

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, 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] and in some meteorites [5]. 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 indicated an average composition consisting of a mixture of Mg-phyllsilicate, (Mg,Ca)-carbonate, a dark absorbing phase, and NH₄-

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 NH₄-phyllsilicates starting from the corresponding NH₄-free minerals.

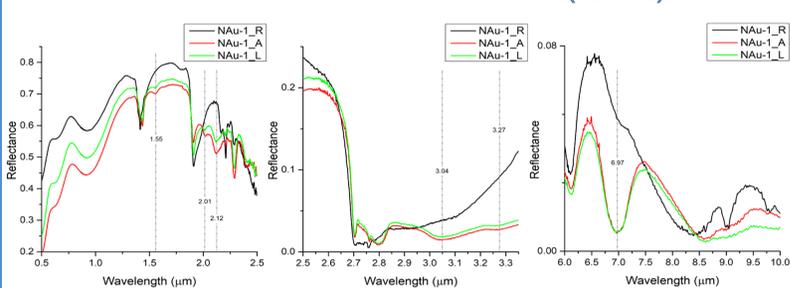
Experimental

For this experiment 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 to remove the excess of water. At this point, all the **R-samples** are ready. To

produce **A-samples** we put the powder samples in a concentrated ammonia solution (30% of NH₃ in H₂O), with a mineral/solution ratio of 1:10 wt/vol. 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 μm) 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

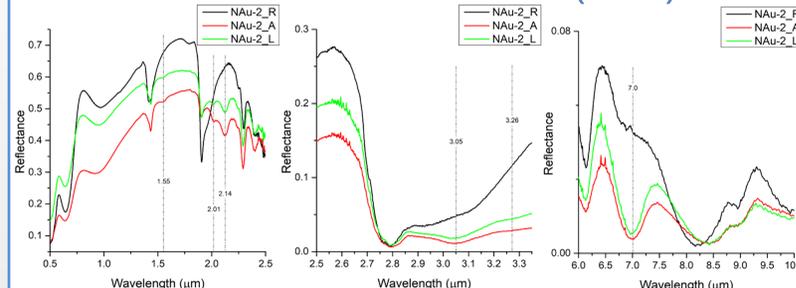
and sieved. All samples (**R**, **A** and **L**) have been spectrally characterized by means of visible/infrared spectroscopy in the INAF-IAPS laboratories. Spectra in the VNIR have been acquired with a FieldSpec Pro in the 0.35-2.5 μm range, with 6 mm spatial resolution and spectral resolution 3-8 nm. 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, 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.

nontronite (NAu-1)



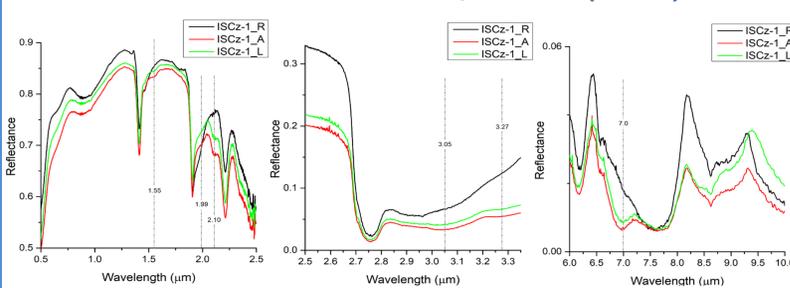
The NH₄-nontronite shows the occurrence of new bands at 1.55 μm, 2.01 μm and 2.12 μm. In the 3 μm region the two treated samples (**NAu-1_A** and **NAu-1_L**) show a strong absorption due to the presence of water; despite that, the presence of two new absorptions near 3.04 μm and 3.27 μm is still appreciable. A new absorption band appears at 6.97 μm due to the presence of the NH₄⁺ in the **NAu-1_A** and **NAu-1_L** samples.

nontronite (NAu-2)



