

DIVERSITY OF SOLUBLE ORGANIC MATTER IN ANTARCTIC MICROMETEORITES, CONSIDERING IN RELATION TO CHONDRITES. K. Yamamoto¹, M. Hashiguchi², T. Yada³, H. Naraoka⁴, T. Nakamura⁵, and T. Okada^{3,1}, ¹Graduate School of Science, University of Tokyo, ²Research Center for Planetary Trace Organic Compounds, Kyushu University, ³Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, ⁴Graduate School of Science, Kyushu University, ⁵Graduate School of Science, Tohoku University (kota@planeta.sci.isas.jaxa.jp)

Introduction: Recent exploration of outer planets and comets have revealed that organic matter exists abundantly in the outer planetary region. This means that the existence of organic matter cannot be ignored in considering the evolution of the solar system, especially the outer planetary area. Micrometeorites (MMs) whose accretion rate to the Earth has been estimated more than ten times as large as that of meteorites [1–4] may quantitatively have contributed more than meteorites. Studies of organic matter in MMs are therefore important in terms of both the evolution of organic matter in the solar system and the origin of life. Organic matter contained in extraterrestrial samples is divided into insoluble organic matter (IOM) which is insoluble in any solvents and acids and soluble organic matter (SOM) which can be extracted with solvents. Pyrolysis prior to melting or sublimation and insolubility of IOM make it difficult to crystallize it for structural analysis. Since IOM has a large molecular weight and a large number of structural isomers, identification by comparison with a standard substance is also difficult. On the other hand, SOM whose structure can be determined is a possible clue to more specifically elucidate chemical reactions in organic evolution [e.g., 5].

Here we report limited diversity of SOM in Antarctic micrometeorites (AMMs) and point out the necessity of a novel method to recover AMMs.

Samples and methods: Four AMMs, T98KS029, T98KS043, T98UT002, and T98UT009, which had been collected from melted water at coastal blue ice near the Syowa station in 1998 by the Japan Antarctic Research Expedition team, were pressed onto gold plates and sequentially analyzed by Fourier-transform infrared spectroscopy (FTIR), desorption electrospray ionization coupled with orbitrap mass spectrometry (DESI-Orbitrap MS), and Raman spectroscopy.

FTIR was performed at ISAS/JAXA using JASCO FT/IR-6100 + IRT-5000 with a ceramic IR light source, a germanium coated KBr beam splitter, a liquid-nitrogen-cooled Mercury-Cadmium-Telluride (MCT) detector, and $\times 16$ Cassegrainian mirror. Reflection spectra were obtained through a square optical aperture $25 \times 25 \mu\text{m}^2$ for T98KS029 and T98UT002, and $50 \times 50 \mu\text{m}^2$ for T98KS043 and T98UT009 with a spectral resolution of 4 cm^{-1} , in the wavenumber range of $4000\text{--}700 \text{ cm}^{-1}$. The spectra of 512 scans were accu-

mulated and then averaged over each sample. Background spectra were collected on each of the gold disks.

DESI-Orbitrap MS was applied to AMMs for the first time at Kyushu University using Omni Spray Ion Source 2D produced by Prosolia coupled with Q-Exactive Plus produced by Thermo Fischer Scientific. The spray solvent was 100% methanol at a flow rate of $2.5 \mu\text{L}/\text{min}$. The electrospray voltage and the nebulizer N_2 gas pressure were set at 3 kV and 0.7 MPa, respectively. The positive ions were collected in full scan mode (m/z 60–500) with mass resolution of 140,000 ($m/\Delta m$ at m/z 200). DESI images were acquired by moving the motorized x-y stage, on which the samples were put, at a constant rate ($\sim 50 \mu\text{m}/\text{sec}$).

After the analyses with DESI-Orbitrap MS, Raman spectroscopy was performed at ISAS/JAXA using JASCO NRS-5100 with a 532 nm exciting laser radiation focused by a microscope equipped with a $20\times$ objective lens, a Peltier-cooled DU420_OE 12 CCD detector with 1024 channels held at $-70 \text{ }^\circ\text{C}$, and a 600 lines/mm grating producing spectral resolution of $\sim 7 \text{ cm}^{-1}$. The laser intensity on the surface of samples was expected less than that of setup 0.8 mW. The spectra of 5 scans with exposure times of 4 seconds each and a spatial resolution of $\sim 10 \times 10 \mu\text{m}^2$ were accumulated.

Results and discussion: The IR spectra of the four AMMs showed some absorption peaks characteristic of organic functional groups including asymmetric stretching of CH_3 and CH_2 groups near 2960 cm^{-1} and 2930 cm^{-1} , respectively (Fig. 1). The peak height of CH_3 and CH_2 were obtained by subtracting a linear baseline in the $3000\text{--}2800 \text{ cm}^{-1}$ region, following earlier studies [6,7]. The peak height ratio CH_2/CH_3 is indicative of the mean aliphatic chain length and branched structure levels. Higher CH_2/CH_3 ratios suggest longer aliphatic chains and/or higher contents of cyclic aliphatic structures, and vice versa. On the basis of a study on chondritic IOM where the CH_2/CH_3 ratios of IOM in type 1, 2, and 3 chondrites roughly increase with progress of thermal processing in the range of 1.2 – 2.0 [6], the four AMMs are primitive in the order of T98KS029 (1.62 ± 0.02), T98UT009 (1.76 ± 0.02), T98KS043 (1.84 ± 0.02), and T98UT002 (1.86 ± 0.03). The errors reflect the uncertainty in defining baselines.

The Raman spectra of the four AMMs showed D- and G-bands around 1350 and 1590 cm^{-1} , respectively.

