Abundant magnesium-containing organic compounds in the Tagish Lake meteorite.
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Introduction: Primitive meteorites contain a wide variety of organic compounds. Recent high mass resolution chemical analyses of the solvent extracts from the Murchison meteorite (CM2) revealed numerous peaks of CHO, CHNO, CHNOS compounds [1] and various alkylated homologues of CHN compounds [2]. Moreover, Mg-containing organics (CHO-Mg compounds) were also identified from methanol extracts of various classes of meteorites including primitive meteorites [3].

To understand formation and evolution of the meteoritic organic matter, we should investigate their relationship with surrounding minerals by in-situ analysis. Close association between organics and clay minerals have been reported by previous in-situ analyses using SEM-EDS [4], near-field IR imaging [5], TOF-SIMS [6], and most recent Nano-scale IR imaging [7].

Our previous studies also revealed spatial distribution of CHN compounds, such as alkylimidazoles, in Murray and Murchison meteorites (CM2) using desorption electrospray ionization coupled with high-resolution MS (DESI-HRMS) [8,9]. The biggest advantage of the DESI-HRMS imaging is that soluble organic matter (SOM) can be ionized without significant fragmentation and identified using the exact mass. In the Murchison meteorite, CHN compounds were distributed in matrix containing clay minerals, but clear relationship with specific minerals was not found [9]. It may be due to gap between spatial resolution of DESI-HRMS imaging and mineral size in matrix. In this study, we carried out DESI-HRMS imaging on the Tagish Lake meteorite containing different lithologies [10] to reveal the relationship between SOM and minerals.

Samples and Methods: Samples were fragments of the Tagish Lake (Ungroup-C2) meteorite, and the Murchison meteorite different from our previous study [8] for comparison. The fragments with a flat surface of each meteorite were embedded in indium or alloy with low melting point (60 °C). The DESI-HRMS imaging was performed using a 2D DESI ion source (Omni Spray Source 2D, Prosolia) equipped with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific). Electrospray voltage was set at 3 kV. A spray solvent was methanol (100%) with the flow rate of 2–3 µL/min. The positive ions were collected in a full scan mode (m/z=60-500) with mass resolution of 140,000 (m/Δm at m/z 200) on the surface of Tagish Lake (~2.5×2.5 mm²) and Murchison (~4.5×4.5 mm²). Because polar organic compounds can be adsorbed into clay minerals [e.g. 11], DESI-HRMS imaging using methanol (100%) spray was also carried on an antigorite grain to understand adsorption effects of organic compounds on surface of clay minerals during storage. The molecular imaging was performed twice on the same surface before/after storage in a clean bench (class 100) inside a clean room (class 1000) for 1 month.

After the DESI-HRMS analysis, mineralogical observation and X-ray elemental mapping were carried out on the two meteorites without coating and polishing using FE-SEM-EDS.

Results and Discussion: Identification of CHNOMg and CHOMg compounds. Any CHN compounds were not detected in Tagish Lake meteorites by DESI-HRMS imaging. In contrast, several alkylated homologues of CHN compounds were identified from Murchison similar to the previous study [9]. This result showed completely different organic characteristics between Tagish Lake and Murchison, which was not consistent with previous reports of bulk analysis that showed its quite low abundance of CHN compounds in Tagish Lake relative to Murchison [12]. Instead of the CHN compounds, abundant Mg-containing organic compounds were identified from Tagish Lake with high mass precision (<3 ppm, mostly <1.5 ppm). Isotopomers of 24–26Mg for compounds with high intensity were also identified using the exact mass and the presence of Mg in these compounds was also suggested by Mg isotope simulation (e.g. Fig. 1). These compounds were assigned as C₅H₅O₃Mg (n=0–10) and C₆H₆N₂O₁Mg (n=1–7) using Kendrick mass defect plot (Fig. 2). Two different slopes in the plots indicate addition/remove of CH₂ units and H₂O units in these Mg-organic compounds (Fig. 2). Total families of CHOMg and CHNOMg compounds were 11 and 6, respectively. Although unknown CHOMg families were identified as negative ions of [(OH)₂MgO₂CR]⁻ from many meteorites by a recent previous study [3], they are different compounds from CHOMg families detected as positive ions in Tagish Lake in this study. Although these Mg-organic compounds were also identified from Murchison, the abundance was quite lower than that in Tagish Lake. The relative ion intensity of the CHOMg and CHNOMg compounds to whole compounds detected from surface of the meteorites were 27% and 21% for Tagish Lake and 0.7% and 0.9% for Murchison, respectively. CHN compounds in Murchison showed 8% of relative intensity.

Among the Mg-organic compounds, C₆H₅O₂+NO₃Mg⁺, C₆H₅O₂+NO₄Mg⁺ and C₆H₅O₂+O₃Mg⁺ families showed high abundance relative to all families (Fig. 2). However, DESI-HRMS imaging on an antigorite grain showed that intensities of these Mg
compounds clearly increased after storage for 1 month which suggests large effect of adsorption of these Mg-organic compounds families on the surface of clay minerals during storage in a clean room. On the other hand, there was almost no effect on other CHOMg or CHNOMg families. This indicates that they were detected from surface or inside of meteorite, not corresponding to the contamination by adsorption.

**Spatial distribution of Mg-organic compounds:** All CHOMg and CHNOMg compounds had a similar spatial distribution with various intensity among the different 11 families (Fig. 3a). SEM-EDS observation revealed some anhydrous silicates (olivine or pyroxene) and numerous framboidal magnetite grains in Tagish Lake (Figs. 3b and 3c). By comparison between DESI-HRMS images and X-ray elemental maps, the Mg-organic compounds seemed to be concentrated in matrix containing less framboidal magnetite. Matrix of Tagish Lake is dominated by saponite or serpentine [9], therefore Mg-organic compounds were relatively concentrated in the saponite/serpentine-rich region. In Murchison, the Mg-organic compounds had almost homogeneous distribution in matrix. Their distributions were different from that of CHN compounds, suggesting different origins between these compounds.

Polar organic compounds could be adsorbed in the surface or into interlayer of clay minerals by ion exchange [e.g. 11]. Particularly, smectite group including saponite has high capability of the ion exchange among clay minerals [11]. Clay minerals in Tagish Lake are mostly saponite, while serpentine is dominant in Murchison [13, 14]. Clearly different abundance of Mg-organic compounds in Tagish Lake relative to Murchison might suggest that these compounds were easily formed during aqueous alteration by interaction between organic ions coexisting with water in fluid and saponite due to high capability of ion exchange of saponite.

**Fig. 1.** Mass spectrum of isotopomers of C$_3$H$_7$O$_2$Mg$^+$. (a) Result of Mg isotope simulation (b) Total intensity from DESI-HRMS images.

**Fig. 2.** Extracted data of Kendrick mass defect plot for Mg-organic compounds detected from Tagish Lake meteorite. Size of symbols correspond ion intensity as shown in the plots.

**Fig. 3.** Spatial distribution of Mg-organic compounds in Tagish Lake. (a) An optical microscope image and DESI-HRMS images of CHOMg or CHNOMg compounds. Color bars indicate ion intensity. (b) A back-scattered electron (BSE) image of sample corresponding to dashed square in an optical microscope image. (c) Combined X-ray Elemental map of Fe (Red), Mg (Green) and Si (Blue). Grains with light green are anhydrous silicate (olivine or pyroxene). Small grains with red color are mostly framboidal magnetite.