

REFLECTANCE SPECTROSCOPY OF AMMONIATED PHYLLOSILICATES. M. Ferrari (1), S. De Angelis (1), M.C. De Sanctis (1), E. Ammannito (2), A. Raponi (1), S. Stefani (1), G. Piccioni (1), (1) Institute for Space Astrophysics and Planetology, IAPS-INAF, Rome Italy, (marco.ferrari@iaps.inaf.it) (2) Italian Space Agency – ASI, Rome, Italy.

Introduction: Nitrogen is a fundamental constituent of many biological compounds, thus being an essential element for life. On Earth, nitrogen is present in any geological environment containing organic matter (e.g., oil shale, coal, marine sediments etc.), but, although in a few ppm, it is present also in igneous and metamorphic rocks as ammonium ion. The presence of nitrogen has been suggested on Mars soil [1] [2] on comets [3] [4] and in some meteorites [5], although the occurrence of NH_4^+ does not necessarily indicate the presence of biotic processes [6]. Ammonium-bearing minerals have been detected on the surface of (1)Ceres by VIR, the Visible and InfraRed imaging spectrometer [7] on-board the Dawn spacecraft [8]. In this case, spectroscopic observations in the range of 1-5 μm indicated an average composition consisting of a mixture of Mg-phyllsilicate, (Mg,Ca)-carbonate, a dark absorbing phase, and NH_4 -phyllsilicates [9]. Ammonium bearing phyllsilicates can be formed by ionic exchange [10], because cations with similar ionic radius can be exchanged within a crystal structure [11]. In this study, we describe the laboratory production and IR spectroscopic measurements of ten NH_4 -phyllsilicates starting from the corresponding NH_4 -free minerals.

Sample preparation and experimental setup:

Previous IR reflectance studies of NH_4 -bearing minerals were done on different mineral species, e.g. [12] [13] [14]. In this work, we focus our attention on the phyllsilicate minerals that are considered putative components of the Ceres surface. A suite of eight clay samples from the Source Clays Repository of The Clay Mineral Society, and a biotite and a serpentine from well-documented geological locations were selected. For each mineral we prepared three types of samples: raw (R), ammoniated (A), and leached (L). All the selected samples were milled and sieved to obtain a fine powder. The sieved samples were dried inside a desiccator to remove the excess of water. At this point, all the R-samples are ready. To produce A-samples we put the dried powder samples in a concentrated ammonia solution (30% of NH_3 in H_2O), with a mineral/solution ratio of 1:10 wt/vol and shaken for two hours. The samples were left in contact with the ammonia solution about 150 hours. Afterwards a centrifuge treatment was made to separate the solid fraction from the solution. After a drying period the samples were milled, sieved (grain size $<36 \mu\text{m}$) and stored in the desiccator. To prepare L-samples, an aliquot of A-samples was re-

suspended in deionized water (mineral/water ratio of 1:10 wt/vol), shaken and separated by centrifuge. This leaching process was repeated three times, then the samples were dried, crushed and sieved. All samples (R, A and L) have been spectrally characterized by means of visible/infrared spectroscopy in the INAF-IAPS laboratories. Spectra in the VNIR have been acquired with a FieldSpec Pro in the 0.35-2.5 μm range, with 6 mm spatial resolution and spectral resolution 3-8 nm. For the FT-IR, we used a Fourier Transform Infrared Spectrometer (Vertex 80) operating in the range of 2 to 14 μm using the MCT detector. The samples were also measured with SPIM [15], an imaging spectrometer operating in the spectral range 0.2 – 5.1 μm , which is a replica of the VIR spectrometer on-board the Dawn mission.

Reflectance measurements results: Reflectance spectra of the ammoniated clays show bands near 1.56 μm , 2.05 μm , 2.12 μm , 3.06 μm , 3.25 μm , 3.55 μm , 4.2 μm , 5.7 μm and 7 μm [13] that are related to the presence of nitrogen complex [16]. Figure 1 shows an example of the spectra acquired on the three samples of nontronite (NAu-1_R, NAu-1_A and NAu-1_L).

