

Organosulfur compounds in carbonaceous chondrites: Implications for organic reaction pathways in the meteorite parent bodies

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Introduction: Sulfur is present as various chemical forms in meteorites. In carbonaceous chondrites, organic sulfur compounds have been found in addition to elemental sulfur as well as metal sulfides (e.g. troilite) and sulfates (e.g. gypsum) [1]. Alkylsulfonic acids such as methyl- and ethyl-sulfonic acids were firstly reported from the Murchison meteorite [2]. The deuterium enrichment and mass-independent sulfur isotope signature suggested that the alkylsulfonic acids may have been an interstellar molecule in origin [3]. Recent high-resolution mass spectral analysis using (Fourier transform-ion cyclotron resonance/mass spectrometry, FT-ICR/MS) has further identified significantly diverse organo-sulfur homologous compounds consisting of CHOS and CHNOS in elemental composition from the various extracts of the Murchison meteorite [4]. However, the chemical structures of the CHOS and CHNOS compounds have not been clarified with respect to their reaction pathways in the extraterrestrial environment. The organic sulfur compounds are generally observed as a negative ion using electrospray ionization. High performance liquid chromatography/high resolution mass spectrometry (HPLC/HRMS) is a powerful tool to deconvolute the occurrence of organic compound mixtures. In the methanol extract of carbonaceous chondrites many CHN compounds were identified as positive ions using HPLC/HRMS [5], in which homologous series of alkylated pyridines and imidazoles were predominant. The alkylated N-containing cyclic compounds could be produced from simple aldehyde and ammonia in the meteorite parent bodies. In this study, we further clarified sulfur-containing compounds in the methanol extract of carbonaceous chondrites.

Sample and Methods: The interior part of the Murchison meteorite (CM2) was powdered using an alumina mortar and pestle in a clean room. The sample powder was sequentially extracted with hexane, dichloromethane (DCM) and methanol by sonication. The DCM extract was analyzed by HPLC/HRMS using an amide column (Inertsil Amide, 1.5 mm i.d. x 25 cm) by hydrophilic interaction liquid chromatography coupled with a hybrid quadrupole-Orbitrap MS (Q-Exactive Plus). The eluent was CH₃CN/HCOONH₄ buffer at a flow rate of 70 μ L/min and was electrically charged to 3 kV followed by spraying into MS using electrospray ionization (ESI). The negative ions were collected in full scan mode from m/z 50 to 600 with mass resolution of \sim 140,000 ($m/\Delta m$ at m/z 200).

Results and Discussion: Abundant inorganic sulfur oxides and organosulfur compounds were detected in the DCM extract of the Murchison meteorite within 2 ppm mass precision. Alkylsulfonic acids up to C₁₅ were identified as homologous compounds (**Fig. 1**), being consistent with the previous studies [2,3]. The most intense peak was hydroxymethane sulfonic acid (HSA, HOCH₂SO₃H), which was found in a meteorite for the first time. It is known that HSA is produced by the reaction of formaldehyde with bisulfite (HSO₃⁻) [6]. Therefore, it is suggested that formaldehyde was abundant prior to the reaction with HSO₃⁻ on the parent body. Because abundant alkylated pyridines (C_nH_{2n-5}N) and imidazoles (C_nH_{2n-2}N₂) detected in the Murchison meteorite could be produced formaldehyde and ammonia [5], formaldehyde is a common starting material for chemical evolution of primitive asteroids.

References: [1] Rubin A. E. & Ma C. 2017. *Chem. Erde*. **77**: 325-385. [2] Cooper G. et al. 1992. *GCA* **37**:1451-1490. [3] Cooper G. et al. 1999. *Science* **49**:1707-1714. [4] Schmitt-Kopplin, P. et al. 2010. *PNAS* **312**: 727-730. [5] Naraoka H. et al. 2017. *ACS Earth Space Chem.* **1**: 540-550. [6] Donnally L. H. 1933. *Ind. Eng. Chem. Anal. Ed.* **5**: 91-92.

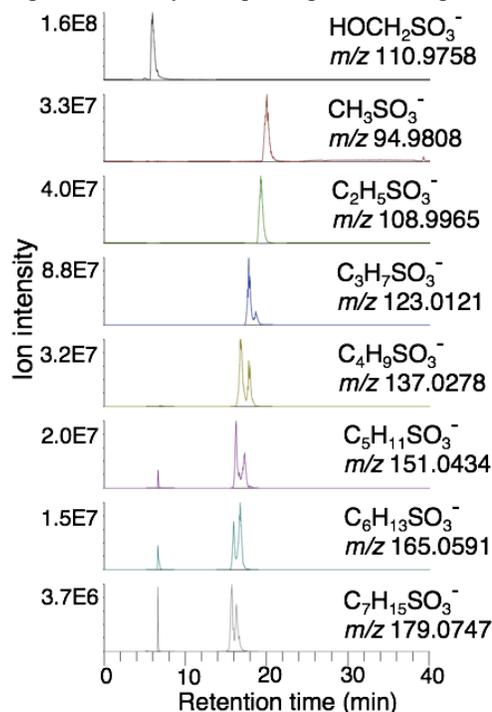


Fig. 1. HPLC/HRMS chromatograms of organosulfur compounds in the Murchison meteorite.