

CHARACTERIZING NH₄-SMECTITES FOR IDENTIFICATION ON PLANETARY BODIES.

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Introduction: Ammonia is present on Ceres [1] and multiple bodies in our Solar System. Ammonia may be present on Mars as well, but has not, to date, been detected in surface materials at Gale Crater, Mars, using the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover. However, the almost ubiquitous presence of perchlorates in surface materials of Gale Crater [2,3] complicates the detection of NH₄⁺ in clays when thermal decomposition methods are used. 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 this 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. We measured visible/near-infrared (VNIR) reflectance spectra for comparison with spectra collected at 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 define the availability of N for prebiotic chemistry, uncover the N cycle on other planetary bodies, and inform the origin of life.

Methods: To prepare the monoionic NH₄⁺ form of smectites, an NH₄Cl treatment was used. 2 g of smectite was dispersed in a 50 ml solution of 1M NH₄Cl for 24 hours, and centrifuged at 5500 rpm for 20 min. The supernatant chloride solution was removed and replaced by a fresh 50 ml solution of 1M NH₄Cl (repeated 5×). The sample was introduced to dialysis tubes, placed in distilled water to remove chloride ions (AgNO₃ test) and dried at 50 °C.

VNIR reflectance spectra were measured under ambient conditions of the smectites and NH₄-smectites using an ASD FieldSpecPro from 0.35-2.5 μm. Additional spectra of SWy-1 montmorillonite and NH₄-SWy-1 prepared for an earlier study [5] are also included here.

Results: The reflectance spectra of these smectite samples were compared in three groups – samples with

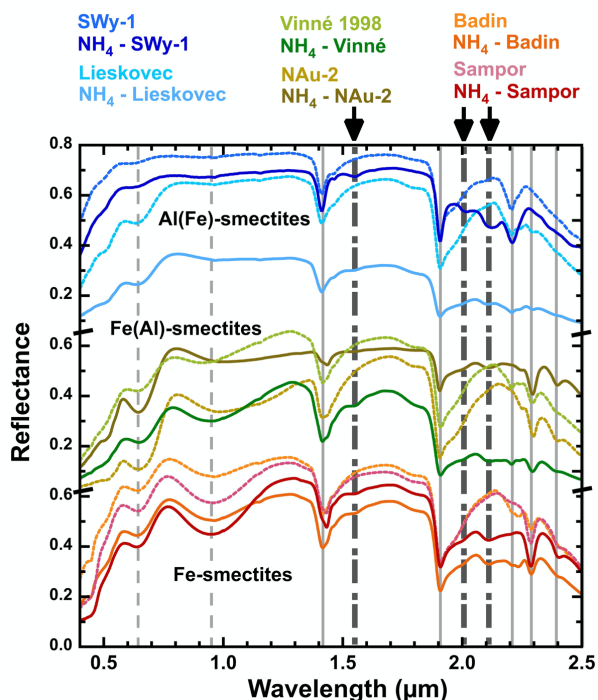


Fig. 1. Reflectance spectra of smectites (dotted lines) and NH₄-smectites (darker colors, solid lines). Bands due to smectites are marked with solid lines, Fe with dashed lines, NH₄ with broken lines.

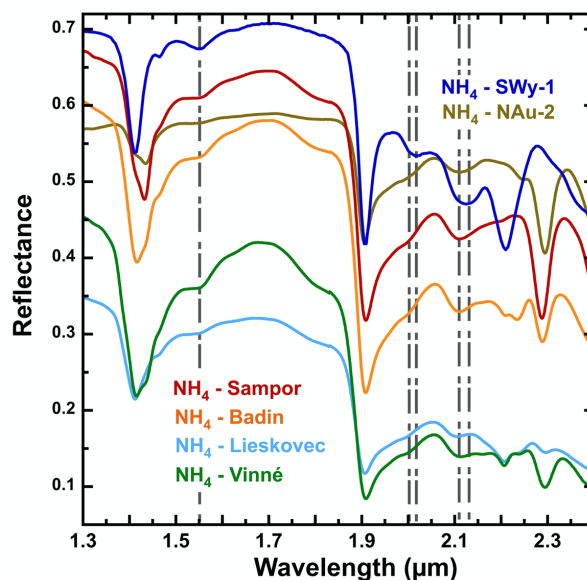


Fig. 2. Reflectance spectra of NH₄-smectites with broken lines marking NH₄ bands.

mostly Al and some Fe, samples with mostly Fe and some Al, and samples with primarily Fe. NH_4 bands were observed in our samples at 1.55, 2.00-2.02, and 2.11-2.13 μm (Figs. 1-2). The NH_4 band near 2.12 μm is strongest and would be easiest to detect in remote sensing data.

Variations are observed near 0.64 and 0.95 μm due to Fe excitations, and near 1.41 and 1.91 μm due to H_2O . OH overtones occur at 1.41 μm for Al-OH and at 1.43 μm for Fe-OH, while OH combination bands occur at 2.21 μm for Al-OH and at 2.29 μm (plus 2.40 μm) due to Fe-OH as in [6]. Changes in these spectral features due to smectite chemistry do not appear to be associated with the small variations in the wavelength position and shape of the ammonia bands (Fig. 2).

