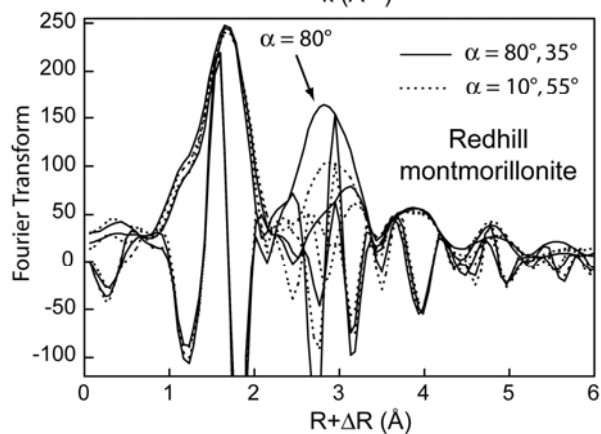
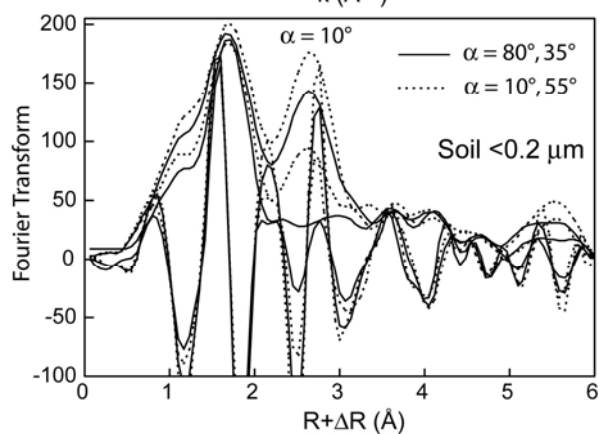
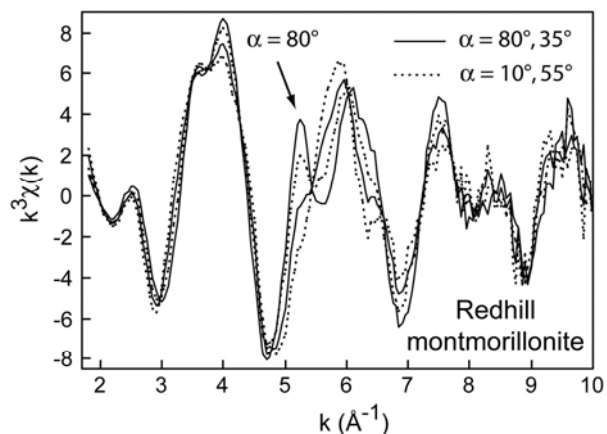
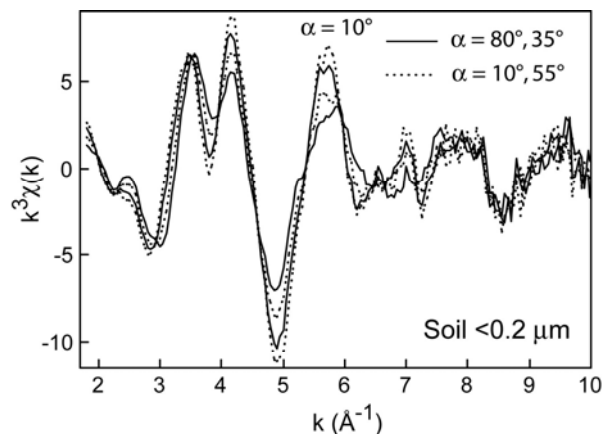


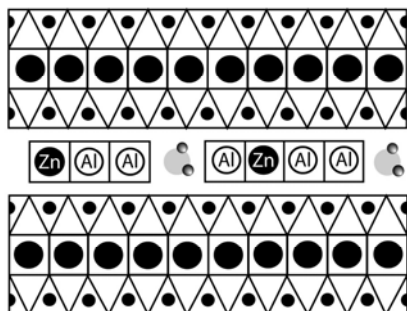
Four articles have been published in leading geochemistry and environmental science journals out of this long-term proposal (abstracts are copied below). Originally, we had planned to study the natural speciation of Ni, Zn, As and Pb, but only the two first elements have been investigated in detail because of beamtime constrain and of technical problems encountered in 2003 at the As K-edge, and especially at the Pb L3-edge. The technical pitfalls (mostly non-linearity of the detectors, and beam instability due to an imperfect regulation of the monochromator cooling) have been reported in our previous yearly reports, and we have been told by Jean Louis Hazemann and Olivier Proux that these problems were solved recently, in particular by the mounting of a new IO detector. For this reason, we intend to complete this long-term program by the study of As and Pb in the coming two years.

