. In addition, a sample box purged with N_2 gas allows for samples to equilibrate to $<1\%$ humidity prior to analysis. Relative humidity measurements in the absence of an N_2 purge averaged 32% (ambient laboratory conditions, Houston, Texas) while the addition of N_2 decreased RH to $<1\%$. Samples were analyzed by summing individual 30 second exposures to obtain a pattern with ample intensity:background ratios. Piezoelectric vibration of the cell is used to randomize the sample to reduce preferred orientation effects.

Results: Figure 1 shows a comparison of the smectite/Kapton peak at 15.5\AA ($6.6^\circ 2\theta$) for mixtures with 3%, 2%, 1%, and 0 wt.% “hydrated” smectite (equilibrated with ambient lab air). For each wt.% presented, three individual patterns, each consisting of 1000 exposures, were summed then compared to one another. Distinct intensity differences are apparent between the 3%, 2%, and 0% smectite samples. The peak intensity evident in the 0% smectite sample results from the Kapton window. The peak intensity shown in the 1% sample has a slight difference (i.e. more intense peak), but likely to be below detection limits for a 15\AA smectite peak in a natural rock or soil sample. These analyses were performed under optimal conditions, with a full sample cell and little to no loss of material throughout the analysis.

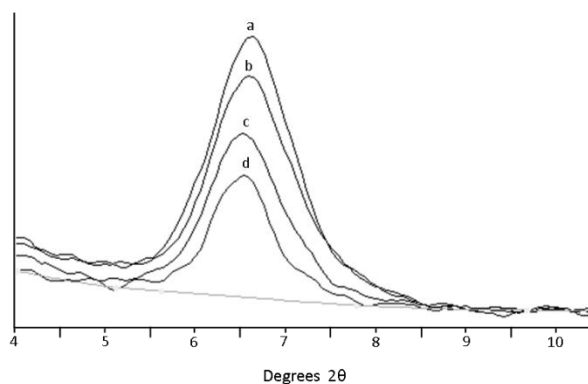


Figure 1 Comparison of the (001) smectite peak for smoothed XRD patterns of (a) 3%, (b) 2%, (c) 1%, and (d) 0% smectite and olivine mixtures for a sample cell with Kapton windows.

Figure 2 shows results from a “dehydrated” 10% smectite sample (i.e. sample equilibrated and analyzed with dry N₂ purging). Prior to analysis the sample was placed in the N₂ purged sample box for 48 hours then analyzed while N₂ flowed to the sample chamber. Humidity measurements recorded during the first hour of analysis show a decrease from 9% to 1.5% RH over the course of 100 exposures (Fig. 2a). The XRD pattern from this time interval shows a distinct shoulder on the higher 2θ side of the Kapton peak, representing the partial dehydration of the smectite through loss of interlayer H₂O. Figure 2b is the summation of patterns 300-399 (approx. 2.5-3.3 hours into the analysis) and shows two distinct peaks; the Kapton peak at 15.3Å and the partially dehydrated smectite peak at 11.7Å.

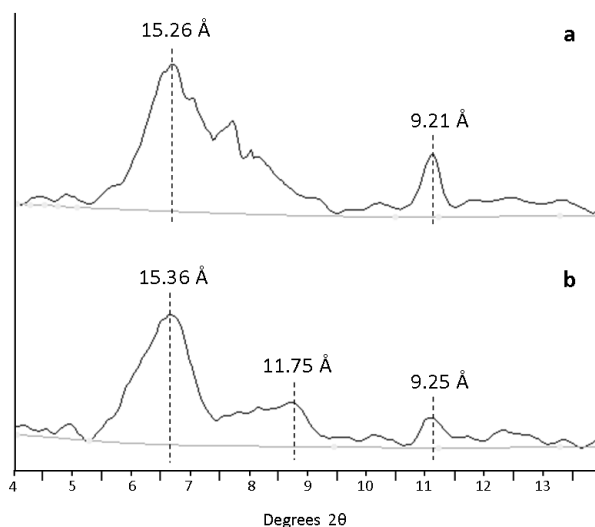


Figure 2 Comparison of smoothed XRD peaks for exposures 0-99 (a) and 300-399 (b). Kapton is represented by the 15Å peak, olivine by the 9.2Å peak and montmorillonite by the 11.7Å peak.

Implications for MSL: The CheMin IV instrument is able to detect 1 wt% smectite in smectite/olivine mixtures when analyzed with a full cell of material and Kapton cell windows in ambient (Houston) laboratory conditions. For natural samples, we conservatively estimate a detection limit of 2 wt% smectite on the basis of Figure 1.

Mixtures with smectite in a dry environment resulted in a distinctly different pattern. Loss of H₂O from the interlayer causes a shift of the (001) peak to higher 2θ values so that the (001) smectite peak does not conflict with the Kapton peak. If smectite minerals on Mars are present in a more dehydrated state, minerals such as montmorillonite and nontronite (which have a hydrated 14-15Å on Earth) are more readily detected in samples measured in sample cells with

Kapton windows. That is, the detection limit for smectite in natural samples under dry conditions is <2 wt% in the presence of Kapton windows.

Further analyses to determine the detection limits of dehydrated secondary minerals, including other phyllosilicates (e.g., mica vs. smectite vs. chlorite/vermiculite) are being conducted at JSC to help quantify secondary phases at Gale Crater.

References: [1] Blake D. F. et al. (2010) *LPSC XLI*, Abstract #1896. [2] Blake D. F. et al. (2009) *LPSC XL*, Abstract #1484. [3] Blake D. F. et al. (2007) *7th Int. Conf on Mars*, Abstract #3220. [4] Milliken R. E. et al. (2010) *Geophys. Res. Lett.*, 37, L04201. [5] Achilles C. N. et al. (2011) *LPSC XLII* Abstract #2671.