HIGHLY PRISTINE ORGANIC MATTER IN A XENOLITH CLAST IN THE ZAG H CHONDRITE.

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Introduction: The Zag meteorite is a halite-bearing H3-6 chondrite [1]. We have been studying a dark Zag clast with abundant organic matter [2,3], which was proposed to be from Ceres [4,5]. Therefore, our systematic research of the Zag clast may provide an important linkage to the recent remote sensing observations obtained by the DAWN mission to Ceres [e.g., 6,7]. We prepared a new sub-sample of this clast for coordinated organic analysis by STXM-XANES and NanoSIMS, in order to understand the nature and origin of the organic matter.

Methods: Carbon-rich areas were located in the clast grains separated from the Zag meteorite with SEM (Hitachi SU8220/Bruker QUANTAX FlatQUAD EDS), and then lift-out sections were prepared with a Hitachi MI4050 FIB instrument. C, N, O-X-ray absorption near-edge structure (C,N,O-XANES) spectra of the sections (~100 nm-thick) were obtained using scanning transmission X-ray microscopes (STXM) on beamline 5.3.2.2 at Advanced Light Source, Lawrence Berkeley National Laboratory, and BL-13A at the Photon Factory, KEK. Subsequently, C and N isotopic imaging were conducted using a CAMECA NanoSIMS 50L ion microprobe at Kochi Institute for Core Sample Research, JAMSTEC.

IR absorption spectra were obtained from the bulk clast grains pressed between two KBr plates, using a Jasco FT/IR-6100+IRT-5200 at Yokohama National University.

Results: Fig. 1 shows IR spectra of the Zag 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. A Si-O band that has a peak center at 1010 cm^{-1} is consistent with phyllosilicates. Carbonates (1460 cm^{-1}) are also abundant. Some organic features are observed at 2955 cm^{-1}, 2925 cm^{-1}, and 2850 cm^{-1} (aliphatic CH_3 and CH_2). A peak at 1630 cm^{-1} can be assigned to adsorbed/interlayer water with some contribution by aromatics.

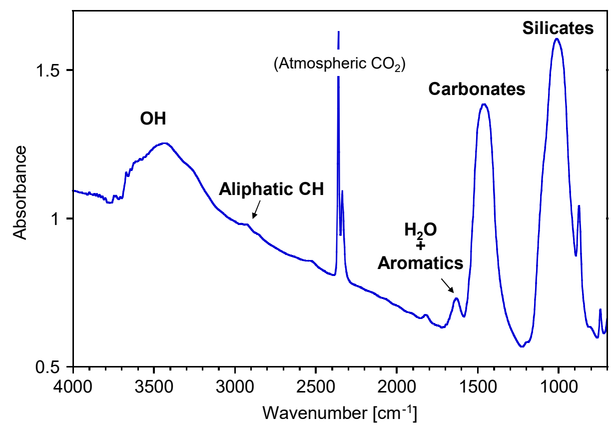

Fig 1: An FTIR spectrum of the Zag clast.

One of the carbon rich areas found with SEM-EDS is shown in Fig. 2. STXM-XANES and NanoSIMS images of the FIB section taken from the C-rich area in Fig. 2 are shown in Fig. 3. The STXM elemental map (Fig. 3a) shows that sub-micrometer organic grains are scattered over the FIB section, some of which have a vein-like structure. The organic matter is somewhat associated with Fe (probably Fe-sulfides), as shown in the EDS elemental map (Fig. 2 right). The Fe (+Ni) and C association is also observed in the clasts in Sharps (H3.4) chondrite, suggesting a potential of catalytic gas–solid reactions such as Fischer-Tropsch type (FTT) synthesis [8,9].

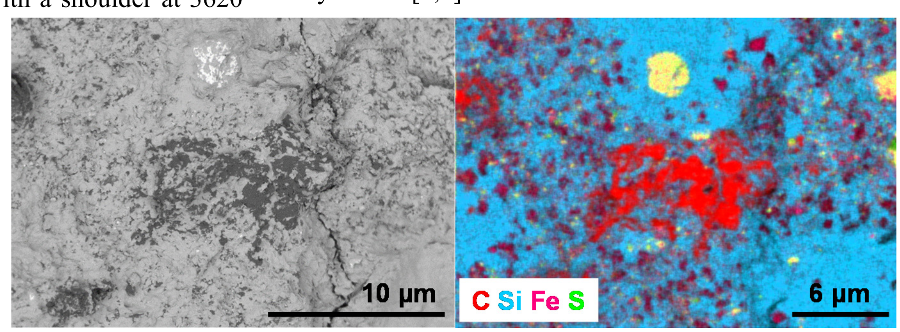

Fig 2: (left) BSE image of a carbon rich area (dark gray), (right) elemental map of the carbon rich area, C is red, Si is blue, and yellow is Fe+S.

A C-XANES spectrum of the organic grains (Fig. 3c red) shows large peaks at 285.2 eV assigned to aromatic carbon, and at 290.3 eV assigned to carbonate (either organic or inorganic), with some features at 287.4 eV (enol C=C-OH), and 287.9eV (aliphatic), and 288.8 eV (carboxyl). Although carbon is not clearly shown in the STXM elemental map (Fig. 3a), C-XANES of surrounding areas shows the presence of organics with less aromatic features (Fig. 3c green). The diffused organic matter in the surrounding area are very fine-grained organic solids and/or soluble organic compounds.

