Preliminary results of Sulfur speciation by µ-XANES and STXM in Extraterrestrial Organics

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Sulfur is one of the major elements in terrestiral and extraterrestrial organics. The elemental compositions of the Murchison IOM (insolble organic matter) are proposed to be $C_{100}H_{70}O_{22}N_3S_7$ [1] or $C_{100}H_{48}N_{1.8}O_{12}S_2$ [2]. Because sulfur shows a wide range in oxidation state (-2 to +6) with both electropositive and electronegative elements, both reduced and oxidized sulfur species have been found in various carbonaceous chondrites [3, 4]. Therefore, understanding of speciation of sulfur and its distribution within organics in a carbonaceous chondrite is crucial to provide the secondary alteration processes of thermal metamorphism and aqueous alteration in the parent body.

X-ray absorption near edge spectroscopy (XANES) is a powerful analytical tool to characterize and quantify chemical speciation, functional group and bonding environment of the sample. In the field of cosmochemistry, many researches were carried out to identify functional groups of C, N and O in extraterrestrial organics (i.e., IOM in carbonaceous chondrites [5], cometary returned sample [6], organics found in Hayabusa Category-3 grains [7], organics in IDPs [8]). However, sulfur study with XANES in the extraterrestrial organics is very rare [3, 9].

In this study, we report preliminary results of sulfur speciation measurements by K- and L_3-edge XANES of the IOM extracted from Asuka 881458 CM2 carbonaceous chondrite. We carried out X-ray fluorescence (XRF) mapping for S and N with a spatial resolution of 20 µm in the IOM (0.8 x 1 mm^2) at BL27SU of SPring-8. We, then, conducted µ-XAFS (sulfur K-edge) measurements to acquire point spectra (#1-#6 in Fig. 1). In addition, we have measured carbon K-edge and sulfur L_3-edge XANES spectra in the FIB section of the AA881459 IOM (8 x 20 µm^2) using scanning transmission X-ray microscope (STXM) at Inst. Mole Sci. UVSOR BL4U.

Figure 1. S and N XRF images of extracted organics from A881458 CM2 chondrite.

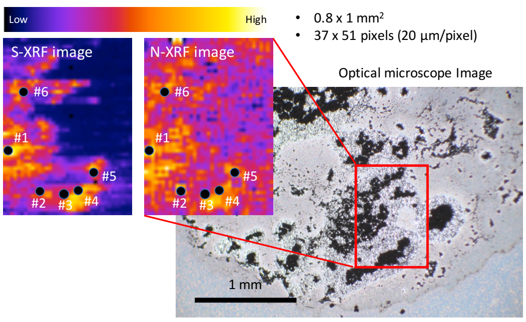


Figure 2. Possible sulfur components in the extracted organics from A881458 obtained by K-edge spectrum.

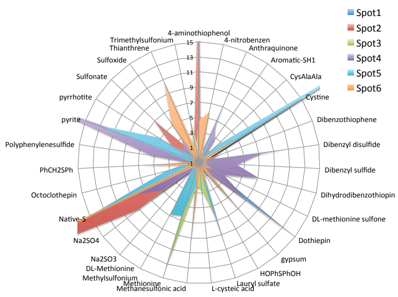
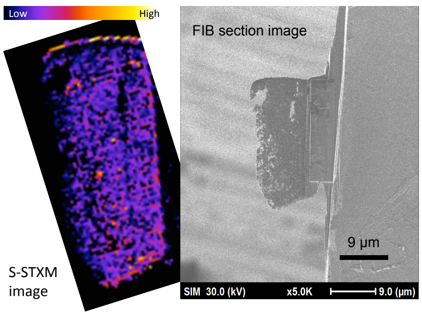


Figure 1 shows S and N XRF images together with optical microscope image of the sample on the Si wafer. The distributions of S and N are similar but slightly different abundances. We used these images to determine XANES analysis spots in the sample (about 20 µm in size, #1 to #6 in Figure 1). Measured S K-edge XANES spectra (#1 to #6) have deconvoluted with a least-square linear combination best fits to reference spectra of S contained organic and inorganic compounds. Figure 2 shows a radar diagram of possible S components and their abundances in each spot (#1-#6). Each spot has different sulfur contained organics and inorganics and their abundances. This suggested that extraterrestrial organics is a complex mixture of several types of sulfur species. Our result is consistent with previous works [3, 9]. S L_3-edge XANES spectra of several S-contained organics with different species (lauryl sulfate, sodium methanesulfonate, L-cysteic acid and DL-methionine sulfone) were obtained as references. Figure 3 shows high-resolution (50 nm) S L_3-edge STXM image of the FIB section of the AA881459 IOM. It is noted that S is homogeneously distribute and tiny S hot spots were observed within the sample. However, it is difficult to deconvolute the L_3-edge spectra of the sample based on fitting by a linear combination of standard materials spectra because of lack of the S L_3-edge spectra for reference materials at this moment.

Figure 3. Sulfur L-edge STXM image and SIM image



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