Two Murchison fragments as large as the AMMs were also measured as references. To make a quantitative comparison, the acquired Raman spectra were fitted in the range between 900 and 2000 cm^{-1} to Lorentzian profiles for the D- and G-bands with a free-floating linear background. The Lorentz profile fits yield three parameters for each band: peak position ω , full width at half maximum Γ and peak height I . Both broad bands indicate the less ordered nature of the carbonaceous materials. It has been reported that chondrites with lower maturation grade show larger ω_D , Γ_D , and Γ_G , and smaller ω_G [8]. On the basis of the previous study, the maturation grade increases in the order of T98KS029, T98UT009, T98KS043, and T98UT002, where Murchison is as primitive as T98KS029 (Fig. 2). This trend is consistent with that of FTIR.

DESI-Orbitrap MS detected a total of eleven kinds of ions from three AMMs except for T98KS029, including those in which molecular formula cannot be assigned with C, H, N, and O (Table 1). Almost all the ions had the degrees of unsaturation of less than 4, indicating that they don't contain benzene ring in their molecular structures. Poorly polar molecules like PAHs which are not easily dissolved in methanol were not detected. The variation among the four AMMs was not observed despite a various degrees of thermal processing, suggesting that SOM in AMMs is originally poor in variation, or most of the compounds inherent in AMMs had been lost during the period from reaching the Earth until measurement. Considering the diversity of SOM found from meteorites so far, the possibility of the latter cause should be examined. Particularly highly polar compounds may have been washed away during melting surrounding ice and filtration recovery of AMMs. Therefore, more various and abundant compounds are expected to be detected by sublimation of surrounding ice to collect AMMs.

Summary: In this study, DESI-Orbitrap MS was applied to AMMs for the first time. The detected ions were poor in variation despite a various degrees of thermal processing of AMMs indicated by FTIR and Raman spectroscopy. Freeze-drying recovery would contribute to detection of more various and abundant compounds inherent in AMMs.

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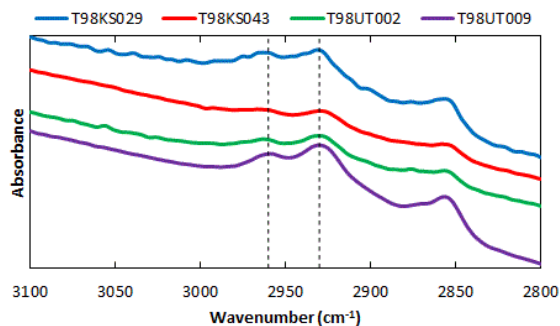


Fig. 1. IR spectra of the four AMMs. Vertical dashed lines represent the peaks due to asymmetric stretching of CH_3 (2960 cm^{-1}) and CH_2 (2930 cm^{-1}).

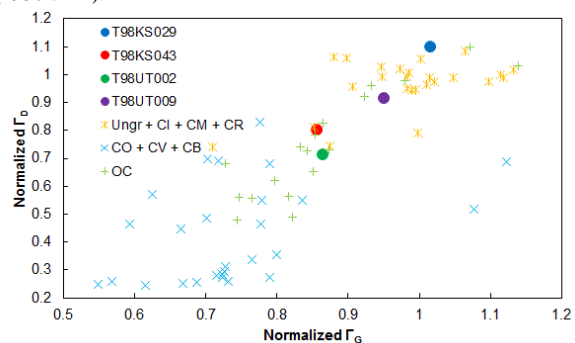


Fig. 2. Correspondence between the AMMs and chondrites [8] on the plot of Γ_D versus Γ_G normalized by the average values of Murchison of each study. Ungr represents Acfer 094 and Tagish Lake.

Table 1. Molecular formula assignment for the ions detected by DESI-Orbitrap MS.

| Sample | Measured m/z | Formula Within 3 ppm of mass accuracy | Degree of unsaturation |
|----------|---|---|---------------------------|
| T98KS029 | | Not detected | |
| T98KS043 | 184.1695 | $\text{C}_{11}\text{H}_{22}\text{NO}^+$ | 2 |
| | 202.1799 | $\text{C}_{11}\text{H}_{24}\text{NO}_2^+$ | 1 |
| T98UT002 | 203.1833 | $\text{C}_{10}^{13}\text{CH}_{24}\text{NO}_2^+$ | 1 |
| | 158.1540 | $\text{C}_9\text{H}_{20}\text{NO}^+$ | 1 |
| | 184.1696 | $\text{C}_{11}\text{H}_{22}\text{NO}^+$ | 2 |
| | 202.1801 | $\text{C}_{11}\text{H}_{24}\text{NO}_2^+$ | 1 |
| T98UT009 | 203.1830 | $\text{C}_{10}^{13}\text{CH}_{24}\text{NO}_2^+$ | 1 |
| | 184.1695 | $\text{C}_{11}\text{H}_{22}\text{NO}^+$ | 2 |
| | 202.1801 | $\text{C}_{11}\text{H}_{24}\text{NO}_2^+$ | 1 |
| | 203.1835 | $\text{C}_{10}^{13}\text{CH}_{24}\text{NO}_2^+$ | 1 |
| | 239.1488 | $\text{C}_{10}\text{H}_{23}\text{O}_6^+$ | 0 |
| | 256.1753 | Not assigned | |
| | 261.1307 | $\text{C}_{10}\text{H}_{22}\text{O}_6\text{Na}^+$ | 0 |
| 338.2535 | $\text{C}_{16}\text{H}_{36}\text{NO}_6^+$ | 0 | |
| | 389.2510 | $\text{C}_{23}\text{H}_{37}\text{O}_3\text{Si}^+$ | |
| | 399.3493 | $\text{C}_{27}\text{H}_{45}\text{NO}^+$ | 6.5 |
| | 447.2929 | Not assigned | |