

Stabilities of metal-thioarsenite complexes: Testing some theoretical predictions

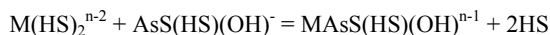
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Clarke and Helz (2000) discovered that dithioarsenite binds Cu^{I} extremely strongly, making an uncharged, 1:1 complex likely to be mobile in subsurface fluids. Such binding of metals by thiometalloids can explain sulfosalts in hydrothermal ores and cotransport of harmful elements near hazardous waste sites. With quantum theory, Tossell (2000a,b) showed why $\text{CuAsS}(\text{SH})(\text{OH})^0$ has high stability and predicted which other metals might bind similarly. Solubilities of Ag, Hg and Pb sulfides in the presence of As sulfide phases are examined here to test some of these predictions. Dissolution of an $\text{Ag}_2\text{S} + \text{Ag}_3\text{AsS}_3$ mixture produces ΣAg concentrations exceeding those from Ag_2S alone. With no UV-Vis spectral evidence of polysulfide ions, excess ΣAg is attributed to:



Similar experiments with $\text{HgS} + \text{S} + \text{As}_2\text{S}_3$ reveal no excess ΣHg compared to experiments with $\text{HgS} + \text{S}$. Thus at thioarsenite concentrations up to As_2S_3 saturation, thioarsenite ligands cannot compete successfully for Hg against HS^- ligands at $[\text{HS}] \geq 10^{-4}$ M. Likewise Pb thioarsenite complexes are not seen. In their trend, these results agree with expectations from theory:



If theory continues to be upheld, Au^+ will be shown to bind less strongly than Cu^+ or Ag^+ with $\text{AsS}(\text{HS})(\text{OH})^-$, but TI^+ , a rare element in nature except in sulfosalts, will be shown to bind much more strongly than metals tested so far.

M^{n+}	Theoretical ΔH_{R}	Measured $\log K_{25\text{C}}$
Cu^+	-26 kJ/mol	+2.64
Ag^+	-19 kJ/mol	-0.37
Hg^{2+}	+1040 kJ/mol	No complex observed
Pb^{2+}	+306 kJ/mol	No complex observed

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Dissolution rate of the lead phosphate mineral pyromorphite

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Traditional remediation methods for lead contaminated soil involve expensive excavation and offsite disposal. However, the formation of insoluble lead phosphate minerals provides a potential *in situ* remediation strategy. To understand immobilization mechanisms of lead and phosphate in soils and the rates of remobilization from contaminated soils, we have used synthetic chloropyromorphite (CPY, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) to assess the dissolution rates. The material was synthesized by mixing 0.15 M H_3PO_4 and 0.25 M PbCl_2 and purging with N_2 at room temperature. The solution was adjusted to pH 7 and aged for 1 month before freeze-drying. Dissolution rates of CPY were investigated in flow-through reactors and batch reactors. Experiments used synthetic chloropyromorphite under different pH, hydraulic residence time, solid concentrations, and solution saturation conditions. Effluent concentrations over time were measured by inductively coupled plasma atomic emission spectrometry (ICP) and inductively coupled plasma mass spectrometry (ICP-MS). The solid characteristics following reaction were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR).

The equilibrium concentrations in batch reactors and steady-state effluent concentrations of lead in flow-through reactors increased with decreasing pH. The steady-state concentrations were close to the equilibrium concentration at each pH. Only slight changes of steady-state concentration occurred with different residence time and solid concentration, which indicates that equilibrium had already been approached. Net precipitation of lead occurred under supersaturated conditions with respect to CPY.

SEM images show that nanoparticles attached to the ripened hexagonal CPY dissolved preferentially at low pH. FTIR data also show that a more soluble amorphous lead phosphate solid was present initially and dissolved preferentially with decreasing pH and increasing reaction time. However, XRD does not show significant changes in crystalline solid phases reacted at different pH conditions. The nanoparticles, which are possibly growing CPY or a $\text{Pb}(\text{OH})_{2(s)}$ impurity, might affect the net dissolution rate because of their different dissolution rates.

