FIB Tomography-STXM-TEM on organic material from Hayabusa-2 grain A0083.

H. G. Changela[1], Y. Kebukawa[2], L. Petera[1], M. Ferus[1] E. Chatzitheodoridis[3], L. Nedjl[4], R. Nebel[1], Z. Hlavenkova[5], J. Moravcova[5], P. Krepelka[5], R. Holbova[5], J. Novacek[5], T. Samoril[6,7], K. Sobotkova[6], H. Tesarova[6] and D. Zapotok[8]

1 J'Heyrovski Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czechia. 2 Tokyo Institute of Technology, Tokyo, Japan. 3 National Technical University of Athens, Greece. 4 Bruno University of Technology, Czechia. 5 Central European Institute of Technology Masaryk University, Brno, Czechia. 6 Central European Institute of Technology Nano, Brno, Czechia. 7 TESCAN GROUP a.s., Brno, Czechia. 8 TESCAN USA Inc, Pennsylvania, USA. Email: changela@unm.edu

Introduction The success of the *Hayabusa-2* mission provides unique insight into prebiotic evolution from a known asteroid free from terrestrial contamination. Asteroid 16273Ryugu (Ryugu here on in) is of CI (Ivuna-type) composition, lacking any distinct chondrules and calcium aluminium inclusions, and is composed mainly of secondary minerals including phyllosilicate, carbonates, (Fe, Ni) sulphides, Fe-oxides and phosphates [1]. Organic material (OM) also pervades Ryugu, characteristic of OM found in primitive chondrite matrices. Micron to submicron organic particles (OPs) – macromolecular organic objects completely surrounded by inorganic material – make up the major mass fraction of OM [e.g. 2], consistent with insoluble organic matter (IOM). A volumetrically diffuse organic component aromatic-poorer and carboxylic-richer than OPs found within chondritic hydrated silicates [3] also occurs in Ryugu [4]. This study is on a grain from the 1st touch-and-go (TAG) site on Ryugu, characterising the distribution, functional chemical variation and mineral setting of OM *in situ*.

Samples & Methods Grain A0083 (Radegast here on in) is a 1.3 and 1.7 mm grain from Chamber A of the *Hayabusa-2* collector TAG site. Radegast was prepared and analyzed taking an approach of minimal damage and material loss for characterisation. Radegast was picked up with vacuum tweezers and placed on a clean Au base with an ~2 mm divot, mounted on an Al stub. An ~1.5 mm circular hole in clean Al foil was placed over the top of Radegast and fastened at the edge of the stub, exposing the grain out of the hole and securing it. This has the advantage that the grain can be turned over by lifting the foil for any further characterization whilst leaving the grain intact. Focused Ion Beam (FIB) ~100 nm lamella of Radegast were prepared for Scanning Transmission X-ray (STXM) and Transmission electron Microscopy (TEM). The TESCAN *AMBERX* and *LYRA3* at TESCAN GROUP and the Central European Institute of Engineering & Technology (CEITEC)-nano, respectively, were used to compare the effects of Xe+ plasma FIB with Ga+ FIB lamella preparation on the STXM measurements of OM in the samples. To minimize sample information losses by destruction from the traditional FIB lamella sample preparation, FIB tomography was performed from the edge of the grain during milling prior to lift-out. Grains of Ivuna were also embedded in molten S for ultramicrotome using methods in [5]. 110 nm samples were cut using a Leica UC7 at CEITEC-Muni to compare the STXM measurements between Xe-, Ga- FIB lamella and microtome samples. Scanning Transmission X-ray Microscopy (STXM) measurements were made at BL 19A at the Photon Factory, Japan. S/TEM was performed with the CEITEC-MUNI Thermofisher *Talos* F200C, and the J'Heyrovski Institute's JEOL 2100.