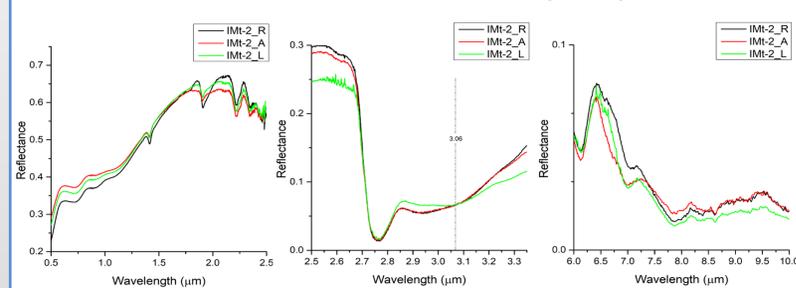
The spectrum acquired on **NAu-2_R** is very similar to that of **NAu-1_R** even if this sample shows a more intense absorption band near 0.6 μm, linked to a greater content of Fe³⁺. The **NAu-2** samples show new NH₄-related bands (1.55 μm, 2.01 μm, 2.14 μm, 3.05 μm, 3.26 μm and 7.0 μm) both in the ammoniated and leached samples in the same position as seen in **NAu-1_A** and **NAu-1_L**.

illite/smectite (ISCz-1)



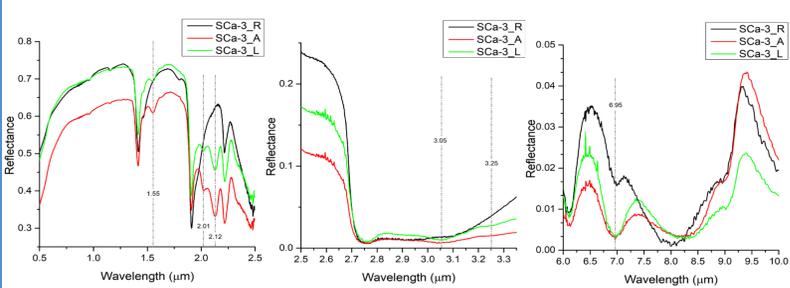
After the ammonium treatment the illite/smectite sample shows the occurrence of new absorptions bands in both the ammoniated (**ISCz-1_A**) and leached (**ISCz-1_L**) versions. New bands near 1.55 μm, 1.99 μm, 2.10 μm, 3.05 μm, 3.27 μm and 7.0 μm shown in the leached sample confirm that the ammonium is effectively bound to the structure of this clay.

illite (IMt-2)



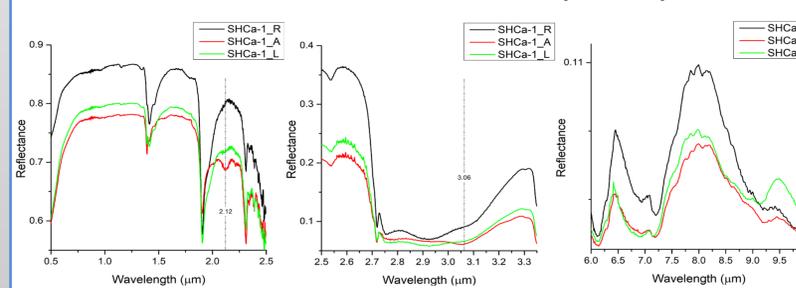
In the range of 0.5 - 2.5 μm, the treated samples of illite **IMt-2_A**, **IMt-2_L** do not show new NH₄-related absorption bands. In the 3 μm region, a weak absorption near 3.06 μm is visible in the ammoniated and leached samples. The raw sample (**IMt-2_R**) shows an absorption band at 7 μm linked to the presence of carbonate; in the ammoniated and leached versions this absorption does not show significant changes.

montmorillonite (SCa-3)



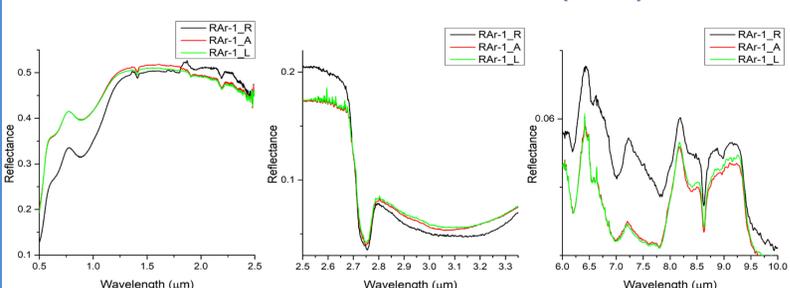
The ammoniated and leached samples (**SCa-3_A**, **SCa-3_L**) show the occurrence of new bands at 1.55 μm, 2.01 μm and 2.12 μm. The 3 μm region shows a wide absorption band due to the presence of water, but the presence of the two new NH₄-related features (3.05 μm and 3.25 μm) is still appreciable. The 7 μm band appears stronger in the **A**- and **L**-samples with respect to that of **R**-sample; this can be interpreted as an addition of NH₄⁺ to a clay that already contained carbonate impurities.

