

The fine structure of Ryugu organic matter unraveled by high spatial resolution monochromated electron energy loss spectroscopy

Christian Vollmer¹, Johannes Lier¹, Demie Kepaptsoglou², Aleksander B. Mosberg², and Quentin M. Ramasse²

¹*Institut für Mineralogie, Universität Münster, Corrensstr. 24, 48149 Münster, Germany*

²*SuperSTEM Laboratory, Keckwick Lane, Daresbury, UK.*

Introduction. The functional chemistry and molecular constitution of Ryugu organic matter (OM) is one of the major science goals of the JAXA Hayabusa 2 mission. The morphological and chemical diversity of extraterrestrial OM is the result of a variety of processes in circumstellar and interstellar environments or the early solar nebula, as well as fluid-induced reactions on asteroids and terrestrial alteration [e.g., 1]. All of these processes can leave fingerprints on the final constitution of OM that have to be disentangled by analysis techniques on Earth. Ryugu OM is of paramount importance in this respect, because in contrast to meteorites found on Earth, terrestrial alteration of Ryugu OM is practically absent [2]. High-spatial resolution investigations such as synchrotron-radiation spectroscopy or electron microscopy on minimally processed Ryugu OM show that it broadly consists of similar organics as detected in other extraterrestrial samples [e.g., 3,4]. However, important differences also exist, such as more dominant aliphatic bonding [5], a higher complexity and heterogeneity of Ryugu OM [6], the close association of more abundant diffuse Ryugu OM with clays and carbonates [7], organic vesicles inside minerals [4], or an exotic NH-rich organic component [8]. This underlines the diversity of Ryugu OM on a μm scale and the need for further high spatial resolution investigations. In this project, we analyzed Ryugu OM by monochromated electron energy loss spectroscopy (EELS) in a dedicated aberration-corrected scanning transmission electron microscope (“SuperSTEM”) equipped with a unique type of spectrometer and detector design [9].

Methods. We investigated two types of Ryugu samples kindly loaned by JAXA during phases AO2 and AO4. The first type are two particles embedded into epoxy and polished during a previous AO (C0033-04 and C0040-02). The second type consists of three pristine particles (A0461, C0396, C0420) that we pressed into high-purity indium foils using a quartz disc. This preparation technique is regularly used by secondary ion mass spectrometry (SIMS) investigations with In and Au foils [e.g., 10]. The pressing procedure leads to some loss of petrographic information, because the material is slightly distorted, but is, in contrast to the epoxy technique, completely iso-chemical. The two preparation techniques therefore also allowed to compare OM chemistry in two types of samples. The samples were then prepared for SuperSTEM analyses using a Hitachi Ethos NX5000 Focused Ion Beam (FIB) system equipped with a third low-energy argon beam enabling the creation of thin lamellae with minimal damage thanks to additional gentle Ga-free polishing. Up to now, we have extracted eight lamellae from the two polished particles and six lamellae from the pressed particles. We located OM-rich regions on the surface of the samples that we targeted for FIB preparation, but we also aimed at nano-scale OM within the lamellae in deeper areas that were unwrapped during the milling process. Ryugu OM was then analyzed on a Nion UltraSTEM100MC “HERMES” aberration-corrected STEM at SuperSTEM Laboratory, operated at 60 kV and in relatively low-dose conditions to reduce beam damage on carbon-based materials. The microscope is equipped with a unique monochromator design for energy resolutions as high as 5 meV and features a Nion IRIS high-energy resolution spectrometer with a high-speed and ultra-low noise Dectris ELA direct-electron detector optimized for EELS. Low-dose imaging modes provide a high spatial resolution even for doses that are $\sim 10^6$ times smaller than standard operating conditions, while distributed dose techniques provide high signal-to-noise analytical data with minimal sample damage.

Results and Discussion. We observe three major morphological forms of OM in our investigated Ryugu FIB lamellae. The first type consists of a large (1-2 μm length and several 100 nm width) irregular vermicular material, that is partly intermixed with small minerals such as sulfides and phyllosilicates. However, the smooth contrast in both bright field and high-angle annular dark field imaging of the major parts of this material indicates that it is chemically homogeneous and amorphous with no internal variations, crystalline inclusions, or subgrains. The second type of OM is an ill-defined nano-sized “diffuse” material ($<< 100$ nm) that is intermingled with the phyllosilicates and also surrounds magnetite and sulfide grains. Some larger veins of framboidal magnetites or single platy magnetites occur in close association with this OM. The third type of OM are globular grains usually only 100 nm large or smaller. Rarely, these globular grains are larger (several 100 nm) or occur in multiglobular clusters. One specific texture of this globular OM are “donut”-shaped regions, where the OM surrounds mineral grains that are morphologically and chemically different to the surrounding matrix. Such globular OM encapsulating mineral phases have also been found in other work [11,12] and are sometimes isotopically anomalous and “twinkie”-shaped [13]. Because morphologies

and chemical compositions are different to the majority of matrix minerals in Ryugu, it can be speculated that this OM represents some pre-accretionary, or even interstellar material [13].

