Organic sulfur compounds and its evolution in carbonaceous meteorites

*Hiroshi Naraoka[1]

1. Department of Earth and Planetary Sciences, Kyushu University

Introduction: Sulfur is an abundant volatile element in meteorites, which is present as various chemical and mineral forms. Metal sulfide (e.g. troilite) is common in iron meteorites and ordinary chondrites. In carbonaceous chondrites, organic sulfur compounds have been found in addition to molecular sulfur (e.g. S_8) as well as and sulfates (e.g. gypsum) [1]. Aromatic sulfur-containing compounds including benzothiophenes and alkylsulfonic acids such as methyl- and ethyl-sulfonic acids were reported from the Murchison meteorite [2, 3]. The alkylsulfonic acids have deuterium enrichment and mass-independent sulfur isotope signature, suggesting an interstellar molecule in origin [3].

Recent ultrahigh-resolution mass spectral analysis using Fourier transform-ion cyclotron resonance/mass spectrometry has further identified significantly diverse organo-sulfur homologous compounds consisting of CHOS and CHNOS in elemental compositions from the solvent extracts of the Murchison meteorite [4]. However, chemical evolution of sulfur-bearing organic compounds is not well understood, because the chemical structures of the CHOS and CHNOS compounds have not been clarified. 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. organic sulfur compounds are generally observed as a negative ion using electrospray ionization. In this study, we further clarified sulfur-containing compounds in the solvent extracts of carbonaceous chondrites.

Sample and Methods: Three carbonaceous chondrites (Murchison, Allende and Tagish Lake) were powdered using an alumina mortar and pestle in a clean room. The sample powder was sequentially extracted with hexane, dichloromethane (DCM) and methanol (MeOH) by sonication. The DCM and MeOH extracts were 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 HRMS using a hybrid quadrupole-Orbitrap MS (Q-Exactive). The eluent was $CH_3CN/HCOONH_4$ buffer at a flow rate of 70 mL/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 ~140,000 (*m/Dm* at *m/z* 200).

Results and Discussion: Abundant inorganic sulfur oxides and organosulfur compounds were detected in the extracts of the Murchison meteorite within 2 ppm mass precision. Alkylsulfonic acids up to C_{15} were identified as homologous compounds. The concentration of the sulfonic acid decreased with increasing carbon number, suggesting carbon-chain elongation by step-by-step single carbon addition. The most intense peak was hydroxymethane sulfonic acid (HSA, $HOCH_2SO_3H$), which was found in a meteorite for the first time. It is known that HSA is produced by the reaction of formaldehyde with bisulfite (HSO_3^-) [6]. In previous studies, formaldehyde was quantified in the Murchison meteorite, but the concentration of formaldehyde was less than 10 % of hydroxymethanesulfonic acid in this study [7, 8]. Therefore, most formaldehyde is likely to be consumed by the reaction with bisulfite in the meteorite. The formaldehyde should be abundant prior to the reaction with HSO_3^- on the meteorite parent body. Because abundant

alkylated pyridines ($C_nH_{2n-5}N$) and imidazoles ($C_nH_{2n-2}N_2$) 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] Naraoka H. et al. 2000. *EPSL* **184**:1–7. [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. [7] Pizzarello S. & Holms W. 2009. *GCA* **73**: 2150-2162. [8] Simkus D. N. et al. 2019. *MAPS* **54**: 142-156.

Keywords: Carbonaceous meteorites, Chemical evolution, Organic sulfur compounds