During the last two years, great strides in our knowledge of the sequestration mechanism of zinc and nickel in soils have been made, despite the generally low concentration of these elements in the analyzed matrices and the high proportion of iron, which gives a parasitic fluorescence signal that is quite intense at the Ni and Zn K-edges. Our most advanced measurements would not have been made possible on other beamlines, at least at ESRF, and I think that all users owe a major debt of gratitude to the FAME team for their excellent technical and instrumental work, and their strong dedication and relentless efforts to maintain this beamline at a cutting-edge.

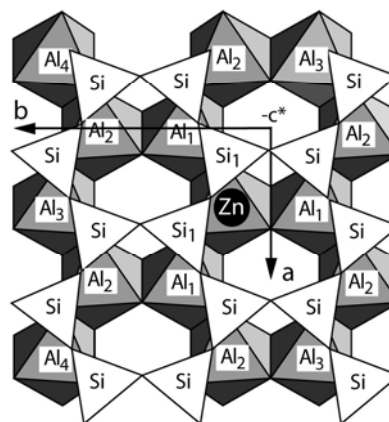
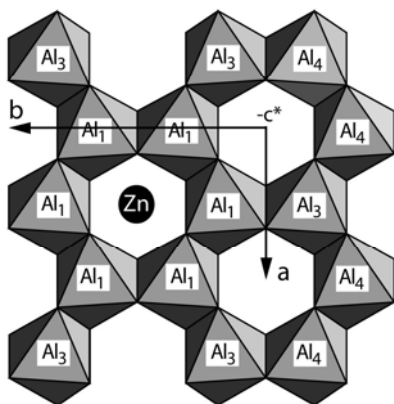
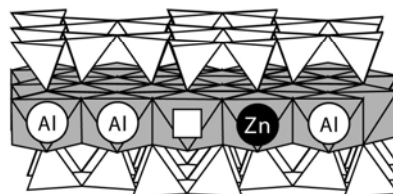
Among all the experiments, which have been performed in the last two years in the framework of this program, I think that the most novel has been, and still is, the development of polarized EXAFS on highly textured (single crystal-like) self-supporting films from the clayey fraction of natural soils and from clay standards. These experiments are technically challenging in many respects (elaboration of high quality films, quality-control by texture goniometry, availability of a focused X-ray beam for grazing-incidence measurements, high stability of the spectrometer during the scans at varying incidence angle, 30-Ge detector for Fe K α rejection, and high flux) and have led to several groundbreaking, and even flabbergasting, results. This research work on P-EXAFS still is completely original and has been a shoo-in for acceptance in premier journals in our field. A glimpse of this accomplishment is shown below with the P-EXAFS data obtained on Zn in a clayey paddy soil from Taiwan ([Zn] = 42 ppm) and on Zn in substitution to Al in the octahedral sheet of montmorillonite ([Zn] = 85 ppm). The two samples exhibit a reversed polarization dependence, although Zn is surrounded by Al in the two samples. This difference is due to the fact that Zn occupies two distinct crystallographic sites: it is located in the octahedral sheet sandwiched between two tetrahedral Si sheets in montmorillonite, and it is located in the vacancy sites of an Al(OH)₃ layer in the soil sample. The two local environments, not only are highly anisotropic, but also dissimilar, thus enabling their differentiation. We believe that the new coordination chemistry of zinc discovered in the paddy soil from Taiwan is ubiquitous, and is the main sequestration mechanism of zinc in acidic to near-neutral aluminium-rich clayey soils at the earth's surface.



