XANES and EXAFS on Worm Jaws

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Introduction

In contrast to vertebrate mandibles that are hardened with calcium-based minerals, the jaws of certain marine sediment worms consist of sclerotized protein and considerable amounts of transition metals [1-3]. The two polychaete worm species investigated here, *Nereis* and *Glycera*, contain zinc and copper, respectively. In *Glycera*, the greater part of the copper has been found to be bound to the mineral atacamite ($Cu_2(OH_3)Cl$) [1]. No zinc-based mineral has been detected in *Nereis* jaws. In the experiment described here, extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) were used to investigate the chemical environment of copper and zinc, respectively, in the worm jaws.

Methods and Materials

EXAFS and XANES experiments on native *Glycera* and *Nereis* jaws had been previously performed at beamline 20-ID at the APS [4]. In this experiment at beamline 20-BM, the emphasis was on measuring proper model compounds. Various Zn- and Cu-containing compounds were analyzed in powder form. The powder was packed into flat sachets of adhesive Kapton® tape. The samples were then mounted on a copper stage that was inserted into a cryostat and cooled down to 4K in order to enhance the x-ray absorption spectroscopy (XAS) signal. X-ray absorption spectra were recorded at the Cu and Zn absorption edges by using ion chambers to record the transmitted intensity and a 13-element detector to record the fluorescence from the sample. The beam diameter was about 1 mm. The data were also compared with and fitted to theoretical standards calculated by using the software FEFF8 [5, 6].

Results

Glycera Jaws

In order to find out how much of the copper in *Glycera* jaws was actually bound to the mineral atacamite and if other copper compounds were present, the *Glycera* XANES was compared to XANES from atacamite powder. The results are shown in Fig. 1. It is obvious that the signals are very similar, except for the

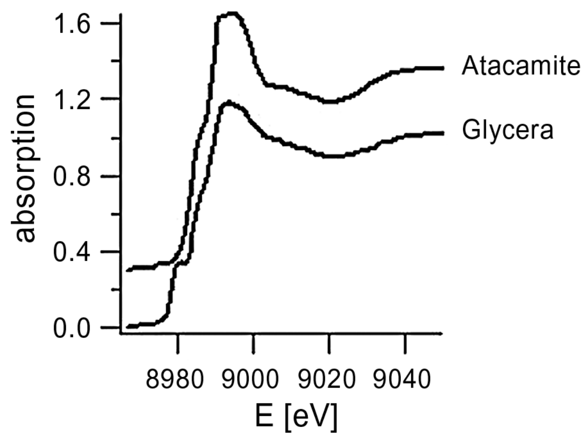

*FIG. 1. XANES spectra of **Glycera** jaw and atacamite powder (experimental data).*

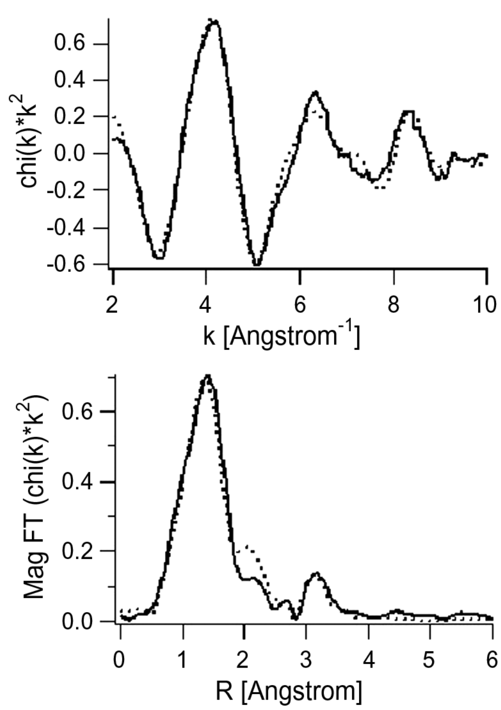

*FIG. 2. EXAFS spectra of **Glycera** jaw (full line) and fit with calculated model spectra of atacamite.*

