SPECTRAL PROPERTIES OF AMMONIATED SMECTITES UNDER DIFFERENT CONDITIONS TO SUPPORT THEIR DETECTION ON CERES AND OTHER BODIES.  S. Andrejkovičová, J. L. Bishop, A. Maturilli, K. A. Wilk, H. Páلكová, and F. Rocha, Geobiote (Aveiro University, Portugal; slavka@ua.pt), SETI Institute (Mountain View, CA, USA), German Aerospace Center (DLR, Berlin, Germany), Brown University (Providence, RI), Institute of Inorganic Chemistry (SAS, Bratislava, Slovakia).

Summary: The purpose of this study is to investigate the reflectance spectra of ammoniated smectites under different environmental conditions in order to characterize the features most likely to be observed on planetary bodies. The spectral properties of hydrous materials, including smectites, change depending on the environmental conditions during measurement. We observed significant reduction in the hydration features and enhancement of the NH₄⁺ features for ammoniated smectite spectra measured under dry air or vacuum.

Introduction: The Dwarf planet Ceres is known to contain ammonia [1] as well as other bodies in our Solar System. Ammonia may be present on Mars, but has not yet been identified. The Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover can detect NH₄⁺ in clays using thermal decomposition methods, but this becomes more complicated in the presence of perchlorates, which are ubiquitous at Gale crater [2,3]. Taking this into account, NH₄⁺-montmorillonite as a potential source of NO evolution in SAM analyses of martian samples was studied [4]. Moreover, previous analyses of the X-ray diffraction [4] and spectral properties [5] of NH₄-treated clay minerals revealed multiple diagnostic features for ammonia in these materials.

For the initial phase of our study we prepared multiple NH₄⁺-smectites using a variety of dioctahedral Fe-bearing smectites to probe the influence of smectite chemistry and structure on the spectral features due to NH₄⁺ [6]. For the current study, we prepared additional NH₄⁺-smectites from trioctahedral Mg-bearing samples. We also measured reflectance spectra under dry air conditions for the dioctahedral NH₄⁺-smectites and tested measuring spectra under vacuum conditions for selected samples. These data will inform the spectral properties of NH₄⁺-smectites expected on planetary bodies, including Ceres, where it has already been detected using the Visible and InfraRed Mapping Spectrometer (VIR) on Dawn [1], and Mars using Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) spectra from orbit and NIR spectra on landed missions. Identifying and characterizing ammonia in our Solar System will help assess the N cycle on other planetary bodies and the availability of N for prebiotic chemistry, and potentially for life.

Methods: Samples were ammoniated as in [6] using an NH₄Cl treatment. XRD was run to confirm the presence of ammonia in the interlayer spacing. VNIR reflectance spectra were measured under ambient conditions using an ASD FieldSpecPro from 0.35-2.5 μm to test the samples.

Reflectance spectra under dry air conditions of the NH₄⁺-smectites with successful NH4 bands were also measured at RELAB, Brown University. IR spectra were measured under dry air with a rough gold standard from ~1-50 μm using a Thermo FTIR instrument and scaled to bidirectional spectra recorded from 0.3-2.5 μm relative to Spectralon under ambient conditions except for the spectrum of rozenite burnt by FTIR beam.

Additional spectra were measured of selected samples at the Planetary Spectroscopy Laboratory (PSL) at the DLR. These spectra were measured from ~1-25 μm using a Bruker FTIR instrument under ~10⁻³ torr vacuum relative to a rough gold surface.

Results: The reflectance spectra of these smectite samples were compared in three groups – samples with mostly Al, Fe, or Mg in their octahedral sites (Fig. 1). Although NH₄ bands were observed in our samples at

![Fig. 1. Reflectance spectra (ambient conditions) of NH₄⁺-smectites with Al, Fe, and Mg octahedral cations. Spectral bands due to Fe are marked with dashed lines, H₂O with solid lines, OH with colored broken lines, and NH₄ with dark gray broken lines and arrows.](image-url)
Variations are observed near 0.64 and 0.95 μm due to Fe excitations, and near 1.41 and 1.91 μm due to H₂O. The OH overtones and combination bands vary depending on the octahedral cation [7] as seen in Fig. 1. The NH₄ bands centers for these smectites appear to be independent of the type of octahedral cation. Shifts observed previously in the NIR and mid-IR spectral features of NH₄ in clay minerals [5,8] are likely due to changes in the phyllosilicate structure rather than the type of octahedral cation present.

Previous studies of NH₄-clays under dry conditions [5,9] noted enhancement in the ammonia bands as the H₂O bands are reduced. In this study, we conducted experiments under vacuum conditions on selected samples (Fig. 2). The strong H₂O bands near 1.41 and 1.91 μm in the ambient spectra decrease quickly under vacuum conditions and little change was noted after 15 minutes. We compared these 10⁻³ torr vacuum PSL spectra to running spectra under dry air conditions at RELAB where the samples were in a chamber for 12 hours under a H₂O purge system. The spectra resulting from both experiments look nearly identical, and even one sample that was heated post vacuum and re-measured under vacuum has similar features to the samples exposed to dry air for 12 hours (Fig. 3). The NH₄ bands near 3.05, 3.29, and 3.52 μm, in particular, are more apparent in the spectra measured under vacuum and could be contributing to spectra of Ceres and other bodies.

**Fig. 2.** Bidirectional reflectance spectra of NH₄-Badin nontronite. The initial measurement was made under ambient conditions, followed by spectra collected under vacuum up to 30 min. Bands due to NH₄ are marked with dark gray broken lines and arrows.

**Fig. 3.** Reflectance spectra of NH₄-smectites with broken lines marking NH₄ bands.

**Implications for detection of ammonia:** Infrared spectra were successfully used to identify ammonia at Ceres via telescopic data [10] and then VIR orbital data collected by the Dawn spacecraft [1]. Ammonia has also been identified on Enceladus [11], Pluto [12], and possibly Titan [13]. Spectral measurement and analysis of NH₄-smectites here and other NH₄-bearing minerals [14] enables detection of ammonia in our Solar System. Identifying ammonia supports understanding of the N cycle and will improve our knowledge of planetary processes (e.g., impacts and reduction) that could have fixed N into a bioavailable form such as ammonia.

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