Primordial organic matter in the xenolithic clast in the Zag H chondrite: Possible relation to D/P asteroids

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Abstract

Some xenolithic clasts in meteorites may have originated from unique primitive Solar System bodies. These clasts would provide novel insights into the early evolution of the Solar System. We conducted multiple analyses of organic matter (OM) in a CI-like xenolithic clast in the Zag (H5) meteorite including bulk elemental and isotopic analysis, FTIR, STXM/XANES, and NanoSIMS. The bulk C and N abundances in the Zag clast were +5.1 ± 0.4 wt.% and +0.26 ± 0.01 wt.%, respectively, which were the highest observed among various chondrite groups. The bulk $\delta^{13}C$ value of the Zag clast was +23.0 ± 4.1 ‰ which was close to the value of the Tagish Lake meteorite; the $\delta^{15}N$ value was +300 ± 3 ‰ which was close to the values of CR chondrites and Bells (a unique CM). The δD values of C-rich regions obtained by NanoSIMS were approximately +600 to +2000‰ which were close to the values of IOM from CI, CM and Tagish Lake. Some isotopic “hot spots” were observed with δD values up to ≈ +4000‰ and $\delta^{15}N$ values up to ≈ +5500‰. The infrared transmission spectrum of the Zag clast was consistent with the abundant phyllosilicates and carbonates observed in the clast. The STXM showed abundant OM in various forms. C-XANES spectra from the OM were generally similar to CI/CM/CR chondrites. However, some variations existed in the molecular structures. OM in the Zag clast was partially associated with carbonates. The functional group, elemental and isotopic signatures of the OM in the Zag clast support the idea that the Zag clast is unique among known carbonaceous chondrite groups and originated from the outer Solar System such as aqueously-altered D/P type asteroids.

1. Introduction

Xenolithic clasts are present in a wide variety of meteorite groups including ordinary chondrites and achondrites (Brearley, 1990; Brearley, 1992; Zolensky et al., 1992; Buchanan et al., 1993; Zolensky et al., 1996; Zolensky, 1999; Rubin et al., 2002; Nakashima et al., 2003; Kebukawa et al., 2017; Nittler et al., 2019). The unshocked ones are most commonly similar to type 1 to 3 chondrites with some differences, and some of these clasts are considered as possible samples from Kuiper Belt Objects

(KBOs) or trans-Neptunian objects (TNOs) (Zolensky et al., 2009). The theory so called "Nice model" proposed that giant planets such as Jupiter and Saturn accreted at positions closer to the sun than the present orbits, and then moved outward to the current orbits (Gomes et al., 2005; Morbidelli et al., 2005; Tsiganis et al., 2005), as well as "Grand tack" model where the giant planets first approached, then moved away from the sun (Walsh et al., 2011). In these models, the migrations of giant planets lead to the insertion of primitive trans-Neptunian objects (TNOs) into the outer asteroid belt, and such bodies could be nowadays known as D/P-type asteroids (Levison et al., 2009; Walsh et al., 2012). Samples available for laboratory studies from such primitive asteroids are highly limited, and as a consequence, most likely highly biased. This bias could be partially due to fragile and volatile-rich natures of the bodies which would not have survived atmospheric entry as material larger than dust. The Tagish Lake meteorite is the only meteorite proposed to be related to D-type asteroids (Hiroi et al., 2001), although some similarities of unusual chondrites—WIS 91600 and PCA 91008—to Tagish Lake have been proposed (Yabuta et al., 2010). However, Tagish Lake reflectance spectra show differences from typical D-types in the asteroid belt and among Jupiter Trojans (Vernazza et al., 2013). Instead, some chondritic interplanetary dust particles (IDPs) and micrometeorites (MMs) may have been derived from D/P-type asteroids (Vernazza et al., 2015; Noguchi et al., 2017). However, we suggest that such primitive and fragile materials could also be protected and delivered to the Earth enclosed as xenolithic clasts in stony compacted meteorites.

The Zag meteorite is an H3-6 chondrite which is known to contain fluid inclusion-bearing xenolithic halite crystals similar to the ones in the Monahans (1998) meteorite (Zolensky, 1999; Rubin et al., 2002; Zolensky et al., 2017). These halite crystals contain organic-rich particles and amino acids (Chan et al., 2018), and trapped aqueous fluids with various δD values ranged from –400 to +1300‰ (Yurimoto et al., 2014). The Zag meteorite also contains a centimeter-sized CI-like xenolithic clast (Zolensky et al., 2003). The clast in Zag (hereafter called the Zag clast) is predominantly a fine-grained mixture of serpentine, saponite, magnetite, Ca-phosphates, organic-dominated grains, pyrrhotite, and Ca-Mn-Mg-Na carbonates, as well as halite indicating a direct link between the clast and the xenolithic halite crystals (Zolensky et al., 2017). We have been studying organic matter (OM) in the clast and found a large and unique OM aggregate, and further propose that the clast possibly originated from D/P type asteroids or TNOs (Kebukawa et al., 2019b). Here we investigate OM in the Zag clast in more detail with additional analytical techniques including bulk elemental and isotopic analysis and Fourier transform infrared spectroscopy (FTIR), in addition to scanning transmission X-ray microscopy (STXM) and nanoscale secondary ion mass spectrometry (NanoSIMS).

