

Soluble organic matter in Ryugu: The first rehearsal analysis

*Hiroshi Naraoka¹, Yoshinori Takano², Nanako O. Ogawa², Minako Hashiguchi¹, Hannah L. McLain³, Eric T. Parker³, Kenji Hamase¹, Francois-Régis Orthous-Daunay⁴, Junko Isa⁴, Dan Aoki⁵, Kazuhiko Fukushima⁵, Philip Schmitt-Kopplin⁶, Jason P. Dworkin³, SOM Analysis Team

1. Kyushu University, Japan, 2. Japan Agency for Marine-Earth Science Technology, Japan, 3. NASA Goddard Space Flight Center, USA, 4. Université Grenoble Alpes, France, 5. Nagoya University, Japan, 6. Helmholtz Zentrum Muenchen, Germany

Introduction: Ryugu is a C-type asteroid possessing a low-albedo surface with low abundance hydrous minerals [1], which is similar characteristics observed for carbonaceous meteorites. Therefore, the asteroid material is expected to contain many types of organic matters including amino acids. The occurrence of organic compounds in Ryugu will provide clues to the evolution of prebiotic molecules, redox and thermal condition as well as aqueous alteration of the asteroids in the solar system. We have organized an international analytical team for the soluble organic matter (SOM) of the Hayabusa2-returned samples. Because the total sampling amount is expected to be small (~100 mg) [2], and because meteoritic SOM usually occurs as a complex mixture consisting of various types of organic compounds with very small concentrations at each compound, we have been developing high-sensitive and high-resolution analytical techniques [3]. The first rehearsal analysis is conducted using small amounts of carbonaceous chondrites.

Samples and Methods: The powdered samples (~50 mg) of CM carbonaceous chondrites and baked serpentine (as a blank) were extracted sequentially with non-polar to polar solvents in a clean room. The solvent extracts were analyzed using: 1) High-resolution mass spectroscopy (HRMS) using Fourier Transform-Ion Cyclotron Resonance/Mass Spectrometry (FT-ICR/MS) [4], 2) HRMS with nano-liquid chromatography (nanoLC) with Orbitrap MS [5], 3) Chiral amino acid analysis using multi-dimensional (2D or 3D) high-performance liquid chromatography (HPLC) with high-sensitive fluorescence detection (FD) coupled with HRMS [6, 7]. 4) Compound-specific isotope analysis using gas chromatography (GC)/Orbitrap MS and GC/combustion/isotope ratio mass spectrometry (GC/C/IRMS), 5) *In situ* organic compound analysis and molecular imaging using desorption electrospray ionization (DESI) equipped with Orbitrap MS [8, 9]. 6) Spatial resolution imaging of organic compounds using time of flight-secondary ion mass spectrometry (ToF-SIMS) [10], and 7) Bulk chemical and isotopic compositions of organic matter (C and N) using nanoEA-IRMS [11].

Results and Discussion: The 3D-HPLC/FD analysis clarified some chiral amino acid distribution using ~mg of the Murchison meteorite, in which non-proteinogenic amino acids were present as racemic mixtures. The FT-ICR/MS analysis of Murchison revealed significantly diverse molecular compositions with the homologous series using both positive and negative ions, being consistent with the previous studies [4]. The various structural isomers (the same molecular composition but different chemical structures) were identified using nanoLC/nanoESI/Orbitrap MS. The nanoLC coupled with nanoESI could enhance the sensitivity of detection by three magnitudes compared to that of conventional HPLC with ESI. The chromatographic HRMS data was deconvoluted by a hand-made software, in which the CHN compounds were predominant, being similar results as the previous study [5]. The heterogeneous distribution of the CHN compounds was revealed using DESI/HRMS. These results indicate that the current analytical methods can be available to reveal organic molecular characteristics of the Ryugu samples, if the returned samples contain SOM similar to the Murchison SOM. We further plan to conduct the second rehearsal

analysis using less samples (~10 mg) of various carbonaceous meteorites.

References: [1] Kitazato K. et al. (2019) *Science***364**, 272. [2] Tachibana S. (2014) *Geochem. J.* **48**, 571. [3] Naraoka H. et al. (2019) *Life* **9**, 62. [4] Schmitt-Kopplin P. et al. (2010) *PNAS USA* **107**, 2763. [5] Naraoka H. et al. (2017) *ACS Earth & Space Chem.***1**, 540. [6] Glavin D. P. et al. (2011) *MAPS* **45**, 1848. [7] Hamase K. et al. (2014) *Chromatography***35**, 103. [8] Naraoka H. & Hashiguchi M. (2018) *Rapid Commun. Mass Spectrom.***32**, 959. [9] Hashiguchi M. & Naraoka H. (2019) *MAPS*, **54**, 452. [10] Naraoka H. et al. (2015) *EPS* **67**, 67. [11] Ogawa N. O. et al. (2019) *82th METSOC Meeting*, Abstract #6208.

Keywords: Hayabusa2, Ryugu, Soluble organic matter, High resolution