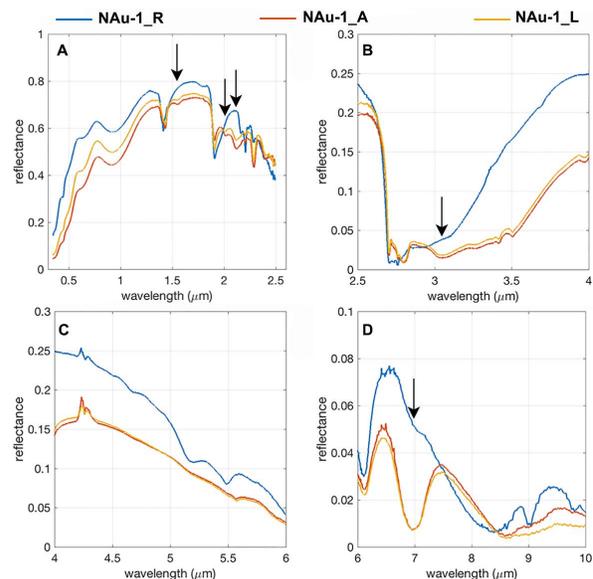


Fig.1. Nontronite NAu-1_R (blue) vs NAu-1_A (red) and NAu-1_L (yellow). Arrows indicate the spectral features linked to the presence of ammonium. The full spectral coverage has been divided into four ranges: A) 0.35-2.5 μm (FieldSpec data); B) 2.5-4 μm ; C) 4-6 μm ; D) 6-10 μm (FT-IR data).

The A-nontronite is characterized by the occurrence of new bands near 2 μm and 2.1 μm and near 3.1 μm and 7 μm . The same bands are present also in the leached sample indicating that the ammonium is effectively bound to the structure of the phyllosilicate. In the NAu-1_R sample, the NH_4^+ features are absent.

In figure 2 a comparison between the spectrum of leached nontronite (NAu-2_L) and the Dawn-VIR average spectrum of (1)Ceres is shown. The bands near 3 μm related to the ammonium are present in both spectra.

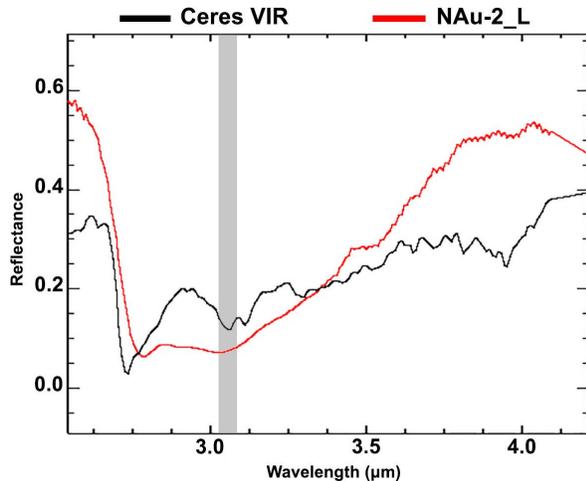


Fig.2. Dawn-VIR average spectrum of (1)Ceres (black) vs leached nontronite (NAu-2_L, red) SPIM laboratory spectrum. The vertical gray strip indicates the spectral region where ammonium shows its absorption.

Summary and Conclusions: The obtained results show that the various types of phyllosilicates respond differently to ammonium treatment. The NH_4^+ ion can replace another ion inside the crystalline structure of a mineral via isomorphic replacement. Its ionic radius of 1.43 Å, similar to that of potassium, can facilitate its substitution. The same can happen with other types of ions such as rubidium, cesium and sodium. This substitution is however also facilitated by other structural and charge-related factors. Among the various minerals used in this study, surely the two nontronites and the montmorillonite were those that better accept the NH_4^+ ion in their structure. Weak NH_4^+ related features are also shown in the spectra of illites and sepiolite. Those minerals have a 2:1 structure with sodium or potassium as interlayer cations. Minerals like serpentine and biotite do not show any absorption band linked to the ammonium. Unfortunately, the presence of the strong absorption band in the 3 μm region, due to the presence of water inside the samples, makes difficult to spectrally identify the features of ammonium at 3.06 μm , 3.25 μm and at 3.55 μm . The chance of measuring samples

in a thermo-vacuum chamber would permit a better recognition of the ammonium absorption bands, e.g. [17]. Performing IR measurements at variable temperatures would allow to identify temperature limits at which the ammonium ion can remain within the structure of clays and facilitate the interpretation of the compositional evolution of bodies like (1)Ceres.

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