2. Methods

2.1. Bulk carbon and nitrogen contents and their isotopic compositions

For the measurements of total carbon and nitrogen contents and their isotopic compositions, we applied an automated elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) system (Flash EA1112 elemental analyzer/Conflo III interface/Delta Plus XP isotope-ratio mass spectrometer, Thermo Finnigan Co., Bremen), which was modified to improve the sensitivity for small sample analysis (>100 ngN, >500 ngC) (Ogawa et al., 2010). A subsample of the clast was rinsed with an organic solvent mixture (dioxin-analysis-grade dichloromethane and methanol, FUJIFILM Wako Pure Chemical Corporation, Japan, mixed with 1:1 by volume) to remove contaminants from the surface, and then dried under a gentle flow of argon gas at ambient temperature. A 55.8 to 73.6 μg aliquot of the sample was weighed in a tin capsule (3.5 × 4 mm smooth wall capsules, Ludi Co., Swiss) and folded into a small packet before being introduced into the EA/IRMS. The tin capsules and forceps used in this study were pre-cleaned by the same mixed solvent described above. The carbon and nitrogen contents and their isotopic compositions were calibrated by three reference materials, L-tyrosine (BG-T; C: 59.7%, N: 7.74%, δ^{13}C: –20.83±0.10‰, δ^{15}N: +8.74±0.09‰) (Tayasu et al., 2011), nickel octaethylporphyrin (Ni-OEP; C: 73.0%, N: 9.47%, δ^{13}C: –34.17±0.06‰, δ^{15}N: +0.86±0.03‰) (Ogawa et al., 2010), L-valine (USGS75; C: 51.3 %, N: 12.0%, δ^{13}C: +0.49±0.07‰, δ^{15}N: +61.53±0.14‰) (Schimmelmann et al., 2016). The analytical errors for the isotopic compositions estimated by repeated analyses of BG-T and Ni-OEP are ±0.66‰ (s.d. 1σ, n=12) for δ^{15}N and ±0.39 ‰

(s.d. 1σ, n=11) for $\delta^{13}C$.

2.2. FTIR

For FTIR analysis, a small amount of the clast was pressed between two KBr plates (~5 × 5 × 1 mm^3). IR absorption spectra were collected using a micro-FTIR (JASCO FT/IR-6100+IRT-5200), equipped with a ceramic IR light source, a germanium-coated KBr beam splitter, a mercury-cadmium-telluride (MCT) detector, and ×16 Cassegrainian mirrors, at Yokohama National University. A total of 512 scans of IR transmission spectra were accumulated with a wavenumber resolution of 8 cm^{-1}, in the wavenumber range of 7000-600 cm^{-1}, with a 80 × 80 μm^2 aperture. Background spectra were acquired through blank areas of the KBr adjacent to the samples.

2.3. FIB-SEM

C-rich positions in the clast were located in subsample grains using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (Hitachi SU8220/Bruker QUANTAX FlatQUAD EDS). Then, 100 nm-thick sections were lifted out from the carbon-rich positions in the clast using a focused ion beam (FIB) instrument (Hitachi MI4050), at Hitachi High Technologies.

2.4. STXM

C and Fe X-ray absorption near-edge structure (XANES) analyses were performed using the STXM at BL-13A of the Photon Factory, High Energy Accelerator Research Organization (KEK) (Takeichi et al., 2014, 2016) and beamline 5.3.2.2 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (Kilcoyne et al., 2003). Measurement conditions were mostly similar to those described in Kebukawa et al. (2019b). The elemental maps were obtained by acquiring pairs of images below (I_b) and on the absorption edges (I), at 280 and 292 eV, respectively for C *K*-edge, 525 eV and 539 eV for O *K*-edge, and 705 eV and 709 eV for Fe L_3-edge, with a dwell time of 3-5 ms, and taking the $-\ln(I/I_b)$ for each pixel, with 0.05-0.1 μm steps per pixel. The C *K*-edge-XANES spectra were acquired with the energy step sizes (ΔE) of 0.1 eV in 283-295.5 eV region, 0.5 eV in 280-283 eV and 295.5-301.0 eV regions, and 1 eV in 301-310 eV region, with a dwell time of 5 ms and 0.1-0.2 μm steps per pixel. The Fe L_3-edge-XANES spectra were acquired with ΔE of 0.1 eV in 705-712 eV region, and 1 eV in 700-705 eV and 712-730 eV regions, with a dwell time of 3 ms and 0.1 μm steps per pixel. The C-XANES peak intensity maps were obtained from "stack" image data sets; for aromatic C, an image at ~285.2 eV by subtracting an image at 283 eV (baseline), and for carbonates, an image at ~290.2 eV by subtracting an image 289.5 eV, after converting $-\ln(I/I_0)$ for each image. The Fe-XANES spectral component map was obtained using the singular value decomposition (SVD) method (e.g., Koprinarov et al., 2002) from a "stack" image data set, in order to visualize the distribution of three different spectral components. STXM/XANES data analysis was performed using a software aXis2000 (http://unicorn.mcmaster.ca/aXis2000.html). Note that we also attempted to obtain N-XANES, but we could not obtain qualified N-XANES spectra due to low N contents in the clast.

2.5. NanoSIMS

H, C, and N isotope imaging measurements of the FIB sections were carried out using a CAMECA NanoSIMS 50L ion microprobe at Kochi Institute for Core Sample Research, JAMSTEC. Detailed measurement conditions are described elsewhere (Ito et al., 2014; Kebukawa et al., 2019b). A focused Cs^+ primary ion beam of 0.8 to 4 pA was rastered over 10 μm × 10 μm to 25 μm × 25 μm areas on the sample and a standard material (1-hydroxybenzotriazole (HOBT) hydrate; $C_6H_5N_3O \cdot xH_2O$, calculated as x=1). The spatial resolution was estimated to be ~100 nm for C and N isotope images, and ~200 nm for the H isotope image. Each run repeatedly scanned (10 to 40 times) over the same area. Individual images consist of 256 × 256 pixels with acquisition times of 5 to 10 ms/pixel (328 to 655 sec/frame) for C and N isotope images, and of 128 × 128 pixels with acquisition times of 5 to 10 ms/pixel (164 or 328 sec/frame) for the H isotope image. Each measurement was only started after stabilization of the secondary ion intensities following a pre-sputtering procedure of approximately 1-3 min. The sample was coated with a 10 nm Au thin film to mitigate electrostatic charging on the surface. During the analysis, the mass peaks were centered automatically every 10 cycles. The final isotope images were generated from regions that had statistically enough counts. Note that hydrogen signals were very low in the matrix region, possibly due to a small amount of phyllosilicate in the matrix, but more likely due to lower ionization efficiency of hydrogen in phyllosilicates compared with that in OM under the Cs^+ primary ion bombardment.

