

HIGH MOLECULAR DIVERSITY AND STRUCTURAL COMPLEXITY REVEALED WITH ULTRAHIGH RESOLUTION MASS SPECTROMETRY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF RYUGU SAMPLES. Ph. Schmitt-Kopplin^{1,2,3}, N. Hertkorn³, M. Harir³, M. Lucio³, H. Naraoka⁴, The Hayabusa2-initial-analysis SOM team, The Hayabusa2- initial-analysis core, ¹Technische Universität Muenchen, Germany; ²Max Planck Institute for Extraterrestrial Physics, Garching, Germany; ³Helmholtz Muenchen, Germany; ⁴Kyushu University, Japan.

Introduction: The surface and possible sub-surface materials of the asteroid Ryugu were recovered during the two touch-down sampling by the Hayabusa2 spacecraft. Here we present the first results on the solvent soluble organic matter (SOM) of the surface sample (A0106) using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) complemented with high field nuclear magnetic resonance spectroscopy (NMR) [1-3].

The goals of the SOM analysis using ultrahigh resolution mass spectrometry and NMR-spectroscopy were (i) to profile organic compounds with the elements C, H, N, O, S, Mg from the Ryugu samples, (ii) to compare these organic signatures to the state of the art in knowledge of meteoritic soluble organic matter, and (iii) to evaluate possible alteration processes that may have occurred on the parent body (temperature and shock stresses, water alteration) leading to organic matter preservation or specific transformations.

The samples A0106 (first touchdown) was sequentially extracted in the Hayabusa2-initial-analysis SOM team with various apolar to polar solvents and demonstrate a never seen molecular complexity and diversity.

Experimental Methods: A small aggregate sample (A0106) of Ryugu grains from the first touchdown site were used in this study. The aggregate sample of A0106 (17.15 mg) was extracted sequentially with hexane, dichloromethane (DCM), methanol, and H₂O sonicated in a 1.5 mL Teflon vial followed by centrifugation. We obtained the SOM solvent sequential extracts and analyzed these using Fourier transform ion cyclotron mass spectrometry (FTICR/MS) equipped with a 12 Tesla superconducting magnet in negative and positive mode electrospray ionization (ESI(-), ESI(+)) and positive atmospheric pressure photoionization (APPI(+)) in direct sample injection and using nuclear magnetic resonance spectroscopy (800 MHz ¹H NMR equipped with a Cryoprobe head), both installed at the Helmholtz Center in Munich. Detailed description of the analysis and data evaluation was described earlier [1, 3, 4].

Results and Discussion: We confirm herewith the close similarity and the possible comparison of the solvent extracts with meteoritic material to the Hayabusa2 return samples. We analyzed the sequential hexane, dichloromethane (DCM), methanol, and water

extracts with NMR and with ESI- and APPI-FTICR/MS systematically for both negative and positive ions. The hundred thousands of signals obtained were filtered, converted and cumulative assigned into more than 34,500 elementary compositions consisting of carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and/or sulfur (S). Organomagnesium compounds (CHOMg, CHOSMg) were not found and this reflects the low temperature processes on the parent body [5, 6].

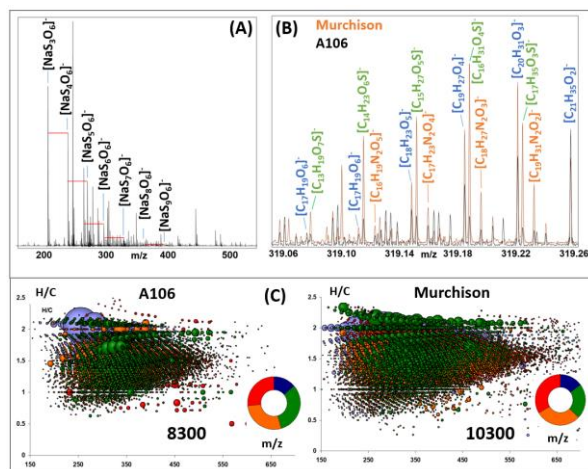


Fig. 1. ESI(-)-FTICR/Mass spectra of the methanol extract of sample A0106 showing in (A) most intensive signals corresponding to homologous chemical series of polythionates with sulfur number from $n=3$ to 12; (B) a detail of the mass spectra in a segment of 0.2 amu of the nominal mass 319, showing the annotated elementary compositions in CHO (blue), CHNO (orange), CHOS (green) compared to Murchison CM2; (C) the mass edited van Krevelen-diagram representation of the 8300 validated formula of A0106 and 10300 formula of Murchison methanol SOM extracts. Pie charts show relative abundances of CHO (blue), CHNO (orange) and CHOS (green), CHNOS (red) molecules.

As shown for carbonaceous chondrites previously, our results confirm that the extraterrestrial chemical diversity is much higher compared to terrestrial biological and the biogeochemical spaces and consists in a regular continuum (i) of small to macromolecules and (ii) of carbon oxidation states from apolar (CH, polycyclic aromatic hydrocarbons and branched aliphatics as analyzed with APPI) to polar small

molecules (CHO) with increasing functionalized groups with varying oxygen and heteroatom contents (CHN, CHS, CHNO, CHOS); these lead to the observed differential solvent type solubility observed in the sequential extraction and with the diverse ionization methods.