Effect of aging on Pb(II) sorption at the calcite-water interface

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Pb(II) sorption experiments with calcite powders were conducted in pH 7.3, 8.2 and 9.4 suspensions equilibrated at atmospheric $PCO_{2(g)}$ and ~22-25°C. Sorption-desorption experiments and X-ray absorption spectroscopy (XAS) were combined to elucidate the effect of sorption time on trends and dominant mechanisms. At pH 8.2, short-term batch experiments, ≤12 d, reveal the predominance of reversibly bound Pb, attributed to the formation of Pb inner-sphere adsorption complexes as confirmed by XAS. At pH 7.3 and 9.4, macroscopic experiments reveal a component of irreversibly bound Pb indicative of dual sorption mechanisms over the short term. Linear-combination fitting of XANES spectra for 12 d samples confirm ~95% adsorbed and ~5% coprecipitated Pb at pH 7.3, and ~75% adsorbed and ~25% coprecipitated Pb at pH 9.4. The irreversibly bound component as observed in batch experiments was attributed to coprecipitated metal.

For long-term sorption, ≥ 60 d, slow continuous uptake occurs at pH 7.3 and 8.2. Complete reversibility of the sorption process in combination with XAS analysis confirms that additional uptake in these samples proceeds via an adsorption mechanism. At pH 7.3, the ~5% coprecipitated component as observed for shorter sorption times is no longer evident suggesting detection may depend on surface loading. At pH 8.2 the fraction of desorbed Pb is greater than that predicted from linear isotherms. This implies enhanced susceptibility of adsorption complexes to exchange when sorbed over the long-term. At pH 9.4 no further uptake occurs, and the reversibility of sorption and solid-phase distribution of Pb is commensurate with that for short-term experiments. This suggests that the relatively high fraction of coprecipitated metal (~25%) may affect the calcite surface topography such that further Pb sorption is precluded. The coprecipitated component is not available for exchange with the aqueous phase, and thus this mechanism may be vital for ultimate metal sequestration.

Structure determination of natural and synthetic nanocrystalline phylломanganates

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In natural phylломanganates, and especially in those resulting from biological activity, the abundance of random stacking faults leads to the occurrence of extremely disordered structures without three-dimensional ordering (turbostratic stacking). One effective way to characterize the actual structure of these defective solids is the trial-and-error fitting of X-ray diffraction (XRD) patterns using the mathematical formalism described by Drits and Tchoubar (1990).

Even in these most defective phylломanganates, XRD patterns exhibit noticeable modulations on the high-angle side of the 20,11 and 31,02 scattering bands (~2.45 and ~1.42 Å, respectively – indexing performed assuming a base-centered two-dimensional cell). It will be shown that these modulations can be used to obtain relevant structural information, which includes not only unit-cell parameters but also atomic coordinates and site occupancies. In particular, these modulations were found to be sensitive to the amount of vacant layer sites capped by interlayer metal cations.

The usefulness of this simulation technique will be illustrated with various natural and synthetic (biogenic and abiotic) turbostratic phylломanganate varieties consisting of diffracting crystallites in the nanometer range. Its complementarity with EXAFS spectroscopy, which is sensitive to the local binding environment of Mn, will be discussed.

Reference

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Sequestration of Pb by hydrous manganese oxide-coated clay

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Mn oxide-coated clay and similar fine-grained fractions have been noted as surfaces that control the behavior of metal contaminants in the environment. The objective of this study was to better understand the effect of coatings on the sorption behavior of Pb. Macroscopic adsorption experiments and X-ray absorption spectroscopy (XAS) were conducted to study sorption mechanisms.