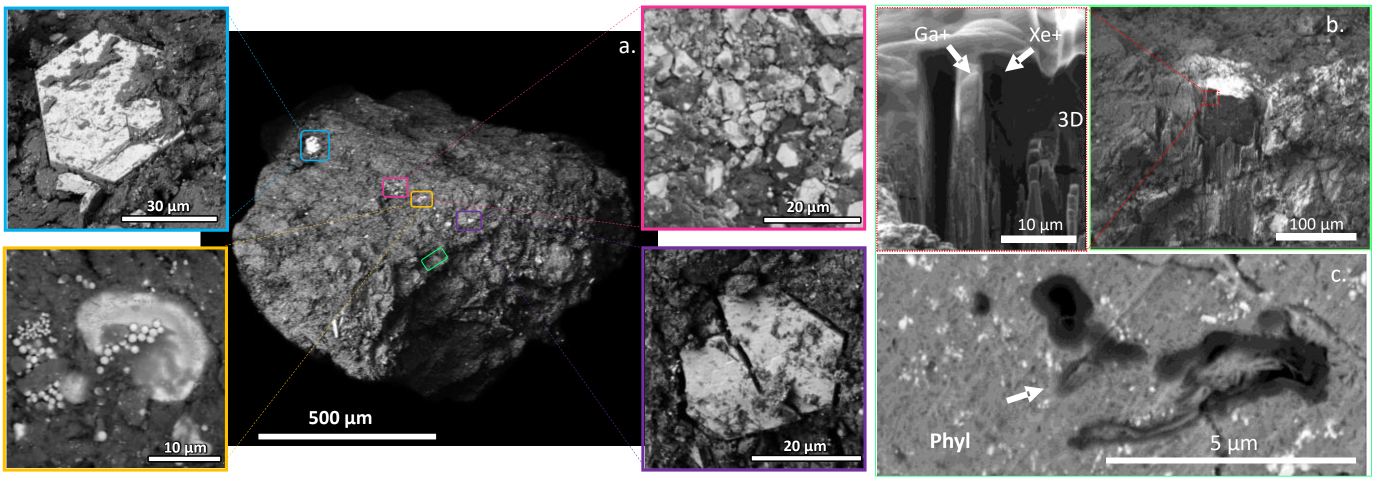


Figure 1. BSE images of particle A0083 (Radegast). (a) Entire image of Radegast. Insets show various phases on the top of the particle. Blue and purple are Fe-Sulphides (probably hexagonal pyrrhotite) Yellow is Fe-oxides (magnetite). Pink is a mixture of minerals. Green rectangle shows the region of tomography from the top edge of Radegast. (b) Tomography and Lamella liftout regions. Inset show the milled regions for tomography and lamella liftout made between Ga+ (*LYRA3*) and Xe+ (*AMBERX*) FIB instruments. (c) A Coarse grained organic particle (arrowed) from 1st cross section of tomography volume.

Results & Discussion Radegast displays CI composition similar to samples from both TAG sites, suggesting widespread alteration across the asteroid. Organic particles are mostly submicron with IOM morphology. Some coarser OPs identified in the tomography completely surround phyllosilicate, suggesting post-formation of the primary mineralogy within them (Fig. 2).

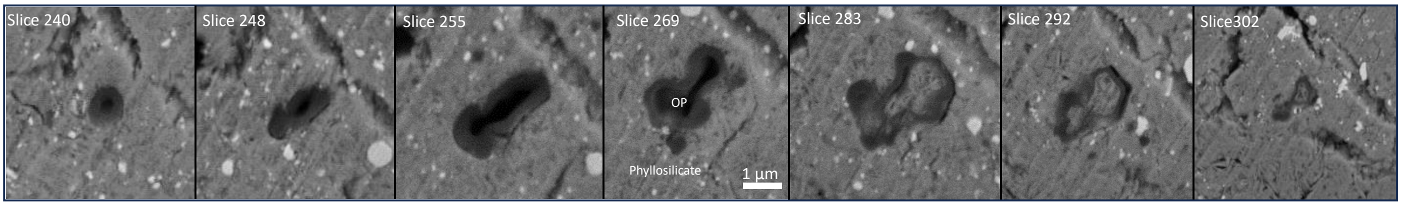
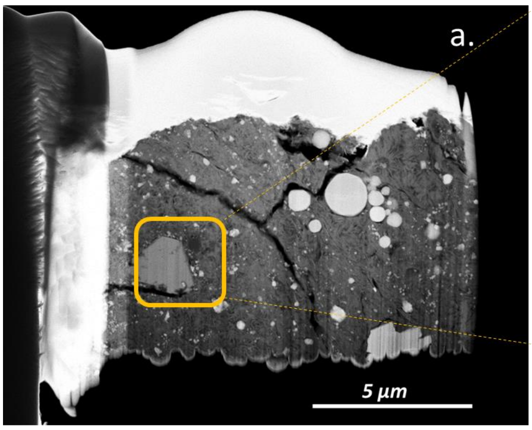


Figure 2. FIB Tomography slices of a coarse-grained organic particle in Radegast.

