

**EFFECTS OF MINERALS ON ORGANIC MATTER EVOLUTION IN HYDRATED CARBONACEOUS CHONDRITE PARENT BODIES BASED ON STXM AND TEM ANALYSES.** K. Kiryu<sup>1</sup>, Y. Kebukawa<sup>1</sup>, Y. Furukawa<sup>2</sup>, Y. Takahashi<sup>3</sup>, Y. Takeichi<sup>4</sup>, D. Wakabayashi<sup>4</sup>, S. Yamashita<sup>4</sup>, T. Ohigashi<sup>5</sup>, M. Ito<sup>6</sup>, Y. Kodama<sup>7</sup>, and K. Kobayashi<sup>1</sup>, <sup>1</sup>Yokohama National University, <sup>2</sup>Tohoku University, <sup>3</sup>The University of Tokyo, <sup>4</sup>High Energy Accelerator Research Organization, <sup>5</sup>Institute for Molecular Science, <sup>6</sup>Kochi Institute for Core Sample Research, JAMSTEC, <sup>7</sup>Marine Works Japan Ltd.

**Introduction:** Organic matter (OM) in carbonaceous chondrites (CCs) mostly occurs in the form of insoluble organic matter (IOM), which is complicated macromolecular compounds [e.g., 1, 2]. The IOM expresses a variety of chemical compositions depending on the extent of the alteration [3, 4]. In the process of OM evolution, specific minerals may play a key role. For instance, phyllosilicates that are major components of hydrated CCs might catalyze organic reactions [e.g., 5-7] because of their peculiar structures [e.g., 8]. Spatial relationships between OM and phyllosilicates in hydrated CCs, in fact, were revealed through scanning electron microscope (SEM) observations [9] and Fourier transform infrared microspectroscopy (FTIR) analyses [e.g., 10]. The objective of this study is relating the degree of aqueous alteration and the specific minerals to OM evolution in these chondrites on the basis of microscopic approaches.

In order to achieve our goal, we selected the Tagish Lake meteorite, since it has various lithologies and similarities to CI and CM chondrites [11]. It is a unique type 2 CC, and presumably experienced heterogeneous aqueous alteration [11, 12]. Herd et al. [12] and Alexander et al. [13] investigated four distinct Tagish Lake lithologies by determining IOM—elemental and isotopic compositions, and functional group chemistries. Their studies showed that the least altered Tagish Lake lithology has the highest H/C ratio and  $\delta D$  value, while the most altered one shows the lowest H/C ratio and  $\delta D$  value, similar to the trend of various chondrite groups [3, 4]. These studies presented the correlation between the extent of aqueous alteration and the properties of IOM. Tagish Lake is ideal for identifying effects of minerals on OM evolution in parent bodies of hydrated CC.

**Methods:** Six ultrathin sections (~100 nm thick) were prepared using a focused ion beam (FIB) apparatus from three different fragments of Tagish Lake (“Pristine [11]”, “KN2 [14]”, “Degraded [11]”). One of the KN2 FIB sections were prepared from particularly Mg-rich area which was surveyed by SEM-EDS before FIB. We analyzed the sections by scanning transmission X-ray microscope (STXM) and obtained C- and Fe-X-ray absorption near-edge structure (XANES) spectra. The aim of utilizing XANES spectra is to associate the degrees of aqueous alteration with OM molecular structures. After STXM analyses, we performed

transmission electron microscope (TEM) observations of the identical sections for the sake of exploring the relationships between the specific minerals to OM distributions in the hydrated CCs. For comparison to Tagish Lake, three CIs—Orgueil, Ivuna, and Alais—were also analyzed with the same way.

**Results and discussion: XANES analyses.** The C-XANES spectra of the sections show peaks at 285.2 eV (aromatic C), 287.3 eV (aliphatic C), 288.5 eV (C(=O)O), and 290.3 eV (carbonate) (Fig. 1). Fig. 2a shows aliphatic/aromatic and C(=O)O/aromatic peak intensity ratios of Tagish Lake and CIs. There is a clear correlation between aliphatic/aromatic and C(=O)O/aromatic ratios, and the abundances of aliphatic and C(=O)O in Tagish Lake are higher compared to the three CIs (Fig. 2a). It implies that the amounts of aliphatic and C(=O)O moieties decreased with increasing aqueous alteration. It is consistent with previous works [12, 13], which showed increasing aromatization and decreasing aliphatic and O-bearing functional groups with increasing alteration among several different lithologies of Tagish Lake. These functional group ratios of Tagish Lake notably disperse (error bars are  $1\sigma$  standard deviations of several different analytical areas) compared to those of the three CIs—the ratios of the three CIs are in close proximity (Fig. 2a). This trend confirms the main feature of Tagish Lake—heterogeneity.

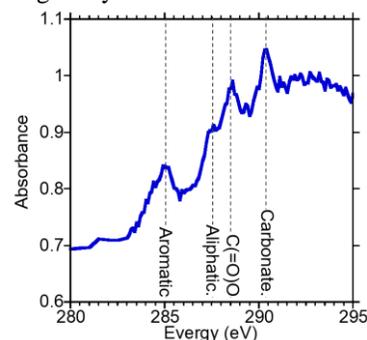


Fig. 1. C-XANES spectrum of Tagish Lake KN2.