Discussion of results

Hydrous manganese oxide (HMO) coatings were prepared according to Boonfueng et al. (2005). Adsorption edges and isotherms revealed that sorption was dominated by the Mn oxide phase. In XAS analysis one type of coordination environment was observed; sorption was invariant of pH, ionic strength, and loading. Specifically, we found approximately 1.7 ± 0.3 atoms of oxygen in the first shell at a distance of 2.29 ± 0.06 Å and 1.0 ± 0.4 atoms of manganese in the second shell at 3.59 ± 0.08 Å. Therefore, the sorption affinity and capacity of the coating was consistent with that of discrete oxide where Pb ions formed inner-sphere complexes. For a contact time up to 4 months, an additional 60% of the sites became occupied and the lead structure was consistent with short-term samples. This slower sorption process was modeled as intraparticle surface diffusion as there was no evidence of surface precipitation or solid solution formation. Best fit diffusivities ranged from 10^{-20} to 10^{-18} cm²/s.

Conclusions

Pb sorption to HMO coated-clay was invariant of pH, ionic strength, and concentration; inner-sphere complexation of Pb involved 1.7 ± 0.3 atoms of oxygen in the first shell at a distance of 2.29 ± 0.06 Å and 1.0 ± 0.4 atoms of manganese in the second shell at 3.59 ± 0.08 Å. This average structure was also observed as a function of time where as much as a 60% increase in adsorption occurred; the result suggests internal surface sites are no different than external ones. Best fit diffusivities ranged from 10^{-20} to 10^{-18} cm²/s, and therefore hydrous Mn oxide present as either coatings or discrete particles acts as an important sink for metal ions.

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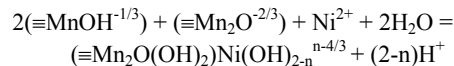
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Sorption of Ni by marine Fe-Mn nodules and crusts: Surface complexation and structural incorporation of Ni in birnessite

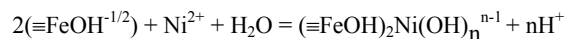
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Marine ferromanganese crusts and nodules contain very high (up to 2 wt. %) Ni contents yet the concentration of Ni in seawater is only ~10 nM. We measured the sorption of Ni(II) onto synthetic birnessite and goethite from pH 3 – 8. EXAFS spectra show that, at pH 8.0, Ni is adsorbed to the birnessite surface by forming a tridentate complex with two edge-sharing MnO₆ polyhedra. We developed a surface complexation model (multisite 1pK with diffuse layer) for Ni on birnessite based on the reactions



(with n=0,1). For Ni sorbing to goethite, we fit our sorption edge to the equilibria



(with n=0,1). Our surface complexation models show that, at the pH of seawater and below, Ni will be strongly preferentially sorbed by birnessite over goethite. This agrees with the Ni-Mn correlation observed in Fe-Mn nodules and crusts. We then characterised the crystal chemistry of Ni in several natural marine ferromanganese crust and nodule samples from the North Pacific. EXAFS spectra show that Ni has been structurally incorporated by replacement of Mn⁴⁺ in the phyllosilicate layer. The surface complex observed in our experiments must be a precursor to structural incorporation of Ni as the nodule grows. Using our surface complex stability constants, we show that in seawater at pH 8.3 the sorption of Ni by marine phyllosilicate phases limits the aqueous concentration of free Ni²⁺ to pM levels. The observed nM concentrations of total dissolved Ni presumably result from Ni complexation by organic ligands. Such ligands must be essential for making biolimiting nutrients available for primary productivity; in their absence, sorption of Ni by birnessite would preclude its bioavailability.

Relation between cis- or trans-vacant character of 1M illite and crystal morphology. Implications for metal sorption

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Sorption of pollutants like heavy metals in contaminated soils or sediments is controlled in part by their strong interactions with micro-crystalline minerals such as phyllosilicates, and numerous studies have been devoted to the determination of possible fixation sites for these adsorbed cations on phyllosilicates. These sites can be located on accessible edges, basal planes and interlayer planes, the relative abundance of which depends on the crystal morphology. In addition the configuration of the edge sites varies as a function of the layer structure.

