Characterization of Sulfur in New York/New Jersey Waterway Sediment

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Abstract. Sulfur plays an important role in the biogeochemical cycle of trace elements and in the diagenetic reactions in sediments/soils. Due to very low solubility of sulfide compounds, metal sulfides are a big concern in the coastal and marine environment. In this study, we investigated sulfur compounds and speciation in contaminated sediments from the waterways of New York and New Jersey in the region of New York City, USA. Measurements were made on particles from the National Institute of Standards and Technology Standard Reference Material (SRM) 1944 (a composite from 6 locations) and from a mud flat on the Passaic River in New Jersey, USA. The experimental measurements were made at the ID21 X-ray Microscopy beamline at the European Synchrotron Radiation Facility (ESRF), France. Maps of the Si, P, and S distributions were made with a sub-µm beam on individual sediment particles. In order to chemically specify sulfur, X-ray absorption near-edge spectroscopy (XANES) measurements were taken from selected areas (regions-of-interest) within these maps.

1. INTRODUCTION

Sulfur exists in natural environment in many inorganic and organic forms with different oxidation state and plays an important role in the complicated biogeochemical cycle of trace elements. Both organic and inorganic sulfur-containing compounds could be changed from one form to another due to bacteria activities and be oxidized to higher oxidation states with the involvement of redox reactions (for prior synchrotron-based studies on this topic, see [1-3]). One of the key biogeochemical components of natural sulfur cycling is the oxidation of reduced sulfur to a higher oxidation state sulfur such as sulfate anion. This can be accomplished by some species of bacteria, *e.g.*, the *Thiobacillus sp.* These thiobacilli are ubiquitous in nature and exist where reduced sulfur is present. In certain environmental conditions, organic sulfur forms in soil arise from the decomposition of organic matter yielding thiols (R-SH), disulfides (R-SS-R), disulfanes (R-SSH) and the S-containing amino acids among others. These sulfur forms can be found in the humic matter of most marine sediments and soils. When redox conditions change from aerobic to anaerobic condition (mediated by organic matter decomposition by bacteria), sulfate can be reduced to sulfide. The sulfide ion plays an important role in binding heavy metals. In areas where there are anthropogenic sources of heavy metals, the significance of toxic metals-sulfide reactions cannot be ignored. In a sense, scavenging metals by sulfide can be a sink for toxic metals. However, if sulfide is oxidized to sulfate (*e.g.*, due to bacterial aerobic respiration), metals can be released; therefore, metal-sulfides can be a source of toxic metals. The migration of contaminants or breakdown products of contaminants in a zone of treatment is a major problem for *in situ* remediation processes. Therefore, study of sulfur compounds and speciation has an environmental significance. In this paper, we present the results from studying sulfur speciation in the contaminated NY/NJ Harbor sediments using synchrotron fluorescence x-ray microscopy.

2. SCANNING FLUORESCENCE X-RAY MICROSCOPY AT ID21

The ID21 scanning X-ray microscope (SXM), operating in the 2 – 8 keV energy range is a unique tool for elemental mapping and near-edge spectroscopy of many *K* edge (Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co) elements in low concentrations (for sulfur down to 300 ag [6]) and at high spatial resolution detecting the fluorescence radiation created in these atoms using an energy-dispersive Germanium detector (Princeton Gamma Tech). An overview of the experimental setup can be found e.g in [4] and a more detailed description of the experimental endstation is available elsewhere [5]. To create a small focal spot (diffraction-limited in the ideal case of fully coherent illumination of the zone plate over its whole diameter), a Germanium zone plate with a diameter of 500 µm and an outermost zone width of 80 nm has been used [6].

