COORDINATED ORGANIC ANALYSES OF HAYABUSA CATEGORY 3 CARBONACEOUS PARTICLES

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Introduction: The first Hayabusa mission has returned to Earth samples from the near-Earth S-type asteroid 25143 Itokawa in 2010 [1]. 943 particles have been picked up and kept in a ISO 6 cleanroom at the Planetary Material Sample Curation Facility of JAXA. Despite a lithology related to ordinary chondrites that typically have low organic contents, 64 particles from the collection are composed predominantly of carbonaceous material [1, 2]. However, the small sizes (~20–200 µm) of the carbon rich 'category (cat.) 3' particles make the characterisation of their organic contents and determination of their origins (terrestrial vs extraterrestrial) challenging [2-5]. In this work, we explore the origins of five Itokawa cat. 3 carbonaceous particles via coordinated analyses of their soluble and insoluble organic contents.

Samples and Analytical Techniques: Five cat. 3 Itokawa particles (RA-QD02-0012, RA-QD02-0078, RB-CV-0029, RB-CV-0080 and RB-QD04-0052) were allocated for this study. Meteorite samples including CM2 Murchison, ordinary chondrites (falls) with similar lithology as Itokawa – LL3.6 Parnallee and LL5 Alta'ameem, and an insoluble organic residue of Murchison were analysed alongside the Hayabusa samples. The Itokawa particles and the meteorite samples of equivalent sizes were picked by a micromanipulator and pressed flat with a spectroscopic grade sapphire window into high-purity gold foils. The samples were analysed with Fourier-transform infrared (FTIR) microspectroscopy at the SMIS beamline of the synchrotron SOLEIL with Nicolet 5700, 8700 FTIR spectrometers coupled to Continuum microscopes and a iS50 with a Nic-Plan IR microscope, and a Cary 670 IR spectrometer coupled to a Cary 620 IR microscope, operating in reflectance mode. Spot and point-by-point mapping Raman spectroscopic analyses were conducted using a Jobin-Yvon Horiba LabRAM HR Raman microprobe at NASA JSC and the Open University using a 514 nm laser for which the power was maintained at ~60 µW. Finally, amino acids were extracted from the samples, derivatised, and analysed with a Waters nano-ACQUITY ultraperformance liquid chromatograph and a Thermo Scientific LTQ Orbitrap XL hybrid mass spectrometer (nLC-HRMS) at NASA Goddard [6]. All tools and materials that were in contact with the particles had been sterilised by baking at 500°C in air for >10h.

Results and Discussion: The five particles are ~86–100 µm in size exhibiting sheet- (#29,52,80), block- (#12) and rod-like (#78) morphologies. The sheet-like particles are flat and have sharp, rugged edges that appear to be produced by tearing. Their appearance is similar to the cat. 3 Itokawa grains described in [7], but their elemental compositions are similar to that reported for cat. 4 particles with a significant contribution of Al, Ti, which are potentially artificial material (e.g., alloy) [2]. Raman analysis shows that only 2 (#52,78) out of the 5 Itokawa grains exhibit the typical first-order defect (D) and graphite (G) band in the ~1350−1600 cm^{-1} region that correspond to the breathing mode of aromatic rings, and in-plane stretching mode of sp^2-bonded C atoms in both rings and chains [8]. The Raman spectral features are similar to that observed for cat. 3 Itokawa particles reported in [5]. It suggests that the organics had been subjected to minimal heating, which is incompatible to the LL4–6 lithology of Itokawa [9]. Yet, FTIR measurements in the mid-IR (650–4000 cm^{-1}) range show that their spectral features are atypical to that of extraterrestrial C. Rather, the main component of the grains are hydrous silicate (#78) and fluorinated-heterocycles (#52). The IR spectra of grains #12&80 are comparable to terrestrial protein dominated by the protein amide I and amide II bands 1500–1700 cm^{-1} corresponding to the C=O stretching and the NH bending of the peptide bond [10]. We are currently preparing the samples for amino acid analysis with nLC-HRMS. If these grains indeed contain terrestrial proteins, they should be easily discernable by the presence of exclusively the L-enantiomers of amino acids.

Implications: Despite the careful contamination control and curation efforts, some fractions of mission-returned samples are still reported to be contaminated by terrestrial material, e.g., Apollo [11], Stardust [12], and Hayabusa missions. The Hayabusa2 (HYB2) mission is now under way with an aim to bring back samples from the near-Earth C-type asteroid 162173 Ryugu at the end of 2020 [13]. Lessons learned from analysing Itokawa particles should be implemented in the analytical protocol of the HYB2 samples and their curatorial procedures.

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