Among the reactive minerals, natural illite (2:1 phyllosilicate of the mica family) crystals were found to occur with several morphologies ranging from 1D "hairy" illite to more isometric pseudo-hexagonal 2D plates. This morphological variability has been correlated with a structural modification from a 1M polytype with the octahedral *trans* site vacant to a 1M polytype with the octahedral *cis* site vacant using X-ray diffraction. However, no direct link has been demonstrated between morphology and structure because only populations of particles were investigated and statistically correlated.

In the present work, Selected-Area Electron Diffraction (SAED) patterns along the [001] zone axis were recorded on individual illite particles exhibiting contrasting morphologies to assess the validity of the hypothesized link. While the position of *hk0* reflections is similar for all illite polytypes, their relative intensity distribution was found to be very sensitive to the nature of the polytype and the *cis- versus trans*-vacant character of the octahedral sheet. Theoretical electron diffraction patterns were calculated and compared with the experimental SAED patterns to identify for individual crystals the polytype and the structure of building layers.

Nucleation and epitaxial growth of Zn phyllosilicate on montmorillonite

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Introduction

Zn retention by phyllosilicates has been documented in heavily contaminated soils. This retention can occur either by adsorption on clay surface or by neoformation of Zn phyllosilicates (e.g., Zn-kerolite), depending on physico-chemical conditions. This study aims to clarify the mechanism of Zn sorption on montmorillonite, the most common phyllosilicate in soils.

Materials and methods

Suspensions of purified MX80 montmorillonite (3.6 g L⁻¹ of solid, 0.5 M NaCl) were reacted with 500 μM Zn at pH 7.3, and with either "low" or "high" concentrations of dissolved Si ([Si]_{aq} = 70 and 500 μM, respectively). Self-supporting films of Zn-sorbed montmorillonite were obtained by slowly filtering suspension aliquots on 0.01 μm cellulose nitrate filters. Zinc K-edge polarized EXAFS (P-EXAFS) spectra of the self-supporting films were collected in fluorescence mode on the FAME beamline (ESRF, France). P-EXAFS data were reduced, and analyzed using standard procedures.

Results and interpretation

Strong angular dependences were observed for all P-EXAFS spectra, meaning that the binding environment of Zn is anisotropic. At low [Si]_{aq} and after 216 h contact time, the magic angle (powder) EXAFS spectrum resembled that of Zn-sorbed hectorite, a magnesian smectite [1] in which Zn is sorbed on layer edges. This same configuration was confirmed for montmorillonite, with Zn being surrounded by 0.6(4) Al at 3.00(2) Å in the film plane, and 0.5(4) Si at 3.21(2) Å in the perpendicular direction.

At high [Si]_{aq}, and t = 4 h, Zn was surrounded by in-plane Zn and Al, and out-of-plane Si, indicating the formation of clay nuclei on layer edges. At t = 313 h, Zn was surrounded on average by 3.7(7) in-plane Zn at 3.10(2) Å and by 3.6(4).4 out-of-plane Si at 3.27(2) Å, as in small Zn-kerolite particles [2]. These results collectively support the nucleation and epitaxial growth of Zn-kerolite on montmorillonite.

References

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Zinc speciation in contaminated soils in relation to soil type

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The formation of surface precipitates is an important retention and sequestration mechanism of trace metals in soils. Laboratory studies have demonstrated that zinc may be incorporated into layered mineral structures such as layered double hydroxides (LDH) and phyllosilicates. Recent studies confirmed the formation of such mineral phases in contaminated soils. The formation of these precipitates depends on the availability of Al and Si from the weathering of primary minerals. Zn may also be incorporated into the gibbsite-like sheets of lithiophorite or Al-hydroxy interlayered minerals (HIM). At present, a general understanding of the influence of geochemical soil properties on the type of the resulting Zn bearing phases and their stability is still lacking.

