

EXAFS Studies of the Iodine and Bromine Metabolism in Brown Algae

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Brown algae, for example of the order of the Laminariales, are able to accumulate iodine and bromine to concentrations that are orders of magnitudes higher than those of the elements in seawater ($10^1 - 10^2$ for Br, $10^4 - 10^5$ for I). The uptake mechanism has been proposed [1] to be one of facilitated diffusion, involving oxidation of the halide anion to a form in which it can pass the cell membrane by a haloperoxidase in the cell wall, requiring low levels of hydrogen peroxide. The objective of the present project is to investigate in what form brown algae, viz. *Laminaria digitata*, accumulate the halogens after passing the cell wall. This accumulation is an important step in the biogeochemical cycle for these elements, and identification of the chemical form of the accumulated elements could give a clue to its physiological significance which has remained largely enigmatic to this date. Halogen metabolism of brown algae is also of interest for ecological reasons, for a general understanding of how marine plants cope with oxidative stress and how they defend themselves against microorganisms and pathogens. Interestingly, under circumstances of oxidative stress increased levels of hydrogen peroxide are present which induce a release of the halogens, partly as volatile organohalogen compounds [2].

In our previous beam time (cf. Annual Report 2001) iodine K-edge X-ray absorption spectra were recorded of *Laminaria* samples as well as of relevant iodine compounds. In 2002 we continued studies on iodine, improving on the data quality and corroborating the conclusions from our exploratory experiments the year before, and extended our studies to the bromine K edge of Laminariales samples and bromine model compounds.

Fresh *Laminaria* samples were collected at Helgoland immediately prior to the experiments, and kept in a tank of aerated seawater in the EMBL cold room. In the first week of our beam time, we did experiments at the Br K edge, and identified the form of the stored bromine in frozen *Laminaria* cells as bromide anion. This did not change upon addition of compounds known to elicit efflux of halogen compounds, such as hydrogen peroxide or oligogulonates [3, 4]. On the other hand, when lyophilized cells, in which the cellular compartmentation has been disrupted but the enzyme haloperoxidase is still active, were exposed to H_2O_2 , bromine was incorporated in aromatic compounds. These results are in line with those obtained from our iodine XAS study on *Laminaria* in the previous year (2001). Some phase-corrected Fourier-transforms of bromine model compounds are presented in Fig. 1.

In the second part of our beam time allocation, we remeasured I XAS spectra of *Laminaria* and some model compounds, and obtained data of a significantly better quality than before. Like bromine, iodine is present as the anion, and is incorporated in aromatic compounds when lyophilized cells are rehydrated in dilute hydrogen peroxide.

Subtle changes in the spectra are observed when intact cells are exposed to oxidative stress, e.g. caused by elicitors [5]. Detailed analysis is in progress to reveal what oxidized form of iodine is formed in this process, which should provide insight into its physiological function.

Acknowledgement. The authors thank the European Community for support in the framework of the Access to Research Infrastructure Action of the Improving Human Potential programme to the EMBL Hamburg Outstation, contract number HPRI-CT-1999-00017.

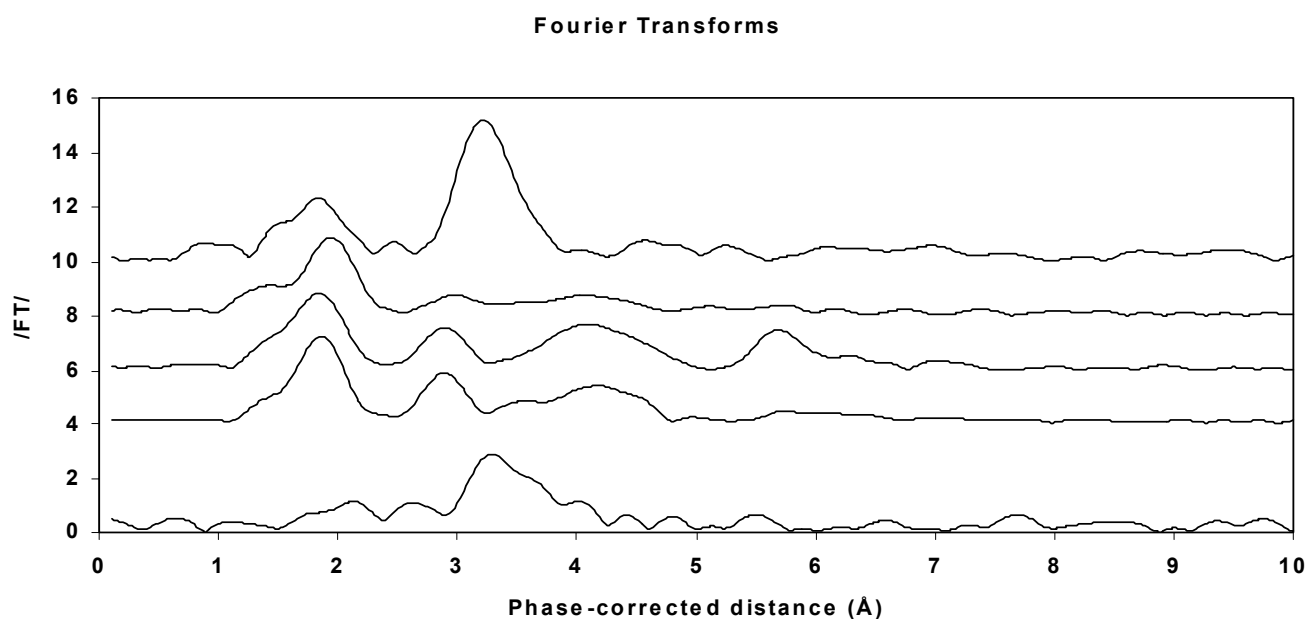


Figure 1: Phase-corrected Fourier transforms of the Br K edge X-ray absorption spectra of (top to bottom) CHBr_3 in water, 11-bromoundecanoic acid in BN (boron nitride), dibromotyrosine in BN, bromophenylalanine in BN, and NaBr (10 mM) in water.

References:

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