X-RAY ABSORPTION SPECTROSCOPIC STUDY OF CARBONACEOUS MATERIALS FROM HAYABUSA-RETURNED SAMPLES.

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Introduction: At the Planetary Material Sample Curation Facility of JAXA (PMSCF/JAXA), several tens of carbonaceous particles of unknown origin have been collected from the sample catcher and classified as Category 3, in addition to the asteroid particles investigated (Categories 1 and 2) [1, 2]. In order to determine whether the materials are terrestrial or extraterrestrial, we have analyzed the functional group compositions of the Category 3 particles by a scanning transmission X-ray microscope (STXM) using X-ray absorption near edge structure (XANES) spectroscopy.

Samples and methods: In this study, four Category 3 carbonaceous samples, RA-QD02-0120, RA-QD02-0180-02, RB-QD04-0037-01-02, RB-QD04-0047-02, were investigated. RA-QD02-0120 and RB-QD04-0047-02 were also analyzed by FE-SEM-EDS [1], micro-Raman, micro-FTIR, NanoSIMS [3], ToF-SIMS, and TEM [2]. The ultra-thin sections (100 nm thick) of the four samples were were fixed by pressing on gold (Au) plates, extracted by focused ion beam (FIB), and analyzed by STXM, at beamline 5.3.2.2, Advanced Light Source (ALS), LBNL. Two different sections of RA-QD02-0120 before and after TEM were analyzed by STXM.

Results and discussion: RA-QD02-0120 and RB-QD04-0047-02 show C-XANES spectra with the typical spectral patterns of heterogeneous organic macromolecules: the set of peaks corresponding to aromatic/olefinic carbon, heterocyclic nitrogen and/or nitrile, and carboxyl carbon. N-XANES spectra of the samples include the developed peak of heterocyclic nitrogen and/or nitrile. Differences in C- and N-XANES spectra of RA-QD02-0120 before and after TEM were observed, demonstrating that the carbonaceous materials are electron beam sensitive. On the other hand, C-XANES spectrum of RB-QD04-0037-01-02 has the well-resolved three peaks of amide, carboxyls, and urea/ether, in addition to an aromatic peak shifted to lower energy (284.8 eV) by 0.3 eV from the two other samples (285.1 eV). Its N-XANES shows a unusually high abundance of heterocyclic nitrogen including R-NH-(C=O)-R' as a peak at 401 eV. C-XANES spectrum of RA-QD02-0180-02 is very similar to that of epoxy resin. N-XANES spectrum of this sample shows a developed peak at 401 eV.

Ca-XANES spectrum and mapping identified a calcium carbonate grain from RA-QD02-0120 and RA-QD02-0180-02. Ti- and Cl-XANES detected titanium and chloride grains from RA-QD02-0180-02. Any fluorine-containing molecular species are not detected from F-XANES of the particles. As one of possibilities, it is implied that the Category 3 functional group features may be reflected by degradation of polymer materials used or contaminated in the Hayabusa spacecraft. Further investigation will be necessary for identification of their sources.

References: [1] Yada et al. 2013. Meteoritics & Planetary Science 49:135-153. [2] Uesugi et al. 2014. *Earth Planets. Space* in press. [3] Ito et al. 2014. *Earth Planets. Space* 66:91.