The OM regions were chosen by distributions of ^{12}C within a section applying 10% threshold of total ^{12}C ion counts. Thus, minerals and OM regions were distinguished by the above method with a spatial resolution of ~100 nm.

3. Results

3.1. Bulk analyses

Three aliquots (0.0581, 0.0553 and 0.0736 mg) of the sample were analyzed by EA/IRMS to obtain average C and N abundances, and $\delta^{13}C$ and $\delta^{15}N$ values with standard deviation (1σ). The bulk C and N abundances in the Zag clast were 5.1 ± 0.4 wt.% and 0.26 ± 0.01 wt.%, respectively, and the N/C ratio (atomic) was 0.043 ± 0.004 (Table 1). The bulk C and N contents of the Zag clast are the highest measured among various chondrite groups, though relatively close to Tagish Lake and CIs (Alexander et al., 2012; Alexander et al., 2018) (Fig. 1).

The $\delta^{13}C$ and $\delta^{15}N$ values of the Zag clast were +23.0 ± 4.1 ‰ and +300 ± 3 ‰, respectively (Table 1). The N/C ratio and $\delta^{15}N$ is among the highest values from primitive chondrites (Alexander et al., 2012). The $\delta^{13}C$ value of the Zag clast is unusual, since most primitive chondrites have negative $\delta^{13}C$ values, except Tagish Lake which has $\delta^{13}C$ of +9 to +14 ‰ (Alexander et al., 2012).

Fig. 2 shows an IR absorption spectrum of the clast. A broad band around 3400 cm^{-1} with a shoulder at 3620 cm^{-1} is characteristic of phyllosilicate OH with some adsorbed/interlayer water. The band is largely affected by atmospheric water since phyllosilicates easily adsorb moisture. Such bands are characteristic of hydrated minerals, and not seen in the IR spectra of anhydrous minerals such as olivine. A peak at 1010 cm^{-1} is consistent with Si–O in phyllosilicates. A peak at 1460 cm^{-1} is assigned to carbonates. Some organic features are observed at 2955 cm^{-1}, 2925 cm^{-1}, and 2850 cm^{-1} assigned to C−H asymmetric stretching of CH_3, C−H asymmetric stretching of CH_2, and C−H symmetric stretching of CH_3+CH_2, respectively. A peak at 1630 cm^{-1} can be assigned to adsorbed/interlayer water with some contribution by aromatic C.

Several C-rich areas were found by SEM-EDS. Most of the C-rich areas are 5 to 10 μm in size and observed in silicate matrix with Fe-rich grains (probably magnetite) and Fe+S rich grains (probably Fe-sulfides). We did not attempt to identify Fe-bearing grains, since the purpose here was to characterize OM-rich areas. FIB sections were prepared from three of these C-rich areas, #03, #25 and #26, as shown in Fig. 3.

3.2. STXM/XANES analyses

STXM images of the FIB section taken from the C-rich areas of #03, #25 and #26 in Fig. 3 are shown in Figs. 4-6, respectively. C-XANES spectra from regions of interest (ROIs) in these FIB sections are shown in Fig. 7. The STXM elemental maps show that sub-micrometer C-rich grains/aggregates are scattered over the FIB section (Figs. 4B, 5B, and 6B); a vein-like structure is observed (#25: Fig. 5B). C-XANES spectra of the C-rich areas show peaks at 285.2 eV assigned to aromatic C and at 290.5 eV assigned to carbonate C (either organic or inorganic), with 287.5 eV (aliphatic C) and 288.8 eV (carboxyl/ester C(=O)O) (Fig. 7). Some areas showed small features at 286.5 eV (C=O). The peak assignments are based on Cody et al. (2008a) and Vinogradoff et al. (2018) and summarized in Table 2.

We generated peak intensity maps that indicate abundances of aromatic and carbonate C (Figs. 4C, 5C, and 6C). Comparing elemental maps and peak intensity maps, C-rich areas (clear red in elemental maps; Figs. 4B, 5B, and 6B) are mostly associated with aromatic C (red in peak intensity maps; Figs. 4C, 5C, and 6C) and thus these areas are mostly organics. C- and O-rich areas (red-green mixture in the elemental maps; Figs. 4B, 5B, and 6B) are associated with carbonate (green in peak intensity maps; Figs. 4C, 5C, and 6C). In most cases (but not all), organic matter is finely mixed with carbonates at the sub-micrometer scale. The vein-like OM in #25 is also closely associated with carbonates (Fig. 5B), indicating its formation during aqueous activity. The #25 also contains a globular OM which is embedded in carbonates (Fig. 5F).

To compare molecular structures of each area, we obtained the peak intensities at 285.2 eV (aromatic C), 287.5 eV (aliphatic C), and 288.8 eV (C(=O)O) by subtracting a linear baseline and normalizing to the intensities at 291.5 eV (approximately at ionization potential energy) (Fig. 8). It should be noted that functional group abundances in Fig. 8 are not exact fractions in OM, but rather are relative indicators to compare molecular structure heterogeneity among each region. The globule in #25 plots away from typical OM areas, and is relatively rich in aromatic C and poor in C(=O)O. The carbonate-rich areas also plot away from typical OM areas (ROIs from #03 and #26). The OM vein (#25) is relatively poor in aliphatic C compared to OM in #03 and #26.