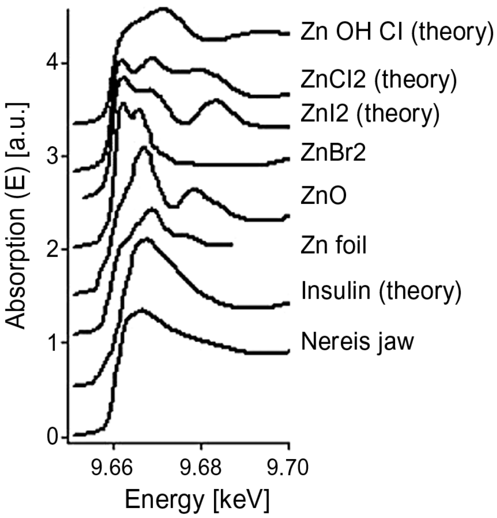

*FIG. 3. XANES of **Nereis** jaw and Zn compounds (experimental data unless stated otherwise).*

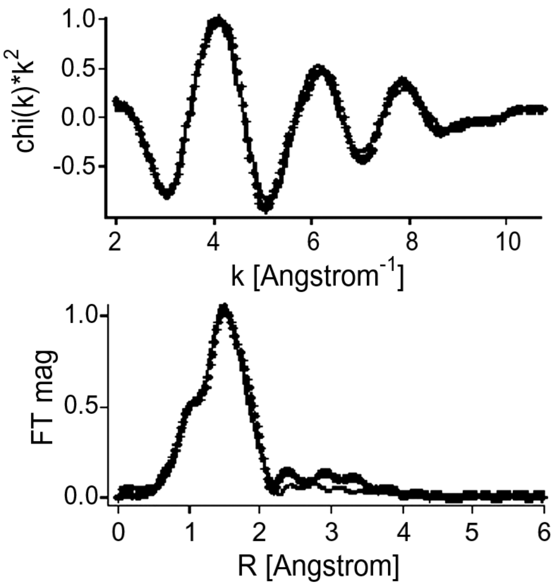

*FIG. 4. Zn EXAFS of **Nereis** jaw. Symbols denote experimental data. The line represents a fit to the calculated EXAFS of Zn-insulin (from Ref. 4).*

extra pre-edge peak in the *Glycera* spectrum. This pre-edge peak is a clear indicator of the oxidation state of copper; its presence denotes the existence of Cu(I). It is not observed in atacamite, because all the copper in atacamite is Cu(II). This suggests that in *Glycera* jaws, there is a small amount of other copper compounds in addition to atacamite.

Figure 2 shows the corresponding EXAFS curves. The full line represents experimental data for the *Glycera* jaw. The dotted line is a fit to the data with the theoretically calculated curve of atacamite. (The top of Fig. 2 shows the EXAFS spectrum in k-space; the bottom shows it in R space.) Whereas the major part of the spectrum is well-fit by the calculated atacamite EXAFS, there is an extra peak at 2 Å in the R spectrum. Thus, the EXAFS data support the interpretation that the major part of the copper is bound to atacamite, but there is a small fraction of other copper-containing compounds.

Nereis Jaws

Zn-XANES and EXAFS spectra of *Nereis* jaws were compared to those obtained from various model substances. In Fig. 3, the XANES data from the Nereis jaw are plotted together with experimentally determined data from Zn-containing model substances as well as selected calculated data. It is obvious that none of the inorganic compounds shown here matched the data. The best match was obtained by using a theoretical standard for Zn-insulin. Taking Zn-insulin as a model also yielded a good fit to the EXAFS data. (Figure 4, where symbols denote experimental data, and the line denotes fit to the model compound.) In Zn-insulin, Zn is surrounded by three N atoms and one Cl atom. It has been suggested that in the *Nereis* jaw, Zn could be directly bound to the histidine-rich jaw protein. Since histidine is a good candidate for metal coordination via its imidazole ring, N atoms appear to be the likely nearest neighbors of Zn. Moreover, in *Nereis* jaws, Cl has been found to occur spatially correlated with Zn-[4]. Thus, Zn-insulin is an appealing model system for the local environment of Zn in *Nereis* jaws.

Acknowledgments

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