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Detailed Spectroscopic Studies in the Aquatic Environment Using Synchrotron Radiation

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Abstract

The important role of metals and metalloids in the aquatic environment can be studied by means of Synchrotron Radiation (SR)-based X-ray spectroscopic techniques. In the present work, we have performed analyses of data sets (μ -XRF, μ -XANES and μ -EXAFS), for coastal sediments and marine precipitates, obtained at the ANKA Synchrotron Facility in Karlsruhe Institute of Technology (KIT, Germany). Preliminary results with regard to the distribution and speciation of toxic (Hg and As) and biocompatible (Fe) metals and metalloids are presented herein. It is therefore demonstrated that Fe is easily precipitated as Fe^{III} oxyhydroxides, most likely related to As, as well as ferrihydrite-type Fe^{III} hydrated oxyhydroxides, whereas Hg is rather accumulated in the form of methyl-containing compounds.

Keywords: synchrotron, μ -EXAFS, aquatic environment

1. Introduction

High-luminosity, micro-focused X-ray beams provided by synchrotrons have been recently on demand, mainly to the variety of applications across several scientific fields, such as biology, geochemistry, environment etc. In the present work, the distribution and speciation of toxic (Hg, As) and biocompatible (Fe) metals and metalloids in distinct aquatic environments are reported as results of a campaign of experiments at ANKA synchrotron facility (KIT, Germany).

Investigating the distribution of Hg in the environment is of high importance due to the element's high toxicity. Surface sediment and sediment cores were collected from aquatic ecosystems in Greece. Chemical analysis showed elevated levels of Hg [1] to a high value of 6000 ppb. Hg and As are in the top-3 places of the list with the most hazardous materials compiled by the US Environmental Agencies [2]. Whereas arsenic may be found in the form of natural compounds, high levels of mercury is more likely to be of anthropogenic origin. The presence, and most importantly, the origin of Hg in chemical compounds can not be determined by traditional chemical or physical techniques.

Arsenic content (the most toxic element in the previously mentioned list) was investigated in geological samples collected from the bottom of the active submarine volcano Kolumbo, NE of Santorini Island, Greece. Arsenic speciation and distribution may be correlated to the bioavailable Fe marine precipitates, in forms frequent in the aquatic environment, such as ferrihydrite. Understanding the formation of Fe compounds in these environmental samples is critical for the understanding of bioprocesses supporting thriving bacterial communities in an anoxic volcanic environment [3].

2. Experimental Details

A campaign of experiments at the SUL-X beamline of the ANKA synchrotron facility (Karlsruhe Institute of Technology) focused on providing insight to the above questions using high-luminosity, micro-focused X-ray beams. The samples were prepared for irradiation and inspected by optical and scanning electron

microscopes. They were mounted in the SUL-X chamber and irradiated with beams provided directly by the SUL-X wiggler (Fig. 1). The detectors collected data to perform advanced spectroscopic techniques: μ -XRF, μ -XANES and μ -XAFS. Reference samples were studied side-to-side with our samples during the experiments.

The μ -XRF data, resulting in elemental maps, were processed using a newly developed open-source software suite [4]. The μ -XAFS (XANES and EXAFS) data were preliminary evaluated using the Demeter Suite [5].

3. The case of Hg in coastal sediments

The sediment samples were examined for Hg distribution and speciation in carefully selected candidate spots identified in SEM prior to irradiation. Elemental maps were created (Fig. 2) to locate micrometer-large Hg compound formations to be examined further by μ -XANES, which can provide direct evidence on the element's oxidation (valence) state. Reference samples were also studied for comparison: HgCl, HgO, cinnabar, methylmercury, mercury(I) nitrate, Hg₂Cl and Hg₂Br.

The deduced μ -XRF maps indicate Hg-rich areas that can be correlated or anti-correlated to other species in the same microspots. Preliminary evaluation of the data using μ -XANES spectroscopy (Fig. 3a) suggests the existence of Hg compounds rather close to methylmercury (CH₃Hg⁺ or MeHg⁺), which is known to be a bioaccumulative environmental toxicant. The source of this compound in the aquatic sediments is currently unknown, despite the fact that it is typically of anthropogenic origin.

4. The case of Fe in marine precipitates

Geological samples from chimneys in the active hydrothermal vents of Kolumbo volcano were collected during an oceanographic expedition with the R/V Nautilus and ROV Hercules. In the aquatic environment the samples were covered by thriving bacterial communities, while in a completely anoxic environment (gas content $\approx 99\%$ CO₂ and $\theta \approx 230^\circ$) [3]. A potential nutrient for such bacteria may be iron, depending on the level of bioavailability Fe ions exist in marine precipitates.