hectorite (SHCa-1)



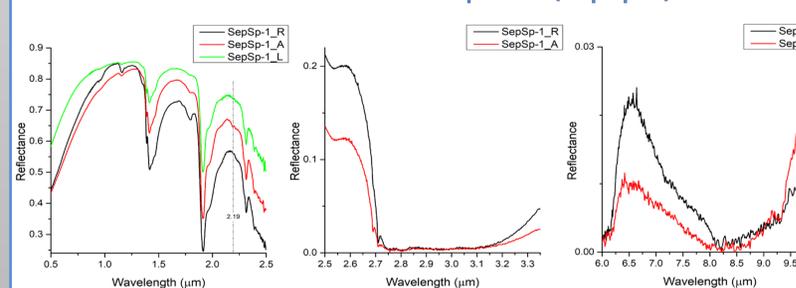
In the 0.5 - 2.5 μm range, hectorite shows the 2.12 μm absorption band only in the **A**-sample, the **L**-sample shows a very weak band, while the **R**-sample does not show any NH₄-related absorption. This happens also in the 3 μm region, where the 3.06 μm band is more appreciable in the ammoniated sample with respect to the leached one; no absorption at that wavelength is shown in the **R**-sample.

rectorite (RAR-1)



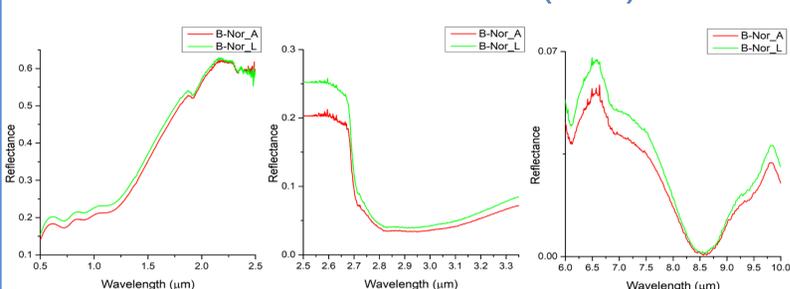
The spectrum of rectorite after the ammonium treatment (**RAR-1_A**) does not show any new NH₄-related absorption bands; as a consequence, neither the leached sample (**RAR-1_L**) shows any change.

sepiolite (SepSp-1)



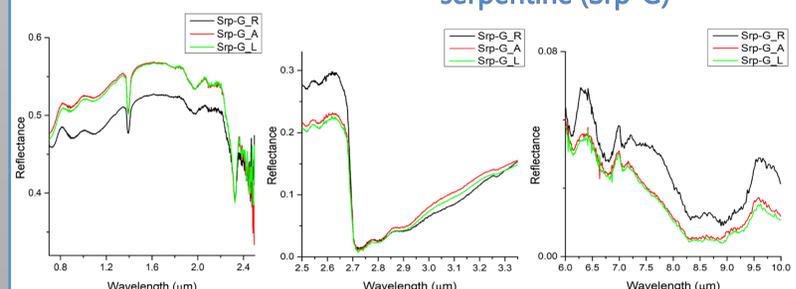
Sepiolite shows only a new weak absorption at 2.19 μm in the ammoniated sample (**SepSp-1_A**), this NH₄-related feature is not present in the leached one (**SepSp-1_L**). In the 3 μm region, the sepiolite seems to be saturated of water, and this could have hidden any new NH₄ absorption in this region.

biotite (B-Nor)



