Sulfur K-edge XANES Spectra for Determining Chemical States of Sulfur Species in the Periostracum of *Corbicula* sp. in Lake Biwa

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In Japan, three native *Corbicula* species have been recognized: *C. Sandai*, *C. Leana*, and *C. Japonica*. The *C. Sandai* (*Setashijimi*) is a species endemic to the Lake Biwa-Yodo River system. In Lake Biwa, only 50 years ago, the freshwater corbicula clam was the main fish resources. However, the catch volume has declined sharply, and the current volume is below 50 t. Accordingly, scientifically-based understanding of the habitat for corbicula clam is required for the resource recovery.

The shell consists of a thin periostracum and a calcium carbonate substrate. The periostracum is an outermost thin organic layer secreted by the inner surface of the outer mantle fold at the mantle margin. Occasionally, the periostracum was peeled off from the substrate. Because the bivalve is unable to self-repair the periostracum, the information of the habitat of *Corbicula* sp. is recorded on the remaining periostracum. Sulfur (S) is one of the main redox-sensitive elements. S K-edge XANES measurements were performed to obtain information on the habitat.

Corbicula clams were collected from Lake Biwa. Two types of corbicula clams, yellowish colors and blackish colors, were used as the samples because it is supposed that the color depends on the habitat. After removing the inside and drying, the shell was smashed and a roughly 10 mm square piece was prepared. The piece was set on the sample plate and S K-edge XANES spectra was taken with XAFS double crystal soft X-ray XAFS beamline (BL-13). The spectra were collected by partial fluorescence yield (PFY) mode with a silicon drift detector (SDD) and the total electron yield (TEY) mode by a sample current.

Figure 1 shows S K-edge XANES spectra of *Corbicula* sp and energies of electronic oxidation states of S atoms. Because there is a strong correlation between the electronic oxidation state of the S atom in an S-containing compound and the peak energy of the white line, the energies were estimated [1]. The PFY-XAFS spectra exhibit only one peak at around 2473 eV. The peak was assigned to reduced S compounds such as S containing amino acid. The TEY-XAFS spectrum of yellowish colored piece exhibits a peak at around 2481 eV in addition to that at around 2473 eV. The peak was assigned to most oxidized S compounds such as sulfate and sulfate esters (S^{6+}). The TEY-XAFS spectrum of blackish colored piece exhibited a peak at 2475.5 eV in addition to those at around 2473 eV and 2481 eV. The peak was assigned to reduced organic S compounds such as sulfoxide (S^{2+}).

The TEY mode is a surface-sensitive technique, while the PFY mode provides near-surface and bulk. It was revealed that the oxidation states of S were different between the outer and inner parts of the periostracum. The outer layer contains S^{6+} and/or sulfate esters, while the black colored outer layer contains S^{2+}. In addition, the yellowish colored shell is more oxidizes than the blackish one.

References

[1] J. Prietzel, J. Thieme, U. Neuhäusler, J. Susini, and I. Kögel-Knabner, *Euro. J. Soil Sci.*, **2003**, *54*, 423.

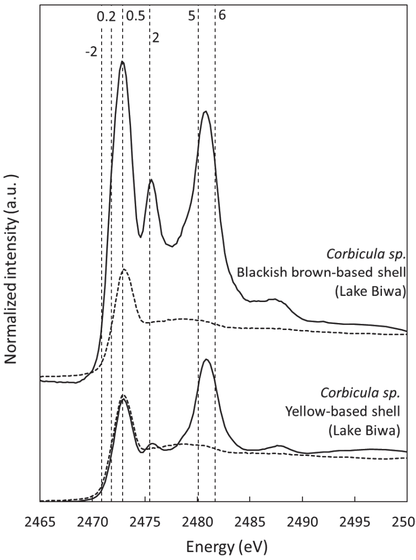

Fig. 1 S K-edge XANES Spectra of *Corbicula* sp and energies of electronic oxidation states of S atoms in S-containing compounds. Sold line: TEY, broken line: PFY.