In this study, the speciation and reactivity of Zn is investigated in a wide variety of soils developed from fluvioglacial sediments, sandstone, limestone, granite and gneiss under different climatic conditions. Contaminated soils were sampled across Switzerland underneath Zn-coated towers of power transmission lines. The speciation of Zn in the soil matrix is studied by bulk Zn K-edge XAFS spectroscopy of soils, clay fractions, and Ca exchanged samples together with μ -EXAFS spectroscopy on a selected set of soils. Principal component analysis (PCA) is applied to a large set of sample spectra (~40 soils) to constrain the number of reference spectra required to describe the data. An extensive set of reference spectra for Zn in mineral structures, organic Zn complexes, and Zn adsorbed to inorganic and organic substrates is subsequently evaluated by target testing (TT) to determine the most suitable reference spectra. The contributions of those reference spectra to the individual experimental spectra are then determined by linear combination fitting (LCF).

First results indicate that Zn layered species are accounting for a significant fraction of the total Zn. The data suggest that Zn-LDH and Zn-phyllosilicates dominate over Zn-HIM and Zn-lithiophorite. The speciation of Zn as determined by PCA-LCF is related to the soil properties (pH, organic matter, soil mineralogy, iron (hydr)oxides, carbonates) and to the reactivity of Zn as determined by single and sequential batch extractions.

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

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The natural speciation of Mn (0.19 g/kg), Ni (46 mg/kg) and Zn (42 mg/kg) in the argillic horizon of an Ultisol from a paddy soil in Taiwan was investigated by advanced X-ray synchrotron techniques. Microchemical associations were imaged by X-ray microfluorescence, host minerals were identified by standard and micrometer-resolved X-ray diffraction, and the local coordination environment of Mn, Ni, and Zn was probed using EXAFS spectroscopy on powdered samples, and polarized EXAFS spectroscopy on a highly textured self-supporting clay film from the <2 μ m fraction of the soil. Manganese was concentrated in Fe-Mn soft mottles as turbostratic hexagonal birnessite and lithiophorite having Mn³⁺/Mn⁴⁺ atomic ratios of about 20 % and 50 %, respectively. Ni ($r = 0.70$ Å) substitutes for Mn ($r(\text{Mn}^{4+}) = 0.54$ Å, $r(\text{Mn}^{3+}) = 0.65$ Å) in the manganese layer in the natural lithiophorite. In contrast, Zn ($r = 0.74$ Å) fills vacant sites in the gibbsitic layer of natural lithiophorite, in a similar manner as lithium ($r = 0.74$ Å) in synthetic lithiophorite. The partitioning of Ni and Zn between the two layers is a result of the general preference of Ni, whose size is intermediate between those of Mn³⁺ and Li⁺, for slightly smaller sites. In contrast with nickel, which is detected only where there is lithiophorite, the Zn-lithiophorite association found in Fe-Mn mottles is not representative of the bulk soil. The combined use of X-ray diffraction, and powder and polarized EXAFS spectroscopy revealed that Zn is predominantly bound to hydroxy-Al interlayers sandwiched between 2:1 vermiculite layers in the fine soil matrix. The incorporation of Zn in the gibbsitic layer of both lithiophorite and vermiculite helps increase the stability of these minerals by providing positive charge to balance the negative charge from the 2:1 phyllosilicate layer and the $[(\text{Mn}^{4+}_{0.68}\text{Mn}^{3+}_{0.32})\text{O}_2]^{0.32-}$ layer of lithiophorite. This binding environment for zinc is probably the main mechanism by which zinc is sequestered in acidic to near-neutral aluminium-rich clayey soils.

The partially deprotonated Fe^{II-III} hydroxycarbonate green rust fougérite mineral and biogeochemistry of the cycles of iron, carbon and nitrogen in hydric soils

