

IN-SITU ANALYSIS OF SOLUBLE ORGANIC COMPOUNDS FOR HAYABUSA CATEGORY 3 PARTICLES.

M. Hashiguchi¹, H. Naraoka^{1,2}, M. Uesugi³, T. Yada⁴, and M. Abe⁴.

¹ Research Center for Planetary Trace Organic Compounds (PTOC) and ²Department of Earth and Planetary Sciences, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, 819-0395 Japan. ³Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Koto, Sayo, Hyogo 679-5198, Japan. ⁴Space Exploration Innovation Hub Center, Japan Aerospace Exploration Agency (JAXA), 3-1-1 Yoshinodai, Sagami-hara 252-5210, Japan.

Introduction: More than 700 Hayabusa-returned particles have been identified by Extraterrestrial Sample Curation Center (ESCuC) of Japan Aerospace Exploration Agency (JAXA) [1]. In preliminary examination on organic materials in silicate particles, no clear evidence was obtained for extraterrestrial organic materials [2]. Some carbonaceous particles composed mainly of C, N, and O were found and categorized as “category 3” based on initial description using FE-SEM-EDS by ESCuC. Previous studies suggested that the category 3 particles were likely contaminants [e.g. 3-6], however, their origin(s) has not been clear yet. In this study, we investigated the category 3 particles by in-situ analysis using desorption electrospray ionization coupled with high-mass resolution mass spectrometry (DESI-HRMS) [7] to characterize the soluble organic compounds in these particles to discuss their origins.

Samples and Methods: Two Hayabusa category 3 particles, RB-CV-0008 and RB-CV-0031 were used in this study. Initial description on by ESCuC showed that C, N, and O were dominant in both particles. The size of both particles is approximately 50 μm . These particles were pressed into an Au plate with a diameter of 3 mm and thickness of 300 μm in a clean booth at ESCuC. They were stored under N_2 or Ar atmosphere and transported to PTOC at Kyushu University for DESI/HRMS analysis. The DESI/HRMS analysis was performed using a 2D DESI ion source (Omni Spray Source 2D, Prosolia) equipped with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific) under the ambient environment in a clean room (Class 1000). Electrospray voltage was set at 3 kV for positive mode, and 4 kV for negative mode. A spray solvent was methanol of Q-ToF-MS grade (100%) with the flow rate of 2.5 $\mu\text{L}/\text{min}$. The positive and negative ions were collected in a full scan mode ($m/z=70\text{--}1,000$) with mass resolution of $\sim 140,000$ ($m/\Delta m$ at m/z 200) on the surface of the sample ($\sim 3.2 \times 3.2$ mm²). After the analysis, a small piece of VITON gloves (~ 2 mm) used in clean chambers was also analyzed using same analytical condition as a possible contaminant for comparison.

Results and Discussion: Numerous peaks as background peaks from a spray solvent and air in the clean room were detected in a range of m/z 70-1000. About 200 positive ions and 30 negative ions, which are concentrated around particle-embedded region, were detected from RB-CV-0008. These ions were identified among the range of m/z 100-990 for positive ions, and m/z 160-680 for negative ions. The spatial distributions (concentrated region) of these positive ions and negative ions was partially matched but different from each other. Particularly, the positive ions were detected from the surface that is slightly (~ 200 μm) shifted from the particle, whereas the negative ions were almost detected from nearly the surface of the particle. These positive ions were possibly be desorbed from the surface of Au disk, however, further investigation is needed to discuss the location difference. For both positive and negative ions, most of them were not identified from a blank Au disk and VITON, which suggests that these compounds were derived from the particle. The RB-CV-0008 particle is not likely a contaminant from VITON glove.

By using their exact masses (< 3 ppm of mass precision) and Kendrick mass defect, an CH_2 homologue (every m/z 14. 0156) with high ion intensity and several different families containing units of m/z 58.042 were identified in the positive ions. A possible candidate for this units is $\text{C}_3\text{H}_6\text{O}$. Some negative ions could be assigned as CHO and CHNO compounds, however, any homologous families could not be identified due to the small number of identified ions. Presence of other elements (e.g. Mg, Si, and S) in the particle reported by previous studies on category 3 particles [e.g. 4, 6] were not clear because that their isotopomers could not be identified in DESI-HRMS images.

We also analyzed RB-CV-0031, however, the particle was lost during the analysis unfortunately by N_2 nebulizing gas and solvent spray of DESI, probably due to high porosity of the particle. Although some compounds were detected from the Au disk and showed concentrated spatial distribution, the position is clearly shifted from the surface of particle and we could not determine whether they were particle origin. Other possible contaminant materials will be analyzed for comparison to discuss the origin and nature of the category 3 particle.

References: [1] Yada T. et al. (2017) *80th Annual Meetings of the Meteoritical Society*, #6204, [2] Naraoka H. et al. (2012) *Geochemical Journal* 46: 61-72. [3] Ito M. et al. (2014) *Earth, Planets and Space*, 66: 102-110. [4] Kitajima F. et al. (2015) *Earth, Planets and Space* 67:20-32. [5] Naraoka H. et al. (2015) *Earth, Planets and Space* 67:67-76. [6] Uesugi M. et al. (2019) *Meteoritics & Planetary Science*, 54: 638-666. [7] Hashiguchi M. and Naraoka H. (2019) *Meteoritics & Planetary Science*, 54: 452-468.