

## Infrared transmission spectra of Ryugu particles and their unique adsorption behavior

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The Hayabusa2 spacecraft successfully obtained samples from two different locations from Ryugu, a C-type asteroid, and returned them to the Earth on December 6, 2020. The first touchdown samples and second touchdown samples were separately stored in sample container chamber A and chamber C, respectively. The initial analyses began in June 2021, after curation at ISAS/JAXA. The insoluble organic matter (IOM) subteam has so far conducted in-situ analyses of the Ryugu particles, in order to decipher the nature of the organic matter and its origin, parent body processing, and interaction with water and minerals. Fourier transform infrared (FTIR) spectroscopy is a nondestructive technique for functional group chemistry and structures which is suitable for both organic and inorganic compounds. To date, IR absorption (transmission) spectra have been obtained from various chondrites and other astromaterials such as interplanetary dust particles (IDPs), micrometeorites and cometary dust particles [e.g., 1-7]. IR spectroscopy is often employed for astronomical observations and remote sensing. The reflectance spectra of solar system bodies provide information of the compositions of their surfaces. To compare the laboratory samples and the surfaces of asteroids, IR reflectance spectra have been commonly used [e.g., 8-10]. Both IR transmission and reflectance spectra give intrinsically similar information as both reflect the absorptions of IR frequencies by the target samples, although some differences do exist. As a part of the initial analysis in the IOM team, IR absorption spectra were obtained using FTIR microspectroscopy, to provide initial characterization of the Ryugu particles and search for organic matter, as well as for comparison with the surface reflectance spectra of Ryugu. Several samples were analyzed in parallel in the team, in Japan (Yokohama National Univ., YNU) and in France (IPAG, Grenoble and Orsay-lab teams) to increase the robustness of the analysis.

Each particle (sub-millimeter in diameter) from the aggregates in chamber A (A0108) or chamber C (C0109), was further decomposed by gently crushing between two glass slides, or by separation of a fragment with a scalpel. The small fragments were then further crushed between two diamond windows (YNU and IPAG) and in a diamond compression cell under an optical microscope to optimize the thickness for further atomic force microscope based infrared spectroscopy (AFM-IR) measurements (Orsay-lab). In YNU, IR absorption spectra were collected from each diamond window with a micro-FTIR (JASCO FT/IR-6100+IRT-5200), equipped with a ceramic IR light source, a germanium-coated KBr beam splitter, a mercury-cadmium-telluride (MCT) detector, and  $\times 16$  Cassegrain mirrors, with typically  $20 \times 20 \mu\text{m}$  aperture. The microscope and the FTIR were continuously purged with dry  $\text{N}_2$ . To remove adsorbed water further from the sample, a heating stage (Linkam 10036L) was employed. The IR absorptions from water were satisfactorily removed typically by  $60^\circ\text{C}$  under  $\text{N}_2$  flow. Micro-FTIR measurements were also conducted at IPAG with a Hyperion 3000 Bruker FTIR microscope, operating with a  $\sim 50 \times 50 \mu\text{m}$  spot and an environmental cell placing the sample under secondary vacuum ( $< 10^{-6}$  mbar) and gentle heating ( $< 80^\circ\text{C}$ ) to remove adsorbed water. IR spectra by the Orsay-lab team were taken during a week of beamtime at the SOLEIL synchrotron (SMIS beam line). The synchrotron beam was coupled to a Nicolet Continuum 2 IR microscope equipped with a MCT detector and a  $\times 32$  Cassegrain optics, under dry air. For these measurements, the IR spot size was optimized with an aperture of  $6 \times 6 \mu\text{m}$ , close to the diffraction limit, and hyperspectral maps of Ryugu samples were acquired over several hundreds of  $\mu\text{m}$  in size.

The IR absorption spectra of both A0108 and C0109 particles were almost identical, and typically consistent with CI chondrites. However, some local heterogeneity exists, e.g., IR spectra from some areas were dominated by carbonate features, and opaque minerals are seen in high resolution hyperspectral maps. They display Mg-rich phyllosilicate bands at  $\sim 1000 \text{ cm}^{-1}$  (Si-O stretching) and  $\sim 3700 \text{ cm}^{-1}$  (OH group in phyllosilicates), organic bands (aliphatic C-H) at  $3000\text{-}2800 \text{ cm}^{-1}$ . The position and narrowness of the OH band fit those observed in spectra collected in-situ by the spacecraft [11]. Compared to the reflectance spectra obtained by JAXA curation [12], the OH band and aliphatic C-H bands features in the absorption spectra were roughly consistent, but the abundance of aliphatic C-H peaks were lower than the reflectance spectra. Such differences could be due to the difference between reflectance spectra and transmission spectra of sample particles. Also, interesting behavior was observed during FTIR analysis, in that the aliphatic C-H peak increased during analysis for a few hours, likely due to adsorption of environmental volatile organic compounds (VOCs). It is known that porous OH bearing silicates adsorb

VOCs [e.g., 13-15], particularly when fresh surfaces are exposed by sample crushing [16], however the Ryugu samples appear unusually reactive and absorb VOC very rapidly, considering that the Ryugu sample analysis was conducted in a clean environment without abundant contamination sources. This behavior indicates that Ryugu samples are fresh and highly porous. Measurements conducted under vacuum and gentle heating reveal a rapid and dramatic disappearance of adsorbed water, along with an increase of the aliphatic band intensity. This has been previously observed for CI chondrites [6,17,18], and confirms the high adsorption properties of Ryugu samples. Tight interactions between organics and -OH in phyllosilicates may account for this spectral evolution.

Overall, the FTIR organic signatures of the Ryugu samples do not point to a significant post-accretionary heating as observed in heated CM/CI chondrites [19]. Acid extraction of Ryugu samples very soon will provide a fresh IOM isolate, and thereby enable quantitative characterization of chemical group abundances.

## References

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