Highest molecular diversity and structural complexity revealed with ultrahigh resolution mass spectrometry and nuclear magnetic resonance spectroscopy of Ryugu´s samples

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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) using ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectroscopy (FTICR/MS) complemented with high field nuclear magnetic resonance spectroscopy (NMR) [1-3]. The two samples A106 (first touchdown) and C107 (second touchdown) were sequentially extracted in the Hayabusa2-initial-analysis SOM team with various polar and apolar solvent extracts and demonstrate a never seen molecular complexity and diversity.

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 electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) [4] FTICR/MS systematically for both negative and positive ions. The hundred thousands of signals were filtered, converted and assigned into more than 24,000 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 biogeochemical spaces and consists in a regular continuum (i) of small to macromolecules (ii) of carbon oxidation states from apolar (CH, polycyclic aromatic hydrocarbons and branched aliphatics) to polar small molecules (CHO) with increasing functionalized oxygen and heteroatom contents (CHN, CHS, CHNO, CHOS) leading to the observed differential solvent type solubility. We revealed specific known molecular targets (CHN^+, $CHNO^+$) [4] and show evidences of multiple chemosynthesis pathways in describing the carbon oxidation state distribution and heteroatom contributions to the assembly of multiple complex endogen molecules; these also 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 [7, 8]. The two fractions analyzed show an extreme coverage in structural features in APPI and only slight differences in the apolar solvents in ESI. The A106 sample showed slight differences only with higher mass range and more oxygenated compounds. The C107 sample had increased abundance and uniqueness of more unsaturated carbon and low oxygenated compounds that may have disappeared due to surface processing (some hypothesis could be cosmic irradiation at the surface). These samples presents a unique opportunity of having a direct and low invasive insight into the complex organic diversity present on 162173 Ryugu.

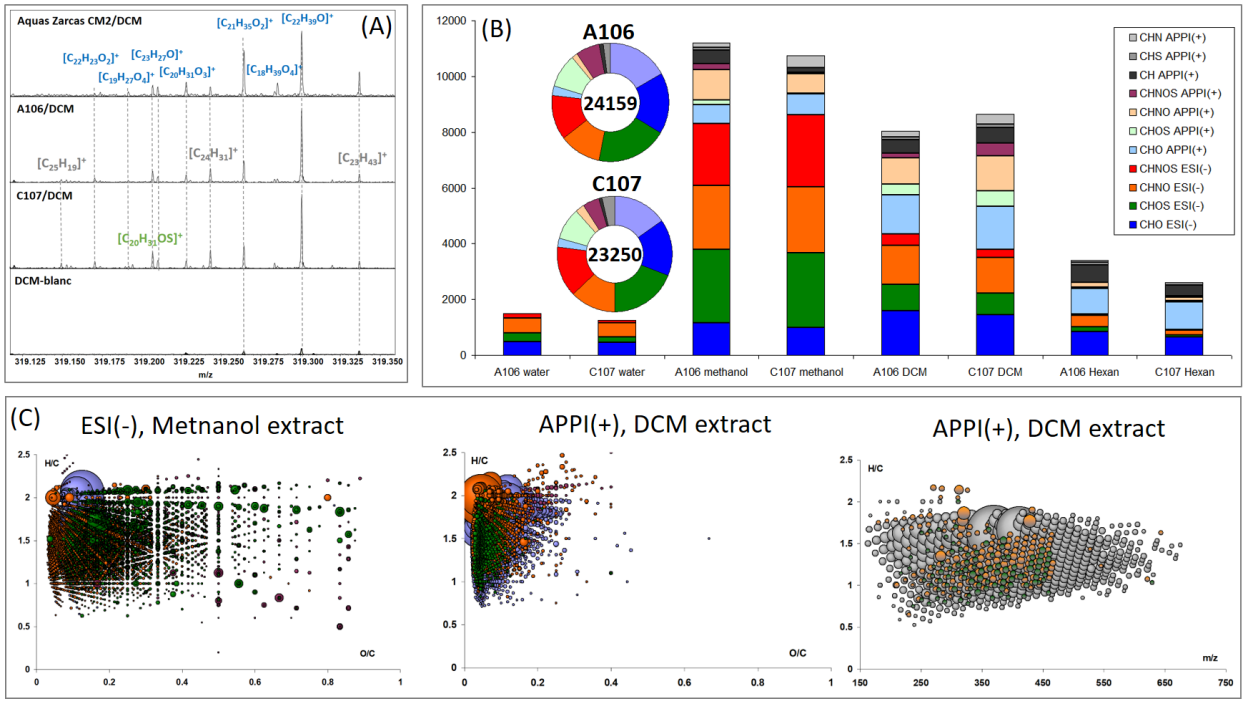

Figure 1. Selected results from the analysis of the solvent extracts of A106 (24159 formula) and C107 (23250 formula) analyzed with Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) in electrospray ionization negative mode (ESI(-)) and atmospheric pressure photoionization (APPI(+)). **(A)** nominal mass 319 details of dichloromethane (DCM) extracts of the CM2 Aguas Zarcas, A106, C107 and the DCM-blank with the annotated elementary compositions as CH, CHO and CHNO from ultrahigh resolution. **(B)** counting of the thousands of elementary compositions in the C, H, O, N, S space as obtained from ESI(-) and APPI(+) and there abundance variations within the different extraction solvents for the A106 and C107 samples. **(C)** visualization of the structural information retrieved from the elementary compositions as van Krevelen diagram plots describing the differences in oxygenations between the two ionization modes ESI(-) and APPI(+) and the profiles of the non-oxygenated CH, CHS and CHN compounds.

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] Danger, G. et al. 2021. *Nat. Commun.*, 12:1. [8] Danger, G. et al. 2020. *Planet. Space Sci.*, 1:55.