Fe-rich nodules (< 1 μm) are also abundant in the Zag clast FIB sections. Considering that these Fe-rich nodules are not O-rich (Figs. 4B, 5B, and 6B), most of them are likely Fe-bearing sulfides rather than Fe-bearing oxides. Fig. 9 shows Fe-XANES of the section #25. The Fe-XANES spectrum of the Fe-bearing sulfides region (Fig. 9A) shows peaks at ~708 eV (Fe^{2+}), and ~709 eV (Fe^{3+}) which is probably due to aerial oxidation. Pyrrhotite and troilite are known to have a peak at 707.7 eV (Calvert et al., 2005; Mikhlin and Tomashevich, 2005). However, a Fe^{3+} absorption could occur at 709.4 eV due to aerial oxidation of pyrrhotite surfaces (Mikhlin and Tomashevich, 2005). A spectral component map indicates that carbonate regions (green in Figs. 5C and 9B) are rich in Fe^{2+} (Fig. 9A), which is consistent with a siderite-like composition. Note that this does not exclude the possibility of the presence of other cations such as Mg^{2+} and Ca^{2+}. The matrix regions (blue in Fig. 9B) that probably consist mainly of phyllosilicates, have smaller Fe-contents but are relatively rich in Fe^{3+} compared to carbonates. The Fe-XANES spectrum of the blue regions (Fig. 9A) is consistent with Fe^{3+}-rich phyllosilicates (Le Guillou et al., 2015). The $Fe^{3+}/\Sigma Fe$ values in silicates could be calculated using the peak intensity ratios of $R_{L3} = I_{Fe3+}/I_{Fe2+}$ (Bourdelle et al., 2013);

$$\frac{Fe^{3+}}{\sum Fe} = \frac{R_{L_3} - 0.1867}{0.01991}\ \% \qquad \text{(eq .1)}$$

The calculated $Fe^{3+}/\Sigma Fe$ ratio of the matrix region (blue in Fig. 9B) is ≈70%. This value is consistent with the values of silicates in CR2 chondrites (66-75%) and CM chondrites (50-70%) (Le Guillou et al., 2015 and references therein). Decreasing Fe^{3+} with progressive alteration is observed and interpreted as a result of the transfer of Fe^{3+} from silicates to oxides (Le Guillou et al., 2015). The silicates in the Zag clast have relatively high Fe^{3+} and thus the matrix may not be fully altered. This proposal is consistent with the analyzed areas containing sulfides rather than oxides.

3.3. NanoSIMS analyses

δD and $\delta^{15}N$ values obtained by NanoSIMS are shown in Table 1 and isotope images are shown in Figs. 4D, 5D, and 6D (δD) and Figs. 4E, 5E, and 6E ($\delta^{15}N$), respectively. The average δD values of entire C regions are approximately +600 to +2000‰. While, the average δD value of entire H regions (which include entire C regions) is lower than the value of entire C regions for section #25, indicating that OM has higher δD than phyllosilicates. The average $\delta^{15}N$ and $\delta^{13}C$ values of entire C regions are approximately +300 to +1900‰ and –22 to –30‰, respectively. Some isotopic "hot spots" are observed with δD values up to ≈ +4000‰ and $\delta^{15}N$ values up to ≈ +5500‰. However, $\delta^{13}C$ is relatively homogeneous. The C-XANES characteristics of these hot spots do not show significant differences from typical OM regions (Figs. 7 and 8).

4. Discussion

4.1. Molecular structure heterogeneity

In the C-XANES peak intensity plot (Fig. 8), there are some regions relatively rich in aromatic carbon. All of these aromatic-rich regions are globular- or irregular-shaped compact OM. One found in #25 is globular with a <500 nm diameter (Fig. 5). ROI#1 in #03 is irregular shape and <1 μm in diameter (Fig. 6). The HS#2 in #03 with high $\delta^{15}N$ (+2640±720‰) is irregular shape, ≈500 nm in diameter, and its aromatic fraction is in between these two aromatic-rich regions and other regions. The OM vein in #25 is less-aliphatic and has less C(=O)O compared to other areas. Our previous study of the same clast from the Zag meteorite showed a large aggregate of OM ("the C-rich aggregate") whose C-XANES is dominated in aromatic structures and little contribution of other functional groups (Kebukawa et al., 2019b). The aromatic, aliphatic, and C(=O)O fractions are plotted in Fig. 8. The C-rich aggregate shows low abundance of aliphatic and C(=O)O and falls close to the globule in #25. In general, compact OM tends to be aromatic-rich compared to diffuse OM. This indicates that compact OM has a higher molecular weight and has massive aromatic units while diffuse OM has smaller molecular weight with smaller aromatic cores which might be very fine-grained organic solids and/or soluble organic compounds. This may be because OM with less-aromatic/more aliphatic and O-bearing functional groups has a higher mobility and has been diffused or scattered during the fluid activity on the clast's parent body (which was not the final Zag ordinary chondrite parent asteroid). This also implies that alteration did not average the molecular structures, but separated it and affected its morphology, likely due to the "geochromatography" effect in the parent body (Wing and Bada, 1991).

There are several isotopic hot spots with higher δD and/or $\delta^{15}N$ (Figs. 4-6, Table 1). We intended to extract C-XANES from the isotopic hot spots (Figs. 7 and 8). However, there are no special characteristics of the isotopic hot spots. Compact OM also shows no specific isotopic anomalies. This result is consistent with our previous analysis of the OM aggregate in the Zag clast that showed isotopic hot spots but no molecular heterogeneity between the hot spots and the average OM area (Kebukawa et al., 2019b). The globule in the #25 (Fig. 5F) shows no isotopic anomalies. Globules in primitive chondrites and cometary dust particles are often, but not always, attributed to isotopic hotspots (Nakamura-Messenger et al., 2006; De Gregorio et al., 2010; De Gregorio et al., 2013; Hashiguchi et al., 2013, 2015).

