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IR Spectroscopy of ammoniated phyllosilicates and mixtures with relevance for dwarf planet (1) Ceres

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Introduction

The surface composition of (1) Ceres has been revealed with great detail by VIR spectrometer high resolution observations [1] on board Dawn spacecraft [2]. Spectroscopic observations in the infrared range 1-5 μm have showed an average surface composition consisting of a mixture of Mg-phyllosilicate, (Mg,Ca)-carbonate, a dark absorbing phase and NH_4 -phyllosilicates [3], and bright areas locally composed by mixtures of Na-carbonates, phyllosilicates, a dark phase and ammonium compounds [4]. The reproduction in laboratory of such mineral mixtures is thus of interest in order to better constraint and interpret remote-sensing observations. In this work we focus on the preparation and IR spectroscopic measurements in laboratory of NH_4 -phyllosilicates and mineral mixtures.

1. Sample preparation and experimental setup

A set of 8 phyllosilicates were chosen from Clay Minerals Society, grinded and dry sieved to a fine grain size ($d < 36 \mu\text{m}$). Ammonium phyllosilicates were then prepared following a procedure similar to what described in Bishop et al. 2002 [5]. All powders were immersed in excess (10:1 vol/mass) solutions of ammonium hydroxide (30% NH_3 in H_2O) for several days, centrifuged and decanted: this cycle was repeated more times, and finally samples were dried. Splits of these samples were separated and treated with a leaching procedure. Other endmembers, concerning the average mixture, were prepared in the form of $d < 36 \mu\text{m}$ -powders, specifically antigorite, (Ca,Mg)-carbonate and magnetite. A set of 8 different mixtures has been then prepared, keeping fixed antigorite, dolomite and magnetite, and varying the NH_4 -clay mineral constituent.

All end-members have been spectrally characterized by means of visible/infrared spectroscopy. 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 $3 \div 8 \text{ nm}$. Fourier Transform Infrared Spectrometer (FTIR-PLAB) Vertex-80 was used in reflectance mode to acquire spectra of powders, with spectral resolution 2 cm^{-1} , spatial aperture of about 6 mm, in the spectral range 1.3-14 μm , using an MCT detector. Each acquisition was performed by summing 256 scans in order to increase S-N ratio. Reflectance spectra were acquired from all endmembers, and separately from phyllosilicates, NH_4 -phyllosilicates and “leached” NH_4 -phyllosilicates, and finally from mixtures.

Clay minerals endmembers		
Sepiolite	SEPSP1	
$(\text{K}_{0.01})[\text{Mg}_{5.54}\text{Al}_{0.35}\text{Mn}_{0.02}\text{Fe}^{2+}_{0.04}\text{Fe}^{3+}_{0.14}][\text{Si}_{7.90}\text{Al}_{0.1}]\text{O}_{20}(\text{OH})_4$		
Rectorite	RAR1	
$(\text{Na,Ca})\text{Al}_4(\text{Si,Al})_8\text{O}_{20}(\text{OH})_4 \cdot 2(\text{H}_2\text{O})$		
Nontronite-1	NAU1	
$(\text{M}^{+}_{1.05})[\text{Si}_{6.98}\text{Al}_{1.02}][\text{Al}_{0.29}\text{Fe}_{3.68}\text{Mg}_{0.04}]\text{O}_{20}(\text{OH})_4$		
Nontronite-2	NAU2	
$(\text{M}^{+}_{0.72})[\text{Si}_{7.55}\text{Al}_{0.45}][\text{Fe}_{3.83}\text{Mg}_{0.05}]\text{O}_{20}(\text{OH})_4$		
Illite-1	IMT2	
$\text{K}_{0.65}\text{Al}_2\text{O}_6[\text{Al}_{0.65}\text{Si}_{3.35}\text{O}_{10}](\text{OH})_2$		
Illite-2	ISCZ1	
Montmorillonite	SCA3	
$(\text{Mg}_{0.45}\text{Ca}_{0.15}\text{Na}_{0.26}\text{K}_{0.01})[\text{Al}_{2.55}\text{Fe}^{3+}_{0.12}\text{Mn}_{\text{tr}}\text{Mg}_{1.31}\text{Ti}_{0.02}][\text{Si}_{7.81}\text{Al}_{0.19}]\text{O}_{20}(\text{OH})_4$		
Hectorite	SHCA1	
$(\text{Mg}_{0.56}\text{Na}_{0.42}\text{K}_{0.05})[\text{Mg}_{4.60}\text{Li}_{1.39}\text{Mn}_{\text{tr}}\text{Ti}_{0.01}][\text{Si}_{7.75}\text{Al}_{0.17}\text{Fe}^{3+}_{0.05}]\text{O}_{20}(\text{OH})_4$		

Tab.1. Clay minerals endmembers.

