THE LASER-INDUCED FLUORESCENCE FROM RYUGU PARTICLES AND THEIR EXTRACTED CARBONACEOUS RESIDUES BY RAMAN SPECTROSCOPY. M. Komatsu[1,2] , H. Yabuta[3], Y. Kebukawa[4], L. Bonal[5], E. Quirico[5], H. Yurimoto[6], T. Nakamura[7], T. Noguchi[8], R. Okazaki[9], H. Naraoka[9], K. Sakamoto[10], S. Tachibana[10, 11], S. Watanabe[12], Y. Tsuda[10] and the Hayabusa2-initial-analysis IOM team, [1]SOKENDAI, The Graduate University for Advanced Studies (Japan), komatsu_mutsumi@soken.ac.jp, [2]Dep. of Earth Sciences, Waseda University (Japan), [3]Hiroshima University (Japan), [4]Yokohama National University (Japan), [5]Université Grenoble Alpes (France), [6]Hokkaido University (Japan),[7]Tohoku University (Japan), [8]Kyoto University (Japan), [9]Kyushu University (Japan), [10]JAXA (Japan), [11]Univ. of Tokyo (Japan), [12]Nagoya University (Japan).

Introduction:

In December 2020, a total of about 5.4 grams of material from C-type asteroid Ryugu was returned to Earth by JAXA's Hayabusa2 spacecraft [e.g.,1]. Ryugu is the fourth extraterrestrial body to be sampled by spacecraft, following past sample return missions including Apollo samples from the Moon, Stardust from comet Wild 2, and Hayabusa from near-Earth S-type asteroid Itokawa. Preliminary analyses of the returned samples showed that the Ryugu samples are most similar to CI chondrites but have lower albedo, higher porosity, and more fragile characteristics [2].

The goal of the Organic Macromolecule Initial Analysis Team is to elucidate the distributions and chemical characteristics of macromolecular organic matter in a C-type asteroid [3]. As a part of the team's investigations, Raman characterization has been conducted independently by two groups in Japan and France on the distinct Ryugu particles.

Raman spectroscopy is a non-destructive, effective tool to assess the thermal records of carbonaceous materials. Many of the carbonaceous chondrites show the two first-order Raman bands of polyaromatic carbon materials, namely the D ("disordered") and G ("graphite") bands [e.g., 4]. It has been shown previously that D and G bands (at ~1350 and 1580 cm^{-1}, respectively) in Raman spectra of organic matter in chondrite matrices reflect the thermal histories of the host meteorite [4-7]. Here we report our preliminary results of the Raman spectral features of the Ryugu particles obtained by the group in Japan. We mostly focus here on the fluorescence signal, whereas the interpretation of the Raman spectral features is led in [8].

Samples and Methods:

Raman point analyses were performed on six intact particles from Chamber A (A0108-5, -7, -17) and Chamber C (C0109-1, -15, -16) aggregates, as well as the extracted insoluble organic matter (IOM) from Chamber A (A0106) and Chamber C (C0107) aggregates [3]. Chamber A and C samples were collected at the first and second touchdown sites, respectively. The Ryugu particles crushed on diamond windows were used for the measurements to ensure continuity with the IR analysis [9]. We also studied primitive carbonaceous chondrites Ivuna, Orgueil (CI chondrites), Tagish Lake, Tarda (C2-ungrouped), Jbilet Winselwan, Murchison, and Y-793321 (CM chondrites) for comparison.

The Raman spectra were acquired using Renishaw InVia Reflex at the Materials Characterization Central Laboratory, Waseda University, Japan. In this study, we first conducted the measurements using a 532 nm (green) laser with 1800 l/mm grating that provides a high scattering intensity and spatial resolution. The laser was focused at the sample surface through a 50× objective (spot size around 3-4 µm) and its power was set at 110 µW, 240 µW, and 1 mW. Each acquisition comprised five integrations of 10 s that were averaged to make the final spectrum.

Test measurements of the Ryugu particles with various laser powers (110 µW–1 mW) showed that the D-band was hidden by the fluorescence background at lower than 240 µW. Therefore we chose to use a 1 mW laser mostly for the intact particles with our spectrometer to calculate both D and G parameters. On the other hand, extracted IOM was more sensitive to laser damage, and we found that a laser power as low as 110 µW would be suitable.

Results and Discussion:

Intact Particles

The intact particles in this study were 300×300 µm in size for the smaller ones and 300×500 µm for the larger ones. They consist mostly of fine-grained, black-colored matrix. Some transparent grains of various sizes are also present, which were identified by Raman analysis as carbonate or phosphate minerals.