We performed EELS analyses on different domains within those organic grains that were thin enough for 60 kV electrons. We usually acquired spectrum images of core-loss spectra with high energy resolution (< 0.1 eV) at the carbon and nitrogen K-edge, but we also recorded some spectra with low energy dispersions over the whole absorption range up to iron to quantify elemental contents and assess the occurrence of other elements. The quantifications of these high-dispersion energy loss spectra confirm previous investigations showing that Ryugu OM is in general very low in nitrogen (N/C usually < 0.01), but rich in carbon and oxygen. Other elements of possible interest such as sulfur were not observed by our analyses within the detection limit. To assess possible modification or loss of labile functional groups, we acquired spectra in various orders, sometimes starting with N-K, and sometimes with C-K. We did not observe any significant changes in spectral fine structure, and thus in inferred bonding environments, during our acquisition sessions which confirms our low-dose STEM approach.

Carbon K-edge spectra are in general very similar to what is observed in meteorites. There are also no differences in spectra of the two types of our Ryugu samples which shows that with due care the epoxy does not impact the observation of the native OM chemistry and that there is no large-scale contamination in the embedded and polished samples. We find highly aromatic OM as well as OM with the typical “three-band” “IOM-like” signature known from other extraterrestrial samples [3]. However, spectrum imaging also allows to visualize the distribution of the “CO” (ketone/aldehyde) and the “COOH” (carboxylic acid) bands with high spatial resolution, not only showing that these bands are often variable from grain to grain but also within the same grain at the nm scale. This may point to parent-body reactions that added oxygen-bearing functional groups to the OM. We also observe that the 285 eV “aromatic” peak has a variable width across the whole dataset, which implies that the sizes of polyaromatic units range from very small two- or three-ring molecules to large kerogen-like OM [6]. Furthermore, although in general the OM is devoid of this functional group, we detect the 287 eV “aliphatic” bonding peak in some regions, sometimes in close association with mineral surfaces. This underlines the fact that this bonding environment is likely highly heterogeneously distributed in Ryugu OM [e.g., 4, 5], but does not rule out the possibility that it is easily destroyed even by very gentle analysis approaches.

Nitrogen K-edges are usually very noisy even by our dedicated sensitive detector setup due to very low nitrogen contents. In some rare regions, however, we observe some slight enrichments of nitrogen contents with the typical two-band N-K edge signature characteristic of C-N double (imine) and triple (nitrile) bonding. This confirms meteoritic observations that nitrogen in extraterrestrial materials is heterogeneously distributed, which likely happens in the solar nebula or via parent body reactions. Only certain regions in meteorites or micrometeorites have retained some more N-rich OM [e.g., 14, 15].

We also acquired spectrum images in the “ultra-low” energy loss region (< 0.5 eV) only accessible due to our extremely high energy resolution (~ 0.01 eV) and only applied to extraterrestrial materials very rarely up to now [14, 16]. A very rich “vibrational EELS” spectrum with numerous identifiable bands can be directly compared to phonon modes known from conventional IR spectroscopy techniques, confirming the presence of intact functional groups inferred from core-loss analyses. In particular, the distribution of the “ 1000 cm^{-1} ” (~ 0.12 eV) Si-O stretch and the “ 3000 cm^{-1} ” (~ 0.4 eV) C-H stretch modes, and the variation of their intensities, can be mapped across these vibrational spectrum images. These investigations further demonstrate that Ryugu OM is a highly complex material whose evolution and origins can be traced from interstellar to parent body environments.

Acknowledgements. We thank the Japanese Aerospace Exploration Agency (JAXA) for giving us the opportunity to work on these precious samples as well as the Deutsche Forschungsgemeinschaft (DFG) for further funding within project VO1816/3-1. SuperSTEM is the U.K. National Research Facility for Advanced Electron Microscopy, supported by the Engineering and Physical Sciences Research Council (EPSRC, UK) via grant numbers EP/W021080/1 and EP/V036432/1.

References. [1] Pizzarello S. & Shock E. 2017. *Origins of Life and Evolution of Biospheres* 47:249. [2] Nakamura T. et al. 2022. *Science* 379: p. eabn8671. [3] Yabuta H. et al. 2023. *Science* 379, eabn9057. [4] Stroud R. M. et al. 2024. *Meteoritics & Planetary Science* 59:2023. [5] Ito M. et al. 2022. *Nature Astronomy* 6:1163. [6] De Gregorio B. et al. 2024. *Nature Communications* 15:7488. [7] Viennet J.-C. et al. 2023. *Geochemical Perspectives Letters* 25:8. [8] Pilorget C. et al. 2022. *Nature Astronomy* 6:221. [9] Vollmer C. et al. 2024. *Nature Communications* 15:778. [10] Nittler L. R. et al. 2024. *Earth and Planetary Science Letters* 637:118719. [11] Phan V. T. H. et al. 2024. *Meteoritics & Planetary Science* 59:1983. [12] Changela H. G. 2024. *Nature Communications* 15:6165. [13] Kraver C. et al. 2024. Abstract #2674, LPSC 55. [14] Vollmer C. et al. 2020. *Meteoritics & Planetary Science* 55:1293. [15] Rojas J. et al. 2024. *Nature Astronomy*, doi: 10.1038/s41550-024-02364-y. [16] Laforet S. et al. 2024. *The Astrophysical Journal Letters* 963:L45.