A Comparative Carbon-XANES and -EELS study of Organic Material from Asteroid 162173 Ryugu and Ivuna.

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Introduction The arrival of samples from carbonaceous asteroids 16273Ryugu [1] 101955Bennu [2] provide a window into early Solar System organic evolution on a known asteroid. Organic material (OM) from carbonaceous asteroids is currently most accurately characterised *in situ* by coordinating synchrotron based scanning transmission X-ray microscopy (STXM) with transmission electron microscopy (TEM) on samples. Organic functional chemical variations can be measured by Carbon K-edge X-ray absorption near edge structure (XANES), whilst organic morphology and its mineral setting is characterised by subsequent TEM. Carbon-energy electron loss spectroscopy (EELS) offers the same possibility as C-XANES but with the advantage of being performed in a stand-alone TEM. Here we compare C-EELS with -XANES on OM from Asteroid Ryugu and the Ivuna CI chondrite prepared by dual beam focused ion beam (FIB)- scanning electron microscopy (SEM) and ultra microtome to assess the effects of electron beam dosage by all techniques.

Methods Two adjacent ~100 nm thick lamella were prepared using FIB-SEM (Fig. 1). Lamella 1 was prepared using Xe-plasma FIB-SEM with the Helios 5 Hydra DualBeam (CEITEC, Masaryk University (MUNI), Czechia) and analysed by TEM-C-EELS with the JEOL ARM200CF (ePSIC, Diamond Light Source, UK), followed by STXM-XANES at Beamline BL19A of the KEK Photon Factory, Japan. Lamella 2 (Fig. 1) was prepared by Xe-plasma FIB-SEM with the TESCAN AMBER X (TESCAN ORSAY holding a.s., Brno, Czechia) followed by STXM-XANES (i.e. no TEM) at the photon factory. Microtome samples of Ivuna were prepared using methods in [3] at CEITEC-MUNI with a Leica UC7. Organic material in a lamella from Ryugu grain C0105-03500000 provided by the Hayabusa-2 preliminary examination SAND team prepared using the University of Leicester's FEI Quanta 3D was also measured by C-EELS at ePSIC.

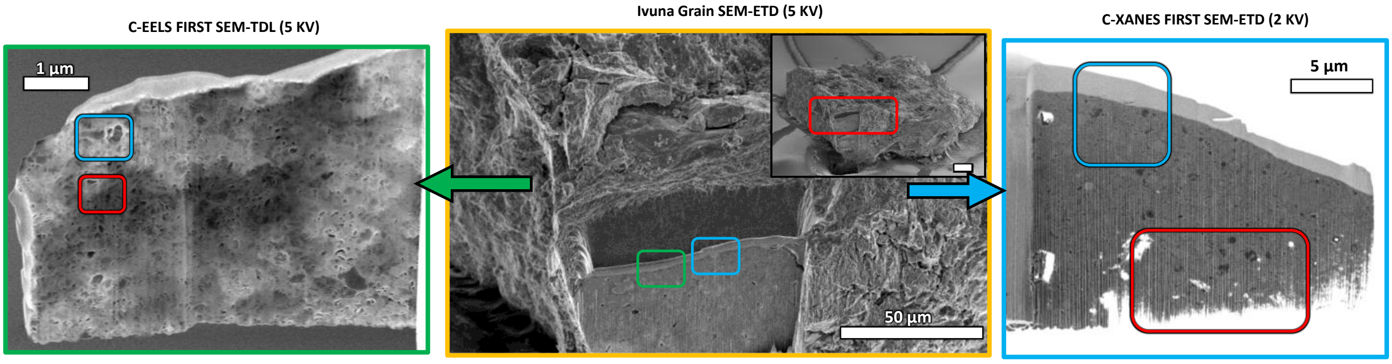

Figure 1. SE image of a grain of Ivuna on carbonate sticky and coated with 5 nm Au. Large cross section at the front of the grain was the location where 2 adjacent FIB lamella were extracted: one with C-K edge EELS then XANES (left extraction) and the other direct XANES (right lamella). Blue and red rectangle mark the ROIs where the EELS and XANES maps were taken (Fig. 2).

