

NANO-IR IMAGING AND SPECTROSCOPY OF A RYUGU ASTEROID SAMPLE Gerardo Dominguez¹, Zack Gainsforth², Kana Amano³, Eiichi Kagawa³, Megumi Matsumoto³, Yuri Fujioka³, Tomoki Nakamura³, Tomoyo Morita³, Mizuha Kikuri³, Hisayoshi Yurimoto⁴, Takaaki Noguchi⁵, Ryuji Okazaki⁶, Hikaru Yabuta⁷, Hiroshi Naraoka⁶, Kanako Sakamoto⁸, Shogo Tachibana^{8,9}, Sei-ichiro Watanabe¹⁰, Yuichi Tsuda⁸, Hayabusa2 Initial Analysis Stone Team,¹ California State University, San Marcos, CA USA (gdominguez@csusm.edu), ²Space Sciences Laboratory, University of California at Berkeley, California, USA, ³Tohoku University, Sendai, Japan, ⁴Hokkaido University, Sapporo, Japan (JP), ⁵Kyoto University, Kyoto, JP, ⁶Kyushu University, Fukuoka, JP, ⁷Hiroshima University, Higashi-Hiroshima, JP, ⁸ISAS/JAXA, Sagami-hara, JP, ⁹The University of Tokyo, Tokyo, JP, ¹⁰Nagoya University, Nagoya, JP

Introduction: The return of specimens from Ryugu by the Hayabusa2 mission presents us with the opportunity to apply laboratory-scale analytical instrumentation to better understand the interrelationship between remote sensing observations and the μm to sub- μm scale variations in the physical-chemical properties of Ryugu. Here we present results of Atomic Force Microscopy (AFM) assisted Nanoscopic InfraRed mapping and spectroscopy (NanoIR) to resolve IR spectral variations and minerals of Ryugu sample A0026-pFIB02 at the micron and sub-micron scales.

Sample Preparation and Mounting: Ryugu sample A0026-pFIB02 from canister A, where grains from the first touchdown site were stored, was mounted on an aluminum SEM stub using carbon paste and polished using a Xe plasma focused ion beam system (Xe FIB; AMBER X, TESCAN ORSAY HOLDING) at TOYO corporation. The polished sample was cut using 30 kV and 2 μA Xe⁺ ions followed by cleaning at 30 kV and 300 nA. The final specimen exposes about 1 mm² for infrared analysis.

NanoIR Instrumentation Setup: We used a Bruker/Anasys NanoIR (NanoIR3-s, [1]) to acquire topographic images, infrared spectral maps, and point spectra. We used a Quantum Cascade Laser (Daylight solutions) tunable IR laser to acquire spectral information between $\sim 900 - 1900 \text{ cm}^{-1}$. The laser is focused near the diffraction limit, but the infrared response is read from the sample surface using an AFM probe which improves the spatial resolution such that infrared spectra can be distinguished from regions on the same order as the radius of the AFM tip – a few tens of nm.

NanoIR Imaging and Point-Spectra Acquisition: NanoIR spectra may be acquired in two distinct data acquisition modes. In the first, the infrared laser wavelength is held fixed while the X-Y stage moves the sample in relation to the AFM tip, allowing us to simultaneously obtain topographic information as well as a signal proportional to the thermal expansion of the surface directly underneath the AFM tip as a function of IR wavelength. Monochromatic IR images can be combined to obtain spectral information on a pixel by pixel basis. In the second mode of operation, the laser's wavelength is changed while the AFM acquires a signal that is proportional to the thermal expansion of

the sample directly underneath a stationary AFM tip.

Post-Processing: NanoIR images were acquired at 4 cm^{-1} intervals with pixel sizes of $\approx 40 \text{ nm}$. Simultaneously recorded topographic images were used to align the monochromatic IR images using pyramid registration[2] in order to produce RGB images and hyperspectral data sets. Point spectra were acquired across the entire spectral range of the laser at 4 cm^{-1} resolution. The spectra were despiked and then smoothed with a Savitzky-Golay filter[3] for further analysis.

Results: Figure 1 displays an RGB image of a region surrounding a carbonate grain that allows us to visualize variations in the phyllosilicate matrix. The phyllosilicate varies at the μm and sub- μm scales which cannot normally be differentiated using traditional far-field IR techniques. The colors correspond to phonon modes for serpentine and saponite phyllosilicates [4]. The red color corresponds to a mix of saponite and serpentine while green and blue correspond to modes present only in serpentine or saponite. Serpentine-rich phyllosilicate appears especially notable on the periphery of the carbonate grain. The identity of the carbonate grain was determined by the presence of the an absorption band at $\sim 1400 - 1500 \text{ cm}^{-1}$ [5].

Figure 2 displays the normalized point spectra of the 3 spots shown in Figure 1 as well as the phyllosilicate phonon modes taken from [4]. The peaks at 1095 and 1128 cm^{-1} differentiate serpentine from saponite due to the high contrast between them. Our point spectra (including a carbonate not shown here) contain the same spectral features observed in the far-field IR spectra of this sample taken by other members of the Hayabusa2 team (Amano et. al, LPSC 2022). These features include both the phyllosilicate and carbonate peaks.

