Abundance and properties of Ryugu diffuse organic matter

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Initial Analysis studies have revealed that Ryugu regolith particles contain abundant organic carbon (3 wt%) [1,2], and that organic matter has the same range of morphologies as previously observed in primitive chondrites, including solid and hollow nanoglobules, nanodiamonds, dense, irregularly shaped particles, and diffuse materials with poorly-defined boundaries [3]. The diffuse organics form coatings on and fill the space between mineral grains, and intercalate into phyllosilicates. Because the diffuse carbon can be very thin (single nm) and intimately mixed with the nanoscale minerals, especially phyllosilicates, it is below the spatial limit for many techniques. Many analyses focus instead on globules or other organic particles > 200 nm. However, the diffuse carbon represents a substantial portion, possibly 50% or more, of the total organic carbon, and must be considered for a complete understanding of the Ryugu organics. To better understand the abundance and properties of diffuse carbon, we used correlated scanning transmission x-ray microscopy (STXM), scanning transmission electron microscopy (STEM) and nanoscale secondary ion mass spectrometry (NanoSIMS) to examine samples from Chambers A and B.

Figure 1A shows a bright-field STEM image montage of a focused ion beam (FIB) lift-out section from particle A108-?? pressed into a Au mount for NanoSIMS analysis. The BF STEM image shows a mixture sulfides and phyllosilicates with domain sizes of 10s to 100s of nm, but no discernable carbonaceous particles. However, STEM-based energy dispersive x-ray spectroscopy (EDS) mapping of the section Fig. 1B reveals carbon distributed throughout. Quantification of the C:Si molar ratio with Cliff-Lorimer routines for areas > $1\mu m^2$ for no visible nanoglobules indicate values of ~ 0.8 ± 0.3 . Similar STEM-EDS analysis of additional FIB sections shows comparable C:Si ratios, confirming that a large portion of the organic carbon is present as diffuse matter rather than globular carbon in general, not only in this specific particle. However, it is difficult to obtain a precise determination of fraction of the diffuse vs. particulate carbon because the ability to resolve individual organic carbon particles < 100 nm depends greatly on the sample preparation and analysis conditions. In 100-nm thick FIB sections such as this, amorphous carbon particles as large as 50 nm could be hidden in images by the greater intensity variation of the phyllosilicates and sulfides, and only revealed by spectroscopy.

Measurement of the carbon K edge x-ray absorption near edge structure (XANES) with STXM can provide the average functional chemistry distribution of the diffuse carbon (Fig. 1D, Fig. 1E). Notably, there are four prominent peaks in the diffuse carbon spectrum from regions across this FIB section, with the typical aromatic (C=C), ketone (C=O), carboxyl (COOH) groups commonly seen in chondritic IOM, plus the CO₃ carbonate peak. Although the carbonate peak is very intense, the additional x-ray absorption peaks associated with crystalline carbonates are absent. In addition, the STEM-EDS shows Ca is absent, and no signs of Fe or Mg carbonate nanocrystals are observed in the STEM images. XANES spectra extracted from smaller ROIs show variability in the relative intensity of the four functional groups and in some cases distinct aliphatic-rich regions can be found (Fig.1D blue box, 1E blue spectrum).

To better constrain the nature of the diffuse carbon, it is also helpful to analyze samples of particle prepared by ultramicrotome and as demineralized acid-insoluble organic matter (IOM) isolates. Those date are discussed but not shown here due to space constraints, but will be presented at the meeting. Some, but not all, of the diffuse organic matter is preserved in the IOM samples, and comprises the fine-grained porous material referred to as "fluffy", distinct from the nanoglobules. Notably, the prominent carbonate peak, easily observed in the FIB sections, is not present in the IOM XANES data. The CO₃ peak is present though difficult to measure in the XANES data from microtomed

particles. Electron energy loss spectroscopy in the STEM, coupled with EDS, shows the carbonate peak is associated with organic carbon in direct contact with phyllosilicates. This suggests that different portions of the diffuse IOM have distinct chemical origins, with the molecular carbonate signature possibly due to reaction of C-rich fluids with phyllosilicates.





Figure 1. A Bright field scanning transmission electron microscope image montage of a FIB section from particle 108xx. B. Energy dispersive x-ray spectroscopy composite elemental map of C, Si, Au and Ga. The Au is the substrate, and Ga from FIB carbon deposition. C. Extracted sum spectrum from the area outlined in white in (C). D. Scanning transmission x-ray absorption microcopy image of the FIB section at 288.9 eV. E. Extracted normalized spectrum in optical density units from representative regions, revealing pervasive molecular carbonate chemistry and localized enhancement in aliphatic content.

References

Yokoyama T et al. 2022. Science abn7850. [2] Yabuta H. et al. 2022. Abstract #2241. 53d LPSC. [3] Stroud R.
M., et al. 2022. Abstract #2052. 53d LPSC.

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