

TOF-SIMS analysis of macromolecular organic matter in Ryugu samples

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Introduction: The Hayabusa2 spacecraft returned samples with total mass of ~5 g from surface of asteroid Ryugu in December 2020 [1]. Chamber A aggregates collected upon the first touchdown and chamber C aggregates collected upon the second touchdown were investigated by the Hayabusa2 initial analysis team from June 2021 to May 2022.

The initial analysis organic macromolecule team has performed chemical, molecular, and isotopic analysis on the intact Ryugu grains and insoluble organic matter (IOM) isolated from Ryugu samples by μ -FTIR, micro-Raman spectroscopy, STXM-XANES, STEM-EELS, AFM-IR, and NanoSIMS [e.g., 4–8]. The result showed that chemical and isotopic compositions are broadly similar between Ryugu IOM and CI chondritic IOM, although some differences between the two IOM were reported by FTIR.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is useful to analyze the molecular species present on the sample surface. This technique has been applied for a variety of organic matter from macromolecular materials [e.g., 9] and extraterrestrial samples [e.g., 10–11]. In this study, we conducted in-situ analysis on bulk Ryugu samples and the isolated IOM using TOF-SIMS to investigate the chemical structure of macromolecular organic matter in asteroid Ryugu.

Experimental: IOM were extracted from two Ryugu aggregate samples (A0106 and C0107) with 6M HCl and 1M HCl/9M HF at Hiroshima University [4]. Those Ryugu IOM samples and intact Ryugu grains A0106 and C0057 were used in this study. For comparison, Tagish Lake IOM and bulk samples of Tagish Lake (C-ungrouped) and Orgueil (CI) were used. All those samples were pressed onto clean copper disks (~2.1 mm ϕ) and mounted in in-house stainless steel holder for TOF-SIMS analysis. Roughness of the sample surface and copper disks were < 10 μ m for fragment samples, < 5 μ m for IOM samples, respectively. The TOF-SIMS measurement was performed using a TRIFT III spectrometer (ULVAC-PHI, Inc., Chigasaki, Kanagawa, Japan) at Nagoya University. Positive and negative ion spectra were obtained using Au⁺ gold primary ion (22 keV, 1.2 nA). The measured surface areas were 200 \times 200 μ m and acquisition time of about 5 min for each sample. The ion intensity of each species was obtained from region of interest (ROI) of the sample of all samples, and were normalized by using total ion intensity of signals at m/z 0 to 150. After the TOF-SIMS analysis, mineralogical observation was performed on the sample using SEM/EDS.

Results and Discussions: Various ions derived from hydrocarbon moieties (C_nH_x⁺), which containing 1-10 carbons, were detected from both of extracted IOM and bulk samples from asteroid Ryugu samples and Tagish Lake and Orgueil meteorites at m/z 10–150 of TOF-SIMS spectra.

Normalized intensities of these fragment ions and the fragment patterns were almost similar between A0106 and C0107 IOM. Most abundant fragment ion was C₂H₃⁺ or C₂H₅⁺ for both extracted IOM and bulk samples from Ryugu and Tagish Lake. Lower mass fragment ions (C₁~C₄) were more abundant than higher mass fragment ions for both Ryugu and the carbonaceous chondrite samples. Furthermore, intensity of C_nH_{2n+1}⁺ ($n=1\sim4$) and C_nH_{2n-1}⁺ ($n=3\sim5$) ions from Ryugu IOM were higher than from Tagish Lake IOM. This trend implies that Ryugu IOM contains more abundant hydrogen than Tagish Lake IOM. On the other hand, Tagish Lake IOM showed higher intensity of C_nH_{2n+1}⁺ ($n>5$) and/or C_nH_{2n-1}⁺ ($n>6$) ions than Ryugu IOM. Although it is not clear whether these ions are derived from aromatic carbon or aliphatic carbon, the high mass fragment ions would indicate the presence of aromatic rings [12]. A previous TOF-SIMS study suggests that C_nH₂⁺ radical cations and C_n⁻ radical anions are the fragmentation ions derived from aromatic moieties [12]. In this study, these radical cations or anions were detected from both Ryugu and Tagish Lake IOM, while their abundances from Tagish Lake IOM were higher than those from Ryugu IOM, except C₅H₂⁺. The result suggests that Ryugu IOM is less molecularly evolved relative to Tagish Lake IOM, which is consistent with the solid-state ¹H-NMR results for organic matter in Ryugu samples [13]. Also, the abundances of intensity of C_n⁻ radical anions from the bulk Ryugu samples were lower than those from Tagish Lake, which also supports our observation for the extracted IOM.

Compared to bulk samples of Tagish Lake and Orgueil, it was hard to see clear difference on hydrocarbon fragment ions such as their intensity and H/C ratio between Ryugu samples like result of IOM samples, except $C_5H_x^+$. This may probably be due to sample heterogeneity. However, Tagish Lake and Orgueil bulk samples showed clearly developed $C_5H_x^+$ peaks relative to the bulk Ryugu samples. On the other hand, the extracted IOM showed the opposite trend: the peak intensities of $C_5H_x^+$ ions from Ryugu IOM, especially $C_5H_7^+$, were very high relative to those from Tagish Lake IOM. Such a large difference between bulk sample and IOM from the same sample has not been observed from meteorites, and therefore the observation implies the different chemical structures of Ryugu IOM and organic matter from bulk samples, which could be result from the acid-susceptible nature of the Ryugu samples. Different chemical structure of organic matter between Ryugu and Tagish Lake may result from freshness of Ryugu organic matter with no or little terrestrial alteration and/or different aqueous alteration process. Further TOF-SIMS analysis on CI chondrite IOM will provide more detailed firm interpretation for chemical evolution of Ryugu OM.

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