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**MOLECULAR GROWTH PATTERN OF SOLUBLE CHN COMPOUNDS FROM RYUGU.** F.-R. Orthous-Daunay<sup>1</sup>, J. Isa<sup>2</sup>, C. Wolters<sup>1</sup>, V. Vuitton<sup>1</sup>, R. Thissen<sup>3</sup>, H. Naraoka<sup>4</sup>, The Hayabusa2-initial-analysis SOM team, The Hayabusa2-initial-analysis core. <sup>1</sup>Univ. Grenoble Alpes, CNRS, IPAG, 38000 Grenoble, France (CS 40700 38058 Grenoble Cedex 9, France (francois-regis.orthous-daunay@univ-grenoble-alpes.fr). <sup>2</sup>Earth-Life Science Institute (ELSI), Tokyo Institute of Technology; Meguro-ku, Tokyo, 152-8550, Japan. <sup>3</sup>Institut de Chimie Physique, Université Paris-Saclay, CNRS, 310 Rue Michel Magat, 91400 Orsay, France. <sup>4</sup>Department of Earth and Planetary Sciences, Kyushu University, Fukuoka 819-0001, Japan.

**Introduction:** Primitive extraterrestrial materials including carbonaceous meteorites contain a variety of organic matter. It has been empirically split into phases depending on the extraction method from the bearing rock. So-called soluble organic matter (SOM) covers everything that can be mobilized in a solvent. The diversity of SOM can be investigated thoroughly down to molecular identification, revealing numerous compounds, some known to be used by terrestrial life and some not. The origin and role in the emergence of life of the SOM are difficult to assess because of multiple synthesis and contamination pathways.

The Ryugu regolith sample brought to Earth by the Hayabusa 2 mission is a unique instance of the material of a C-type asteroid and can be compared to carbonaceous chondrites. For this sample, contamination is under control. The travel from the parent body extraction to the surface of the Earth included collection in situ followed by ~15 months of storage in a very protective environment in the spacecraft sampling module. This mitigates against organic contamination or modification during atmospheric entry.

In this study, we focused on the description of the ‘complexity’ the molecular mixture, probed by high resolution mass spectrometry and chromatographic separation. By mixture complexity, we mean mass spectrometric features that exist only because of the presence of several compounds or types of compounds. The main descriptor of complexity we use is the distribution of masses observed by mass spectrometry and associated with molecular formulas that share molecular characteristics as much as possible (e.g., the mass distribution of all compounds bearing no oxygen, 1 nitrogen atom, with DBE=4 and retention time of  $1200 \pm 100$  seconds). These proxies have been selected because they involve tens of items and are unlikely to be found in two different sample by chance. This statement of ‘complexity’ has been shown to provide robust fingerprints of synthesis processes in applications to polymer science [1], [2].

Recently, the evolution of such distribution has been used to help tracking the effect of aqueous alteration on a carbonaceous chondrite [3] as well as the effect of UV irradiation [4]. These interpretations

relied on the identification of a typical polymerization pattern thanks to a good match with a theoretical model and its alteration, and agreement with independent markers like clay abundance or experimentally received photon dose.

**Experimental Methods:** In order to access the organic compounds in the Ryugu regolith sample, liquid extractions were performed at Kyushu University under the supervision of H. Naraoka. A small aggregate sample of Ryugu grains from the first touchdown site (A0106) were used in this study. The aggregate sample of A0106 (17.15 mg) was extracted sequentially with hexane, dichloromethane (DCM), methanol and H<sub>2</sub>O using a sonicator in a 1.5 mL Teflon vial followed by centrifugation. All extraction procedures were performed on an ISO 5 (Class 100) clean bench inside an ISO 6 (Class 1000) clean room. All glassware used in this study were heated in an oven at 500°C for 3 h prior to analysis to remove possible organic contaminants. Baked serpentine powder (500°C for 3h) was analyzed as a procedural blank.

The chromatographic separation and high-resolution mass spectral analysis was achieved by nano-liquid chromatography coupled with Orbitrap mass spectrometry using electrospray ionization (ESI). The positive mass spectra were acquired by full scan over a range of  $m/z$  62 to 500 with a mass resolution  $m/\Delta m$  at  $m/z$  200. For the rest of this study, we’ll focus on the methanol extracts separated on an Amide HILIC column (75  $\mu\text{m}$  i.d.  $\times$  15 cm) with an acetonitrile to water elution gradient before electrospray ionization (ESI) and Q-Exactive-Orbitrap mass spectrometry.

