

Characterization and formation mechanism of soluble organic molecules through the formose-like reaction

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Extraterrestrial organic matter records chemical processes occurred in different physicochemical environments in the early history of the Solar System. Cody et al. [1] and Kebukawa et al. [2] showed that organic solids, synthesized from formaldehyde through the formose-like reaction, resemble chondritic insoluble organic matter, and concluded that the insoluble organic matter could form from simple molecules such as formaldehyde and ammonia under a hydrothermal condition in small bodies. Soluble organic molecules (SOMs) such as amino acids are also synthesized through the formose-like reaction [3-5]. However, bulk characteristics of SOMs formed by the formose-like reaction have not been well investigated yet. In this study, we characterize SOMs synthesized by the formose-like reaction and discuss the contribution of SOMs by the formose-like reaction to the meteoritic SOMs.

Hydrothermal organic synthesis was performed following [2]. A starting mixture of paraformaldehyde, glycolaldehyde, calcium hydroxide and ultrapure water was heated at 90, 150 and 200°C for 1-30 days. The experiments with ammonia were also performed. Supernatant liquids of the run products were filtered and diluted by ultrapure water to reduce concentrations of SOMs for the analysis with a liquid chromatography mass spectrometer (Orbitrap Elite). The obtained mass spectra were analysed with a software ATTRIBUTOR.

The total ion current (TIC) chromatogram of the LC-HRMS analysis showed that total ion intensities for all the experimental samples were larger than that of the blank because SOMs formed through the formose-like reaction. The larger TIC was observed for samples heated at higher temperatures for the same duration.

Mass spectra obtained from a peak of the TIC chromatogram showed thousands of peaks of m/z in the range of 50 to ~650 for all the samples. More than several hundreds of molecular composition formulas were obtained from the 3000 highest peaks in each mass spectrum. Bulk compositions of SOMs were estimated by averaging all the chemical compositions of assigned molecules using their ion intensities as weights [6]. The bulk H/C ratios are 1.10-1.16, 1.15-0.1.18, and 1.23-1.30 at 90, 150 and 200°C, respectively, and they tend to be higher for the SOMs formed in the presence of ammonia. The bulk O/C ratios are estimated to 0.36-0.42, 0.29-0.30 and 0.20-0.24 at 90, 150 and 200°C, respectively. The increase of H/C and decrease of O/C of bulk molecular compositions with temperature suggest that SOMs becomes more reduced at higher temperatures.

The average composition of a growth unit of SOMs was also estimated from the increments of C, H, and O against the molecular mass. The H/C ratios of the growth unit are 1.19-1.24, 1.20-1.26 and 1.25-1.32 at 90, 150 and 200°C, respectively, and the O/C ratios are 0.4-0.42, 0.32-0.33 and 0.27-0.29 at 90, 150 and 200°C, respectively. The composition of the growth unit and its temperature dependence are similar to the bulk compositions of SOMs.

The more reductive nature of SOMs and their growth unit at higher temperatures can be explained by the

effective reduction of molecules by formic acid, a product of a disproportionation reaction of formaldehyde [7].

A bulk composition of methanol-soluble organic components of Murchison meteorite was estimated to be $C_{100}H_{155}O_{20}N_3S_3$ [7], of which H/C and O/C ratios are not consistent with those in the present study. This implies that a more reducing condition was required to form the Murchison SOMs through the formose-like reaction on the parent body.

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Keywords: meteorites, soluble organic matters, high resolution mass spectrometer, molecular evolution, formose reaction