Raman spectra were obtained from randomly selected matrix areas from the Ryugu intact particles A0108-5 and A0108-7. They show wide D and G bands, in addition, they are superimposed to a high fluorescence background (Fig. 1). These features are consistent with the generally observed significant fluorescence background in CI chondrites and Tagish Lake. Our study shows that CI chondrites have four to fifteen times higher fluorescence than CM chondrites; for example, ~197,200 counts for Ivana, vs. ~13,400 counts for CMs at 1000 cm^{-1}, whereas ~96,300 counts for A0108-5. Our observation is consistent with those by the French group [8].

Raman spectra on the intact Ryugu particles measured under 1 mW with our spectrometer produce better D and G band signatures (Fig. 2). Although the laser power is higher than the value we applied for CM chondrites (240 μW), visible laser damage due to the exposure to laser light was not observed. The intensity of the fluorescence background of the intact particles from both Chamber A and Chamber C particles are comparable, but Chamber A particles seem to have slightly higher fluorescence than Chamber C particles.

Extracted IOM

Average spectra of the extracted IOM from Ryugu particles and Murchison are shown in Fig. 3. The extracted IOM from Chamber A (A0106-IOM-r2) shows higher fluorescence than those from Chamber C (C0107-IOM-r8 and -r13) (Fig. 3). A similar trend is also observed in the intact particles (Fig. 2). We also observe the spectra from Ryugu's extracted IOM show higher fluorescence than the CM chondrite's extracted IOM, which is also in good agreement with the results from intact particles (Fig. 1). It is unclear what caused the difference in fluorescence, but it may reflect the sample heterogeneity or chemical variations between the two collecting sites.

Implications of the observed fluorescence

Raman scattering and fluorescence emission are two competing phenomena, which have similar origins. The cause of the fluorescence is not fully explained yet; it is caused by the presence of conjugated C bonds, as polyaromatic groups in the case of meteorites. The size of these groups and their concentration play a role, resulting in a control by the aliphatic/aromatic ratio of organic matter, thereby the degree of thermal metamorphism [7].

We observed significant fluorescence in intact particles, consistent with poorly ordered carbonaceous matter [8]. At this point, the fluorescence is not likely controlled by the chemical composition of the IOM residue. Rather, the higher fluorescence intensity in matrix grains from the asteroid Ryugu grains may be due to the fact their organic matter are present as tiny nanoparticles [10] and limits photons reabsorption. Our observation suggests that the fluorescence characteristics of the Ryugu particles indicate (i) a weak or lack of thermal metamorphism, and (ii) a close similarity to those of CI chondrites and Tagish Lake, which is in good agreement with FT/IR analyses and others [e.g., 3, 9,11]. The intensity of the fluorescence also varies depending on the laser wavelength [12], therefore Raman measurements at the different laser wavelengths as well as measurements under inert atmosphere to avoid photo-oxidation will be needed in the future.

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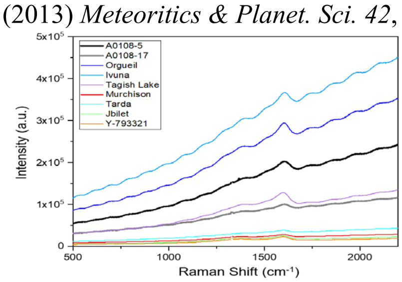

Fig. 1. Representative spectra of the intact Ryugu particles from A0108, together with average spectra of carbonaceous chondrites. The sinusoidal signal visible on the spectra is the artifact related to the detector. All analyses were performed under the same analytical settings (laser power: 240 μW).

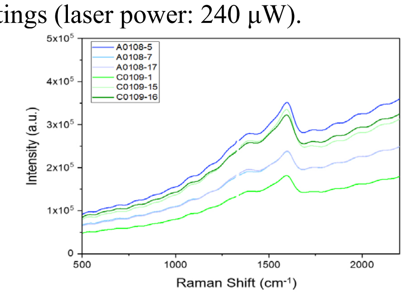

Fig. 2. Average spectra of the Ryugu intact particles, measured under the laser power of 1 mW. The spectrum shown here was obtained by averaging about 20 spectra taken from different locations of the particle.

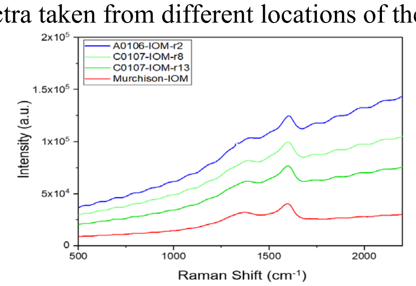

Fig. 3. Average spectra of the extracted IOM from Ryugu particles and Murchison, measured under the same conditions (laser power: 110 μW).