An initial look at the distributions and compositions of organic macromolecules in the asteroid Ryugu samples

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Hayabusa2 is JAXA's asteroid sample return mission that targeted the carbonaceous (C-type) asteroid (162173) Ryugu. The mission aims to unveil the origin and evolution of organic compounds and water in the early Solar System as life's building blocks [1]. Following the arrival of the Hayabusa2 spacecraft at Ryugu on June 27, 2018, observations by onboard remote sensing instruments revealed that Ryugu is a top-shaped asteroid with a very low geometric albedo [2-4] and that its surface is probably partially dehydrated [5]. The Mobile Asteroid Surface Scout (MASCOT) lander observed two types of boulders on the surface of Ryugu: one type was dark and cauliflower-like with a similar morphology to primitive carbonaceous chondrites, and another type was bright and smooth [6]. The lander's radiometer revealed that Ryugu has low thermal conductivity and high porosity unlike any chondritic meteorites, while these thermal properties have similar values to comets [7]. Thanks to the formation of the artificial crater on Ryugu's surface by a small carry-on impactor [8], two successful touchdowns on February 22 and July 11, 2019 have enabled collections of samples from two distinct locations on the asteroid, providing an advantage for investigating the origin and evolution of the Solar System as well as the surface processes of the asteroid. After the sample return on December 6, 2020, the curatorial work on the Ryugu sample has been conducted at JAXA for the first 6 months [9]. With the significant guidance from the observations and curation, the initial sample analysis has a one-year mission from June 2021 to June 2022 to address the question of what kind of asteroid Ryugu is.

Organic compounds are a major component of interstellar dust as along with silicates and water ice due to the high abundances of their elements (C, H, O, N, S, P) in the Galaxy. The initial molecular inventory of the Solar System, inherited from the parental molecular cloud, was modified and new complex molecules formed through a variety of processes in the protoplanetary disk and planetesimals, which resulted in the diverse compositions of asteroids and comets. These small bodies are thought to have contributed to the formation of our habitable planet, through exogenous delivery of organics and water as life's building blocks to the early Earth.

Organic macromolecules from chondritic meteorites have been often characterized as a dark, complex, acid-insoluble organic matter (IOM). IOM accounts for a major portion of total organic carbon in primitive carbonaceous chondrites (CCs). The intact chemical structure of IOM in CCs is still unknown, although a number of previous studies have suggested that it is composed of aromatic network crosslinking with short-branched aliphatic chains and various oxygen-bearing functional groups [10, 11]. Whether IOM was formed in interstellar cloud [12], outer solar nebula [13] or planetesimals [14], is still under debate. Nevertheless, elemental, molecular and isotopic variations of IOM from various types of small body materials, such as chondritic meteorites [15-20], interplanetary dust particles (IDPs) [21], cometary dusts [21-23], and Antarctic micrometeorites (AMMs) [24-27], have enabled our comprehensive understanding of chemical history of the early Solar System.

The Hayabusa2-initial-analysis IOM team consists of 36 members from Japan, USA, France, and Portugal. The scientific goals of IOM team include: i) Decoding the chemical relationship(s) between organics and minerals on a C-type asteroid parent body, ii) Elucidating formation pathways of organic macromolecules in a C-type asteroid, iii) Determining the origin(s) of organics in a C-type asteroid, iv) Investigating the asteroid-comet continuum, v) better understanding Solar System formation and volatile delivery, and vi) Understanding the role of organic macromolecules in the origin of life. In order to accomplish the goals, we aim to unveil the elemental, isotopic, and functional group compositions, structures and textures of organic macromolecules from the Ryugu samples. The analytical procedures are configured by combination of micro-Fourier

Transform Infrared Spectroscopy (FTIR), micro-Raman spectroscopy, synchrotron-based scanning transmission x-ray microscope (STXM), Scanning Transmission Electron Microscopy (STEM) coupled with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-ray Spectroscopy (EDS), Atomic Force Microscope based Infrared Spectroscopy (AFM-IR), and nano-secondary ion mass spectrometry (NanoSIMS). The analytical procedures are applied to the intact Ryugu samples and the IOM isolated by HCl/HF treatment of the Ryugu samples, respectively.

For the first measurements, Chamber A aggregates (A0108) collected upon the first touchdown and Chamber C aggregates (C0109) collected upon the second touchdown have been analyzed. The individual particles from A0108 and C0109 range from 200 to 900 μm in size. Some of the particles were crushed on a diamond window for micro-FTIR, micro-Raman, and NanoSIMS. Slices of other particles were prepared with a focused ion beam workstation (FIB) and/or an ultramicrotome to obtain ultra-thin sections for STXM, STEM-EELS, AFM-IR and NanoSIMS. The water/solvent/HCl extraction residues of other aggregates of Chamber A (A0106) and Chamber C (C0107), which were transferred by SOM team, were treated with 6N HCl and 1N HCl/9N HF to yield IOM for future measurements.

Organic macromolecules have been identified from the Ryugu samples by all the analytical techniques. The organic macromolecules were associated with secondary minerals formed through aqueous alteration [28], and they often exhibited D and/or ^{15}N-rich regions [29, 30]. These results show that the observed organics are of extraterrestrial origin. The FTIR [31] and Raman [32] spectroscopic features as well as the isotopic features [29, 30] of organic macromolecules from the Ryugu samples were comparable with those of the primitive carbonaceous CI/CM chondrites, while the other features were not necessarily consistent with the typical CI/CM, demonstrating that Ryugu samples record heterogeneous chemical history in a pristine state [28, 29].

References

[1] Tachibana et al. 2014. Geochem. J. 48:571. [2] Watanabe et al. 2019. Science 364:268. [3] Sugita et al. 2019. Science 364: eaaw0422. [4] Tatsumi et al. 2020 A&A, 639:A83. [5] Kitazato et al. 2019. Science 364:272. [6] Jaumann et al. 2019. Science 365:817. [7] Grott et al. 2019. Nature Astronomy 3:971. [8] Arakawa et al. 2020. Science 368:67. [9] Yada et al. et al. 2021. under review. [10] Glavin et al. 2018. In: Primitive Meteorites and Asteroids: Physical, Chemical and Spectroscopic Observations Paving the Way to Exploration (Ed. Abreu N.) pp. 205-271. [11] Martins et al. 2020. Space Sci. Rev. 216:54. [12] Alexander et al. 2007. GCA 71:4380. [13] Remusat et al. 2010. Astrophys. J., 713:1048. [14] Kebukawa et al. 2013. Astrophys. J. 771:19. [15] Cody and Alexander, 2005. GCA 69:1085. [16] Yabuta et al. 2005. GCA 40:779. [17] Bonal et al. 2006. GCA 70:1849. [18] Cody et al. 2008. Earth Planet. Sci. Lett. 272:446. [19] Kebukawa et al. 2011. GCA 75:3530. [20] Quirico et al. 2018. GCA 241:17. [18] Messenger, 2000. Nature 404:968. [21] Sandford et al. 2006. Science 314:1720. [22] Cody et al. 2008. MAPS 43:353. [23] De Gregorio et al. 2011. MAPS 46:1376. [24] Duprat et al. 2010. Science 328:742. [25] Yabuta et al. 2017. GCA 214:172. [26] Noguchi et al. 2017. GCA 208:119. [27] Mathurin et al. 2019. A&A 622:A160. [28] Stroud et al. this conference. [29] Nittler et al. this conference. [30] Remusat et al. this conference. [31] Kebukawa et al. this conference. [32] Bonal et al. this conference.