

The results from our experiments have been reported in an article, which is in press to *Geochimica et Cosmochimica Acta*. Its abstract is copied below. The research has been conducted partly at the ALS for the microspectroscopy part, and at ESRF on the FAME beamline for the EXAFS part on powdered samples. One of the main outcome from this study is the first identification in a natural sample of Zn-rich trioctahedral phyllosilicate. This species had been inferred in the literature by our team several years, but its existence had been questioned. Its existence is now firmly established. Frédéric Panfili defended his Ph. D. thesis in June 2004.

The effect of phytostabilization on Zn speciation in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence, EXAFS spectroscopy and principal components analysis

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ABSTRACT

The maintenance of waterways generates large amounts of dredged sediments, which are deposited on adjacent land surfaces. These sediments are often rich in metal contaminants and present a risk to the local environment. Understanding how the metals are immobilized at the molecular level is critical for formulating effective metal containment strategies, such as phytoremediation. In the present work, the mineralogical transformations of Zn-containing phases induced by two graminaceous plants (*Agrostis tenuis* and *Festuca rubra*) in a contaminated sediment ($[Zn] = 4700 \text{ mg kg}^{-1}$, $[P_2O_5] = 7000 \text{ mg kg}^{-1}$, $\text{pH} = 7.8$), untreated or amended with hydroxylapatite (AP) or Thomas basic slag (AS), were investigated after two years of pot experiment by scanning electron microscopy coupled with energy-dispersive spectrometry (SEM-EDS), synchrotron-based X-ray micro-fluorescence (μSXRF), and powder and laterally-resolved extended X-ray absorption fine structure (μEXAFS) spectroscopy. The number and nature of Zn species were evaluated by principal component (PCA) and least-squares fitting (LSF) analysis of the entire set of μEXAFS spectra, which included up to 32 individual spectra from regions of interest varying in chemical composition. Seven Zn species were identified at the micrometer-scale : sphalerite, gahnite, franklinite, Zn-containing ferrihydrite and phosphate, (Zn-Al)-hydrotalcite, and Zn-substituted, kerolite-like,

trioctahedral phyllosilicate. Bulk fractions of each species were quantified by LSF of the powder EXAFS spectra to linear combinations of the identified Zn species spectra.

In the untreated and unvegetated sediment, Zn was distributed as ~50 % (mole ratio of total Zn) sphalerite, ~40 % Zn-ferrhydrite, and ~10-20 % (Zn-Al)-hydrotalcite plus Zn-phyllosilicate. In unvegetated but amended sediments (AP and AS), ZnS and Zn-ferrhydrite each decreased by 10 to 20 % and were replaced by Zn-phosphate (~30-40 %). In the presence of plants, ZnS was almost completely dissolved and the released Zn bound to phosphate (~40-60 %) and to Zn phyllosilicate plus (Zn,Al)-hydrotalcite (~20-40 %). Neither the plant species nor the co-addition of mineral amendment affected the Zn speciation in the vegetated sediment. The sediment pore waters were supersaturated with respect to Zn-containing trioctahedral phyllosilicate, near-saturation with respect to Zn-phosphate, and strongly undersaturated with respect to (Zn,Al)-hydrotalcite. Therefore, the formation of (Zn,Al)-hydrotalcite in slightly alkaline conditions ought to result from heterogenous precipitation on mineral surface.