

AMMONIATION OF PHYLLOSILICATES, CARBONACEOUS CHONDRITE METEORITES, AND IMPLICATIONS FOR THE NATURE OF AMMONIATED MATERIALS ON CERES. B.L. Ehlmann^{1,2}, R. Hodys², E. Ammannito³, G.R. Rossman¹, M.C. De Sanctis⁴, C.A. Raymond². ¹Division of Geological and Planetary Science, California Institute of Technology, 1200 E California Blvd, MC 150-21. Pasadena, CA, 91125. (ehlmann@caltech.edu), ²Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, Pasadena, CA 91109. ³Dept. of Earth Planetary and Space Sciences, University of California, Los Angeles, California, ⁴Istituto di Astrofisica e Planetologia Spaziali, Istituto Nazionale di Astrofisica, Rome, Italy

Introduction: Ammoniated- and phyllosilicate-bearing materials were discovered on Ceres and globally mapped with the VIR imaging spectrometer on the Dawn mission [1-3]. Key Ceres infrared spectral features are located at $\sim 3.05 \mu\text{m}$, indicating NH_4 -bearing materials, and $2.72 \mu\text{m}$, indicating Mg-OH-bearing materials. Their co-occurrence everywhere on the surface [3] makes it likely, but not certain, that Mg phyllosilicates are the carrier of the ammonium. Readily available spectral libraries have ammoniated, Al-phyllosilicates, which have been used in radiative transfer unmixing models to estimate the composition of the Ceres surfaces [2]. Yet, more suitable may be Fe- or Mg-phyllosilicates, which are more likely from meteoritic materials. Here, we obtain, purify, and ammoniate a variety of Ceres-relevant analog materials, including both phyllosilicates and meteorites. We then evaluate (i) which phases ammoniate; (ii) which ammoniated phases exhibit absorptions with similar positions, widths, and shapes to those observed for Ceres; and (iii) if/how the NH_4 -related absorptions change at different temperatures under vacuum [detailed further in 4]. The overarching goals are to refine the identification of the ammoniated species on Ceres and develop a spectral library suitable for accurate, quantitative radiative transfer models that estimate Ceres' composition.

Methods: Fe/Mg phyllosilicates from the smectite, chlorite, and serpentine families were obtained, powdered, checked for purity with FTIR and/or XRD, purified by settling to diminish the non-phyllosilicate fraction or treated with acetic acid to remove associated carbonates (if needed), and sieved to $<150 \mu\text{m}$. Similarly, powdered fractions from CM and CI meteorites with spectral properties similar to some asteroids [5] were obtained. Samples listed in Table 1 were measured with a iS50 FTIR instrument in biconical diffuse reflectance mode over 2-25 μm at room temperature. Samples were then ammoniated at room temperature with ammonium acetate followed by acquisition of spectra, also at room temperature, to evaluate whether ammoniation occurred. Samples showing signs of ammoniation were then measured while being cooled from 300 K to 90 K,

under vacuum (base pressure $\sim 3 \times 10^{-5}$ Torr) using a Nicolet 6700 FTIR fitted with a diffuse reflection accessory (Pike Technologies DiffusIR) at a 30° incidence.

Table 1. Materials ammoniated in this study

Phyllosilicates	Fe-smectite	Nontronite	NAu-1
	Fe-smectite	Nontronite	NAu-2
	Fe-serpentine	Cronstedtite	CIT-17639
	Fe-serpentine	Cronstedtite	H-2320
	Mg-smectite	Saponite	IMV
	Mg-smectite	Saponite	Sap_Gr
	Mg-smectite	Saponite	Sap_Baja
	Mg,Li-smectite	Hectorite	SHCa-1
	Mg,Li-smectite	Hectorite	SynH-1
	Mg-Serpentine		OM12_003
	Mg-Serpentine		OM12_016
	Mg-chlorite	Ripidolite	CCa-2
	Al-smectite	Montmorillonite	SAZ-2
	Al-smectite	Montmorillonite	SWy-3
Meteorites	Murchison (CM2)		
	Murray (CM2)		
	Cold Bokkeveld (CM2)		
	Orgueil (CI1)		
	Mighei (CM2)		
	Tagish Lake		

Results: Smectite minerals readily ammoniated at room temperature. Al smectite spectra matched those in existing databases [e.g., 6], while Mg smectite materials showed absorptions between $3.03\text{-}3.06 \mu\text{m}$ due to NH_4 and at $2.72\text{-}2.78 \mu\text{m}$ due to Mg-OH (Fig. 1). The latter were sometimes in a doublet. These spectral characteristics of the ammoniated Mg smectites persist in vacuum and down to 90 K (Fig. 2). Fe smectite materials

Figure 1. SWIR spectra of two Mg smectites before (black) and after (orange) ammoniation

