

# Investigating the ammonium-bearing phase in Ryugu samples

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## Introduction

The JAXA/Hayabusa2 mission collected 5.4 g of samples from two different sites (i.e., A and C) on the surface of the C-type asteroid (162173) Ryugu [1; 2]. This asteroid is characterized by a low albedo and by the presence of hydrous and carbonaceous materials [3]. The Ryugu surface spectra collected by the Hayabusa2/NIRS 3 spectrometer reveal a narrow absorption feature at 2.72  $\mu\text{m}$  [4] resembling that observed on the surface of Ceres by the Dawn/VIR spectrometer [5; 6]. Laboratory analysis of returned grains confirmed that Ryugu samples contain hydrated silicates, sulfides, oxides, carbonates, and organics and have spectroscopic similarities to CI chondrites [7]. MicrOmega hyperspectral microscope observation [8] revealed the presence of a band at 3.06  $\mu\text{m}$ , indicating the possible presence of NH-bearing phases in most of the returned grains [9]. This ammonium-related absorption feature was confirmed by FTIR measurements [10]. The 3.06  $\mu\text{m}$  band was also observed in the spectra of Ceres by telescopic observations [11] and by the Dawn/VIR spectrometer that accurately characterized its distribution on the dwarf planet's surface [12]. Current interpretations of Ceres spectra suggest that the most likely mineralogical phases hosting ammonium are phyllosilicates [13; 14], but the presence of ammonium salts has also been inferred in specific areas of the Cerean surface [15; 16]. Hydrated silicates represent the main reservoir of water in Ryugu samples, and their presence is indicative of extensive aqueous alteration in the parent body, likely the alteration path that occurred on Ceres. Even if phyllosilicates are the most likely carriers, the specific ammonium-bearing phase determining the 3.06  $\mu\text{m}$  band on Ryugu samples and the surface of Ceres is not fully constrained, nor are the processes that led to ammonium enrichment on these C-type bodies.

## Sample selection

Our selection criterion of the samples among those available in the first allocation (2022A) was the presence of the absorption band at 3.06  $\mu\text{m}$  as observed in the spectroscopic data obtained from the preliminary screening by FTIR and MicrOmega. We have considered: 1. Similarities of the 3.06  $\mu\text{m}$  absorption between Ryugu samples and Ceres spectra, in terms of wavelength range and band center position; 2. The presence of surface features or morphological structures suggests some mineralogical diversity.

Through the first allocation, we obtained two samples: A0198 and C0091. The preliminary FTIR data provided by JAXA collected on particle C0091 show the presence of a remarkable absorption close to 3.06  $\mu\text{m}$ . On the contrary, the spectroscopic data collected on particle A0198 show a shallow absorption ascribed to the presence of ammonium and several surface features that comply with our scientific requirements. Moreover, the two assigned samples were collected at different sites which will allow us to make further considerations.

## Objectives and research plan

With this work, we aim to contribute to the definition of the physical and mineralogical characteristics of the Ryugu asteroid to understand the initial stages of formation and evolution of C-type bodies; particular attention will be given to the identification of the ammonium-bearing phase(s) and its/their interplay with hydrated silicates. In addition, we aim to define Ryugu's path of alteration and its similarities with Ceres.

The following laboratory analyses will be used to characterize the samples:

- VIS-IR imaging spectroscopy (0.4-5  $\mu\text{m}$ ) will be carried out with the SPectral IMager (SPIM) facility [17] on whole samples. Data will allow a first characterization of the mineralogic composition of their external surface, including an assessment of the presence of water, organic matter, and ammonium in addition to the minerals. Furthermore, by using the SPIM facility (i.e., the Dawn/VIR replica), we can perform a compelling comparison between the data collected on the samples with those provided by the Dawn/VIR spectrometer on Ceres;

- X-ray microscopy (XRM). This non-destructive technique has been used to obtain a high-resolution (submicron scale) 3D tomography of the samples, revealing their internal structure (including pore structure and fracturing), as well as the morphology and composition of the individual grains contained in them; XRM data will also enable the location of regions of interest (ROIs) within the samples to be analyzed by transmission electron microscopy (TEM);

- Raman  $\mu$ -spectroscopy, to obtain compositional maps of the surface of the samples at the micro-metric scale;
- Focused ion beam-field emission gun-scanning electron microscopy (FIB-FEG-SEM) will be used to identify the main mineralogical phases and to extract the electron-transparent lamellae for TEM analyses;
- Transmission Electron Microscopy (TEM), electron diffraction, and energy-dispersive X-ray spectroscopy (EDS) will be used to identify cryptocrystalline mineral phases and crystal defects through high-resolution techniques.

## Results

The VIS-NIR spectra obtained with the SPIM facility on the surface of the two particles show the almost ubiquitous presence of a deep V-band centered at lengths slightly above 2.7  $\mu\text{m}$ , and absorptions near 3.4  $\mu\text{m}$  and in the range 3.7-3.9  $\mu\text{m}$ , however, limited at specific points on the surface returning an inhomogeneous surface composition at the scale of  $\sim 40$   $\mu\text{m}$  (SPIM pixel size). These absorption features can be related to the presence of phyllosilicates and carbonates, respectively.

In addition, at some specific points, the band at 3.06  $\mu\text{m}$  is found indicating the presence of ammonium-bearing compounds.

The Raman spectra acquired on the two particles are characterized by a high fluorescence background and by the presence of the Raman D and G-bands related to the presence of poorly ordered carbonaceous matter. The spectral parameters derived from the mathematical fitting of the acquired spectra as band positions, and band intensity ratio do not differ significantly between the two particles. Raman analysis identifies dolomite as the most common carbonate on both particles.

The interpretation of spectral data acquired by both particles is currently in progress. However, at the moment there do not appear to be notable differences in spectral terms (VIS-NIR and Raman) between the two particles coming from the two different sampling sites.

The two samples (A0198 and C0091) are characterized by a generally similar composition in terms of phase abundance and composition. Energy Dispersive X-ray spectroscopic (EDX) data obtained using the FE-SEM confirmed the presence of hydrated silicates, sulfides (Ni-rich and Fe-rich), carbonates, fosfates, and oxides (mainly magnetite). Sulfides form dominantly euhedral grains (up to 5  $\mu\text{m}$  in size), whereas oxides form submicrometric framboid, platy, or columnar structures. The internal distribution of silicates, sulfides, and oxide in the interior of the two samples, as revealed by XRM data, is rather homogeneous. Notably, sample C0091 displays a slightly smaller grain size and a slightly higher porosity compared to particle A0198.

## Conclusions

The notable similarities of the spectra of some Ryugu samples with Ceres' average spectrum [18] sparked scientific curiosity. To date, interpretation of remotely sensed data coupled with spectroscopic investigation of analogs has not enabled a full understanding of the mechanisms of ammonium enrichment and the nature of the mineral assemblage hosting ammonium on the surface of C-type objects. Furthermore, studies on meteorites have not provided morphological and compositional information on the mineral phases that preceded the alteration of their progenitor body.

Therefore, we consider that spectroscopic measurements and nanoscale mineralogical investigations that we are conducting on the samples returned from Ryugu represent a unique opportunity to definitively establish the link, if any, between ammonium and the mineralogy of this type of object.

## References

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