MOLECULAR ATLAS AND STRUCTURAL COMPLEXITY REVEALED WITH ULTRAHIGH RESOLUTION MASS SPECTROMETRY AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF RYUGU.

Ph. Schmitt-Kopplin[1,2,3], N. Hertkorn[3], M. Harir[3], M. Lucio[3], H. Naraoka[4], The Hayabusa2-initial-analysis SOM team, The Hayabusa2- initial-analysis core, [1]Technische Universität Muenchen (Schmitt-Kopplin@tum.de), Germany; [2]Max Planck Institute for Extraterrestrial Physics, Garching, Germany; [3]Helmholtz Muenchen, Germany; [4]Kyushu 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 spectroscopy (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 (i.e. organosulfurs, organomagnesiums). 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.

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 of A0106 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 conservatively cumulative assigned into more than 25,000 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]. 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. 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 molecules. Compared to SOM of meteorites these specific profiles of sample A0106 reflect cold hydrothermalism involved on the parent body [5, 6]. We also confirm the 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.

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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, Toshiki 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, Sei-ichiro Watanabe.