4.2. Interaction with minerals?

The Zag clast is predominantly a fine-grained mixture of serpentine, saponite, magnetite, Ca phosphates, organic-dominated grains, pyrrhotite and Ca-Mn-Mg-Na carbonates (Zolensky et al., 2017). The IR spectrum of the Zag clast is similar to those of CI/CM/CR chondrites (Kebukawa et al., 2019a), but with a higher abundance of carbonates. A globule within carbonate is observed (Fig. 5F). The structure indicates that carbonate precipitated around this globule, and thus implies that the globule formed before carbonate precipitation, possibly before accretion of the Zag clast parent body or at least at an early stage of aqueous process. In contrast, the vein-like OM in #25 is mixed with carbonates, indicating that the OM precipitated or deposited with carbonates during aqueous activities. There could be two possibilities; (1) solid OM formed in-situ from water soluble precursor molecules and precipitated (e.g., Cody et al., 2011; Kebukawa et al., 2013), or (2) physical deposition of insoluble OM. In any case, the globule and the vein-like OM may have been formed at different periods of time. This result is also consistent with the difference in C-XANES between the globule and the vein-like OM. The carbonates would have either precipitated from an aqueous fluid (Brearley, 2006), and/or been produced from OM by oxidation (Cody and Alexander, 2005).

The association of OM and carbonates is commonly observed in many (but not all) carbonaceous chondrites. STXM/XANES and transmission electron microscopy/electron energy-loss spectroscopy (TEM/EELS) studies have shown a OM-carbonate association in Tagish Lake, Murchison, Orgueil, and some CR2 (Renazzo, NWA 852, and GRA 95229) (Zega et al., 2010; Le Guillou et al., 2014; Vollmer et al., 2014), as well as IDPs from the comet 26P/Grigg-Skjellerup (Busemann et al., 2009). Infrared spectroscopic mapping studies reported distribution of OM (aliphatic C-H features) and carbonates at one to several micrometer spatial resolution. Carbonates show some association with organics (but at a much lesser extent than the association between organics and phyllosilicates) in the Tagish Lake meteorite (Yesiltas and Kebukawa, 2016). In the Bells meteorite, the organic matter is distributed adjacent to, but not overlapping carbonates (Kebukawa et al., 2010). The carbonate-OM association are not observed in NWA 852 (CR2) and Sutter's Mill (unusual CM) (Yesiltas et al., 2014; Yesiltas et al., 2015). A Raman study (~1 μm spatial resolution) reported that OM-carbonate associations are observed in some CMs; Jbilet Winselwan, Nogoya, Santa Cruz, and WIS 91600, but not observed in Murchison (Chan et al., 2017).

Sulfides are often observed to be rimmed by carbonaceous compounds in various extraterrestrial materials such as Tagish Lake, IDPs, and comet Wild 2 particles (Nakamura et al., 2002; Keller et al., 2004; Matrajt et al., 2008, 2012). These associations are often attributed to the formation of OM by catalytic gas-solid reactions such as Fischer-Tropsch type (FTT) synthesis. In the Zag clast, the association of OM with Fe-bearing grains (probably Fe-sulfides) is not obvious (Figs. 4B, 5B, and 6B), except for one grain in #26 where a Fe-rich grain surrounded by OM is observed at the bottom of the FIB section (Fig. 6B).

4.3. Insights from isotopic compositions

Fig. 10 compares the C-, N- and H-isotopic compositions in the Zag clast and various extraterrestrial materials. The bulk $\delta^{13}C$ (Fig. 10A) of most of the CM/CI/CR chondrites are in the range of –15 to +4‰ (Alexander et al., 2012). While the $\delta^{13}C$ of IOM from these chondrites are in the range of –27 to –17‰ (Alexander et al., 2007). The bulk $\delta^{13}C$ of the Zag clast is +23.0 ± 4.1 ‰, which is relatively similar to the values of Tagish Lake (Alexander et al., 2012). The $\delta^{13}C$ value of OM regions in the Zag clast is –28 to –22‰ that is similar to the value of IOM from CI/CM/CR chondrites, particularly close to CRs and Bells (Alexander et al., 2007). The lower $\delta^{13}C$ (–14.7 to –13.3‰) of Tagish Lake IOM (Herd et al., 2011) is consistent with the case of the Zag clast. The differences between bulk and OM are likely due to contributions from carbonates with higher $\delta^{13}C$. In fact, carbonates in CM/CI/CR chondrites range from ≈ +30‰ to ≈ +70‰ (Alexander et al., 2015). The significantly higher $\delta^{13}C$ values of bulk Tagish Lake could be attributed to the observed higher abundance of carbonates in Tagish Lake compared to other carbonaceous chondrites (Zolensky et al., 2002), as well as for the Zag clast.

The bulk $\delta^{15}N$ values (Fig. 10B) of CM (except Bells), CI, CR chondrites, and Tagish Lake are –6 to +50 ‰, +35 to +45 ‰, +160 to +180 ‰, and +60 to +76 ‰, respectively (Alexander et al., 2012). The $\delta^{15}N$ of IOM is similar to bulk values, and –9 to +8 ‰ for CMs, ≈ +30 ‰ for CIs, +150 to +230 ‰