Results Eelectron beam exposure to chondritic OM during SEM, TEM and EELS changes its functional chemistry, in both its macromolecular and particularly in soluble/insoluble form within phyllosilicate (Fig. 2). A peak at ~290.4 eV attributed to carbonate -O-C=O-O- bonds is observed under 200 KV electron doses by TEM, STEM imaging and by EELS spectral mapping. This feature is absent from microtome samples measured by XANES. A bulge in the EELS spectra consistent with amorphous an carbon σ * peak (~288 – 315 eV) is found in organic particles. The carboxylic (288.5 eV) peak found in diffuse OM within phyllosilicates (e.g. Graph 2) is replaced by the carbonate one at 290.4 eV (Graphs 1 & 4).

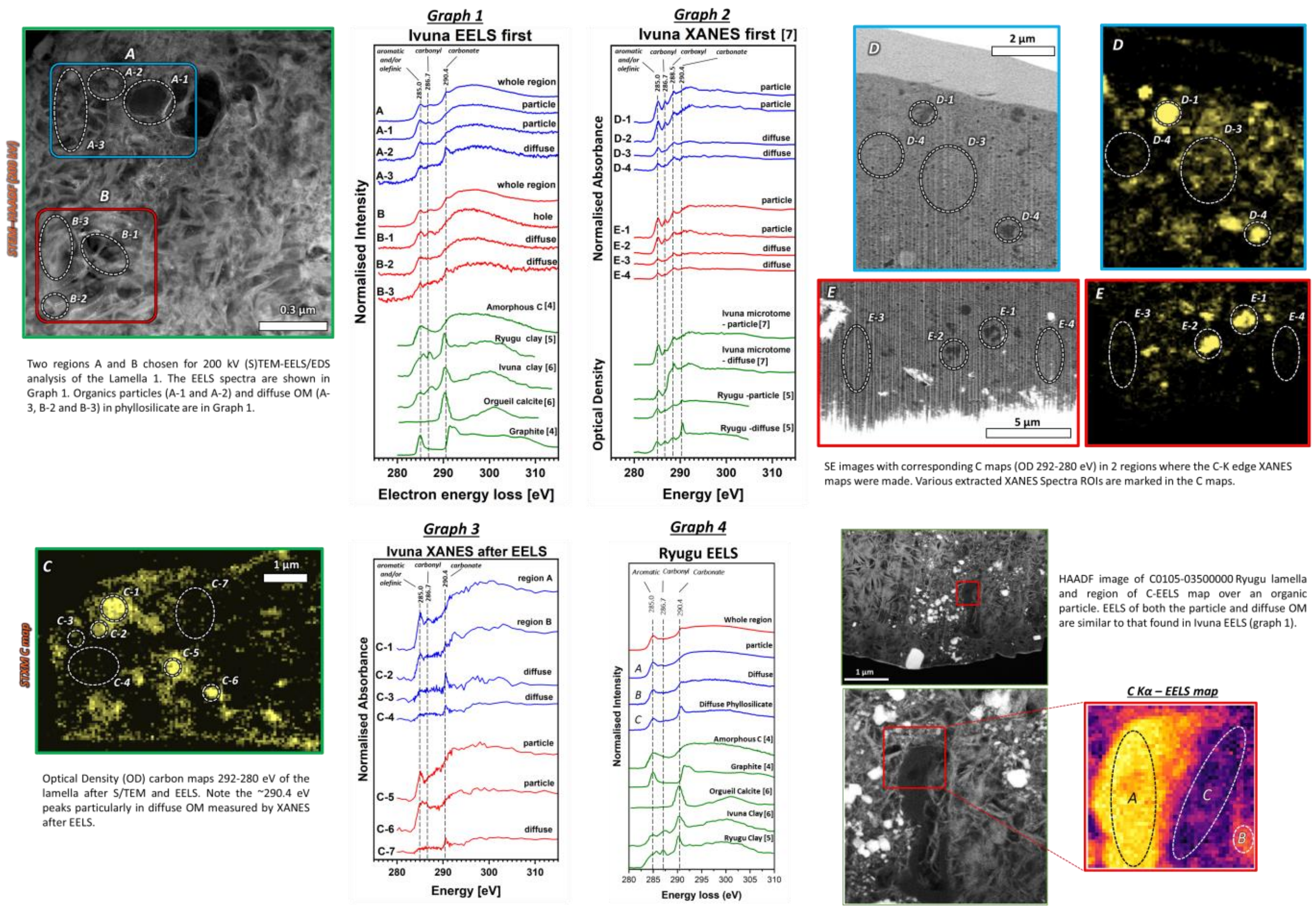

Figure 2. Carbon-EELS and -XANES on the Ivuna lamella and Ryugu sample.

Discussion The amount of radiation damage has been shown much lower in STXM-based XANES spectroscopy than in TEM-based EELS [8]. Our observations particularly of organo-carbonate bonding in diffuse OM shows its formation sensitive to e-beam exposure rather than X-ray exposure. This was also identified by [9] in terrestrial coals imaged with 5KV SEM during FIB lamella preparation. Furthermore, Yabuta et al. 2023 [5] reported the lack of any carbonate peak in microtome samples measured by XANES, but occurring in FIB sections with organic particles and diffuse OM in Ryugu samples (referred to as clay bound OM in their study). Our microtome samples of CI chips also lack this peak in any XANES measurements, suggesting that e-beam exposure during FIB-SEM preparation also formed the organo-carbonate bonds observed in previous STXM studies [e.g. 10] and recently in [5]. However, potential mixture of indigenous organo-carbonate cannot be ruled out.

