**ORGANICS AND THEIR RELATIONSHIP TO PHYLLOSILICATES IN RYUGU, ORGUEIL AND IVUNA: IN SITU TEM AND XANES STUDY.**

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**Introduction:** The origin and the further transformation of organic matter in chondrites are major questions in cosmochemistry. For the first time, the Hayabusa 2 sample return mission gives us an opportunity to investigate a "fresh", perfectly preserved sample from a carbon-rich asteroid.

Organic matter in chondrites is known to occur as submicrometric individual particles and as finer scale material intimately intricated with phyllosilicates and is suspected to have been modified by hydrothermal processes [1]. To reveal the nature of the organic-phyllosilicates relationship in Ryugu and compare it to that of Orgueil, Ivuna, we need analytical techniques with spatial resolution better than 100 nm, such as transmission electron microscopy (TEM) and scanning transmission X-ray microscopy (STXM). The former gives access to the organic-inorganic spatial relationship, while the latter gives access to the functional chemistry of the organics.

We analyzed four FIB sections of Ryugu (from-chamber A) prepared by the "Min-pet fine team", as well as one section of Ivuna (Institut of meteoritics, UNM) and 4 FIB sections of Orgueil (MNHN, France). We also compared the *in situ* results to insoluble organic matter (IOM) extracted from Orgueil.

**TEM and STXM-XANES measurements:** TEM data were acquired on a Titan Themis equipped with a four quadrant SDD EDS detector, calibrated for major elements but also for light elements (C, N, O). Quantified maps are produced offering a wealth of data.

All the STXM data presented here were acquired on the HERMES beamline at the SOLEIL synchrotron (www.synchrotron-soleil.fr/en/beamlines/hermes). We collected stacks of images at the carbon K-edge on areas as large as possible, typically 15 to 40 µm$^2$. The data are processed as hyperspectral dataset, using the hyperspy python library. We perform a series of operation (background subtraction, normalization to the carbon amount, fit of Gaussian function) in order to quantify the abundance of some of the functional groups for each pixel-spectra using calibration obtained on standards [2]. This approach allows to shed a new light on STXM-XANES data, in terms of visualization, quantification and statistical assessment of variabilities.

**Carbon spatial distribution:** Organics occurs as micrometer-sized individual particles of more or less rounded shapes. Some nanoglobules are present. However, the mapping by TEM and EDS reveals that carbon is present everywhere, i.e. finely embedded within the phyllosilicates. We call this component diffuse organic matter (OM). It appears that this diffuse OM is the main carrier of organics. In the example below, it represents ~ 80 % of the total carbon (Fig. 1). Similar carbon distribution is also observed in Orgueil and Ivuna.

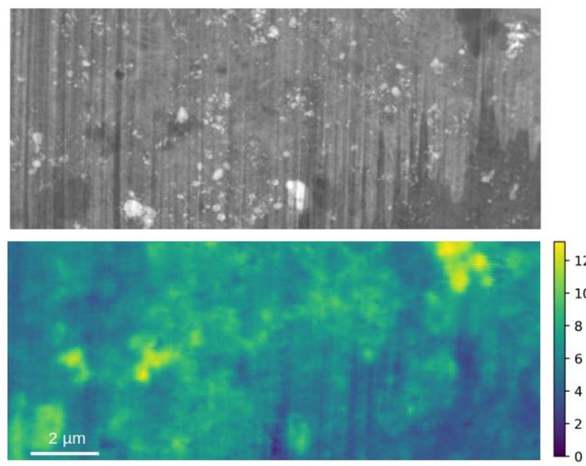


*Fig. 1: Above: STEM-HAADF image. Below: Carbon abundance map (arb. units) based on STXM analysis (spectral integration up to 291.5 eV).*

**Molecular signatures:** In Ryugu and CI chondrites, the organic particles are always more aromatic than their diffuse counterpart, which is in contrast more aliphatic rich. There is a correlation between the abundance of carbon at one pixel and its aromatic content (Fig. 2). There is a strong variability both among the particles and among the diffuse OM. Aromaticity varies between 20-30% for the diffuse OM and 40-50 % for particles.

**Comparison with Orgueil and Ivuna:** Ryugu shares strong connection with CI chondrites from the chemical and mineralogical point of views. However, their XANES spectra shows significant differences (Fig. 3). In CI chondrites, the organic particles are richer in oxygenated functional groups such as ketones and/or phenols. The diffuse OM in CIs is richer in carboxylic and ketone+phenol functional groups and depleted in aromatics compared to Ryugu.