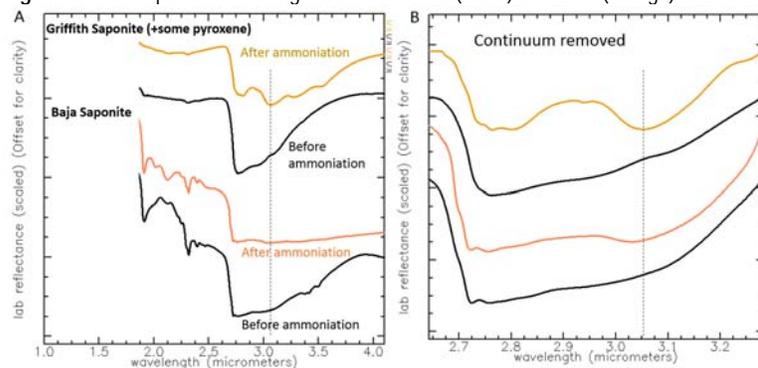
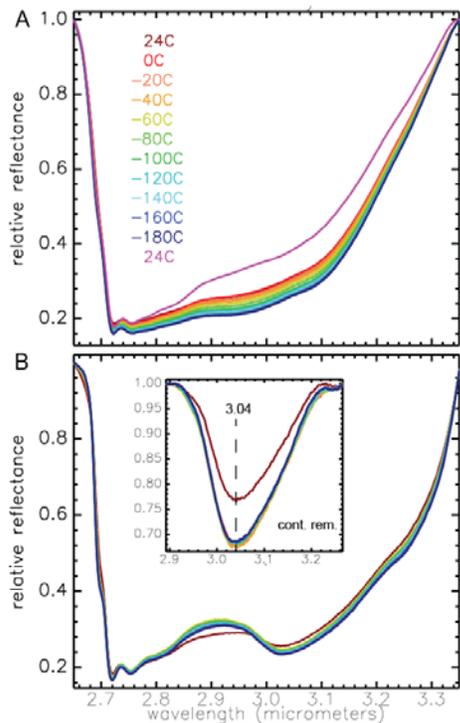


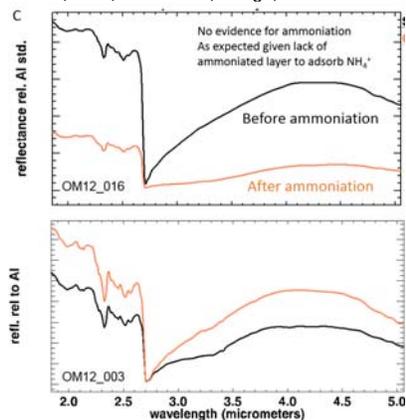
Figure 2. SWIR spectra of the Baja Rosarita saponite (an Mg smectite), (a) not ammoniated and (b) ammoniated and acquired under vacuum temperatures from 297 K to 93 K.



showed signs of ammoniation, but also the formation of a dark precipitate, perhaps due to reaction of the iron to form Fe oxides. Future work will include XRD of the ammoniated Fe smectites. As anticipated, serpentines and chlorites did not ammoniate. These phyllosilicates lack the interlayer of smectites for hosting of species with positive charge. No evidence for loosely bound (e.g., adsorbed) NH₄ was seen in their spectra (Fig 3).

Meteorite spectra from Murray and Mighei did not show appreciable change upon ammoniation. The Cold Bokkeveld sample did develop an absorption between 3.0-3.1 μm, which might be attributed to ammoniation, although the shape and position of the band are not a good match for the shape and position of the ~3.05 μm absorption band in VIR data from Ceres

Figure 3. SWIR spectra of two Mg serpentines before (black) and after (orange) ammoniation



from Ceres

(Fig 4). Sample hydration may instead be responsible. Future work will examine the effects of treatment with water alone for comparison to determine if the effect is one of (re-)hydration, rather than ammoniation. Future work will also examine the more smectite-rich Tagish Lake and additional data from Orgueil.

Key Findings Related to Ceres & Future Work:

Smectite family minerals readily ammoniate under the conditions whereas serpentines and chlorite family minerals do not. This is as expected, given that smectites can readily exchange interlayer cations for NH₄ in solution whereas other phyllosilicates lack this high cation exchange capacity. Materials from some carbonaceous chondrites may ammoniate while most do not, possibly related to the proportion of expandable clay minerals like smectites vs. serpentines in the sample. Smectite-rich meteorite samples will be treated to examine for evidence of ammoniation. Interestingly, so far, only the Mg smectites produce an ammoniation feature that robustly matches the Dawn VIR and Dawn telescopic data (Fig. 4), robust against changing temperature (Fig. 2). However, the deepest metal-OH absorption feature of the Mg-smectites occurs at a different absorption position (2.76 μm) than observed on Ceres (2.72 μm). This implies there may be two distinct phases responsible for the Ceres spectrum. Speculatively, both ammoniated Mg-smectites and Mg-serpentines may be present, further reinforcing the similarity with highly altered carbonaceous chondrites, which possess both of these phases.

References: [1] King et al., 1992, *Science* [2] DeSanctis et al., 2015, *Nature* [3] Ammannito et al., 2016, *Science* [4] Ehlmann et al., 2017, in prep for submission to *Met. & Plan. Sci.*, Ceres special issue [5] Takir et al., 2013, *Met. & Plan. Sci.* [6] NASA Keck RELAB database, Brown University [7] DeSanctis et al., 2016, *Nature*

Figure 4. SWIR spectra of Ceres [7] compared to the Cold Bokkeveld meteorite, serpentine, and ammoniated Mg smectite