Conclusions Chondritic OM is sensitive to electron radiolysis particularly by the formation of organo-carbonate bonding, although the formation mechanism is unclear. Carbon-EELS of organic particles also convolute the 288.5 eV carboxyl peak by an amorphous bulge. This means that synchrotron XANES coordinated with subsequent TEM more accurately provides a measure of functional chemical variation of chondritic OM than EELS-TEM.

FIB-SEM lamella preparation of chondritic matrices require electron energies lower than 5KV (e.g. 1.5KV) during imaging to minimize e-beam damage by radiolysis. It is unclear though whether SEM lower than 5KV could prevent the formation of this carbonate -O-C=O-O- ~290.4 eV feature, and how other regions of C-XANES and -EELS spectra are effected.

References [1] Yada T. et al. 2014. Nature Astronomy 6:214-220. [2] Lauretta et al. 2015. Meteoritics & Planetary Science 50:834-849. [3] Noguchi et al. 2020. Life 10(8):135. [4] Yuan J. & Brown L. M. 2000. Micron 31: 515-525 [5] Yabuta H. et al. 2023 Science 679:6634. [6] Garvie and Buseck 2007. Meteoritics & Planetary Science 42(12):2111-2117. [7] Changela. H. G. et al. 2023. Abstract #2848. 54th LPSC. [8] Wang J. et al. 2009. Journal of Electron Spectroscopy and Related Phenomena 170:25-36. [9] Bassim N. et al. 2012. Journal of Microscopy 245:288-301. [10] Changela. H. G. et al. (2018) Meteoritics & Planetary Science 53:1006-1029.

Acknowledgements Special thanks to the Hayabusa-2 preliminary examination SAND team for useful discussions and access to Ryugu sample C0105-03500000 in this study. We thank Diamond Light Source and electron Physical Imaging Centre ePSIC (instrument EO1, proposal MG30752). We also thank TESCAN GROUP, a.s. for use of their instrumentation and Dr. Hana Tesarova for her help. We acknowledge CF CryoEM of CIISB, Instruct-CZ Centre, supported by MEYS CR (LM2023042) and European Regional Development Fund-Project UP CIISB" (No. CZ.02.1.01/0.0/0.0/18_046/0015974).We thank KEK Photon factory for use of Beamline BL 19A for STXM.