FIRST IDENTIFICATION OF INDIGENOUS ORGANIC MATTER ALONGSIDE WATER IN ITOKAWA PARTICLE RETURNED BY THE HAYABUSA MISSION. Q. H S. Chan[1,2], R. Brunetto[3], Y. Kebukawa[4], T. Noguchi[5], A. Stephant[1], I. A. Franchi[1], X. Zhao[1], D. Johnson[6], N. A. Starkey[1], M. Anand[1], S. S. Russell[7], P. Schofield[7], M. C. Price[8], K. H. McDermott[8], R. Bradley[9], J. D. Gilmour[9], I. Lyon[9], P. J. Withers[9], M. Lee[10], Y. Sano[11] and M. M. Grady[1,7], [1]The Open University, Walton Hall, Milton Keynes MK7 6AA, UK (Queenie.Chan@open.ac.uk; Queenie.Chan@rhul.ac.uk), [2]Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK, [3]Université Paris-Saclay, CNRS, Institut d'Astrophysique Spatiale, 91405, Orsay, France, [4]Yokohama National University, Yokohama, 240-8501, Japan, [5]Kyushu University, Fukuoka, Japan, [6]University of Exeter, UK, [7]Natural History Museum, UK, [8]University of Kent, UK, [9]University of Manchester, UK, [10]University of Glasgow, UK, [11]University of Tokyo, Japan.

Introduction: The first Hayabusa mission returned samples from the near-Earth S-type asteroid 25143 Itokawa to Earth in 2010 [1]. Despite a lithology related to ordinary chondrites (OCs) that typically have low organic contents, several Itokawa particles were found to contain organic matter (OM) [2-5]. The origin of the observed OM has yet to be established with certainty, as the carbon and hydrogen isotopic compositions of the OM fall within a zone that overlap with both terrestrial and extraterrestrial OM [2, 6].

Itokawa particle RA-QD02-0162 provides a unique opportunity to investigate the H_2O and organic contents of Itokawa in a single study. This sample is polycrystalline, containing a wide distribution of structurally distinct OM across the particle. The relatively large sizes of some nominally anhydrous minerals also enable the study of the abundance and isotopic composition of the H_2O (as hydroxyl group).

Methods: The Itokawa particle was transferred from the JAXA glass slide with a micromanipulator and then mounted into indium on an aluminium stub. Spot and point-by-point mapping Raman spectroscopic analysis was conducted using a Jobin-Yvon Horiba LabRAM HR Raman microprobe at the Open University using a 514 nm laser for which the power was maintained at ~60 μW. The H isotopic compositions and abundances of H_2O, and H, C and N isotopic compositions of the OM were obtained by a NanoSIMS 50L ion microprobe. For organic analysis, the probe currents were 2 pA for C and N isotopes, and 4 pA for H isotope, respectively, rastered on an 8 × 8 μm² surface of the particle. For H_2O analysis in silicates, a 16 keV Cs^+ primary beam of ~600 pA was rastered on a 6 × 6 μm² surface of the particle. Blanking was made and only the 3 × 3 μm² (25%) interior of the surface area was analysed. Subsequently, energy dispersive X-ray micro-analysis with an accelerating voltage of 5kV was carried out with a Phenom XL Scanning Electron Microscope. Three 3 μm focused ion beam (FIB) sections will be lifted from the particle at Kyushu University, and the molecular structure of the OM will be analysed with Fourier-transform infrared (FTIR) microspectroscopy at the SMIS beamline of the synchrotron SOLEIL, and scanning transmission X-ray microscopy (STXM) coupled with X-ray absorption near edge structure (XANES) at BL-19 of the Photon Factory, High Energy Accelerator Research Organization.

Results and Discussion: The Itokawa particle RA-QD02-0162 was given the nickname "*Amazon*", to recognise its unique shape that was preserved after soft pressing into indium (Figure 1).

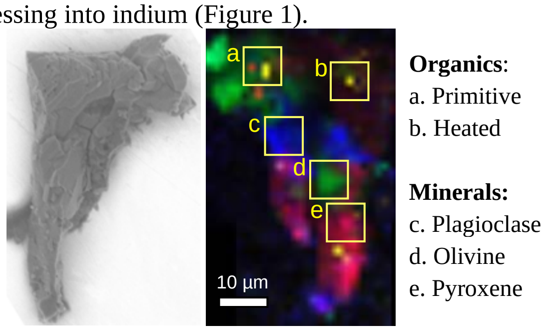

Figure 1. SEM (left) (JAXA) and Raman (right) maps of *Amazon* showing mineralogical distribution of olivine (green), plagioclase (blue), pyroxene (red) and OM (yellow). Five ROIs (a-e) are marked by the yellow boxes.

Raman spectroscopy. The compositions of the main mineral components can be determined based on the peak positions of the characteristic Raman modes [7-9]. *Amazon* is composed predominantly of olivine ($Fo_{77\pm8}$) and orthopyroxene (En_{80}), with a small contribution of albite (Figure 2). The mineral compositions of *Amazon* is comparable to that of L or LL chondrites, and that reported for Itokawa samples based on chemical and isotopic analyses [10, 11].

