

CRYSTALLINITY EFFECTS ON SPECTRAL FEATURES OF AMORPHOUS SAPONITE AND IMPLICATION FOR POORLY CRYSTALLINE PHYLLOSILICATES ON MARS

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Introduction: VNIR Spectral observations from the CRISM on MRO and the OMEGA on Mars Express, have detected spectral signatures indicative of clay minerals at numerous locations across the martian surface^[1-3]. The identification is based on the detection of H₂O combinations and overtones (near 1.4 and 1.9 μm) and metal-OH combination absorptions (2.2-2.5 μm). The Chemistry & Mineralogy X-Ray Diffraction (CheMin) on the Curiosity rover confirmed the presence of phyllosilicates at Gale Crater^[4-5]. XRD patterns of Martian surface soil (Rocknest) and mudstones (John Klein and Cumberland) present a low-angle rise (4-10° in 2θ) and the elevated background between 15 and 40° in 2θ, which indicates the presence of poor-crystalline smectite and amorphous mineral component, respectively^[5]. The CheMin XRD analyses pose an urgent question on the crystallinity of phyllosilicates found by orbital remote sensing in Mars global scale, which is directly relevant to aqueous alteration conditions (e.g., pH, temperature, water to rock ratio, and the duration of liquid water presentation) during geologic history of Mars^[6-7]. It is therefore a necessity to develop a capability to better constrain the crystallinity of Martian clays based on the VIS-NIR data.

Experiments: Mg-endmember smectite, saponite, was synthesized with a sol-gel method modified from [8]. 0.07 mol sodium metasilicate powder (Na₂SiO₃·9H₂O) was dissolved in 40 mL NaOH and NaHCO₃ buffer solution (pH=11). The obtained solution was added in the 0.01 mol AlCl₃ and 0.06 mol MgCl₂ mixture solution with an eyedropper under magnetic stirring. The white precipitation was observed immediately. The white gel was collected, put into a Teflon cup, then into a Parr Bump to run a hydrothermal synthesis that lasted for two weeks at 200°C in an oven. At the end, the solid phase was separated by vacuum filtration and dried overnight at 50°C. The initial amorphous saponite A was characterized by EDS, XRD, and Raman spectroscopy to be saponite with extremely low crystallinity. This sample was sealed in a silica tube and heated at different temperatures with different durations for the purpose of increasing its crystallinity.

The chemistry of initial saponite A was determined by FE-SEM equipped with EDS. On all samples, XRD patterns were collected on a Bruker D8 Advance powder diffractometer. Raman spectra were obtained using

both the 532 nm and 785 nm excitation laser line on a Renishaw inVia system. A Nicolet Nexus 670 FTIR spectrometer was used to collect Mid-IR ATR measurements of saponite. VNIR spectra were collected using an ASD portable spectrometer.

Results: On the basis of EDS results, we calculated the chemical formula of synthetic saponite. The derived stoichiometric formula for synthetic saponite is Na_{0.67}[Mg_{4.94}Al_{1.06}][Si_{7.56}Al_{0.44}]O_{20.00}(OH)₄.nH₂O.

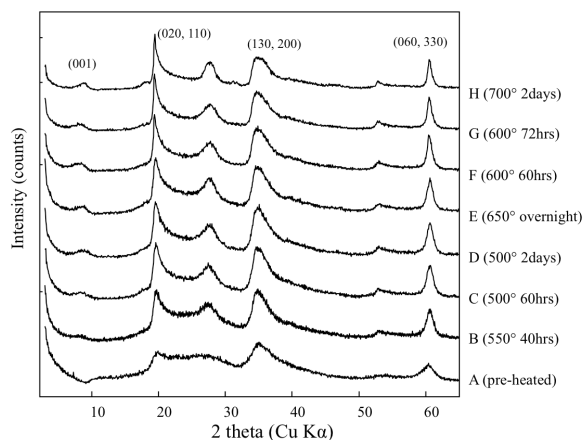


Fig. 1 XRD patterns of synthetic saponite. Heating temperature and duration are listed in parentheses.

In Figure 1, the initial saponite (sample A) shows an elevated background from 15 to 50° in 2θ. This suggests the amorphous structure in the product of hydrothermal experiment. Almost non-existence of (001) peak at low diffraction angle (near 10°) implies that the layers are not stacking well along *c*-axis in sample A. The position of the (060) reflection of sample A indicates it is a trioctahedral phyllosilicate.

After being heated at 500-700° (sample B-H), there are two major changes in the XRD patterns: (1) the (001) peak intensity gradually increases, indicating the increasing of stacking order (basal spacing of 10.1-10.9 Å); (2) the intensity increasing and width narrowing of the (060) peak, which indicates the increase of regularity of MgO₄(OH)₂ in octahedral sheet (*d*₀₆₀ spacing of A-H sample is 1.525-1.528 Å). In order to link XRD results with multiple spectroscopic data, we calculated a smectite crystallinity index (or Biscaye's index^[9]) using the obtained XRD data, as a measure of degree of crystallinity of saponite in this study.