Zn-incorporated
hydroxy-Al phyllosilicate



Zn-substituted montmorillonite



Zinc mobility and speciation in soil covered by contaminated dredged sediment using micrometer-scale and bulk-averaging X-ray fluorescence, absorption and diffraction techniques

Marie-Pierre Isaure, Alain Manceau, Nicolas Geoffroy, Agnès Laboudigue, Nobumichi Tamura, Matthew A. Marcus

Geochimica et Cosmochimica Acta, in press

ABSTRACT

The mobility and solid-state speciation of zinc in a pseudogley soil (pH = 8.2-8.3) before and after contamination by land-disposition of a dredged sediment ($[\text{Zn}] = 6600 \text{ mg kg}^{-1}$) affected by smelter operations were studied in a 50 m^2 pilot-scale test site and the laboratory using state-of-the-art synchrotron-based techniques. Sediment disposition on land caused the migration of micrometer-sized, smelter-related, sphalerite (ZnS) and franklinite (ZnFe_2O_4) grains and dissolved Zn from the sediment downwards to a soil depth of 20 cm over a period of 18 months. Gravitational movement of fine-grained metal contaminants probably occurred continuously, while peaks of Zn leaching were observed in the summer when the oxidative dissolution of ZnS was favored by non-flooding conditions. The Zn concentration in the $<50 \mu\text{m}$ soil fraction increased from $\sim 61 \text{ ppm}$ to $\sim 94 \text{ ppm}$ in the first 12 months at 0-10 cm depth, and to $\sim 269 \text{ ppm}$ in the first 15 months following the sediment deposition. Higher Zn concentrations and enrichments were observed in the fine ($<2 \mu\text{m}$) and very fine ($<0.2 \mu\text{m}$) fractions after 15 months (480 mg kg^{-1} and 1000 mg kg^{-1} , respectively), compared to 200 mg kg^{-1} in the $<2 \mu\text{m}$ fraction of the initial soil. In total, 1.2 % of the Zn initially present in the sediment was released to the environment after 15 months, representing an integrated quantity of $\sim 4 \text{ kg Zn}$ over an area of 50 m^2 . Microfocused X-ray fluorescence (XRF), diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy techniques were used to image chemical associations of Zn with Fe and Mn, and to identify mineral and Zn species in selected points-of-interest in the uncontaminated and contaminated soil. Bulk average powder EXAFS spectroscopy was used to quantify the proportion of each Zn species in the soil. In the uncontaminated soil, Zn is largely speciated as Zn-containing phyllosilicate, and to a minor extent as zincochromite (ZnCr_2O_4), $^{\text{IV}}\text{Zn}$ -sorbed turbostratic birnessite ($\delta\text{-MnO}_2$), and Zn-substituted goethite. In the upper 0-10 cm of the contaminated soil, about $60 \pm 10 \%$ of total Zn is present as ZnS inherited from the overlying sediment. Poorly-crystalline Zn-sorbed Fe (oxyhydr)oxides and zinciferous phyllosilicate amount to about $20\text{-}30 \pm 10 \%$ each and, therefore, make up most of the remaining Zn. Smaller amounts of franklinite (ZnFe_2O_4), Zn-birnessite and Zn-goethite were also detected. Further solubilization of the Zn inventory in the sediment, and also remobilization of Zn from the poorly-crystalline neoformed Fe (oxyhydr)oxide precipitates, are expected over time. This study shows that land deposition of contaminated dredged sediments is a source of Zn for the covered soil and, consequently, presents environmental hazards. Remediation technologies should be devised to either sequester Zn into sparingly soluble crystalline phases, or remove Zn by collecting leachates beneath the sediment.

Mn, Fe, Zn and As speciation in a fast-growing ferromanganese marine nodule

Matthew A. Marcus, Alain Manceau and Michael Kersten

Geochimica et Cosmochimica Acta, 2004, 68, 3125-3136

ABSTRACT

The speciation of Mn, Fe, As and Zn in a fast-growing (0.02mm/yr), shallow-marine ferromanganese nodule has been examined by micro X-ray fluorescence, micro X-ray diffraction, and micro X-ray absorption spectroscopy. This nodule exhibits alternating Fe-rich and Mn-rich layers reflecting redox variations in water chemistry. Fe occurs as two-line ferrihydrite. The As is strictly associated with Fe and is mostly pentavalent, with an environment similar to that of As sorbed on or coprecipitated with synthetic ferrihydrite. The Mn is in the form of turbostratic birnessite with ~10 % trivalent manganese in the layers and probably ~8 % corner-sharing metal octahedra in the interlayers. The Zn is enriched on the rim of the nodule, associated with Mn. The Zn is completely (>90 %) tetrahedrally coordinated and sorbed in the interlayers of birnessite on vacant layer Mn sites. The Zn and Mn species are similar to ones found in soils, suggesting common structural principles, despite the differing formation conditions in these systems.