for CRs (Alexander et al., 2007), and +53 to +73 ‰ for Tagish Lake (Herd et al., 2011). ^{15}N-enriched hot spots up to ≈ +3000 ‰ are often found in these chondrites (Busemann et al., 2006; Hashiguchi et al., 2015). Such high ^{15}N/^{14}N ratios are generally considered to be the result of ion-molecule reactions in the ISM or in the cold regions of the disk surrounding the protostar, and/or photodissociation of N_2 by UV light from the proto-Sun or from nearby stars, so called self-shielding (Füri and Marty, 2015). The ^{15}N-enrichment generally increases with distance from the Sun (Füri and Marty, 2015). As a result, D/H ratios also show similar trends with ^{15}N/^{14}N (Marty, 2012). Similar to the ^{15}N, the D-enrichments are considered to be the result of ion-molecule reactions in low temperature environments such as molecular clouds (Kerridge, 1983; Millar et al., 1989). It has also been suggested that D-fractionation occurred in the protoplanetary disk by UV irradiation to ionized molecules in the early solar system (Remusat et al., 2006; Remusat et al., 2010; Aikawa et al., 2018). However, generally more complexity exists compared to nitrogen, since hydrogen is easy to exchange between water and OM, e.g., D-enrichments of OM decrease by alteration due to exchange with D-depleted water (e.g., Alexander et al., 2010). The bulk δD values (Fig. 10C) of CM (except Bells), CI, CR chondrites, and Tagish Lake are –200 to +100 ‰, +70 to +80 ‰, +250 to +750‰, and +500 to +550 ‰, respectively (Alexander et al., 2012). The δD of IOM is similar to bulk values, and +640 to +890 ‰ for CMs, ≈+970 ‰ for CIs, and +2600 to +3500 ‰ for CRs (Alexander et al., 2007), and +600 to +1800 ‰ for Tagish Lake (Herd et al., 2011). D-rich hot spots reach up to ≈ +20,000 ‰ (Busemann et al., 2006). In addition, ^{15}N-rich hotspots are not always associated with D-enrichments, supporting the view that the D-enrichments are easily modified by aqueous alteration processes on the parent body (Hashiguchi et al., 2015). On the other hand, adsorption of ammonia on phyllosilicate surfaces could induce N isotopic fractionation and result in ^{15}N-enrichment of ammonia on phyllosilicates (Sugahara et al., 2017). Considering that ammonia and phyllosilicates are common constituents of primitive chondrite parent bodies, the adsorption of ammonia on mineral surfaces might partly explain the ^{15}N enrichment, although the observed N fractionation by this mechanism is relatively low (Sugahara et al., 2017). The bulk δ^{15}N of the Zag clast is +300 ± 3.3 ‰, and the δ^{15}N value of OM region in the Zag clast is ≈ +300 to +1900 ‰ (Figs. 10B and 10C). These are closest to the bulk $\delta^{15}N$ values of Bells (≈+350 ‰) and CRs (≈+160 to +180‰) (Alexander et al., 2012), and the $\delta^{15}N$ of IOM from CRs (≈ +150 to + 300 ‰) and Bells (+415‰) (Alexander et al., 2007), but generally higher than these values. The δD of the OM regions in the Zag clast varies in the range of +600 to +2000 ‰, which is similar to the value of IOM from CI/CM chondrites and Tagish Lake (Alexander et al., 2007). The $\delta^{15}N$ of the OM regions in the Zag clast are also somewhat similar to cometary (IDP) values (Busemann et al., 2009; Floss et al., 2011; Davidson et al., 2012) (Fig. 10B), although some IDPs show δD values much higher than the Zag clast (Fig. 10C). However, the phyllosilicate-rich nature of the Zag clast is probably not consistent with a cometary origin. The Isheyevo meteorite (CH/CB) has dark xenolithic clasts that have a wide range of $\delta^{15}N$, up to +4900 ± 300 ‰ (Briani et al., 2009; Bonal et al., 2010b). However, their δD values are ≈ –300‰ to +400‰, and no localized D-enrichments were observed (Briani et al., 2009; Bonal et al., 2010b).

4.4. Insights from molecular compositions

The C-XANES spectra of the Zag clast (Fig. 7), in general, show various functional groups such as C(=O)O, and aliphatics, but there is no 1s-σ* exciton at 291.7 eV indicating graphene structures as in the case of thermally metamorphosed chondrites (Cody et al., 2008b). It indicates that the clast did not experience long-term thermal metamorphism as in H3-6 chondrite parent body(ies). However, short-term heating, e.g., impact heating, cannot be excluded.

The C-XANES spectra show large to moderate aromatic C at 285 eV, some aliphatic C at 287.5 eV, and some C(=O)O at 288.5 eV, but no or little C=O at 286.5 eV (Fig. 7). These features generally agree with C-XANES of primitive chondritic IOM, such as Murchison and Tagish Lake (5b and 11i) which have abundant aromatic C, some aliphatic C, moderate C(=O)O and no or little C=O (De Gregorio et al., 2013; Alexander et al., 2014). However, some IOM, e.g., that in a CR2 (EET 92042), is rich in C=O (De Gregorio et al., 2013). The C-XANES features of nanoglobules are variable; some are similar to IOM and some are rich in C=O and/or aromatic (De Gregorio et al., 2013). Also, variable chemical structures are found in in-situ observations of OM in primitive meteorites, e.g., Renazzo (CR2), Murchison, and Orgueil; generally OM particles or globules are rich in C=O but “diffuse” OM has less C=O than particles/globules (Le Guillou et al., 2014). The in-situ C-XANES spectra of Renazzo, Murchison and Orgueil are similar to our Zag clast except for the C=O features. In-situ C-XANES analysis of Tagish Lake showed aromatic C, C(=O)O, and minor aliphatic C with no or little C=O (Chan et al., 2019), and these features are common in the Zag clast.

Cometary particles also show similar C-XANES features with chondritic OM, but with larger variations (Cody et al., 2008a). Major differences between OM in cometary particles and primitive chondrites are that cometary OM is less aromatic and higher C=O (Cody et al., 2008a; De Gregorio et al., 2010). Also IDPs are less aromatic and rich in C=O and C(=O)O (Flynn et al., 2003; Keller et al., 2004). Overall, the C-XANES features of the Zag clast are similar to OM in CMs, CIs, and Tagish Lake rather than CRs, IDPs, and cometary particles.

