XAFS Study of Iron Oxides in Oyster Digestive Processes

M. M. Sarker,[1] R. A. Gordon,[1] E. D. Crozier,[1] L. Bendell-Young,[1] G. Kruzynski[2]
[1]Simon Fraser University, Burnaby, British Columbia, Canada
[2]Institute of Ocean Sciences, Sidney, British Columbia, Canada

Introduction

Bivalves, especially oysters, are hyperaccumulators of trace metals. Of concern are known metal toxicants such as Cd. Once ingested via diet, Cd in oysters becomes bound to a specific protein, metallothionein, and the complex turns over very slowly. As a consequence, Cd concentrations within the organism increase with time and become a health risk to frequent consumers.

One possible source of Cd to the filter-feeding oyster is local upland factors, such as runoff from a recently disturbed watershed (e.g., logging). This runoff, which ultimately makes it way to embayments through streams and then estuaries, may be high in mineral components, such as iron and manganese oxides, to which Cd can partition. Particles of these oxides may, in turn, act as intermediaries that provide an efficient Cd pathway from the water to the mineral surface to oysters through filter feeding [1].

Here, we present the results of a scanning micro x-ray absorption fine structure (micro-XAFS) study that suggests a link between metal exposure to the oyster and upland sources, specifically through the occurrence of oxides of iron in the gut of the oysters. Further, by comparing the oxidation states of iron in the gut and feces of the oyster, we provide evidence that oxides of iron are being reduced in the oyster gut.

Methods and Materials

Samples of oyster guts and feces were collected from Barkley Sound on the west coast of Vancouver Island, British Columbia (about 48° 59' N and 125° 04' W.). Feces were collected by suspending a sediment collection trap under a raft of cultured oysters for 24 h. Collected deposits from the oysters were placed in a plastic container and kept cool until the feces were removed. Feces, identified by long intact strands, were removed via glass pipette and refrigerated. Oysters were collected from a nearby beach at mid-tide and frozen until required. One oyster whose size was representative of the oysters collected was dissected, and the complete contents of its gut were removed.

Samples for x-ray analysis consisted of thin coatings that were spread onto tissue paper, covered with Kapton® tape, and adhered to a fused silica disk. Sample areas 1×1 mm in size were imaged by using KB mirrors focused to 5 μm in the Pacific Northwest Consortium Collaborative Access Team (PNC-CAT) beamline ID-B hutch. The fluorescence radiation was collected with a Canberra single-element Li-drifted Ge detector. Regions with high Fe concentrations were identified, and K-edge XAFS spectra were acquired.

Results

For six randomly selected regions in the guts, the Fe x-ray absorption near-edge structure (XANES) spectra were the same, suggesting that the Fe is homogeneously distributed with the same oxidation state and coordination. A representative spectrum is shown in Fig. 1. A comparison with the XANES of reference compounds indicates that the Fe is in a 3^+ oxidation state. While the XANES of Fe in the gut is similar to that of α–FeO(OH) (geothite), the differences suggest that either different or additional phases are present. The gut XANES cannot be fit with simple linear combinations of geothite, γ–FeO(OH) (lepidocrocite), α–Fe_2O_3 (hematite), or γ–Fe_2O_3 (maghemite). The near edge of the feces XANES (Fig. 1) is chemically shifted ~2.5 eV to lower energies relative to the gut, indicating that the Fe is in a lower average oxidation state (~2.6) with a coordination geometry different from the guts. In addition, as shown in Fig. 2, the XANES spectra of feces vary from region to

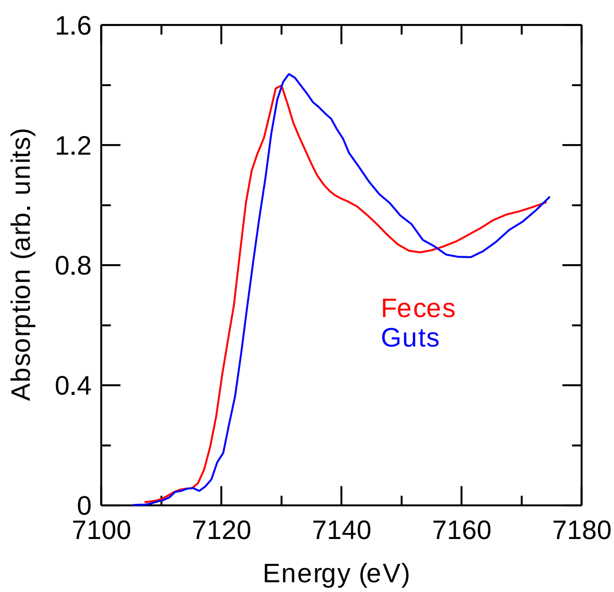

FIG. 1. Fe K-edge micro-XANES of 5 ´ 5-mm regions in oyster guts and feces.

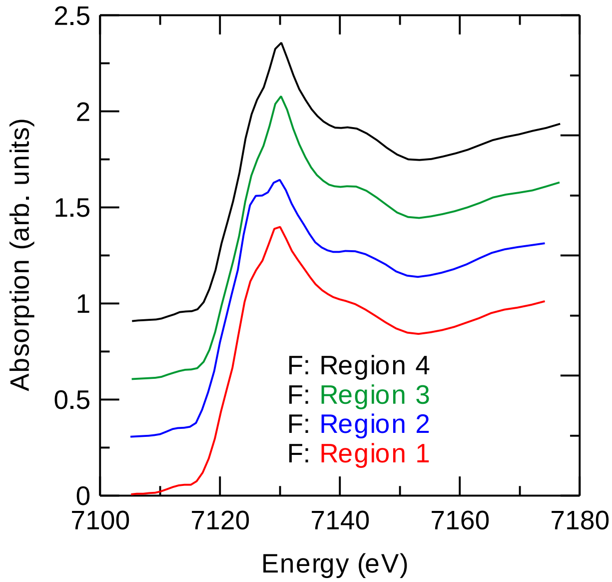

FIG. 2. Fe K-edge micro-XANES of four regions in oyster feces.

region, indicating an inhomogeneous distribution of different Fe structures.

Preliminary analysis of the Fe K-edge EXAFS indicates that the Fe near-neighbor bond length is shorter in the feces than it is in the guts. This is consistent with the feces Fe having a lower oxidation state.

Discussion

Two important findings came from these results: (1) oysters are clearing inorganic material, specifically oxides of iron, from the water column and (2) digestive processes are reducing the oxides of iron from a higher to a lower oxidation state. Oxides of iron are known sites of trace metal sorption. Hence, it is likely that as the oyster clears the oxide from the water column, it also clears metal adsorbed onto the oxide surface. This then becomes a potential source of trace metal (such as Cd) exposure to the oyster. We are currently analyzing our XAFS data to complete the identification of the iron oxides present in both the gut and feces of oysters.

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Reference

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