Shifts observed previously in the NIR and mid-IR spectral features of NH_4 in clay minerals [5,7] appear to be due to changes in the phyllosilicate structure rather than the type of octahedral cation present (Fig. 3). Spectra measured under dry conditions [5,8] reveal enhancement in the ammonia bands as the H_2O bands are reduced. This is especially noted under vacuum or high temperature conditions [8].

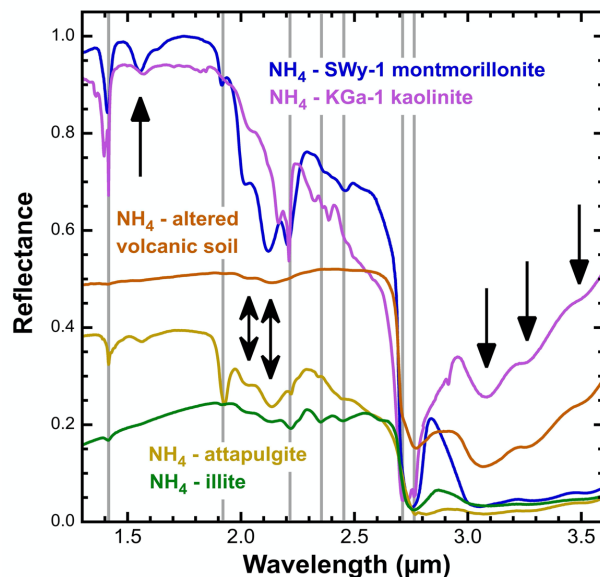


Fig. 3. Reflectance spectra of NH_4 -phyllsilicates and altered volcanic soil [5] with solid lines marking phyllosilicate bands and arrows marking NH_4 bands.

The NH_4 band near 3.06 μm in ammonia-treated phyllosilicates and altered volcanic soil (Fig. 3) is consistent with a spectral feature in VIR images of Ceres attributed to ammonia [1]. The bands near 1.55, 2.01, and 2.12 μm have not yet been identified, but could be found in future studies.

Implications for detection of ammonia: Infrared spectra were successfully used to identify ammonia at Ceres via telescopic data [9] and then VIR orbital data

collected by the Dawn spacecraft [1]. Ammonia has also been identified on Enceladus [10], Pluto [11], and possibly Titan [12], and could be present on Mars and other bodies as well. The Curiosity rover at Gale crater on Mars has observed low levels of N, although its detection with SAM is challenged by perchlorates [3]. Infrared spectroscopy at the surface of Mars could identify ammonia if present.

Spectral measurement and analysis of NH_4 -smectites here and other NH_4 -bearing minerals [13] enables detection of ammonia in our Solar System. Identifying ammonia supports understanding 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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References: [1] De Sanctis M. et al. (2015) Ammoniated phyllosilicates with a likely outer Solar System origin on (1) Ceres, *Nature*, 528, 241-244. [2] Ming D. et al. (2014) Volatile and Organic Compositions of Sedimentary Rocks in Yellowknife Bay, Gale Crater, Mars, *Science*, 343(6169). [3] Sutter et al. (2017) Evolved gas analyses of sedimentary rocks and eolian sediment in Gale Crater, Mars, *JGR*, 122, 2016JE-005225. [4] Andrejkovičová S. et al. (2018) NH_4 -smectite, a potential source of N compounds (NO) in SAM analyses, *LPSC L*, Abstract #1998. [5] Bishop J.L. et al. (2002) Detection of soluble and fixed NH_4^+ in clay minerals by DTA and IR reflectance spectroscopy, *PSS*, 50, 11-19. [6] Bishop J.L. et al. (2008) Reflectance and emission spectroscopy study of four groups of phyllosilicates, *Clay Minerals*, 43, 35-54. [7] Ehlmann B.L. et al. (2018) Ambient and cold-temperature infrared spectra and XRD patterns of ammoniated phyllosilicates and carbonaceous chondrite meteorites, *MAPS*, 53, 1884-1901. [8] De Angelis S. et al. (2021) High-Temperature VIS-IR Spectroscopy of NH_4 -Phyllosilicates, *JGR Planets*, 126, e2020JE006696. [9] King T. V. V. et al. (1992) Evidence for ammonium-bearing minerals on Ceres, *Science*, 255, 1551-1553. [10] Waite J. H. et al. (2006) Cassini Ion and Neutral Mass Spectrometer: Enceladus Plume Composition and Structure, *Science*, 311, 1419-1422. [11] Cruikshank D. et al. (2019) Ch. 22: Spectroscopy of Pluto and its satellites, in *Remote Compositional Analysis* (Cambridge) 442-452. [12] Niemann H. et al. (2005) The abundances of constituents of Titan's atmosphere from the GCMS instrument on the Huygens probe, *Nature*, 438, 779-784. [13] Berg B. et al. (2016) Reflectance spectroscopy (0.35-25 μm) of ammonium-bearing minerals and qualitative comparison to Ceres-like asteroids, *Icarus*, 265, 218-237.