3. EXPERIMENTAL RESULTS AT THE SULFUR-*K*-ABSORPTION EDGE

3.1 Measurements on NIST Marine sediment standard reference material (SRM) 1944

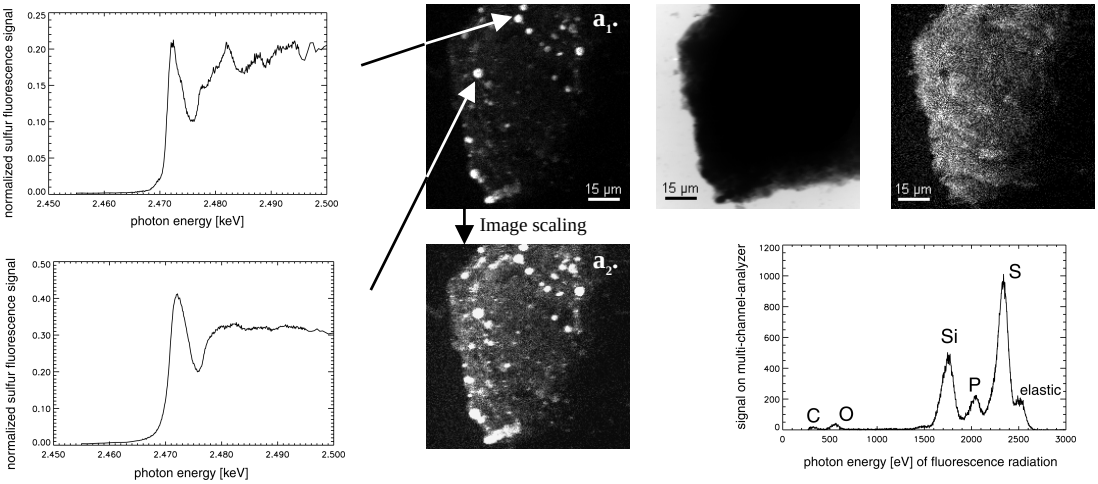

Figure 1: Data of the NIST standard reference material 1944 (coarse fraction), taken at 2.5 keV photon energy: (a_1 & a_2) Sulfur fluorescence map, (b) transmission (thick, low transmission particle), (c) Silicon fluorescence map, (d & e) Sulfur-XANES spectra taken from regions as indicated by the arrows, (f) fluorescence spectrum integrating over the whole particle, acquired using a 200 µm diameter 2.5 keV beam.

First measurements were made on a Marine sediment standard reference material (SRM 1944, coarse fraction) from the U.S. National Insitute of Standards and Technology (NIST). This material was taken from 6 regions near urban areas in New York/New Jersey, freeze dried and chemically well characterized in its bulk properties [7]. Figures $1a_1$ & a_2 show sulfur fluorescence maps of a big particle within this sample in different image scalings. Sulfur can be seen in relatively high concentrations (hot spots on the particle, see fig. $1a_1$) as well as in low concentrations (covering the whole particle, best seen in fig. $1a_2$). Measuring sulfur-near edge spectra helps to reveal the chemical state of sulfur: Figure 1e shows a resonance at 2472 eV (sulfide), figure 1d shows resonances at 2472 eV (sulfide), less pronounced at 2477 eV (most likely sulfoxide) and a resonance at 2482 eV (ester or inorganic sulfate peak). Both figures $1a_2$ and 1c show some 'shadowing effect', meaning that the right side of the particle shows less Sulfur or silicon signal than the left side. This is due to the fact that the fluorescence radiation generated by the incident X rays are absorbed by the relatively thick particle and are not seen by the fluorescence detector (mounted perpendicular to the beam). Figure 1f shows a fluorescence spectrum representing all elements with absorption edges below 2.5 keV present in the sample. As a side effect, even low signals of fluorescence radiation from carbon and oxygen, present in high concentrations in the polymer sample support, can be seen, although the fluorescence yield for these elements is extremely low.

3.2 Characterization of freshly dredged contaminated sediment from Passaic river

Further studies dealt with characterizing a real marine sediment sample that was taken in Newark Bay, New Jersey, USA (see figure 2) just one week before the experiment. Results are shown in figure 3.

