

HIGHLY PRISTINE ORGANIC MATTER IN A XENOLITH CLAST IN THE ZAG H CHONDRITE. Y. Kebukawa¹, M. Ito², M. E. Zolensky³, A. Nakato⁴, H. Suga⁵, Y. Takahashi⁶, Y. Takeichi⁷, K. Mase⁷, Q. Chan³, M. Fries³, and K. Kobayashi¹, ¹Faculty of Engineering, Yokohama National University (kebukawa@ynu.ac.jp), ²Kochi Institute for Core Sample Research, JAMSTEC, ³ARES, NASA Johnson Space Center, ⁴Graduate School of Science, Kyoto University, ⁵Department of Earth and Planetary Systems Science, Hiroshima University, ⁶Department of Earth and Planetary Science, The University of Tokyo, ⁷Institute of Materials Structure Science, High-Energy Accelerator Research Organization (KEK).

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. 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 3620cm⁻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 CH₃ and CH₂). A peak at 1630cm⁻¹ can be assigned to adsorbed/interlayer water with some contribution by aromatics.

One of the carbon rich areas found with SEM-EDS is shown in Fig. 2. STXM-XANES and

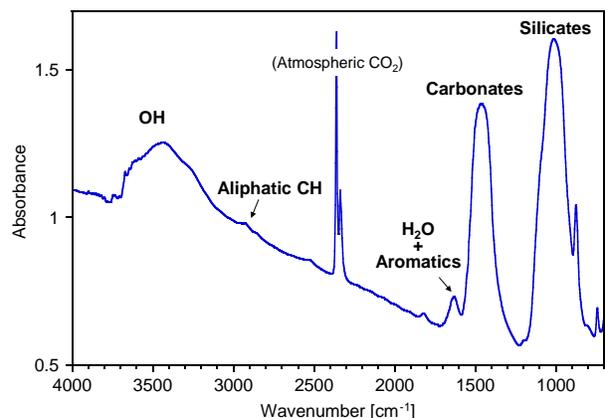


Fig 1: An FTIR spectrum of the Zag clast.

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 closely associated with Fe that is probably in Fe-sulfides, as shown in the EDS elemental map (Fig. 2 right). 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 organic features with less aromatic (Fig. 3c green). The diffused organic matter in the surrounding area would be very fine-grained organic solids and/or soluble organic compounds.

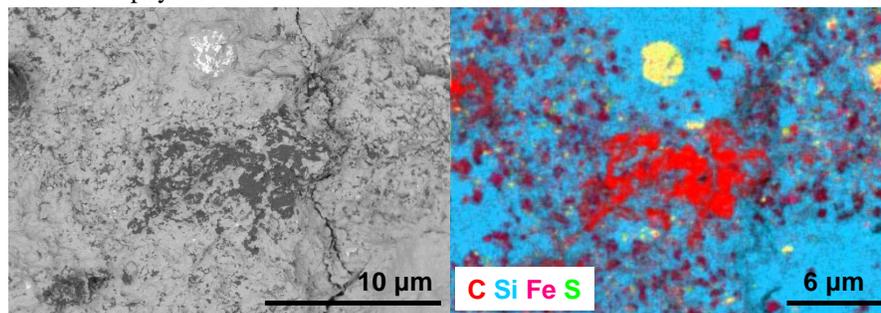


Fig 2: (left) BSE image of a carbon rich area, (right) elemental map of the carbon rich area, C is red, Si is blue, and yellow is Fe+S.

NanoSIMS isotope images are shown in Fig. 3d ($\delta^{13}\text{C}$) and Fig. 3e ($\delta^{15}\text{N}$). $\delta^{13}\text{C}$ is relatively homogeneous with an average $\delta^{13}\text{C}$ of $-28 \pm 10 \%$. $\delta^{15}\text{N}$ has a highly heterogeneous distribution within the organic matter, and the average $\delta^{15}\text{N}$ value is $+324 \pm 35 \%$. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ is similar to the value of insoluble organic matter (IOM) from Bells (an unusual CM chondrite) and CRs [6]. However, nitrogen is undetected with STXM, indicating that the nitrogen abundance is small.

