Soluble Organic Matter (SOM) analysis of the Hayabusa2 samples: The first results

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The Hayabusa2 spacecraft successfully collected the surface and possible sub-surface materials of the asteroid 162173 Ryugu. Ryugu is a C-type asteroid characterized by a low-albedo surface probably consisting of hydrous minerals and carbonaceous materials. [1] The direct optical and spectral analysis of the returned samples indicates that Ryugu material is dominated by hydrous carbonaceous chondrite-like matter (similar to CI chondrites) [2]. Since carbonaceous chondrites have generally yielded various types of organic matter, the collected Ryugu grains are expected to contain diverse types of organic compounds including bio-related molecules. The occurrence of organic compounds in the Ryugu surface will provide clues to the evolution of prebiotic molecules and their preservations associated with aqueous alteration of the primitive asteroid. The initial analysis of soluble organic matter (SOM) of the Hayabusa2-returned samples has been performed by an international team consisting of 32 members. Because the sample amount available for comprehensive SOM analyses is limited, and because the SOM is expected to be present as a complex mixture of various types of organic compounds with very small concentrations of each compound, high-sensitivity and high-resolution analytical techniques have been developed using carbonaceous meteorites [e.g. 3].

Two aggregate samples of the Ryugu grains (A106 and C107) were allocated for the solvent extractions and bulk carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) measurements. The A106 sample was collected during the 1st sampling in February 2019 and the C107 sample was collected during the 2nd sampling in July 2019 after the Small Carry Impactor (SCI) operation. They consist mainly of particles smaller than 1 mm in diameter, and each sample mass was 38-39 mg. They were firstly investigated spectroscopically in the near infrared wavelength range by the Stone Team prior to the solvent extractions. Other small grains (A0080 and C0057) were also allocated for this study to investigate the spatial distribution of organic compounds on the sample surface. The extraction and analytical measurements implemented by the SOM Team are summarized in Figure 1. Each powder sample was extracted sequentially with non-polar to polar solvents, i.e., hexane, dichloromethane (DCM), methanol (MeOH) and H_2O, for non-targeted analysis to reveal the compound composition. Each solvent extract was analyzed by solution state nuclear magnetic resonance (NMR) spectroscopy [4], Fourier transform-ion cyclotron resonance/mass spectrometry (FT-ICR/MS) with ESI and APPI ionization [5] and by high-resolution mass spectroscopy using Orbitrap MS coupled with nano-liquid chromatography (nanoLC/Orbitrap MS) [6], and using two dimensional gas chromatography/mass spectrometry (GC×GC/MS). The extracted residues were passed to the Chemistry Team for further inorganic element analysis. The other powder sample was subjected to the hot water extraction for amino acid analyses including chiral isomer separation, which was performed by three-dimensional (3D) high-performance liquid chromatography (HPLC) with high-sensitivity fluorescence detection (FD) [7] and by HPLC/FD coupled with quadrupole-time of flight/mass spectrometry (QToF/MS) [8]. After the hot water extraction, the residue was split into two halves. One half was further extracted with hydrochloric acid (HCl) to analyze for amino acids in bound-form. The other half was sequentially extracted with DCM/MeOH (1/1) to analyze semi-polar compounds such as polycyclic aromatic hydrocarbons (PAHs) by GC/MS, followed by further extraction with formic acid to analyze polar heterocyclic compounds, and subsequent extraction with HCl to detect bound-form polar compounds. The extracted residues were passed to the IOM Team for the analysis of insoluble organic matter (IOM). Compound-specific stable isotope analyses will be performed using GC/combustion/isotope ratio mass spectrometry (GC/C/IRMS) if the compound concentration is high enough to enable such an isotopic measurement. All extraction procedures were performed on an ISO 6 (Class 100) clean bench inside an ISO 5 (Class 1000) clean room. Baked serpentine powder was also analyzed as a procedural blank. *In situ* organic compound analysis with the molecular imaging was performed using desorption electrospray ionization (DESI) equipped with Orbitrap MS [9, 10], followed by

spatial imaging of organic compounds using ToF/secondary ion mass spectrometry (ToF/SIMS) [11]. The bulk chemical and isotopic compositions of CNS and HO were determined using nano-elemental analysis/isotope ratio mass spectrometry (nanoEA/IRMS) [12] and EA/pyrolysis/IRMS, respectively.

We have identified a variety of indigenous organic compounds in the extracts of both A106 and C107 samples. The Ryugu grains host organic molecules under the high-vacuum and cosmic-ray irradiation environment of the asteroid surface. The analysis of extracted molecules is in progress, and the first results will be presented at the symposium.

