

SOLUBLE ORGANIC MATTER (SOM) ANALYSIS PLAN OF THE HAYABUSA2-RETURNED SAMPLES

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Introduction: The Hayabusa2 spacecraft successfully performed the first touch and go sampling of the surface materials of asteroid 162173 Ryugu on 22nd February, 2019. The collected surface materials of Ryugu will be delivered to Earth in late 2020. Because Ryugu has the surface of C-type reflectance spectra with a low abundance hydrous minerals [1], the asteroid surface appears composed of materials similar to that of carbonaceous chondrites. Such primitive meteorites are expected to yield various soluble organic matter (SOM) including amino acid, carboxylic acid, etc. The occurrence of SOM in Ryugu will provide clues to the formation pathways of organic compounds as well as prebiotic molecules with respect to origins of life in the primitive solar system. In order to investigate the organic evolution of Ryugu, an international team consisting of 24 members currently is organized for the initial SOM analysis for the Hayabusa2-returned samples. In this study, we propose the comprehensive SOM analyses using high-sensitive and high-resolution analytical methods.

Methods: We have been developing the advanced techniques to analyze the trace amounts of soluble organic compounds in very small extraterrestrial materials, because the sampling amount is expected to be >100 mg [2]. The analytical procedures must be performed under clean conditions to avoid terrestrial contaminations. Meteoritic SOM usually occurs as a complex mixture consisting of various types of organic compounds with very small concentrations at each compound, therefore, high resolution analyses are required under high sensitivity. Currently we are planning to perform four techniques. 1) High-resolution mass spectroscopy (HRMS) of various solvent extracts coupled with or without nano-liquid chromatography by electrospray ionization (ESI) using Fourier Transform-Ion Cyclotron Resonance/Mass Spectrometry (FT-ICR/MS) [3] and/or Orbitrap MS [4]. 2) Chiral amino acid analysis using multi-dimensional (2D or 3D) high-performance liquid chromatography with high-sensitive fluorescence detection (FD) coupled with HRMS [5, 6]. 3) *In situ* organic compound analysis and molecular imaging using desorption electrospray ionization (DESI) equipped with HRMS [7, 8]. 4) Spatial resolution imaging of organic compounds using time of flight-secondary ion mass spectrometry (ToF-SIMS) [9]. If the sample is available, we will also perform 5) compound-specific isotope analysis using gas chromatography/combustion or pyrolysis /isotope ratio mass spectrometry (GC/C or pyrolysis/IRMS). In addition, we plan to measure bulk chemical and isotopic compositions of organic matter (C, H, N, O and S) using nanoEA-IRMS and/or laser-tunable FT-IR spectroscopy. The returned samples will be extracted sequentially with non-polar (e.g. hexane) to polar (H₂O) solvents and/or polar to non-polar solvents in a clean bench (ISO Class 5) set inside of a clean room (ISO Class 6). The extracts will be delivered to some research institutes for the detailed analyses. In addition, grain-level minimally-destructive analysis will be performed by nanoLC/Orbitrap MS and DESI/HRMS.

Results and Discussion: The preliminary result of one grain analysis of the Murchison meteorite (~ a few tens µg) demonstrated the organic compound identification by nanoLC/Orbitrap MS. The predominance of CHN compounds in the methanol extract of Murchison is similar between the two analytical methods (nanoLC vs. HPLC). The nanoLC coupled with nanoESI could enhance the sensitivity of detection by three magnitudes compared to that of conventional HPLC with ESI. The 2D-HPLC/FD analysis clarified the enantiomer distribution of amino acids using ~µg fragments of Murchison. The result suggests heterogeneous distribution of amino acid enantiomers in the meteorite, which is consistent with previous studies. [10]

We will further conduct preliminary tests of the sequential analysis for various types of SOM using 30 mg, 10 mg, and 1 mg samples of the carbonaceous meteorites and baked serpentine (as a blank). After the sequential extraction of samples, the residues will be used for the analysis of insoluble organic matter (IOM).

References: [1] Kitazato K. et al. (2019) *Science* 364:272-275. [2] Tachibana S. (2014) *Geochem. J.* 48:571–587. [3] Schmitt-Kopplin P. et al. (2010) *Proc. Natl. Acad. Sci. USA* 107:2763-2768. [4] Naraoka H. et al. (2017) *ACS Earth & Space Chem.* 1:540-550. [5] Glavin D. P. et al. (2011) *Meteoritics & Planetary Science* 45:1848-1972. [6] Hamase K. et al. (2014) *Chromatography* 35:103-110. [7] Naraoka H. & Hashiguchi M. (2018) *Rapid Commun. Mass Spectrom.* 32:959-964. [8] Hashiguchi M. & Naraoka H. (2019) *Meteoritics & Planetary Science* 54:452-468. [9] Naraoka H. et al. (2015) *Earth, Planets & Space* 67:67. [10] Pizzarello et al. (2003) *Geochim. Cosmochim. Acta* 67:1589-1595.