$Fe^{3+}/\Sigma Fe$  ratios in silicates are calculated using the method of Bourdelle et al. [15] using the peak intensities at 706.8 eV ( $Fe^{2+}$ ) and 708.5 eV ( $Fe^{3+}$ ) from Fe-XANES spectra. Le Guillou et al. [16] proposed that  $Fe^{3+}/\Sigma Fe$  ratio of silicates gradually decreased with increasing aqueous alteration for CRs. They interpreted the cause

as the transfer of  $\text{Fe}^{3+}$  from silicates to oxides during aqueous alteration. However, the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios of Tagish Lake and CIs in our study do not show significant correlations with aliphatic/aromatic and  $\text{C}(=\text{O})\text{O}/\text{aromatic}$  peak intensity ratios (Fig. 2b,c). Although petrologic type of Tagish Lake is higher (lower aqueous alteration degree) than CIs, the  $\text{Fe}^{3+}$  abundances of Tagish Lake are lower than CIs. It is probably due to the difference of phyllosilicate assemblages between Tagish Lake and CIs [11].

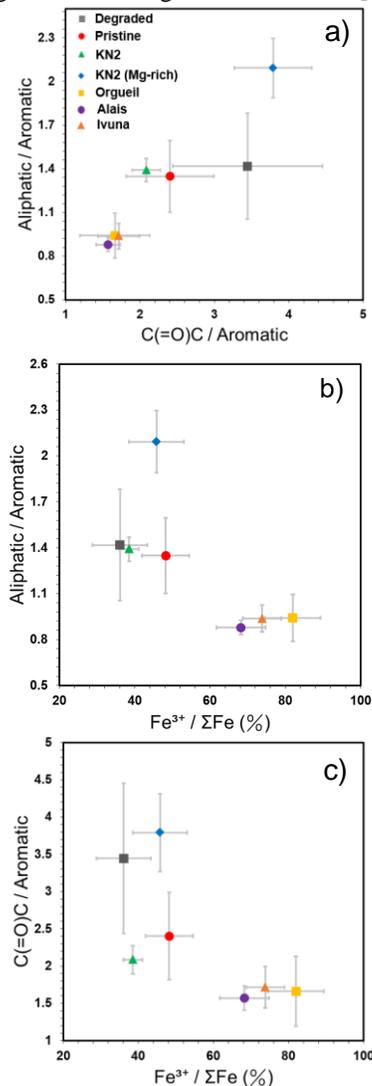


Fig. 2. (a) Aliphatic/aromatic and  $\text{C}(=\text{O})\text{O}/\text{aromatic}$  peak intensity ratios, and (b, c) their relationship with  $\text{Fe}^{3+}$  abundances in Tagish Lake and three CIs.

**TEM analyses.** We found several peculiar areas from Tagish Lake KN2 (Mg-rich) (Fig. 3a, b). In Fig. 3a, we can see a clear boundary between phyllosilicates (the black-left side) and OM (the white-right side). It is interesting that sulfides (secondary minerals) exist in the border.

Fig. 3b shows the distinctive structure of phyllosilicates in KN2 compared to typical ones in Tagish Lake analyzed in this study. The TEM-EDS and the STXM C-map of this region show that the abundance of OM in this area is considerably lower than other phyllosilicate areas. It indicates that phyllosilicates do not be always associated with OM.

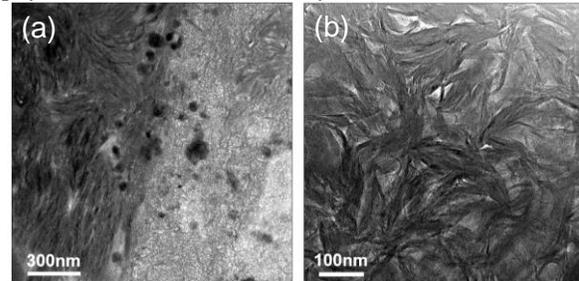


Fig. 3. TEM images of peculiar areas in Tagish Lake KN2 (Mg-rich).

**Perspectives:** TEM analyses are still on the way, we will analyze more details of associations between OM and minerals, and compare with STXM-XANES data. It will bring us new insights into the relationships of OM and minerals in the unique Tagish Lake meteorite, as well as their co-evolution during parent body alteration and possibly before accretion.

**Acknowledgments:** We would like to acknowledge Dr. M. Zolensky and Dr. W. Fujiya for providing the meteorite samples. This study was supported by JSPS KAKENHI.

**References:** [1] Botta O. and Bada J. L. (2002) *Surveys in Geophysics*, 23, 411–467. [2] Pizzarello S. et al. (2006) In *Meteorites and the early solar system II*, eds. Lauretta D. S. et al., Tucson, AZ: The university of Arizona Press. pp. 625–651. [3] Alexander C. M. O. D. et al. (2007) *Geochim. Cosmochim. Acta*, 71, 4380–4403. [4] Alexander C. M. O. D. et al. (2010) *Geochim. Cosmochim. Acta*, 74, 4417–4437. [5] Varma R. S. (2002) *Tetrahedron*, 58, 1235–1255. [6] Yadav J. S. et al. (2004) *Tetrahedron*, 60, 1767–1771. [7] Ferris J. P. (2005) *Elements*, 1, 145–149. [8] Murray R. S. and Quirk J. P. (1990) *Langmuir*, 6, 122–124. [9] Pearson V. K. et al. (2002) *Meteorite. Planet. Sci.*, 37, 1829–1833. [10] Yesiltas M. and Kebukawa Y. (2016) *Meteorite. Planet. Sci.*, 51, 584–595. [11] Zolensky M. E. et al. (2002) *Meteorite. Planet. Sci.*, 37, 737–761. [12] Herd C. D. K. et al. *Science*, 332, 1304–1307. [13] Alexander C. M. O. D. et al. (2014) *Meteorite. Planet. Sci.*, 49, 503–525. [14] Brandon A. D. et al. (2005) *Geochim. Cosmochim. Acta*, 69, 1619–1631. [15] Bourdelle F. et al. (2013) *Contrib. Mineral. Petrol.*, 166, 423–434. [16] Le Guillou C. et al. (2015) *Earth Planet. Sci. Lett.*, 420, 162–173.