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A green rust has been recognised as a new mineral (IMA 2003-057) and given the name fougérite. Its chemical counterpart is Fe^{II-III} hydroxycarbonate GR1(CO₃²⁻) compound, which is partially deprotonated since formed by reduction of ferric oxyhydroxides through the activity of dissimilatory iron-reducing bacteria (DIRB) in anaerobic gley soils. Preparation of GR1(CO₃²⁻) by co-precipitation of Fe^{II} and Fe^{III} cations in carbonated medium shows by using Mössbauer spectroscopy that the domain of existence of GR1(CO₃²⁻) for $x = \{[\text{Fe}^{\text{II}}] / [\text{Fe}_{\text{total}}]\}$ lies within $[\sim 0.25, 0.33]$ with ordered limit $[\text{Fe}^{\text{II}}_4 \text{Fe}^{\text{III}}_2 (\text{OH})_{12}]^{2+} \cdot [\text{CO}_3 \cdot \sim 3 \text{H}_2\text{O}]^{2-}$. GR1(CO₃²⁻) gets oxidised into ferrihydrite evolving to goethite by oxidation, or into ferric green rust GR1(CO₃²⁻)*, $[\text{Fe}^{\text{III}}_4 \text{Fe}^{\text{II}}_2 (\text{OH})_4 (\text{OOH})_4]^{2+} \cdot [\text{CO}_3 \cdot \sim 3 \text{H}_2\text{O}]^{2-}$ by OH⁻ deprotonation. A mass balance of iron ox(yhydro)xides is drawn accordingly in the carbonated medium. Mössbauer spectra measured at 12 K show quite different magnetic properties and the three quadrupole doublets, comprising 2 ferrous and 1 ferric in GR1(CO₃²⁻), becomes 3 magnetically split sextets in GR1(CO₃²⁻)*. Crystallographic structure of ordered GR1(CO₃²⁻) and GR1(CO₃²⁻)* are drawn from XRD, XAS and Mössbauer spectroscopy, whereas E_{SHE} -pH diagrams are presented. Extension to other hydrotalcite-like compounds is proposed whereas occurrences of fougérite mixed with clay minerals are displayed. *In situ* Mössbauer measurements using the Mars probe MIMOS in the field will be discussed according to weather and depth variations in gley soils. The coupling between the cycles of Fe, C and N in hydric soils and the nitrate reduction by fougérite through ferric oxyhydroxides bioreduction due to DIRB is forwarded. The partially deprotonated green rust fougérite mineral is Fe^{II}_{6(1-x)}(OH)_{12(1-x)}Fe^{III}_{6(x-1)}(OOH)_{6(x-1)}Fe^{III}₂(OH)₄CO₃ where $1/3 \leq x < 2/3$. The proposal advocating a ferrosic hydroxide Fe(OH)_(2+x) is outdated.

Distribution and speciation of metals and metalloids at microbe/mineral interfaces

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Sorption and precipitation reactions at microbial and mineral surfaces provide critical controls on the speciation of trace and toxic elements in natural aquatic and sedimentary systems. Changes in speciation are particularly dynamic at microbe-mineral interfaces, yet our ability to directly probe the localized distribution, redox activity and chemical form of metals and metalloids at these interfaces has been limited. We will discuss how the coupling of several spectroscopic and scattering techniques (e.g. Reflectivity, TR-XRF, XSW, grazing-angle XANES) has enabled us to quantitatively determine the partitioning of metal(loid)s (e.g. Pb and Se) between microbial biofilms and the underlying mineral (e.g. metal-oxide) surfaces, and to identify the local structure and oxidation state of sorbed vs. precipitated or biomineralized species. We will also discuss recent advances in the ability to quantitatively measure the transfer of metal ions into microbial biofilms (or aqueous solutions) *from* minerals and rocks colonized by microbial organisms, and to define localized oxidation fronts of metals (e.g. Fe and Mn) at the nanometer scale, using the oxidative dissolution of basaltic glasses as an example.

Identification of trace metal speciation in environment using Z-contrast imaging

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A major challenge to understanding the fate of contaminants in environment is the direct identification of trace concentrations (ppm to ppb) at the nano-scale. In order to efficiently characterize the trace metals, we have utilized high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). In general, the image contrast in the HAADF-STEM is correlated to the atomic mass.