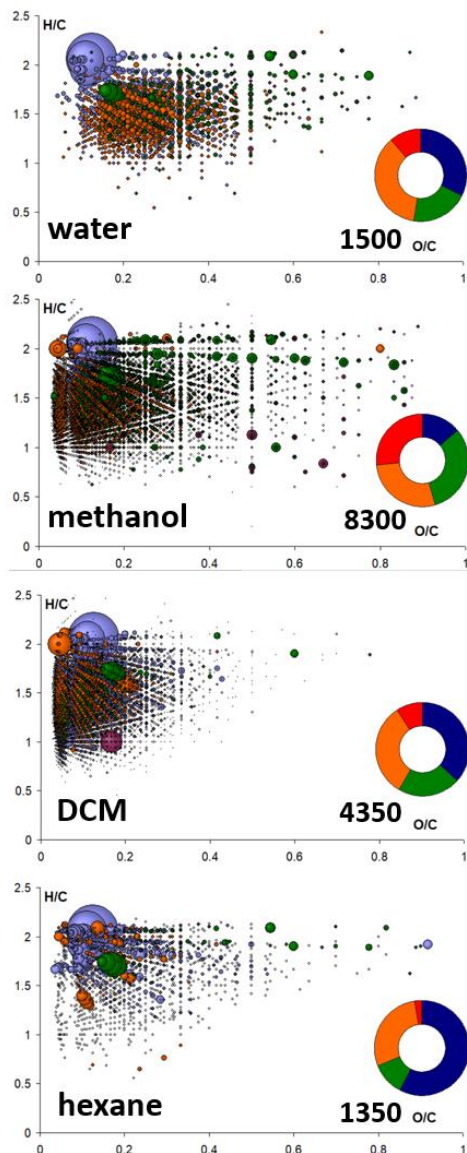


Fig. 2. van Krevelen diagram representation of the ESI(-)-FTICR MS annotated oxygenated formula (CHNOS) of the sequential solvent extraction of sample A0106 (Bubble size is proportional to the intensity in the mass spectra and color as in Fig.1). For water, methanol, DCN, and hexan extracts, 1500, 8300, 4350, and 1350 chemical formulas were validated, respectively. Relative abundances of CHO, CHNO, CHOS, and CHNOS molecules are shown in pie charts.

Combining the sequential solvent extraction of increasing polarity with the various ionization sources prior FTICR/MS showed evidences of multiple chemosynthesis pathways in describing the mass ranges, the carbon oxidation state distribution, and heteroatom contributions to the assembly of multiple complex endogen molecules. Compared to knowledge from SOM of meteorites these specific profiles of sample A0106 reflect cold hydrothermalism involved on the parent body [5, 6]. We also confirm the high importance of chemical processes involving specific nitrogen and sulfur chemistry. We also revealed specific known molecular targets such as PAHs and alkylated N-containing heterocyclic compounds and alkylpyridine homologues ($C_nH_{2n-4}N^+$) such as described on the sample with DESI/HRMS [7] and as described with Murchison meteorite previously [4].

Conclusions: Ryugu sample A0106 showed extreme chemical diversity and complexity, close to low temperature water altered meteoritic materials. These samples present a unique opportunity of having a direct and low invasive insight into the complex organic diversity present on 162173 Ryugu.

References: [1] Schmitt-Kopplin P. et al. (2010) *Proc. Natl. Acad. Sci. U.S.A.*, 107, 2763. [2] Ruf A. et al. (2018) *Life* 8, 18. [3] Hertkorn N. et al. (2015) *Magn. Reson. Chem.*, 53, 754. [4] Herzog J. et al. (2019) *Life*, 9:48. [5] Ruf A. et al. (2017) *Proc. Natl. Acad. Sci. U.S.A.*, (2017) 114, 2819. [6] Matzka M. et al. (2021) *Astrophys. J. Lett.*, 915, L7. [7] Hashiguchi M. et al. (2022) *LPS LIII*.

The Hayabusa2-initial-analysis SOM team:

Hiroshi Naraoka, Yoshinori Takano, Jason P. Dworkin, Kenji Hamase, Aogu Furusho, Minako Hashiguchi, Kazuhiko Fukushima, Dan Aoki, José C. Aponte, Eric T. Parker, Daniel P. Glavin, Hannah L. McLain, Jamie E. Elsila, Heather V. Graham, John M. Eiler, Philippe Schmitt-Kopplin, Norbert Hertkorn, Alexander Ruf, Francois-Regis Orthous-Daunay, Cédric Wolters, Junko Isa, Véronique Vuitton, Roland Thissen, Nanako O. Ogawa, Saburo Sakai, Toshihiro Yoshimura, Toshiaki Koga, Haruna Sugahara, Naohiko Ohkouchi, Hajime Mita, Yoshihiro Furukawa, Yasuhiro Oba, Yoshito Chikaraishi.

The Hayabusa2-initial-analysis core:

Shogo Tachibana, Tomoki Nakamura, Hiroshi Naraoka, Takaaki Noguchi, Ryuji Okazaki, Kanako Sakamoto, Hikaru Yabuta, Hisayoshi Yurimoto, Yuichi Tsuda, Seichi Watanabe.