Anomalous SAXS on Copper-containing Worm Jaws

H.C. Lichtenegger,^{1,3} H. Birkedal,¹ G.D. Stucky,¹ J.H. Waite,² D.M. Casa,⁴ T. Gog⁴

¹Department of Chemistry and Biochemistry and

²Department of Molecular, Cellular and Developmental Biology,

University of California, Santa Barbara, CA, U.S.A.

³Institute for Materials Science and Testing, Vienna University of Technology, Wien, Austria

⁴Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

The jaws of the marine sediment worm Glycera dibranchiata have been found to contain considerable amounts of copper [1]. The major part of the copper is bound in a copper-based biomineral that is organized in polycrystalline fibers that reinforce the sharp jaw tip [2]. However, there appears to be copper in the matrix as well. In previous small-angle x-ray scattering (SAXS) experiments conducted at the CMC-CAT beamlines, a pronounced, anisotropic SAXS signal was obtained from the fiber-containing regions. If the copper is mainly restricted to the fibers, the SAXS signal in the fiber region should be highly sensitive to variations of the incident beam energy around the copper absorption edge. Anomalous SAXS (ASAXS) was, thus, the method of choice to determine the distribution of copper in the system.

Methods and Materials

Glycera worm jaws were used as dissected from the animal and dried. The samples were mounted on a thin glass fiber with a small drop of super glue. ASAXS experiments were carried out at CMC-CAT beamline



Fig. 1. SAXS curves recorded below (solid symbols) and at the copper absorption edge (open symbols).

9-ID. The diameter of the x-ray beam was 0.1 mm. The incident beam energy was varied around the Cu absorption edge (8.979 keV). Scattering images were recorded using a SMART charge-coupled device (CCD) camera (Bruker AXS) positioned at a distance of 5.25 m from the sample. The flight path of the scattered photons was evacuated to reduce the background. The intensity I_0 of the incident beam was monitored continuously by using an ion chamber. The transmitted total intensity was measured with a pin-diode at each point before the SAXS scan and used to calculate the absorption. The measured SAXS patterns were normalized with respect to I_0 , background corrected and corrected for absorption. Subsequently, the 2-D scattering images were integrated over the azimuth and the intensity plotted versus q.

Results and Discussion

Figure 1 shows typical scattering curves recorded below and at the Cu absorption edge. The shape of the curve is the same at both energies, but at the Cu absorption edge, a considerable loss of intensity occurs (note the logarithmic scale).

Figure 2 shows the total SAXS intensity (i.e., the area under the scattering curves) as a function of energy. It is obvious that the scattering varies considerably with energy. The intensity is a smooth



Fig. 2. Total SAXS intensity as a function of energy.

function of energy that reaches its minimum at the copper absorption edge and corresponds well with the shape that would be expected from theory. The result, thus, strongly supports the assumption that the scattering contrast in the *Glycera* jaw tips is due to the high concentration of copper in the mineralized fibers and its very low concentration in the protein matrix.

Acknowledgments

H.C. Lichtenegger was supported by Fonds zur Förderung der Wissenschaftlichen Forschung (FWF, Austria) under Award No. J2184. H. Birkedal thanks the Danish Natural Sciences Research Council for financial support. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

[1] P.E. Gibbs and G.W. Bryan, J. Mar. Biol. Assoc. U.K. **60**:1, 205-214 (1980).

[2] H.C. Lichtenegger et al., Science **298**:5592, 389-392 (2002).