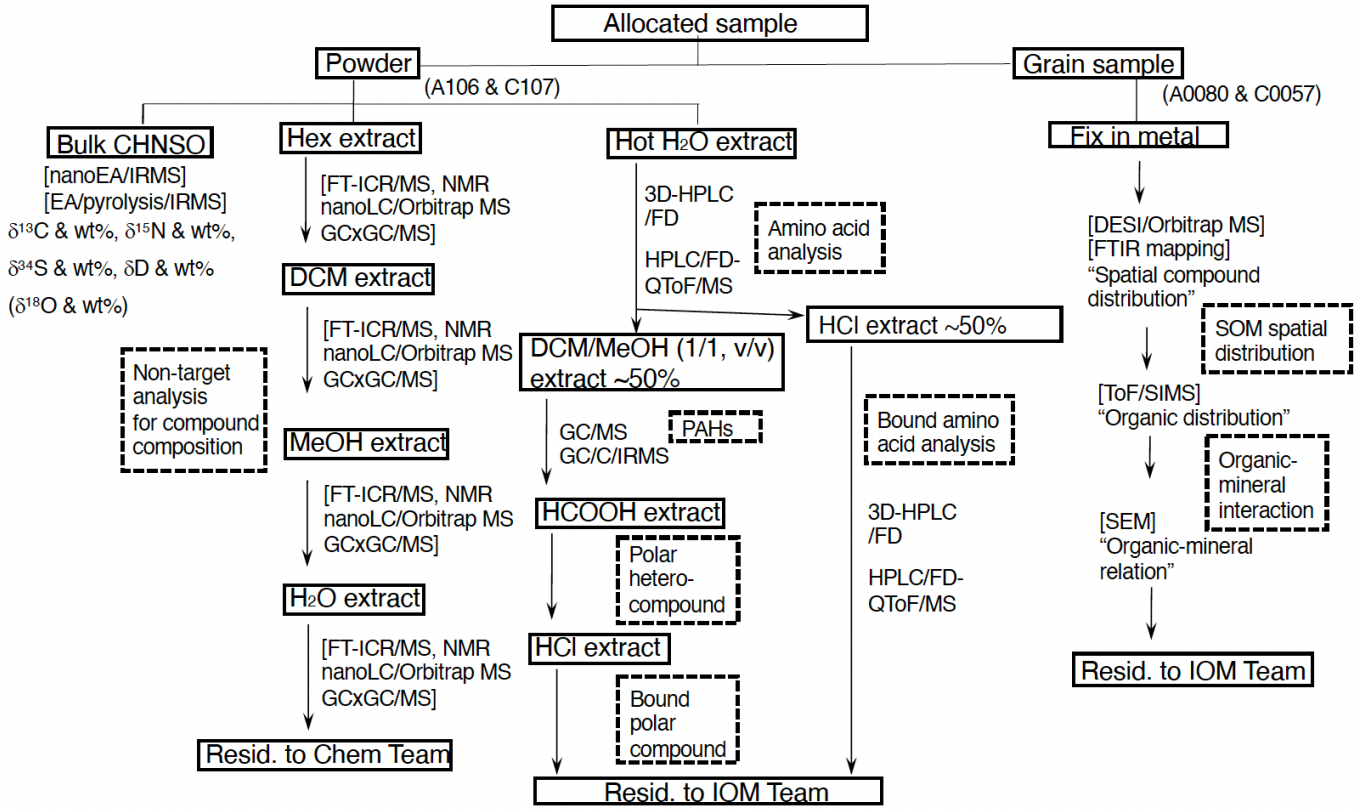

Figure 1. Analytical scheme for the Ryugu samples by the SOM Team.

References

[1] Kitazato K. et al. (2019) *Science* **364**, 272. [2] Yada T. et al. (2021) *Nature Astron*. in press. [3] Naraoka H. et al. (2019) *Life* **9**, 62. [4] Hertkorn N. et al. (2015) *Magn Reson. Chem.* **53**, 754. [5] Schmitt-Kopplin P. et al. (2010) *PNAS USA* **107**, 2763. [6] Naraoka H. et al. (2017) *ACS Earth & Space Chem.* **1**, 540. [7] Furusho A. et al. (2020) *J. Chromatogr. A* **1625**, 461255. [8] Glavin D. P. et al. (2021) *MAPS* **56**, 148. [9] Naraoka H. & Hashiguchi M. (2018) *Rapid Commun. Mass Spectrom.* **32**, 959. [10] Hashiguchi M. & Naraoka H. (2019) *MAPS,* **54**, 452. [11] Naraoka H. et al. (2015) *EPS* **67**, 67. [12] Ogawa N. O. et al. (2019) *82nd METSOC Meeting*, Abstract #6208.