Sulfur-XANES of intact Ryugu grains and the isolated IOM

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Introduction: The Hayabusa 2 spacecraft was launched on December 2014 to collect samples of the near-Earth C-type (carbonaceous) asteroid (162173) Ryugu [1]. This mission aims to investigate the origin and evolution of the early Solar System and life. In December 2020, the spacecraft returned 5.42 g of the Ryugu surface samples to the Earth [2]. The initial sample analysis team and the JAXA phase2 curation found that the elemental compositions, mineralogy, and organic chemistry of asteroid Ryugu were identical to those of CI chondrites [e.g., 3-6].

A variety of sulfur-bearing organic molecules have been identified from both soluble organic matter (SOM) and insoluble organic matter (IOM) in carbonaceous chondrites [e.g., 7-9]. Sulfur has a wide range in oxidation states from -2 to +6, so it can be used as a cosmochemical indicator of redox conditions; therefore, it contributes to elucidating the formation of organic molecules in the early Solar System. X-ray Absorption Near Edge Structure of Sulfur (S-XANES) can be used to estimate oxidation states of sulfur from a large chemical shift, and the chemical species can be discussed by the spectral profile. In this study, we conducted the S-XANES analysis on intact Ryugu grains and the isolated IOM to determine the sulfur composition.

Samples and Method: The Ryugu aggregate samples A0109-21 and C0057-1&2 were selected for S-XANES measurements. The acid treatment protocol of IOM isolation is described in [3] in detail. The intact Ryugu grains and the isolated IOM were analyzed by non-destructive bulk S K-edge XANES analysis at BL27SU in SPring-8.

Results and Discussion: Sulfur-XANES spectra were obtained from the intact Ryugu grains and the isolated IOM. The spectral profile of the intact grains is composed of the dominant peak around 2470.4 eV and broad spectra ranging from 2475.0 to 2484.0 eV. The peak of 2470.4 eV corresponds to the inorganic sulfide (S^{1-}) [8]. Compared with the spectral profile of standard materials in the previous study [e.g., 10], it corresponds to pyrrhotite, a common sulfide in Ryugu [5]. In addition, a peak derived from sulfate (S^{6+}) was observed at 2482.6 eV from A0109-21.

The S-XANES spectra of Ryugu IOM were entirely different from those of the intact grains. The peak around 2472.0 eV corresponding to organic sulfides (C-S-S-C, C-S-C) was the most prominent from the spectra of Ryugu IOM. The shoulder feature at 2474.3 eV is consistent with the presence of heterocyclic sulfur (S^0) [9]. The broad profile ranging at 2477.0–2484.0 eV could be a mixture composed of oxidized organic sulfur species; such as sulfonate (R-SO_2O-R'), sulfone (R-SO_2-R'), and sulfites (R-SO_3) [8]. A moderate peak of sulfates was also observed, which is likely to be correspond to organic sulfate (R-O-SO_3) because inorganic sulfate compounds should have already been dissolved from the Ryugu samples during acid treatment to extract IOMs. No significant difference was found between IOMs extracted from A0109 and C0057.

The spectral shapes of the isolated Ryugu IOM were broadly similar to those of IOM from carbonaceous chondrites [8,9], except that the peak derived from inorganic sulfide was not detected from the Ryugu IOM. In particular, moderate abundances of heterocyclic sulfur and oxidized organic sulfur functional groups in Ryugu IOM were closer to those in IOM isolated from CM rather than that of CI. CI experienced a higher temperature (100–150 °C) than CM, and heterocyclic sulfur and oxidized organic sulfurs in them are the aqueous alteration products related to the alteration temperature [8]. Our study shows that Ryugu experienced as low temperature as CM chondrites during the parent body aqueous alteration, which is consistent with the discussion by [5].

Conclusion: In this study, organic sulfur functional groups were identified from the IOM isolated from Ryugu samples by S-XANES. Our results indicate that reductive organic sulfur components, i.e., organic sulfides (C-S-S-C, C-S-C), are dominant relative to oxidized organic sulfurs in Ryugu IOM. Ryugu IOM experienced low-temperature parent body aqueous alteration.

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