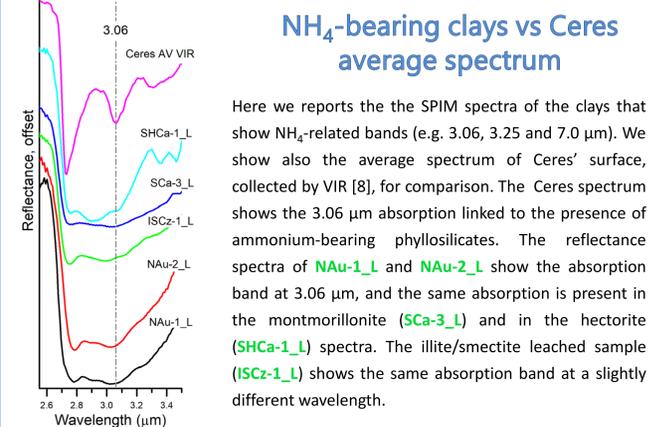
The biotite (B-Nor) do not show any evidence of ammoniation, nor new ammonium-related absorption bands appear in its reflectance spectra, neither before, nor after the ammonium treatment.

serpentine (Srp-G)



The serpentine (Srp-G) samples do not show any evidence of ammoniation, nor new NH₄-related features appear in its reflectance spectra, neither before, nor after the ammonium treatment.

NH₄-bearing clays vs Ceres average spectrum



Here we reports the the SPIM spectra of the clays that show NH₄-related bands (e.g. 3.06, 3.25 and 7.0 μm). We show also the average spectrum of Ceres' surface, collected by VIR [8], for comparison. The Ceres spectrum shows the 3.06 μm absorption linked to the presence of ammonium-bearing phyllsilicates. The reflectance spectra of **NAu-1_L** and **NAu-2_L** show the absorption band at 3.06 μm, and the same absorption is present in the montmorillonite (**SCa-3_L**) and in the hectorite (**SHCa-1_L**) spectra. The illite/smectite leached sample (**ISCz-1_L**) shows the same absorption band at a slightly different wavelength

Conclusions

Tab. 1. Summary table reporting (✓) the occurrence and (x) the absence and of a specific absorption band found in the ammonium treated and leached phyllsilicates.

SAMPLE	1.6	2.1	2.1	3.1	3.3	3.6	7.0	TYPE
NAu-1_L	✓	✓	✓	✓	✓	-	✓	Fe-smectite
NAu-2_L	✓	✓	✓	✓	✓	-	✓	Fe-smectite
ISCz-1_L	✓	✓	✓	✓	✓	-	✓	illite/smectite
SCa-3_L	✓	✓	✓	✓	✓	-	✓	Na, Ca smectite
SHCa-1_L	-	-	✓	✓	-	x	x	Mg, Li smectite
IMt-2_L	x	x	x	-	x	x	x	illite
B-Nor_L	x	x	x	x	x	x	x	mica
RAR-1_L	x	x	x	x	x	x	x	mica/smectite
Srp-G_L	x	x	x	x	x	x	x	antigorite
SepSp-1_L	x	x	-	x	x	x	x	sepiolite

- This experiment indicates that the clays belonging to the **smectite group** (NAu-1, NAu-2, ISCz-1, SCa-3 and SHCa-1) are those that best accept the NH₄⁺ in their structure;
- At room temperature and pressure the NH₄⁺ ion does not replace the K⁺ inside the crystalline structure of illite, this can occur in the diagenesis process during the smectite→illite transformation [11];
- The absence of the NH₄-related bands in the rectorite (RAR-1) spectrum could be due to the presence of Ca²⁺ as interlayer cation;
- The sepiolite (SepSp-1) sample shows a very weak absorption near 2.2 μm. In this case, the NH₄⁺ ion could be hosted inside the channels of the sepiolite structure.
- On Earth, the occurrence of ammonium in minerals of primary magmatic origin (e.g. biotite and muscovite) indicates that ammonium enter in mica structure during the anatexis process or hydrothermal alteration (Hall, 1999) and that it is thermally stable [12];
- The unambiguous recognition of the phyllsilicates bearing NH₄⁺ (eg. smectite, illite, mica) on planetary surfaces can discriminate the geological history of a body;
- The chance of measuring the ammoniated clays in a thermo-vacuum chamber would permit a better recognition of the NH₄ absorption bands. To this end... we have developed it! (see panel 455 by De Angelis et al. abstract n #1428).