Natural speciation of Zn at the micrometer scale in a clayey soil using X-ray fluorescence, absorption, and diffraction

Alain Manceau, Matthew A. Marcus, Nobumichi Tamura, Olivier Proux, Nicolas Geoffroy, Bruno Lanson

Geochimica et Cosmochimica Acta, 2004, 68, 2467-2483.

ABSTRACT

Combined use of synchrotron-based x-ray fluorescence (SXRF), diffraction (XRD), and absorption (EXAFS) with an x-ray spot size as small as five micrometers allows us to examine noninvasively heterogeneous soils and sediments. Specifically, the speciation of trace metals at low bulk concentrations and the nature of host minerals can be probed with a level of detail unattainable by other techniques. The potential of this novel analytical approach is demonstrated by determining the Zn species in the solid phases of a pristine horizon of a clayey acidic soil (pH 4.5 – 5.0) having a Zn concentration of 128 mg/kg. The sample presents a differentiated fabric under the optical microscope with traces of localized manganiferous, ferriferous and argillaceous accumulations. The high chemical and textural heterogeneity of this soil offers an opportunity to identify new Zn species and to confirm the existence of others proposed from published least-squares fits of bulk averaged EXAFS spectra. As many as five to six Zn species were observed: sphalerite (ZnS), zincochromite (ZnCr₂O₄), Zn-containing phyllosilicate and lithiophorite, and Zn-sorbed ferrihydrite or Zn-phosphate, the results being less definitive for these two last species. Bulk EXAFS spectroscopy applied to the powdered soil indicated that Zn is predominantly associated with phyllosilicates, all other species amounting to less than about 10-20 % of total zinc. The role of lithiophorite in the sequestration of zinc in soils had been inferred previously, but the firm

identification of lithiophorite in this study serves as an excellent demonstration of the capabilities of combined micro-SXRF/XRD/EXAFS measurements. The micro-EXAFS spectrum collected in an area containing only phyllosilicates could not be simulated assuming a single Zn structural environment. Two distinct octahedrally-coordinated crystallographic sites (i.e., two EXAFS components) were considered: one site located within the phyllosilicate structure (isomorphic cationic substitution in the octahedral sheet) and another in the interlayer region in the form of a Zn-sorbed hydroxy-Al interlayered species. This second subspecies is less certain and further investigation of the individual EXAFS spectrum of this component is needed to precise its exact nature and the uptake mechanism of zinc in it.

Molecular-scale speciation of Zn and Ni in soil ferromanganese nodules from loess soils of the Mississippi basin

Manceau A., Tamura N., Celestre R.S., MacDowell A.A., Geoffroy N., Sposito G., Padmore H.A.

Environmental Science & Technology, 2003, 37, 75-80.

Determining how environmentally important trace metals are sequestered in soils at the molecular scale is critical to developing a solid scientific basis for maintaining soil quality and formulating effective remediation strategies. The speciation of Zn and Ni in ferromanganese nodules from loess soils of the Mississippi Basin was determined by a synergistic use of three noninvasive synchrotron-based techniques: X-ray microfluorescence (*i*XRF), X-ray microdiffraction (μ XRD), and extended X-ray absorption fine structure spectroscopy (EXAFS). We show that Ni is distributed between goethite (α -FeOOH) and the manganese oxide lithiophorite, whereas Zn is bound to goethite, lithiophorite, phyllosilicates, and the manganese oxide birnessite. The selective association of Ni with only iron and manganese oxides is an explanation for its higher partitioning in nodules over the soil clay matrix reported from soils worldwide. This could also explain the observed enrichment of Ni in oceanic manganese nodules. The combination of these three techniques provides a new method for determining trace metal speciation in both natural and contaminated environmental materials.