2. IR Spectral measurements: results

In fig.1 an example of spectra acquired on nontronite endmember (NAU-1) is shown, in which the non-

treated sample (blue line) is compared with the NH_4 -treated sample (green). The full spectral coverage has been subdivided in five ranges for clarity, specifically 0.35-2.5 μm (FieldSpec) and then 1.3-2.5 μm , 2.5-4.1 μm , 4-6 and 6-14 μm for FTIR data. The ammoniated sample is characterized by the occurrence of several new features in four of the five displayed ranges, although a global change in the overall spectrum is visible in the full range; namely a substantial decrease in reflectance level is observed, together with a reduction of spectral contrast. New absorption bands putatively attributable to NH_4^+ ions appear near 2 and 2.1 μm , near 3.1 μm and at 7 μm .

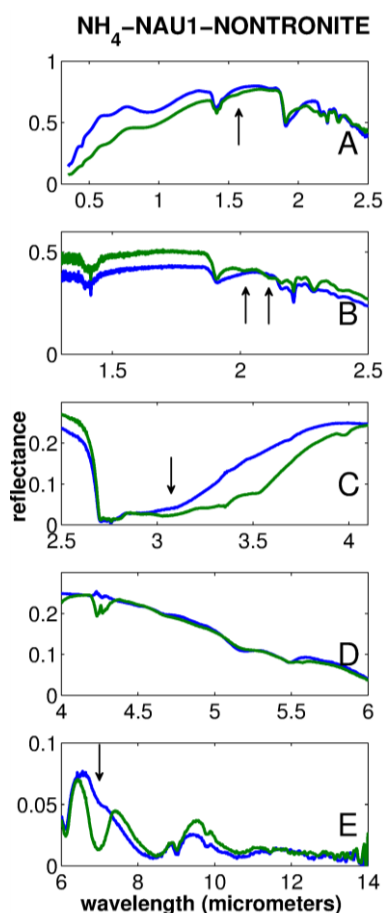


Fig.1. Nontronite NAU-1. Untreated sample (blue line) vs NH_4 -treated sample (green line). A: 0.3-2.5 μm . B: 1.3-2.5 μm . C: 2.5-4.1 μm . D: 4-6 μm . E: 6-14 μm . The NH_4^+ 3.1- μm band here appears as a bump overlapped with the water band at 3 μm , which is difficult to remove unless heating the sample in vacuum.

In fig.2 the VIR average spectrum of Ceres (purple line) [3] is compared with mixture spectra measured with FTIR. Here the mixture is composed by serpentine-antigorite, dolomite, magnetite and NH_4 -

NAU1 (nontronite). Laboratory spectra show a good matching with VIR spectrum; the agreement is better for what concerns the OH⁻ 2.7 μm -band of serpentine and the 4 μm -band of carbonate. The feature near 3.1 μm due to NH_4^+ in laboratory spectra is evident, although additional adsorbed water is present in the sample and influences the band.

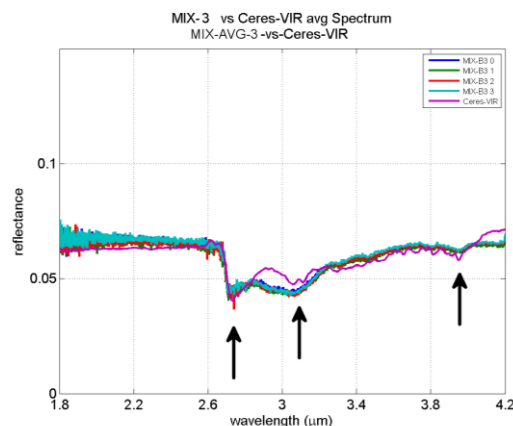


Fig.2. Dawn-VIR average spectrum of Ceres (purple line) vs Mixture AVG-3 laboratory spectra. Arrows indicate, from left to right, absorptions in the mixture due to antigorite (2.72 μm), NH_4^+ + H_2O (3-3.1 μm) and dolomite (4 μm).

3. Summary and Conclusions

Treatment of phyllosilicates with ammonia shows that different minerals behave in different ways: NH_4^+ ions are easily accepted by several crystal structures (nontronite, montmorillonite), while other structures accept these ions with difficulty. Laboratory spectra of the mixture show a good agreement with VIR spectrum. Further work is ongoing to remove adsorbed water from phyllosilicates, in order to facilitate NH_4^+ inclusion in mineral structures, and to separate NH_4^+ and OH⁻ absorption features in the 3- μm spectral region.

Acknowledgements

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