Meteoritic organic compound analysis by nano-liquid chromatography/mass spectrometry

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[Introduction]
Carbonaceous chondrites, which have the primitive chemical composition in the solar system, contain volatile materials including water and organic matter. Since biologically-relevant molecules such as amino acids, nucleobases were detected in meteorites(e.g. Burton et al., 2012), meteoritic organic matter has been investigated with respect to the origin of life. So far the organic compounds have been generally analyzed using the powder sample of sub-g to g meteorite with solvent extraction followed by chromatography. The powdered sample has lost its location information such as mineral textures, even though the primitive meteorites have heterogeneous composition in chemistry and mineralogy. Since most carbonaceous chondrites experienced aqueous alteration on the parent bodies, the understandig of mineral associaton with organic compounds is necessary to reveal chemical evolution in extraterrestrial environments. Futhermore, non-destructive organic analysis is preferred especially for precious samples. In this study, we will develop an analytical method of organic compounds using an intact micro-meter sized grain of extraterrestirial meterial with high-sensitive nano-liquid chromatography (nanoLC) coupled with high-resolution mass spectrometry(HRMS).
[Materials and Methods]
A single grain (~300 to 900 μm) was obtained by chipping from carbonaceous chondrites (Murchison and Murray; CM2). Each grain (0.168-2.392mg) was soaked in 5.0μL of methanol(MeOH) followed by sonication or mixing. One micro-litter of each extract was subjected to nanoLC/HRMS ($m/\Delta m$=~140,000 at m/z 200) with electrospray ionization (positive ion) using C18 reversed phase column or amide column. The eluent solvents were mixture of acetonitrile, water and formic acid. All analytical procedures were performed in a clean room.
[Results and Discussion]
Apparent changes were not observed on the grain surface before and after the analysis. Many alkylated homologous CHN and CHNO compounds were distinguished by every 14.0156 (m/z; $-CH_2-$) and peaks shift in the retention time of mass chromatogram. The occurence of homologous series is consistent with previous studies (Schmitt-Kopplin et al., 2010; Yamashita and Naraoka, 2014), suggesting the carbon-chain elongation by stepwise reactions from small molecules. The homologous series of $C_nH_{2n-5}N$(n=5-26), C_nH_{2n-7N}(n=9-28), $C_nH_{2n-1}N_2$(n=5-23), $C_nH_{2n-1}NO$(n=3-20), $C_nH_{2n-3}NO$(n=9-12) and $C_nH_{2n-5}NO$(n=6-26) were detected from the Murray meteorite. In contrast, the only series of $C_nH_{2n-5}N$(n=5-24) and $C_nH_{2n-7}N$(n=10-26) homologous series were detected in Murchison meteorite. The range of carbon number in the homologous series varied depending on the meteorites, whch may imply heterogeneity of organic compounds in the meteorites. Such a heterogeneous distribution may be associated with the mineral occurance. The fluid flow on the parent body may also affect the compound distribution by the (geo)chromatographic effect. Further investigations are needed to clarify the relationship between the meteoritic texture and the distribution of organic compounds.

Keywords: organic compound, carbonaceous chondrite, nanoLC/HRMS, heterogeneity