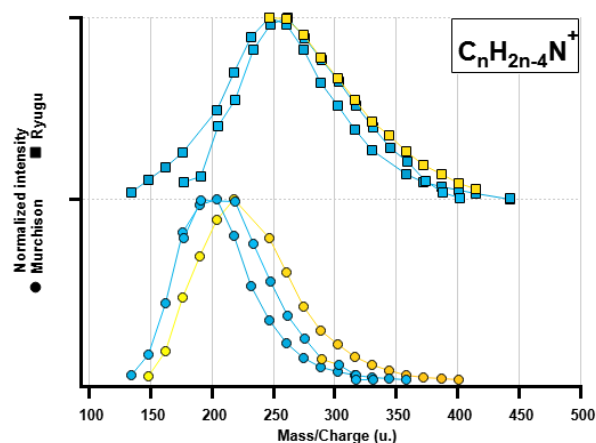
The treatment of the resulting time-versus-mass data field took place at IPAG in Grenoble, France. It consisted of the isolation of each peak and automatic splitting of peaks into so-called plexuses. Those plexuses are used for the complexity description referred to in the introduction. Results from A0106 were compared to Murchison with the same extraction method.

#### **Results and Discussion:**

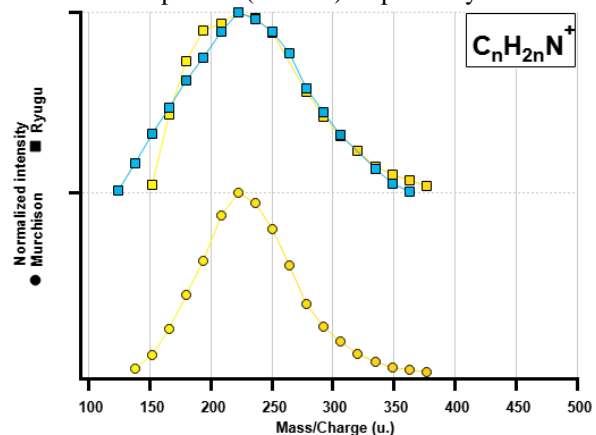
The organic compound complexity of the Ryugu methanol extract is, to first order, like that for extracts from Murchison samples. Specifically, the

chromatographic separation resulted into one single major split between water soluble and water insoluble compounds, as described in [5] for the homologous series of 1-N bearing molecules. This discrepancy affects the whole sample, and compounds as well as plexuses will be referred to as belonging to either the low retention time (low RT, less water soluble) and high RT (more water soluble).

The most remarkable feature of our measurements of the Ryugu sample extract is a ubiquitous, bell-shaped distribution in the  $\text{CH}_2$ -plexuses. This is the typical polymerization pattern found as evidence of pristine preservation of organic matter in Tagish Lake [3]. The pattern is detected in the extract regardless of the retention time (solubility in water) and the saturation degree of the molecules. Figure 1 and 2 show couples of plexuses found in A0106 and Murchison for some 1-N bearing molecules. Comparable features are seen for other chemical compositions.



**Figure 1:** Three polymerization patterns found in Ryugu (square, top) and Murchison (circles, bottom) extracts with DBE=4. Yellow and blue indicate the water-soluble compounds (high RT) and water-insoluble compounds (low RT) respectively.



**Figure 2:** Two patterns found on Ryugu extract as well as one found in Murchison.

For some degrees of saturation, a slight shift toward higher masses is observed for Ryugu's extract compared to Murchison.

Distributions on an asteroid regolith and a meteorite being similar is consistent with a common origin of their constituents. Furthermore, the fact that A0106 is in some cases shifted to higher masses is inconsistent with the prediction from solar wind irradiation or heavy ions bombardment that could have occurred on the asteroid surface.

The mass distribution of various classes of compounds in the Ryugu extract is among the broadest ever measured in laboratory experimental analogues simulating gas phase synthesis, liquid phase polymerization or UV irradiation of ices. This means that to-date, the complexity pattern found in Ryugu extracts is dissimilar from those in any prior terrestrial experiments. The synthesis process responsible for the measurements of Ryugu extracts remains to be determined.

**References:** [1]Glusker, D. L.Lysloff, I.and Stiles, E. 1961.*J. Polym. Sci.*vol. 49, no. 152.pp. 315–334 [2]Weßlau, V. H. 1956.*Die Makromol. Chemie.*vol. 20, no. 1.pp. 111–142 [3]Isa, J.Orthous-Daunay, F.Beck, P.Herd, C. D. K.Vuitton, V.and Flandinet, L. Oct. 2021.*Astrophys. J. Lett.*vol. 920, no. 2.p. L39 [4]Orthous-Daunay, F. R. *et al.* 2019.*Geochem. J.*vol. 53, no. 1.pp. 21–32 [5]Naraoka, H.Yamashita, Y.Yamaguchi, M.and Orthous-Daunay, F. R. 2017.*ACS Earth Sp. Chem.*vol. 1, no. 9.pp. 540–550

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