Based on the observation of the Raman parameters (e.g. the peak locations and widths of the first-order defect (D) band at ~1350 cm^{-1} and the graphite (G) band at ~1580 cm^{-1}) [12], a significant variety of carbonaceous materials has been observed in *Amazon*. The carbonaceous materials include primitive and unaltered OM (ROI-a) that shares similarity with the IOM in primitive (CI,CM,CR) carbonaceous chondrites, as well as OM that has been heavily graphitised (ROI-b) (Figure 3). The Raman parameters of the most heated OM in *Amazon* are comparable to that of the

IOM in CV3.2 Allende, CO3.7 Isna and CH4 Indarch, suggesting peak metamorphic temperatures of as high as 590−640 °C [13] and the onset of large-scale graphitisation. The thermal history of the heated OM in *Amazon* is comparable to the high peak metamorphic temperatures estimated for Itokawa (600−800 °C), which is equivalent to the LL4 to LL6 lithology [11].

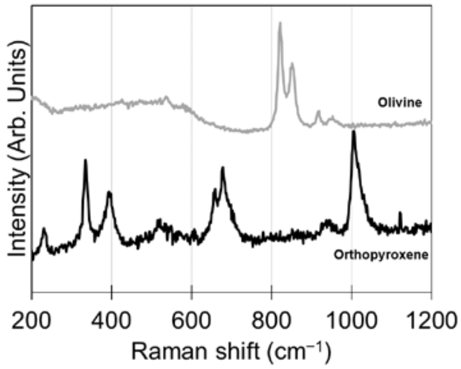

Figure 2. Representative Raman spectra of olivine and orthopyroxene in *Amazon*.

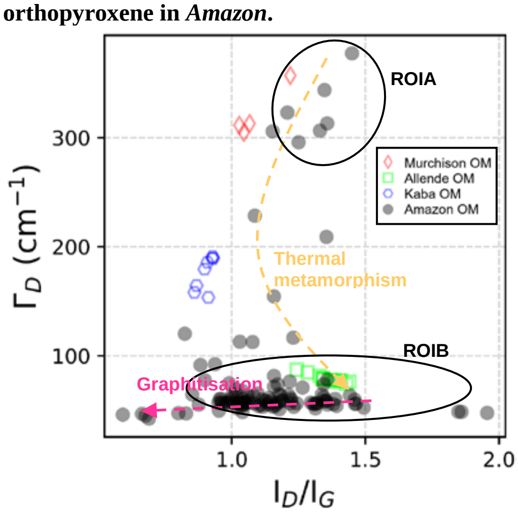

Figure 3. Raman D and G bands intensity ratio (I_D/I_G) plotted against D band width (Γ_D).

H_2O abundance and isotopic composition. We have obtained the H_2O abundances for the pyroxene, and for the first time, for the olivine and albite grains in Itokawa particle. The water contents of olivine and pyroxene are 242 ppm and 250 ppm, respectively. While the H_2O abundance of olivine is comparable to that of OC olivine, *Amazon* pyroxene contains lower H_2O abundance than typical OC pyroxenes. This likely suggest a lower initial ice/rock ratio, or a smaller size of the Itokawa parent asteroid and thus a faster rate of water loss. The δD value of olivine (δD = −95‰) is similar to that reported for olivine in OCs and pyroxene in Itokawa [14]. Albite, on the contrary, has a high H_2O abundance (1,278 ppm) with a δD value of −208‰, which likely indicates that the Itokawa asteroid has undergone low-T hydration by isotopically evolved or extraneous H_2O [15].

H,C,N isotopic compositions of the OM. We have obtained the H,C,N isotopic compositions for the primitive OM (ROI-a) in *Amazon*. The OM is heterogeneous at the sub-micrometre level. The primitive OM exhibits clear extraterrestrial isotopic signatures (δD = +3,820‰; $\delta^{13}C$ = −18‰; $\delta^{15}N$ = +212‰). Despite the comparable δD and $\delta^{13}C$ values of the OM in *Amazon* to OCs, the $\delta^{15}N$ is higher than that typically observed for OCs ($\delta^{15}N$ = −47 to +36‰), and is similar to that of CRs ($\delta^{15}N$ = +153 to +309‰) [16].

OCs and CRs share notable similarities in their isotopic compositions, e.g., (1) δD of the IOM from the most primitive OCs are comparable to that from the CRs, (2) the $\delta^{13}C$ values of OC and CR become heavier with increasing petrologic type. Our findings support the view that Itokawa has recorded the dynamical history of small bodies in the solar system via material mixing between S- and C-type asteroids [17]. It is consistent with a rubble-pile asteroid model of Itokawa, which has re-agglomerated primitive OM with material that has been severely altered by the impact process and extraneous H_2O. For the heated OM, since it is either buried deep below the surface of the particle, we will obtain its isotopic compositions after the ROI-b section is subsampled by FIB.

Implications: This study demonstrates that the current instrumental capabilities are able to unravel the complex formation and evolution histories of multiple components of volatiles and organics in very small samples, and underscores the importance of sample return missions. This analytical protocol is suitable for analysing samples returned by future missions, e.g., Hayabusa2 and OSIRIS-REx.

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