Discussion and Analysis: Consistent with far-field IR results applied to Ryugu samples (Amano et. al, LPSC 2022), our nanoIR measurements show that Ryugu's mineralogical composition appears to be dominated by phyllosilicates and carbonates. Our measurements show heterogeneity of these minerals at the micron and sub-micron scales. Observations at these scales should provide constraints on the formation mechanisms of phyllosilicate minerals on Ryugu or its parent body.

The "color" variations seen in Figure 1 point to under-

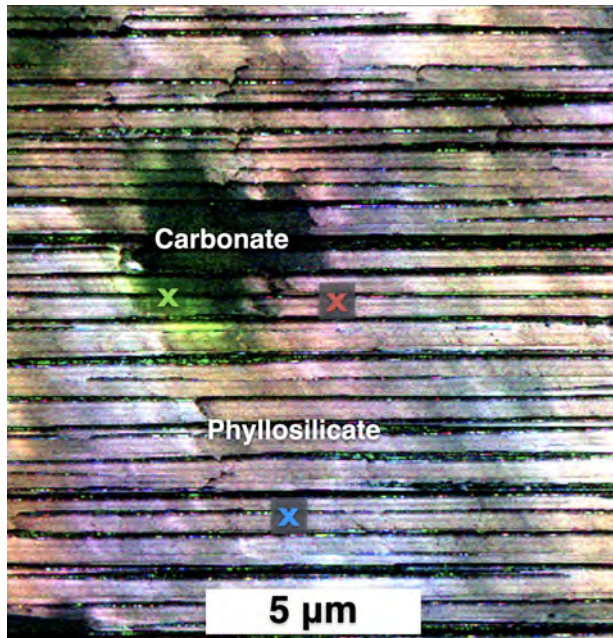


Figure 1: IR view of Ryugu sample A0026-pFIB002 dominated by phyllosilicates and a $\approx 4 \mu\text{m}$ carbonate grain. Red is the average intensity between $1050\text{--}1067 \text{ cm}^{-1}$ corresponding to an Si-O stretch present in both serpentine and saponite, green is $1087\text{--}1100 \text{ cm}^{-1}$, an Si-O mode present in serpentine, but not saponite, blue is $1117\text{--}1150 \text{ cm}^{-1}$, a mode present in saponite but not serpentine. Colored 'X' locations correspond to point spectra shown in Figure 2. Horizontal stripes are an artifact caused by FIB polishing.

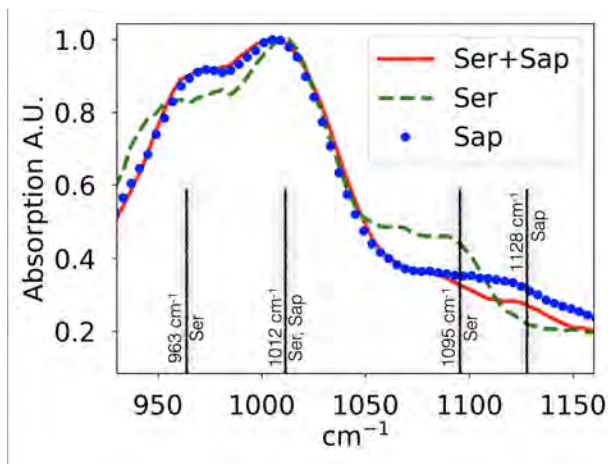


Figure 2: Point spectra taken at the locations shown in Figure 1. Phonon modes for serpentine and saponite have been placed on the plot per [4]. The solid red spectrum contains a mix of serpentine and saponite (Ser+Sap), while the green dashed spectrum is mostly serpentine (Ser) and the blue dotted spectrum is mostly saponite (Sap).

lying variations in the relative strength of the IR absorptive properties of Ryugu nanophases. These variations could be attributed to varying Al/Si ratios and/or minor element abundances[6]. However, the point spectra shown in Figure 2 suggest that these color variations may also be caused by phyllosilicate stacking. Spectral fitting of the IR point spectra taken in different phyllosilicate regions shown in Figure 2 are consistent with a superposition of serpentine and saponite, with peak assignments taken from [4].

Fourier analysis of the RGB image displayed in Figure 1 reveals phyllosilicate spectral variations extending down to the 40 nm scale, with significant power at the submicron to several micron length scales, especially at 1.7 and 5 microns. These variations would not be resolvable without NanoIR imaging. One potential mechanism for producing IR variations on the smallest size scales would be interlayer mixing and stacking of clay minerals [7]. We are currently working on understanding the physical-chemical causes of these spatial variations.

The serpentine enrichment around the carbonate grain is interesting given the similarities and differences in the layered structure of saponite and serpentine. Saponite consists of one layer of octahedral sites sandwiched between two tetrahedral sites and the freedom to fill the interstitial region with filler cations such as Ca. Serpentine, by comparison, has one layer of octahedral and one layer of tetrahedral sites. We suggest that the carbonate grain depleted Ca cations from the brine and pushed the local kinetics to favor the formation of serpentine. This explanation is also consistent with the observation that phyllosilicate is more enriched in saponite at greater distances from the carbonate. More detailed analysis is needed to better understand this system.

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