(i) Fine- and ultra-fine particles in urban aerosols from Detroit were examined to investigate metal concentrations and speciation. The trace element speciation: Pb, As, Sb, La, Ce, Sr, Zn, Cr, Se, Sn, Y, Zr, Au, Ag and U have been characterized. We have identified nanocrystals of uraninite encapsulated in carbonaceous matter (~50 nm). The “carbon-caged” nanocrystals of uraninite are protected from the immediate oxidation that would lead to increased mobility of uranium in the environment. Still, the presence of uranium in the very fine-fraction (PM_{2.5}) of atmospheric particulates provides another pathway for radiation exposure [1].

(ii) A direct, near atomic-scale characterization of Pb is demonstrated in zircon (3.3-4.4 Ga). Two forms of Pb have been identified: Pb concentrated at ~3 atom% as a nanoscale patch in zircon structure, and Pb concentrated within the amorphous domain created by fission fragment damage. The first result suggests that the Pb atoms directly substitute for Zr⁴⁺ in the zircon structure, and the latter observation demonstrates that Pb diffusion can occur through amorphous regions created by radiation damage, although volume diffusion is typically considered to be the dominant diffusion mechanism for Pb [2].

These examples illustrate the value of HAADF-STEM as a powerful technique for the direct characterization of trace elements. This is a particularly useful technique for the heavy metals that occur at low bulk concentrations in a lighter element matrix [3].

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Hydrogeochemical signature of various amorphous As^V-Fe^{III} phases

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The precipitation of amorphous As^V-Fe^{III} phases is widely used as a remediation method for As-contaminated effluents from mining and processing industries. A better description of these phases (and of water/mineral interactions during ageing) is needed for the modeling of their long-term stability in tailing ponds. The hydrogeochemical signature of a synthetic “coprecipitate” (CPT) and of its equivalent “adsorbed ferrihydrite” (ADS) were the subject of a recent investigation the results of which are presented here.

The CPT and ADS amorphous Fe^{III}-As^V precipitates were synthesized, under the following specific conditions: 21°C, a sulphate medium, a final pH=4, a molar ratio As/Fe=0.28. Duplicates of CPT and ADS were aged for 6 months at 21±1°C, following a self-drift method, with a liquid to dry solid ratio of L/S=15±1. The aqueous matrix was composed of pure water oversaturated with respect to gypsum and calcite. This water (filtered at 0.025 µm poresize) in contact with ADS and CPT was analysed during ageing. The initial solids showed some significant chemical and morphological differences.

Hydrogeochemical signatures were representative of major differences between ADS and CPT: both of these showed a fast decrease of pH values from 7.5 (buffered in the blank matrix over 6 months) to pH 5.6 and pH 3.6 for ADS and CPT respectively. Dissolved iron was released from CPT (up to 1.3 mg/l), whereas arsenic remained on the solid. Arsenic was released from ADS until its equilibrium concentration to reach [As] = 2.5 mg/l. This behaviour was interpreted as resulting from initial different Fe^{III}-As^V-H₂O binding mechanisms between ADS and CPT.

This study demonstrates the distinct nature of the “coprecipitate” when compared to “As-adsorbed ferrihydrite”. It sheds new light on the ageing behaviour of these nanomaterials, with implications for the quality of porewater in tailings ponds and for long-term stability modeling of Fe^{III}-As^V phases.

Acknowledgments

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Oxidation of natural groundwater from Bangladesh: Arsenic speciation evolution assessed by XAS

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Arsenic poses a grave threat to human health in the southern portions of Bangladesh, where Arsenic concentrations are above 10 µg/l in over 50% of the wells, placing an estimated 20 million people at risk of developing neurological, skin diseases and cancer. The aim of our experiments was to determine As speciation in complex environment where Fe^{II}, Fe^{III}, Si and P contribute to As mobilization.

Fe and As K-edge XAS experiments have been carried out on the new XAS CRG French beamline (FAME) and on the D42 beamline of the LURE synchrotron.

XAS results confirm water oxidation kinetics that were realized on field which highlight that phosphates, silicates and natural organic matter may inhibit As-Fe complexation. The low intensity of the Fourier transforms peaks at As K-edge in the 2-4 Å range for the natural samples strongly suggests that the As-Fe interaction is not as important as believed and that the As mobility is not totally controlled by Fe. One interesting point is that Fe oxidation is catalyzed by the presence of As(III) in solution. But the most unexpected point is concerned with the highly probable As-Si interaction.