Organic particles and diffuse OM are consistent between FIB and microtome samples of Ivuna (diffuse OM in microtome samples have not been previously reported), implying that both Ga+ and Xe+ FIB preserve the functional chemistry of OPs and diffuse OM (Fig. 3). Carbon-XANES shows that individual OPs in closer proximity to one another are more equilibrated, suggesting that the alteration recorded in the grain was a common process evolving them. They have aromatic-rich, 3-peak spectra similar to the 'aromatic' particles in [4]. Notably, OPs in Ivuna are aromatic poorer, with lower aromatic/ketone ratios than those in Radegast and other Ryugu samples. Aromatic-rich OPs are however in higher abundance in the CR1 GRO 95577 [2] and Orgueil [3] than the type 2/3 carbonaceous chondrites. Diffuse OM (aromatic-poorer and aliphatic/carboxylic-richer OM than OPs) in Radegast is also more similar to diffuse OM found in Ivuna (Fig. 3) and GRO 95577 [2], with higher carboxyl/aromatic peak ratios than type 2/3. It is also similar by being in phyllosilicate rather than amorphous hydrated silicates found in type 2/3 chondrites. SEM and TEM (Fig. 5) shows coarse and finer domains of phyllosilicate. Diffuse OM occurs in both domains of phyllosilicate but is less concentrated in the coarse domains than the finer ones that are also intermixed mostly with Fe and Fe,Ni-rich sulphides (Fig. 3a). HRTEM shows the coarse domains as mixed layers of serpentine and smectite, consistent with previous studies [6].



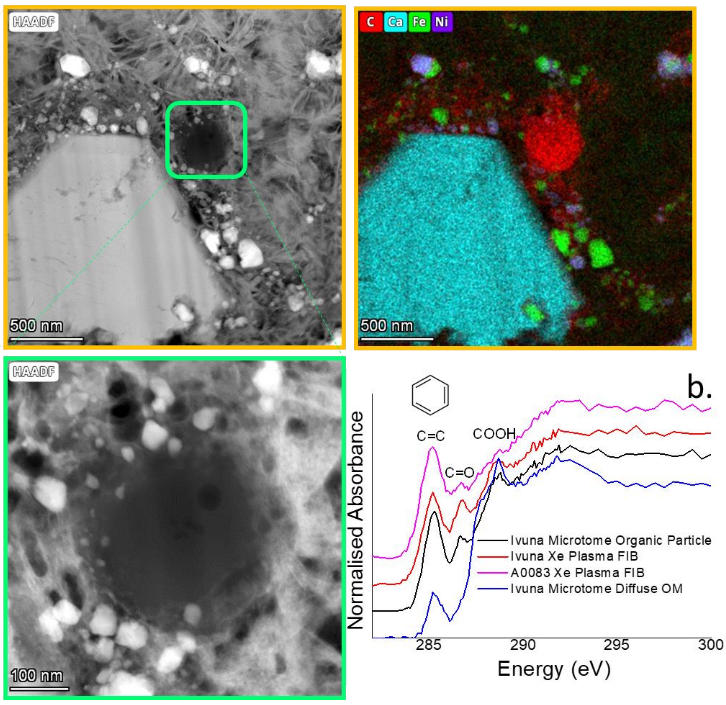


Figure 3. STXM-TEM on Radegast. (a) HAADF image of Xe+ prepared lamella. Inset is magnified region where the C-XANES Stack was made, showing a calcite grain adjacent to an OP. (b) C-XANES of OPs and diffuse OM in Ivuna and Radegast. The OP in (a) is pink. Note the higher aromatic/ketone ratio of OPs in Ryugu than in Ivuna.

Conclusion Organic material in Radegast evolved into aromatic-rich organic particles and aliphatic/carboxyl-rich diffuse OM by alteration on Ryugu, similar to those found in type C1 planetary materials.

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Acknowledgements This research was funded by the Czech Science Foundation Project Reg. No. 21-11366S with financial support by ERDF/ESF Centre of Advanced Applied Sciences (CZ.02.1.01/0.0/0.0/16_019/0000778). 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 Takis Theodossiou of the Greek Meteorite Museum for the curation of the Ivuna meteorite.