NanoSIMS isotope images are shown in Fig. 3d (δ^{13}C) and Fig. 3e (δ^{15}N). δ^{13}C is relatively homogeneous with an average δ^{13}C of –28 ± 10 ‰. δ^{15}N has a highly heterogeneous distribution within the organic matter, and the average δ^{15}N value is +324 ± 35 ‰. The δ^{13}C and δ^{15}N is similar to the value of insoluble organic matter (IOM) from Bells (an unusual CM chondrite) and CRs [10]. However, nitrogen is undetected with STXM, indicating that the nitrogen abundance is low.

Discussion: There are large differences between the organics analyzed in this and our previous study of the same Zag clast [2,3]. Morphologically, organic matter in this study appeared as scattered sub-micrometer grains, in contrast with our previous observation which showed that the organic matter appeared as micrometer-sized chunks. Structurally, enol, aliphatic and carboxyl carbon are significantly more abundant than the previous sample. δ^{13}C values are comparable, but less ^{15}N-rich than the previous study [3]. Relationships between this and previous studies are ambiguous, but overall, there appears to be a rough trend between the size of organic matter and its molecular structure. The smaller size of organics tend to have diminished aromatic nature. This might indicate that organic species with less-aromatic/more aliphatic and O-bearing functional groups have a higher mobility and have been diffused or scattered during the fluid activity on the clast's parent body (which was not the Zag parent body).

The C-XANES spectra in the Zag clast show some similarity with organic matter from Comet Wild 2, rather than with primitive chondritic IOM [11], except for the abundant carbonate in the Zag clast. The high δ^{15}N value also indicates a primitive nature for the organic matter, and that its precursor, at least, originated in interstellar space or at an outer region of the Solar System.

Conclusions: We conducted a coordinated molecular structure and isotopic study using STXM and NanoSIMS on an aqueously-altered xenolithic clast in the Zag meteorite. Both molecular structure and isotopic signatures indicate highly pristine (less altered) nature of organic matter in the clast, and it may be related to cometary organics and/or primitive chondritic IOM (Bells and CRs).

References: [1] Zolensky M. E. et al. (1999) *Science, 285,* 1377–1379. [2] Kebukawa Y. et al. (2016) *47th LPSC,* Abstract #1802. [3] Kebukawa Y. et al. (2016) *79th MetSoc,* Abstract #6233. [4] Fries M. et al. (2013) *76th MetSoc,* Abstract #5266. [5] Zolensky M. E. et al. (2015) *78th MetSoc,* Abstract #5270. [6] Nathues A. et al. (2015) *Nature, 528,* 237–240. [7] De Sanctis M. C. et al. (2015) *Nature, 528,* 241–244. [8] Brearley A. J. (1990) *Geochim. Cosmochim. Acta, 54,* 831–850. [9] Kebukawa Y. et al. (2017) *Geochim. Cosmochim. Acta, 196,* 74–101. [10] Alexander C. M. O'D. et al. (2007) *Geochim. Cosmochim. Acta, 71,* 4380–4403. [11] Cody G. D. et al. (2008) *Meteorit. & Planet. Sci., 43,* 353-365.

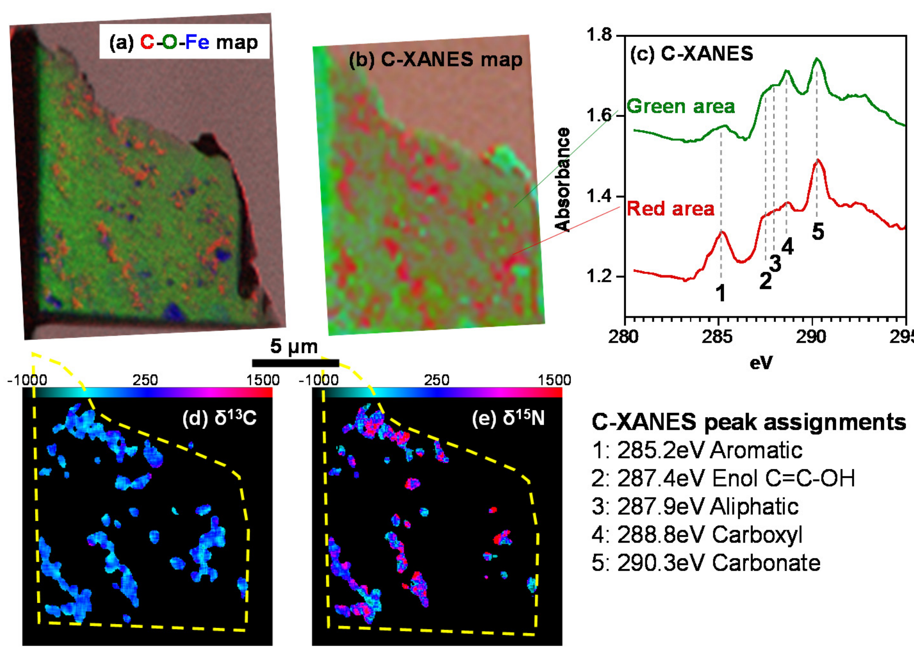

Fig 3: (a) STXM elemental map of the Zag clast FIB section. C in red, O in green, and Fe in blue. (b) C-XANES map and (c) C-XANES spectra of aromatic-rich organic grains (red) and less-aromatic diffused organic matter (green). (d) δ^{13}C and (e) δ^{15}N images obtained by NanoSIMS.