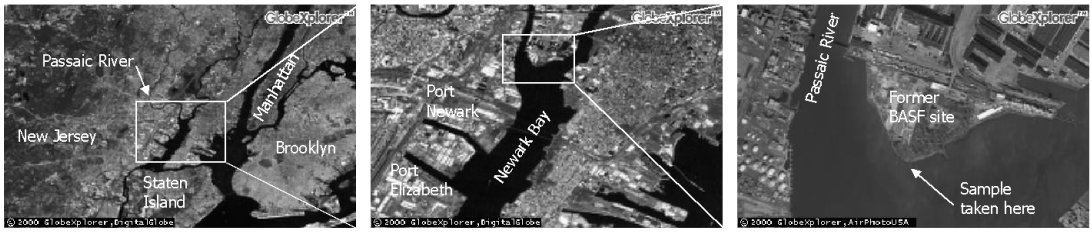

Figure 2: Satellite images of the NY/NJ bay area. Upstream the Passaic river, the region is traditionally industrialized with heavy activity for the last 200 years.

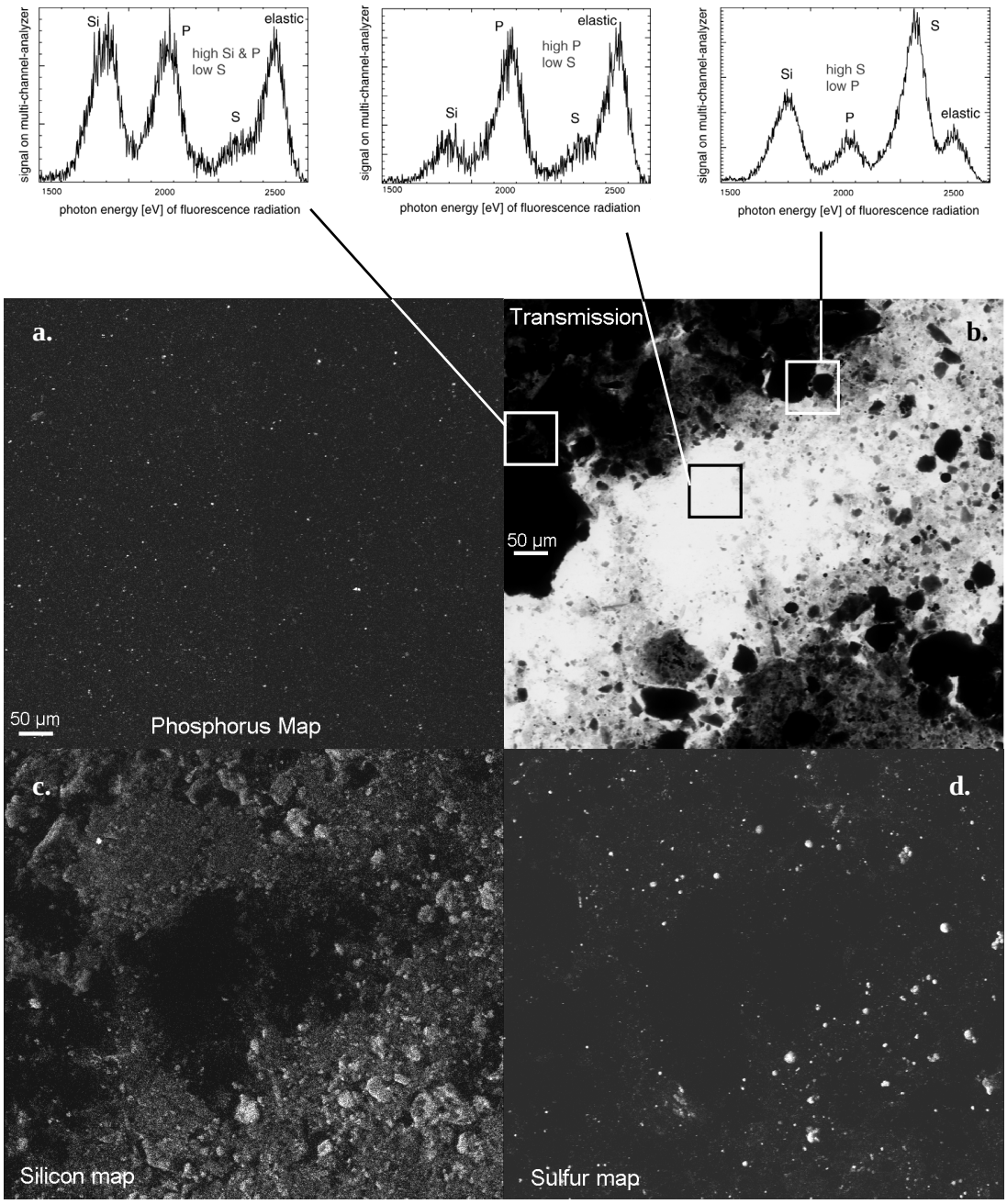

Figure 3: X-ray micrographs of a marine sediment, dredged from Newark Bay just at the mouth of the Passaic river. Transmission image (right-top, fig. 3b), sulfur fluorescence map (right-bottom, fig. 3d), silicon fluorescence map (left-bottom, fig. 3c) and phosphorus map (left-top, fig. 3a).

This large field of view image was obtained by stitching 10 x 9 piezo scan images together. For each image pixel (80 msec dwell time), a full fluorescence spectrum is available. The element maps (figs. 3 a,c,d) were calculated from these spectra by selecting appropriate channel intervals for the respective element using the ARTEMIS – software [8].

The fluorescence spectra (shown on the very top) are obtained by integrating the fluorescence spectra for all pixels from different square regions (75 x 75 μm^2) as indicated in the transmission image (fig. 3b). The spectra prove that there are in-homogeneities not only on the micrometer scale (as demonstrated in figure 1), but also on a length scale almost 2 orders of magnitude larger.

Using the elemental maps for S, Si and P (figure 3), the spatial correlation between elements was studied:

- Phosphor barely comes along with sulfur**,** so the phosphor seen (fig. 3a) is most likely of inorganic origin (e.g., phosphor minerals)
- a weak sulfur coating can be found on the silicate mineral particles (the silicate minerals are localized by the silicon fluorescence signal).