The bulk C and N contents of the Zag clast are 5.1±0.4 wt.% and 0.26±0.01 wt.%, respectively (Table 1). The bulk C and N contents of the Zag clast are the highest observed among various chondrite groups, but relatively close to Tagish Lake and CIs (Alexander et al., 2012; Alexander et al., 2018) (Fig. 1A). The C and N contents in IDPs and cometary particles are generally much higher (Alexander et al., 2017), although no precise C and N abundances are available since the samples are too small. Extremely C-rich (~50-85% of OM) particles are sometime found among Antarctic micrometeorites called ultracarbonaceous Antarctic micrometeorites (UCAMMs), which are considered to be cometary in origin (Duprat et al., 2010). The dust particles from comet 67P/Churyumov-Gerasimenko (67P/CG) analyzed by the cometary secondary ion mass analyzer (COSIMA) on Rosetta had ~30 wt.% carbon and the organic/mineral ratio is suggested to be as high as ~45/55 (w/w) (Bardyn et al., 2017). The C and N abundances in the Zag clast—higher than typical chondrites but smaller than comets—also support the idea of primitive asteroids such as D/P type or asteroids somewhat intermediate between asteroids and comets.

The N/C ratio (atomic) of the Zag clast was 0.043 ± 0.004 (Table 1) which is consistent with the values of bulk carbonaceous chondrites (Fig. 1B). These values are much lower than the N/C ratio of OM in an anhydrous chondritic IDPs (N/C = 0.12) and the cometary particles from 81P/Wild 2 (N/C = 0.07 to 0.24) (Sandford et al., 2006; Cody et al., 2008a; Flynn et al., 2008). It indicates that the Zag clast is less primitive compared to comets (and the IDPs possibly originating from comets). However, the N/C atomic ratio of the comet 67P/CG particles ranges from 0.018 to 0.06 with an averaged value of 0.035 ± 0.011 (Fray et al., 2017), which is rather similar to the values of chondrites as well as the Zag clast.

4.5.Origin?

The aqueously altered nature of the Zag clast (Zolensky et al., 2017) probably excludes the possibility of cometary origin—although a possibility of aqueous alteration in comets cannot be excluded (Gounelle et al., 2006)—, as well as ordinary chondrites and thermally metamorphosed carbonaceous chondrites (CV, CO, CH, CB). However, as discussed in the above two sections and summarized in Table 3, the isotope and molecular structure characteristics of the OM in the Zag clast lie somewhat in-between primitive chondrites and IDPs/comets, and share significant similarities with the Tagish Lake meteorite. Fujiya et al. (2019) showed that the Tagish Lake parent body (plausibly D-type asteroid) have accreted in the cold outer Solar System where the ice giant planets formed, or in the trans-Neptunian regions, and have subsequently migrated inwards. It should be noted that, although surfaces of D/P type asteroids are dominated by anhydrous materials (Emery et al., 2006; Vernazza et al., 2012), one cannot exclude the possibility of aqueous alteration in the interior (Yang et al., 2013).

In addition, the texture (e.g., weakness) of the Zag clast is similar to Tagish Lake, and much weaker than typical carbonaceous chondrites such as Murchison and Orgueil. However, the Zag clast is apparently less porous than cometary IDPs (Busemann et al., 2009; Davidson et al., 2012). It is possible that the clast experienced compaction and lithification during alteration and/or impact. These processes would explain less-primitive nature of the clast compared to cometary particles and IDPs. On the other hand, it may not have required thermal processing, but could have resulted from, e.g., something akin to “cold welding” that effects spacecraft (Lu et al., 2010).

Our additional and more detailed analyses of the Zag clast further support the idea that the Zag clast originated from the outer Solar System such as D/P type asteroids, as we suggested previously (Kebukawa et al., 2019b). Thus, this result would be supporting evidence of the giant planet migration models which lead to the insertion of primitive trans-Neptunian objects (TNOs) into the outer asteroid belt (Levison et al., 2009), and even into main asteroid belt region ($<$2.5 AU) (Vokrouhlicky et al., 2016), crossing the orbit of the probable parent body of the H chondrites, asteroid 6/Hebe (2.4 AU) (Gaffey and Gilbert, 1998). Indeed, four D-type asteroids are confirmed at 2.3-2.5 AU (DeMeo et al., 2014).

5. Conclusions

We conducted detailed analyses of OM on an aqueously-altered xenolithic clast in the Zag meteorite using EA/IRMS, FTIR, STXM/C-XANES and NanoSIMS. The STXM/C-XANES analyses show that OM in the Zag clast is heterogeneously distributed and include globule-like structures and vein-like structures. The vein-like structures are associated with carbonates which indicates formation during aqueous activities. C-XANES spectra of OM indicate the presence of aromatic C, aliphatic C, and C(=O)O structure, as well as carbonates that are finely mixed with OM. Some areas show small contributions of C=O structures. The bulk C and N abundances in the Zag clast are +5.1±0.4 wt.% and +0.26±0.01 wt.%, respectively, with the N/C ratio (atomic) of 0.043±0.004. The $\delta^{13}C$ and $\delta^{15}N$ values of the bulk Zag clast are +23.0±4.1‰ and +300±3‰, respectively. The $\delta^{15}N$ and $\delta^{13}C$ are among the highest values measured from astromaterials. NanoSIMS isotope analyses show local heterogeneity of $\delta^{15}N$ and δD with the highest $\delta^{15}N$ of +5540±2760‰ and the highest δD of +4150±1710‰. The molecular structures and elemental and isotopic compositions support the idea that the Zag clast originated from the most primitive asteroids such as D/P type asteroids, as we suggested previously.

