

**SOLUBLE ORGANIC COMPOUNDS IN ASTEROID 162173 RYUGU.** Hiroshi Naraoka<sup>1</sup>, Yoshinori Takano<sup>2</sup>, Jason P. Dworkin<sup>3</sup>, The Hayabusa2-initial-analysis SOM team, The Hayabusa2- initial-analysis core, <sup>1</sup>Department of Earth and Planetary Sciences, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka, 819-0395; <sup>2</sup>Japan Agency for Marine-Earth Science Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan; <sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.

**Introduction:** Asteroid 162173 Ryugu is a C-Type asteroid characterized by a low-albedo of IR reflectance spectrum consisting of hydrous minerals and carbonaceous materials [1]. The C-type asteroids are distributed primarily in the main belt between Mars and Jupiter, and regarded as parent bodies of carbonaceous meteorites [2]. Primitive carbonaceous meteorites often contain wide ranges of soluble organic matter (SOM) including prebiotic organic compounds such as amino acids [3]. Therefore, C-type asteroids might have delivered prebiotic organic molecules essential to the emergence of life in the primitive Earth [4]. The meteoritic organic matter is among the oldest material in the Solar System, possibly recording a long history from molecular cloud and protosolar nebulae to planetesimal and parent body processes. Furthermore, the alteration and preservation processes of SOM on an asteroid surface requires investigation since the asteroid surface is subjected to impacts, cosmic rays and solar radiation under a high-vacuum condition. The surface material of Ryugu can provide the first opportunity to examine the occurrence of organic compounds with respect to chemical evolution and organic resource distribution of the Solar System.

Objectives of the SOM analysis for the Ryugu samples are: (i) What organic compounds are present (or absent) in the C-type asteroid Ryugu? (ii) What kind of meteorite corresponds to the organic contents of the Ryugu samples? (iii) What are the origins and formation mechanism(s) are considered for the organic compounds in Ryugu? (iv) What are the alteration and preservation processes of the Ryugu organic materials? In this study, the SOM occurrence of the Ryugu samples was examined using several high-sensitive and high-resolution analytical techniques [5].

**Experimental Methods:** A small aggregate sample of Ryugu grains (A0106) from the first touchdown site was used in this study. The aggregate sample of A0106 (17.15 mg) was extracted sequentially with hexane, dichloromethane (DCM), methanol (MeOH) and H<sub>2</sub>O using a sonicator in a 1.5 mL PTFE vial followed by centrifugation at room temperature. A separate aggregate sample of A0106 (13.08 mg) was subjected to the hot-water extraction at 105°C for 20 h in an N<sub>2</sub> purged glass vial. The hot-water extract residue was split into two halves; one was extracted with HCl for bound-form amino acid analysis, and the other was

extracted with DCM/MeOH followed by formic acid and hydrochloric acid sequentially to analyze SOM and ionic species. All extraction procedures were performed on an ISO 5 (Class 100) clean bench inside an ISO 6 (Class 1000) clean room. All glassware used in this study was baked at 500°C for 3 h in air prior to analysis to remove possible organic contaminants. Baked serpentine powder (500°C for 3h in air) was also analyzed as a procedural blank.

A small portion of the A0106 grains was also analyzed for elemental and isotopic compositions of carbon (C), nitrogen (N) and sulfur (S) as well as hydrogen (H) and pyrolyzable oxygen (O) using elemental analyzer/isotope ratio mass spectrometer (EA/IRMS). A single ~1 mm-sized grain (A0080) was analyzed for the spatial distribution of organic compounds by *in-situ* analysis using desorption electrospray ionization/high-resolution mass spectrometry (DESI/HRMS). Electrically charged MeOH was sprayed directly on the sample surface and positive ions were collected.

**Results and Discussion:** The Ryugu sample (A0106) contained 3.76 wt% C, 1.14 wt% H and 0.16 wt% N, indicating that Ryugu is the richest in C, H and N compared to various types of carbonaceous chondrites. The heavy isotope enrichment of H ( $\delta D = \sim +250\%$ ) and N ( $\delta^{15}N = \sim +40\%$ ) was observed, showing a similar isotopic signature to CI-type chondrites such as Ivuna and Orgueil.

The extracts of hexane, DCM, methanol and H<sub>2</sub>O were subjected to non-target ultrahigh-resolution mass spectral analysis using Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR/MS) coupled with electrospray ionization (ESI) and atmospheric pressure photo-ionization (APPI). Hundreds of thousands of ion signals were detected between *m/z* 100 and 700 in the methanol extract, in which almost 20,000 molecular compositions consisting of C, H, N, O and/or S were assigned [6]. The organic solvent extracts were also analyzed using a two-dimensional gas chromatography with high-resolution (time of flight) mass spectrometry (GC×GC-HRMS), by which various organic compounds including aromatic hydrocarbons were identified [7]. In addition, nano-liquid chromatography coupled with high-resolution Orbitrap mass spectrometry (nanoLC/HRMS) revealed the

occurrence of alkylated N-containing heterocyclic compounds in the methanol extract of Ryugu. The alkyipyridine homologues ( $C_nH_{2n-4}N^+$ ) identified in the Ryugu extract had a different distribution pattern from those of CM chondrites. The Ryugu compounds contained a range from 11 to 22 carbons with the maximum at 17, while the Murchison meteorite has a lower carbon range mainly from 8 to 16 with the maximum at 11 [8].

The hydrolyzed hot-water extract of the A0106 sample was analyzed for amino acids using a combination of 3-dimensional high precision liquid chromatography with a high-sensitivity fluorescence detector (3D-HPLC/FD) and ultrahigh precision liquid chromatography with tandem UV fluorescence detection and Orbitrap high-resolution mass spectrometry (LC-FD/HRMS). More than 10 amino acids were identified above the blank levels. Proteinogenic amino acids such as glycine, D,L- $\alpha$ -alanine as well as non-proteinogenic amino acids including  $\beta$ -alanine, D,L- $\alpha$ -aminobutyric acid were identified. The chiral amino acids are present as racemic mixtures (D/L  $\sim$  1), which is indicative of extraterrestrial, non-biological origins [9]. The H<sub>2</sub>O extract as well as HCOOH and HCl extracts were also analyzed by ion chromatography to measure anion and cation species with relevant to aqueous alteration of Ryugu [10].

The DESI/HRMS analysis of A0080 revealed molecular distribution on the grain surface. The molecular imaging shows  $\mu$ m-scale differences in spatial distribution of the CHN compounds depending on their molecular sizes and families. Various spatial distribution among different molecular sizes and compound classes were also observed among CHO and CHNO compounds [11].

**Conclusions:** The high molecular diversity and spatial distribution of the SOM was observed in the Ryugu sample. The SOM concentration of the A0106 sample was less than that of Murchison. The Ryugu organic matter is likely to have been affected by aqueous alteration. However, the Ryugu material has not experienced the high temperatures like those observed for the heated CI (CY-type) chondrites, such as B-7904 and Y-86720, since the CY-type chondrites yielded the least or no detectable amino acids and polyaromatic hydrocarbons [e.g. 12, 13].

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