- regions with high sulfur concentration do not coincide with silicate minerals. One explanation is that this sulfur comes from organic materials such as fecal pellets or it is just metal sulfide precipitate. Due to the strong signal and the XANES measurements, these regions can be identified to consist of sulfides.

4. CONCLUSIONS AND OUTLOOK

Sulfur, Silicon and Phosphor were mapped in dry marine sediment standards (NIST SRM 1944) and freshly dredged material with sub-µm spatial resolution using the ID21 scanning transmission X-ray microscope at 2.5 keV photon energy in fluorescence mode. Sulfur was chemically specified using S-*K* edge XANES.
A heterogeneity of the elemental distribution within the samples studied was shown on the micrometer as well as on the 100 µm length scale. Therefore, spatially resolving measurements (like available by X-ray microscopy techniques) are essential for this kind of samples.
For future studies, the metal bound to the sulfides found need to be specified. Experiments at the Iron-*K*-edge (7.1 keV) could help to rule out or confirm pyrite (a form of iron sulfide) versus other heavy metal sulfides. Correlations could also be made with data on carbon compounds as accessible by carbon edge imaging/XANES around 280 eV [9] and the information should be cross-linked to the information on sulfur in organic/inorganic form.
Finally, there is a need for further studies comparing contaminated and treated material that has undergone some decontamination process within the NY harbor decontamination project, aiming towards the removal of organic contaminants as well as heavy metals in many million of cubic meters of dredged material every year.

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