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Figures captions

Fig. 1. (A) The bulk C and N abundances (wt.%) of the Zag clast, and various carbonaceous chondrites. (B) The N/C ratios of the Zag clast, various chondrites (bulk and IOM), an IDP, and Comet Wild 2. Chondrite, IDP, and cometary particle data from: Grady and Pillinger (1990); Alexander et al. (2007); Cody et al. (2008a); Ivanova et al. (2008); Alexander et al. (2010); De Gregorio et al. (2010); Herd et al. (2011); Alexander et al. (2012); Alexander et al. (2018).

Fig. 2. Infrared absorption spectrum of the clast from the Zag meteorite.

Fig. 3. (Upper) Backscattered electron (BSE) images of the carbon-rich areas in the Zag clast. (Lower) Elemental composition maps by energy-dispersive X-ray spectroscopy (EDS) of the carbon-rich areas in the Zag clast.

Fig. 4. The FIB section from the C-rich area #03 in the Zag clast. (A) A STXM image at 395 eV (darker area corresponds to lower transmission), (B) C-O-Fe elemental map, (C) Peak intensity map, aromatic C in red, carbonates in green, and blue corresponds to background, (D) δD image, and (E) δ^{15}N image. Yellow circles indicate δD and δ^{15}N hot spots.

Fig. 5. The FIB section from the C-rich area #25 in the Zag clast. (A) A STXM image at 395 eV (darker area corresponds to lower transmission), (B) C-O-Fe elemental map, (C) Peak intensity map, aromatic C in red, carbonates in green, and blue corresponds to background, (D) δD image, and (E) δ^{15}N image. A yellow rectangle contained an organic nanoglobules. An enlarged peak intensity map of the yellow rectangle area is shown in (E).

Fig. 6. The FIB section from the C-rich area #26 in the Zag clast. (A) A STXM image at 395 eV (darker

area corresponds to lower transmission), (B) C-O-Fe elemental map, (C) Peak intensity map, aromatic C in red, carbonates in green, and blue corresponds to background, (D) δD image, and (E) δ^{15}N image.

Fig. 7. The C-XANES spectra of the Zag clast FIB sections #03, #25 and #26. The spectra were obtained from regions shown in Figs. 4-6.

Fig. 8. The C-XANES peak intensities normalized by the intensities at 291.5 eV. (A) Aliphatic vs. aromatic, (B) aliphatic vs. C(=O)O.

Fig. 9. (A) The Fe-XANES spectra of the Zag clast FIB section #25. (B) The spectral component map generated from the spectra shown in (A). Red region corresponds to Fe-rich nodules, green region corresponds to carbonates, and blue region corresponds to the matrix. (C) The C-O-Fe elemental map (same as Fig. 4B) was shown next to the composition map for comparison.

Fig. 10. The isotopic compositions of the Zag clast comparing to various chondrites, IDPs and cometary particles. (A) The C isotopic compositions, (B) the N isotopic compositions, and (C) the H isotopic composition. Data: IOM, Alexander et al. (2007); Alexander et al. (2010); Tagish Lake IOM, Herd et al. (2011), Bulk chondrites, Alexander et al. (2012); Alexander et al. (2018); CH/CB, Prombo and Clayton (1985); Franchi et al. (1986); Grady and Pillinger (1990, 1993); Sugiura and Zashu (2001); Ivanova et al. (2008); Briani et al. (2009); Bonal et al. (2010a); IDPs, Floss et al. (2006); Busemann et al. (2009); Floss et al. (2011); Davidson et al. (2012); Hotspots, Busemann et al. (2006); Hashiguchi et al. (2015); Comet 81P/Wild 2, De Gregorio et al. (2010); De Gregorio et al. (2011); Matrajt et al. (2013).

Table 1. The C and N contents, N/C elemental ratios and isotopic compositions of the Zag clast.

	δD (‰)	δ^{15}N (‰)	δ^{13}C (‰)	C wt.%	N wt.%	N/C (at.)
Bulk[1]		300 ± 3.3	23.0 ± 4.1	5.1 ± 0.4	0.26 ± 0.01	0.043 ± 0.004
NanoSIMS[2]						
#03						
Entire H	810 ± 210					
Entire C		390 ± 80	-22 ± 21			
HS#1	4150 ± 1710					
HS#2		2640 ± 720				
#25						
Entire H	1700 ± 60					
Entire C	2030 ± 90	1850 ± 190	-22 ± 9			
HS#1	3150 ± 1510	5540 ± 2760				
HS#2	3600 ± 760					
#26						
Entire C	640 ± 130	324 ± 35	-28 ± 10			
HS	1760 ± 790					
Previous[3]						
OM aggregate	2370 ± 74	696 ± 100	-43 ± 20			0.022 ± 0.004
HS#1	4200 ± 550	3413 ± 1070				0.032 ± 0.006
HS#2	4500 ± 900	724 ± 780				
Matrix		301 ± 98	10 ± 41			0.036 ± 0.007

[1] Errors are standard deviation (1σ) of 3 analyses, [2] Errors are standard deviation (1σ) of each pixel, [3] Data from Kebukawa et al. 2019

Table 2. C- and Fe-XANES peak positions and assignments.

Energy/eV	Structures
285.2	Aromatic C
286.5	C=O
287.5	Aliphatic C
288.8	C(=O)O
290.5	Carbonate
707.8	Fe^{2+}
709.5	Fe^{3+}

Table 3. Similarities between the Zag clast and various astromaterials.

	$\delta^{13}C$	$\delta^{15}N$	δD	C & N contents	N/C	C-XANES
CMs	+	–	++	–	++	+
Bells	+	++	–	–	++	nd
CIs	+	–	++	+	++	+
CRs	+	+	–	–	++	+
Tagish Lake	++	–	++	+	++	++
Isheyevo clasts	–	+	–	nd	–	nd
IDPs	+	++	+	nd	nd	+

+: consistent, –: inconsistent., nd: no data