Discussion: There are large differences between this study and our previously analyzed organics in this Zag clast [2,3]. In morphology, organic matter in this study appeared as scattered sub-micrometer grains, in contrast with organic matter that appeared as micrometer-sized chunks in our previous study of this Zag clast. For molecular structure, enol, aliphatic and carboxyl carbon are highly abundant in the clast studied here as compared to the previous one. $\delta^{13}\text{C}$ values are comparable, but less ^{15}N -rich than the previous study [3]. Relationships between the sample from the clast studied here and the previous one is ambiguous, but it seems that there is a rough trend between the size of organic matter and its molecular structure. The smaller-sized organics might have less aromatics. This might indicate that less-aromatic organics have a higher mobility and have been

easily diffused or scattered during 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 Wild2, rather than with primitive chondritic IOM [7], except for the abundant carbonate in the Zag clast. The high $\delta^{15}\text{N}$ 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 for an aqueously-altered xenolithic clast in the Zag meteorite. Both molecular structure and isotopic signatures indicate the highly pristine 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] Alexander C. M. O'D. et al. (2007) *Geochim. Cosmochim. Acta*, 71, 4380–4403. [7] Cody G. D. et al. (2008) *Meteoritics & Planet. Sci.*, 43, 353–365.

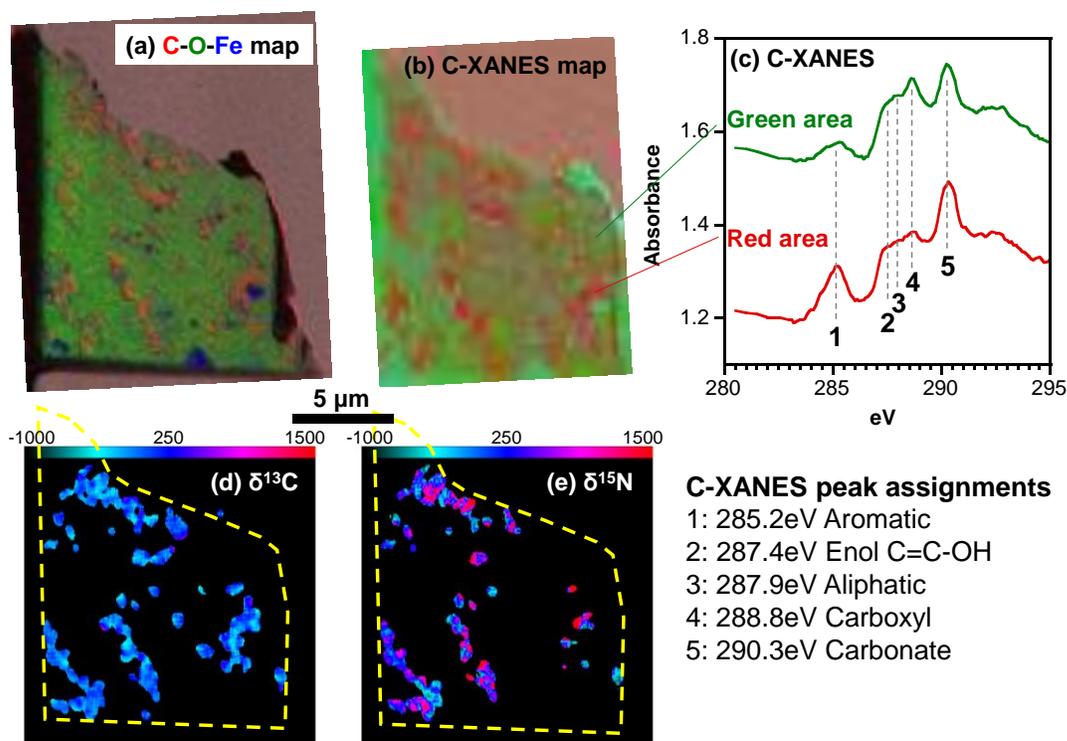


Fig 3: (a) STXM elemental map of the Zag clast FIB section. C in red, O in green, and Fe in blue. (b) C-XANES map and (c) C-XANES spectra of aromatic-rich organic grains (red) and less-aromatic diffused organic matter (green). (d) $\delta^{13}\text{C}$ and (e) $\delta^{15}\text{N}$ images obtained with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