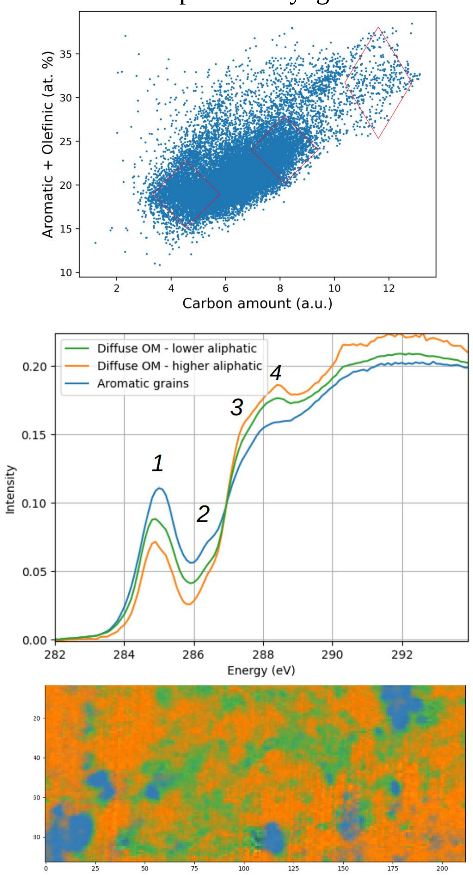


*Fig. 2: On top: Carbon content vs. aromatic content (at.%) at each pixel. Particles plot apart from the diffuse OM. Center: Carbon K-edge spectra of the organic particles and the two end-members of the diffuse OM. [1: aromatics+olefinics; 2: ketones+phenols; 3: aliphatics; 4: Carboxylics]. Bottom: component map obtained based on linear fitting of the above spectra.*

**Orgueil IOM:** The IOM resembles the diffuse OM, despite a slightly higher aromatic content. In any case, the IOM is closer to the diffuse component than to the organic particles. Therefore, we identified at least three chemically different components in Orgueil: i) minor aromatic-rich particles (see also [3]), mixed in various amounts with the other components, ii) IOM-like molecules, present everywhere and iii) an aliphatic-rich (and soluble?) component.

**Discussion:** A number of observations points to a more oxidized state of the CI chondrites compared to Ryugu (CI chondrites show absence of nanosulfides, presence of ferrihydrite, higher $Fe^{3+}$ content of the phyllosilicates). One key question is whether these differences are due to terrestrial weathering only or, in contrast, result -at least in part- from different alteration conditions on their respective parent body. Sulfates have been shown to appear on the surface of the sample during curation, and are undoubtedly terrestrial [4]. However, the other differences are not definitely proven to be terrestrial.

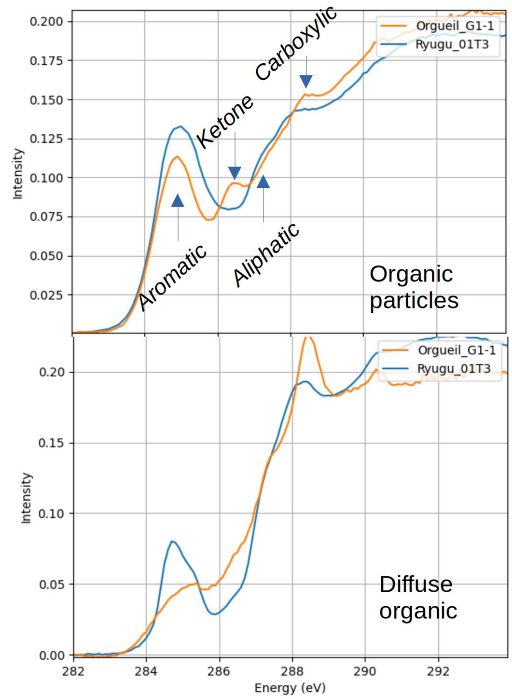


*Fig. 3: Spectra of the particles (above) and diffuse OM (below) from averaged areas of Ryugu (blue) and Orgueil (orange). Clear differences are present between Ryugu and Orgueil that are mostly due to the oxygenated functional groups (ketone, phenol, carboxylic).*

The clear differences observed for the organic matter point to a higher abundance of oxygenated functional groups in Orgueil. This strengthens the case for a generally less oxidized state of matter in Ryugu. We thus reach two hypothetic conclusions, opposite to each other, but important in both case:

- If one assumes that OM in CI chondrites was weathered on earth, then it would be the first evidence of strong terrestrial alteration of organics. It would thus require a reassessment of previously obtained conclusions for all other chondrites.
- If one assumes that these differences are indigenous, then it would imply that CI-like parent bodies experienced varied hydrothermal conditions and that organics are highly sensitive to these variations.

**References:** [1] Le Guillou C. et al. (2014) *GCA*, *131*, 368-392. [2] Le Guillou C. et al. (2018) *Anal. Chem.*, *90*, 8379-8386. [3] De Gregorio et al. (2013) *MAPS*, 48, 904–928. [4] Gounelle et al. (2001) *MAPS*, *36*(10), 1321-1329.