In Raman spectra, the initial saponite (sample A) has three main Raman peaks at 190, 360, and 678 cm^{-1} , which is consistent with that of terrestrial saponite SapCa-2^[10]. The strongest Raman peak at 678 cm^{-1} is due to Si-O_{bridging}-Si bending vibration, which implies that synthetic saponite has a trioctahedral structure character. After heating, no significant peak shifts were observed, but an obvious narrowing of the 678 cm^{-1} peak width is observed: the full-width-half-maximum (FWHM) changes from 25 (sample A) to 19 cm^{-1} (sample B-E). This change suggests improved ordering of Si-O bonds in tetrahedral sheet.

In the MIR-ATR spectra, the strong band at 1006 cm^{-1} is contributed by Si-O asymmetric stretching mode in tetrahedral sheet. The band at 665 cm^{-1} could be assigned to Mg-OH bending vibration. We found the FWHM of Si-O band gradually decrease from 108 to 75 cm^{-1} with the increases of heating temperature and heating duration. A linear correlation exists between the FWHM and the smectite crystallinity index extracted from XRD data ($R^2=93.42\%$). Both Raman and MIR observations imply the increased structural order of tetrahedral sheet of saponite with heating, i.e., the irregularity among tetrahedral units in the layer has been reduced. However, the band area ratios (A_{1006}/A_{665}) and crystallinity index are uncorrelated, which suggests no losing of structural OH during high temperature heating.

In VNIR spectra (Figure 2), the initial saponite sample A exhibits strong and broad water overtone near 1.41 μm with a sharp peak at 1.39 μm due to Mg-OH overtone, and HOH combination stretching plus bending vibrations due to bound and interlayer water at 1.90 μm ^[11]. The two features mainly derive from molecular water in the interlayer region and adsorbed on the surface. We note the depth of these two bands gradually decrease with increasing heating temperature and duration, except the sharp peak at 1.39 μm .

The initial saponite (sample A) has a broad band centered at 2.31 μm . Following the increase of heating temperature and duration, the 2.31 μm band became sharper and stronger, and a new band at 2.29 μm (sample B) appeared. All the heated saponites (sample B to G) show a diagnostic NIR doublet at 2.29 and 2.31 μm corresponding to the combination of Mg-OH stretching and bending vibrations in octahedral sheet^[11]. Following the increase of heating temperature and duration, three changes were observed in the Mg-OH band: (1) the increases of the band depth and spectral contrast; (2) the increase of separation of spectral components, as a multi-peak band; (3) the decrease of band width, especially the central doublet at 2.29 and 2.31 μm . We found the 2.31 μm band depth has a strong correlation with the crystallinity index extracted from XRD data.

This phenomenon suggests the increase of Mg-OH bond ordering in octahedral sheet of our saponite.

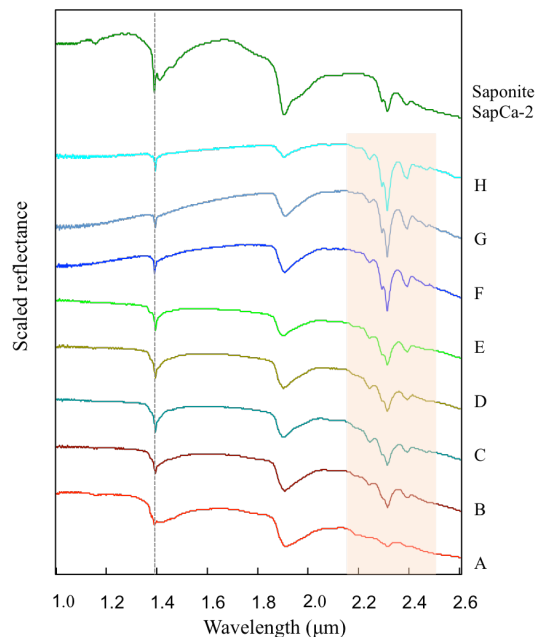


Fig. 2 NIR reflectance spectra of synthetic saponite. Natural saponite SapCa-2 is used as the reference.

Implications: Our synthetic Mg-saponite with low crystallinity has similar XRD patterns with the smectites of Sheepbed mudstones found on Mars: i.e., the locations of 001 and 021 diffraction peaks, octahedrally coordinated cations, the low degree of crystallinity. Furthermore, the correlation we found through this study, i.e., the shape and intensity of metal-OH band in the range 2.2-2.4 μm vs. smectite crystallinity index, can be used to assign the structural ordering of smectite found on Mars in global scale using VNIR spectroscopy. The VNIR, MIR, Raman spectra of saponite with gradually changed crystallinity would complement the current spectral libraries, which will eventually help assigning the crystallinity of saponite during landing/rover exploration at Martian surface, and therefore to help constrain their formation conditions.

References: [1]Bibring et al., 2006, *Science*, 312(5772), 400-40. [2]Mustard et al., 2008, *Nature*, 454(7202), 305-309. [3]Poulet et al., 2005, *Nature*, 438(7068), 623-627. [4]Bish et al., 2013, *Science*, 341(6153), 1238932. [5]Vaniman et al., 2014, *Science*, 343(6169), 1243480. [6]Rice et al., 2013, *Icarus*, 223(1), 499-533. [7]Smith et al., 2013, *Icarus*, 223(2), 633-648. [8]Decarreau and Bonnin, 1986, *Clay Minerals*, 21(5), 861-877. [9]Biscaye, 1965, *GSA Bulletin*, 76(7), 803-832.[10]Wang et al., 2015, *J. Raman Spectrosc.*, 46(10), 829-845. [11]Bishop et al., 2008, *Clay Minerals*, 43(1), 35-54.