

## Characterization of S-containing concretions from the North Sea

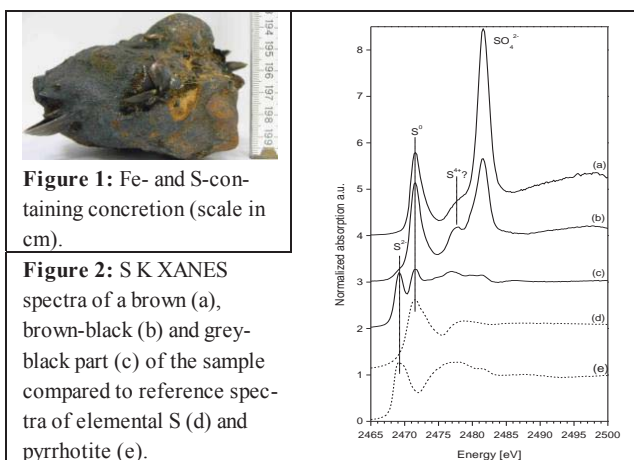
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Sulfur containing concretions can be found from time to time on the German North Sea shore, e.g., on the beach of the island Juist. They show grey to black and yellow to red-brown colors (Fig. 1). Macroscopically they consist of cemented sand intergrown with shell fragments. Because of the red brown colors Fe might be present.

So far, a few of them have been investigated by X-ray powder diffraction and additionally with X-ray absorption spectroscopy (SUL-X beamline, ANKA) at the S K-edge to determine the chemical form of sulfur. The latter technique has been applied because the grey black colored parts may indicate iron sulfides. XANES spectra have been processed with the Athena program [1]. From the X-ray diffractograms quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>) and calcium sulfate hydrate have been identified. Two sharp reflections (at d values of 3.24 and 3.19 Å) could not yet be assigned. And there are no reflections left that indicate an iron oxyhydroxide or iron sulfide phase because their amounts might be too small or they are not or not well crystalline. Peaks from the S K XANES spectra of the brown parts have been assigned to sulfate ( $\approx 2481.4$  eV, close to the calibration energy of sulfate in scotch tape) and to elemental sulfur (2471.6 eV) by comparison with a spectrum of elemental sulfur (Fig. 2). Brown-black parts show additionally a peak at about 2477.6 eV which is close to S<sup>4+</sup>. In the grey-black areas mono-sulfide (S<sup>2-</sup>) has been identified by comparison with a spectrum of pyrrhotite (Fe<sub>1-x</sub>S).

Because of the intergrowth with shells the location of the iron, sulfide, elemental S and sulfate containing concretions may take place on the sea floor. One possibility could be that around a nucleus in the tideland concretions of sand and shells are forming, where Fe and reduced sulfur are delivered from the sediment to form iron mono-sulfides around the quartz grains and shells that partially oxidize to elemental sulfur and sulfate. Fe K XANES spectroscopy is planned to get more information of the Fe mineral phase.



**Figure 1:** Fe- and S-containing concretion (scale in cm).

**Figure 2:** S K XANES spectra of a brown (a), brown-black (b) and grey-black part (c) of the sample compared to reference spectra of elemental S (d) and pyrrhotite (e).

[1] Ravel & Newville (2005). *JSR*, **12**: 537–541

## MULTI-ISOTOPE TRACING OF ATMOSPHERIC EMISSIONS FROM AN ALUMINUM SMELTER

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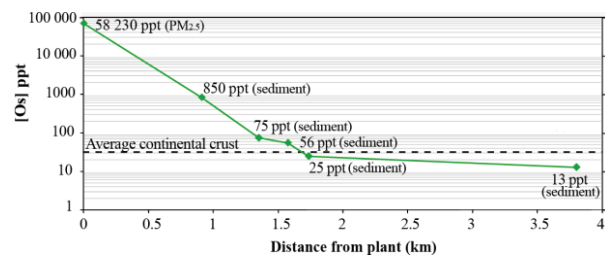
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Evaluating the net contribution to atmospheric fine particulates of an aluminium smelter is a challenge. For the first time here, we combine osmium (Os) and lead (Pb) isotopes as tracers of the atmospheric emissions from an aluminum smelter in Saguenay (Canada). This smelter reduces alumina (extracted from bauxite) into metallic aluminum using carbonaceous anodes. These anodes are consumed during the electrolytic process and produce atmospheric emissions (mainly CO<sub>2</sub>) during reaction with Al<sub>2</sub>O<sub>3</sub>. Anodes are made of petroleum coke, which is characterized by isotopic compositions of lead and osmium that are significantly different from other typical anthropogenic sources [1]. These metal's isotopic compositions are transferred into particulate matter emitted along with gases from the smelter process, and can then be traced in the environment. In the immediate surroundings of the aluminum smelter (i.e. on the industrial property) we observed a high Os content in surface deposits, which gradually decrease away from the factory, down to average eroding continental crust at the sampling point closest to the boundary of the industrial property (Fig. 1). For this study, we will compare these findings with Pb isotope results obtained on the same set of samples; Pb stable isotopes systematics being a powerful tool in environmental studies.



**Figure 1.** Decrease of osmium content in the near environment of the aluminum smelter.

[1] Boullemant (2011) *Journal of the Air & Waste Management Association*, **61**, 311-318.