Detailed spectroscopy using μ -XAFS (both μ -XANES and μ -EXAFS) on the samples exhibited a good agreement with the ferrihydrite reference material (Fe(III) hydrated oxyhydroxide) 3b. Ferrihydrite is an enigmatic phase which is very frequently formed in the aquatic environment. Ferrihydrite may also accommodate toxic metal- and metalloid-ions into its disordered (and nanoporous) "structure" (see Fig. 4). This feature is important for the understanding of the existence of arsenic in the same marine precipitates, which is currently under investigation.

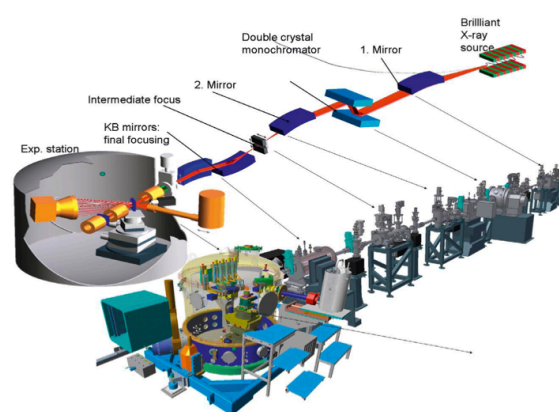


Figure 1: The SUL-X beamline at ANKA

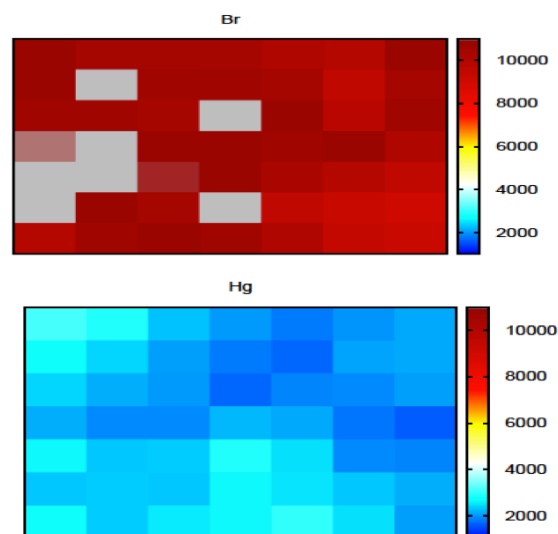
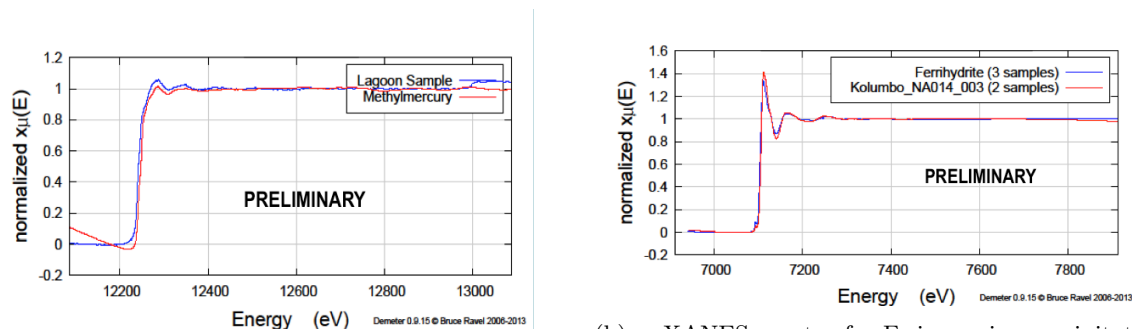


Figure 2: μ -XRF elemental map.



(a) μ -XANES spectra. The Hg compound in the sediment sample seems to agree most with the methylmercury structure.

(b) μ -XANES spectra for Fe in marine precipitates from the Kolumbo volcanic cone. The sample's structure seems to be in very good agreement with the ferrihydrite reference material.

Figure 3: μ -XANES spectra

5. Conclusions

A study on samples from various aquatic environments in Greece was undertaken by means of synchrotron radiation. The role of toxic metal and metalloids, as well as bioavailable metals was investigated in the samples. Preliminary results show an agreement with known structures. Detailed investigation is underway.

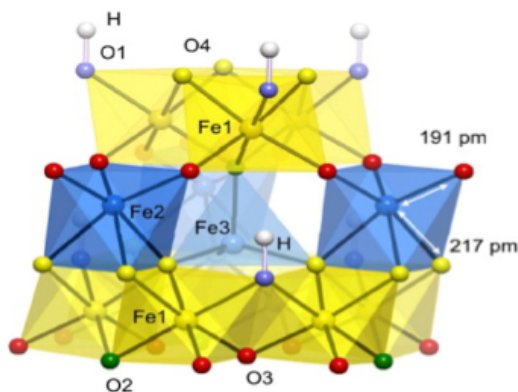


Figure 4: Suggested surface and mineral "structure" of ferrihydrite (Ref. [6])

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