TRACE ORGANIC COMPOUND ANALYSES OF MICROMETER-SIZED ASTEROIDAL MATERIALS.

Hiroshi Naraoka
Department of Earth and Planetary Sciences and Research Center for Planetary Trace Organic Compounds, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. (naraoka@geo.kyushu-u.ac.jp)

Introduction: Organic compounds are distributed widely in terrestrial and extraterrestrial environments, and are characterized by their diverse structures. The asteroidal organic compounds are generally very small in amount, and the quantities of sample materials obtained from precious meteorites, cosmic dusts or sample-return missions from asteroids are extremely limited. The micrometer-sized particles from the Hayabusa spacecraft have been examined for the occurrence of organic compounds by amino acid analysis and time of flight-secondary ion mass spectrometry (ToF-SIMS). However, no indigenous organic compounds were identified [1, 2] due to thermal metamorphism of asteroid Itokawa. In order to obtain detailed information on organic compounds from tiny asteroidal carbonaceous materials, the development of ultra-high sensitivity and resolution analyses is needed. The research center for Planetary Trace Organic Compounds (PTOC) of Kyushu University was founded in March 2016 to study trace organic compounds of extraterrestrial materials under clean conditions.

Clean environment: The clean room technology is essential to analyze trace organic compounds in tiny planetary materials in order to avoid terrestrial contamination and to reduce the analytical background. The PTOC center has two clean rooms (class 1000) for sample preparation and mass spectral analysis. The sample preparation has a clean bench (class 100). Both clean rooms and bench bear 4-layers filters (acid, alkaline, organic chemical and HEPA) for air cleaning to avoid contaminants.

Ultrahigh-resolution mass spectrometry: Recent ultrahigh-resolution mass spectral (UHRMS) analysis using FT-ICR/MS detected tens of thousands of different mass peaks consisting of C, H, N, O, and/or S from the Murchison meteorite [3]. Considering the structural and optical isomers, the current organic contents identified in the meteorite correspond to only approximately 1% of the total compounds present. Recently we found > 600 compounds consisting of C_nH_mN and $C_nH_mN_2$ in elemental composition using HPLC coupled with an Orbitrap MS [4]. An advantage of Orbitrap MS is that the UHRMS analysis can be achieved in the clean room.

Ultrahigh-resolution chromatography: Meteoritic organic compounds are generally present as very complex mixtures having suites of homologues with various functional groups. In addition, they often have many structural isomers (including stereoisomers), in which the isomer distribution sometimes reflects physical and chemical conditions of the extraterrestrial environment. Ultrahigh-resolution analysis in liquid chromatography will be achieved to identify many isomers by a long silica monolithic capillary column using nanoLC coupled with an Orbitrap MS. The nanoLC technique also can enhance the sensitivity of detection by three orders of magnitudes compared to that of conventional HPLC.

In-situ analysis for imaging of organic compound distribution: Trace organic compounds have been generally analyzed using the solvent extracts of powdered samples. In-situ analysis of organic compounds has been limited for volatile compounds such as PAHs [5]. In order to clarify the distribution for various organic compounds, the molecular imaging on the surface of carbonaceous meteorites has been performed using desorption electrospray ionization (DESI, [6]) coupled with an Orbitrap MS. Alkylated N-containing cyclic compounds including alkylimidazoles ($C_nH_{2n-1}N_2^+$) and alkylpyridines ($C_nH_{2n-4}N^+$) were identified on the surfaces of the Murray meteorite by in situ analysis using DESI/Orbitrap-MS [7]. The distribution of alkylimidazoles and alkylpyridines appeared different on the meteorite surface, suggesting different their source regions or asteroidal chromatographic effect on the parent body.

Summary: The technical development of ultrahigh-resolution mass spectral and chromatographic analyses as well as in-situ analysis with molecular imaging by DESI will allow for the improved identification of organic compounds compared to current analysis, and will advance comprehensive studies of the formation pathways and origins of asteroidal organic compounds. Furthermore, the new analytical techniques will allow for the definitive identification of organic compounds in greatly reduced sample sizes (using ~μg of sample vs. current ~mg requirement), thereby contributing to the successful analysis for future sample-return missions (e.g. Hayabusa 2 and OSIRIS-REx).

References: [1] Naraoka H. et al. 2012. *Geochemical Journal* 46: 61-72. [2] Naraoka H. et al. 2015. *Earth, Planets and Space* 67:67 DOI 10.1186/s40623-015-0224-0. [3] Schmitt-Kopplin P. et al. 2010. *Proceedings of the National Academy of Sciences* 107:2763-2768. [4] Yamashita Y. and Naraoka H. 2014. *Geochemical Journal* 48: 519-525. [5] Clemett S. J. et al. 1993. *Science* 262:721–725. [6] Takáts Z. et al. 2004. *Science* 306: 471–473. [7] Naraoka H. and Hashiguchi M. 2016. *79th Annual Meeting of the Meteoritical Society*, August 6-12, *Berlin, Abstract #6169*.