Geochemical and mineralogical controls on arsenic release from uranium mine tailings

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One of the most important environmental issues facing the uranium mining industry in Saskatchewan, Canada is the long-term stability of arsenic in its mine wastes. Decommissioning of these mine wastes requires that the long-term source contaminant potential of these primary contaminants of concern to the regional groundwater be known. Arsenic-rich uranium mine tailings from the Rabbit Lake in-pit tailings management facility (RLITMF) in northern Saskatchewan were investigated to determine the mineralogy and long-term stability of secondary arsenic precipitates. Tailings material was continuously sampled from the RLITMF to a depth of 72 m below the tailings surface. Detailed characterization of the geochemical parameters; pH, Eh and temperature, as well as solid- and pore-fluid chemistry and arsenic mineralogy were completed on the tailings samples.

Total arsenic concentrations in the mine tailings and their associated pore fluids ranged from 56 to 9,871 µg/g and 0.24 to 140 mg/l, respectively. Synchrotron-based X-ray absorption spectroscopic studies of tailings material showed that the arsenic in iron-rich areas of the tailings existed as the stable As⁵⁺ and was adsorbed to 2-line ferrihydrite through inner sphere bidentate linkages. Single reservoir diffusion cell test work and synchrotron based X-ray absorption spectroscopic studies showed that aged tailings (up to 10 years) continue to adsorb arsenic via inner sphere bidentate linkages. Using results from field- and laboratory-based studies, the redistribution (via diffusion) and attenuation (via adsorption) of arsenic in the RLITMF was modelled using a three-dimensional mass transport model (MT3DVS) to provide the source term (mass flux) of arsenic migration from the tailings to the regional groundwater systems over the next millennia.

Speciation and surface complexation of As on hydrous ferric oxide in soils modified by *in situ* chemical fixation

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Soils contaminated with arsenic-bearing herbicides in the 1940s and 1950s may leach arsenic into surface and ground water supplies and thus pose a potential environmental hazard. A soil sample containing 900 ppm arsenic was selected for study and characterized using XRD, SEM/EDX, EMPA and synchrotron techniques (micro-XRD and XANES). The arsenic was found to be As(V) and primarily disseminated on the surfaces of fine-grained soil particles in close association with aluminum. Although no crystalline arsenic phases were identified by XRD or SEM/EDX analyses, a few arsenic-rich particles were observed by EMPA and determined to be phaunouxite ($\text{Ca}_3\text{AsO}_4 \cdot 11\text{H}_2\text{O}$) using micro-XRD and XANES.

The arsenic-contaminated soil sample was treated with a solution of ferrous sulfate, which immobilized or "fixed" the arsenic within the soil. The treated soil sample was examined using synchrotron radiation techniques to deduce the mechanism of the *in situ* chemical fixation technique. Micro-XRF mapping performed on treated and untreated soil samples showed arsenic and iron were highly correlated after treatment. However, XANES analysis of the treated soil gave no indication of crystalline arsenic and iron phases being formed by the treatment process. Sequential chemical extractions performed on treated and untreated soil samples showed that arsenic becomes associated with amorphous ferric hydroxide produced by the treatment. EXAFS analysis of the treated soil sample shows similarities with the EXAFS spectrum of synthetic ferrihydrite precipitated from an arsenic-bearing solution. Interpretation of the treated soil's EXAFS spectrum indicates that soil arsenic is fixed as inner-sphere bidentate surface complexes on the precipitated ferric hydroxide. EXAFS analysis of a treated soil sample aged more than a year showed no significant variation in the arsenic chemical bonding environment compared to the newly treated samples, which indicates that soil arsenic held as arsenate surface complexes on ferric hydroxide is stable in an aerobic environment.

Transformation of arsenic species in solids and porewaters from Yellowknife Bay, NWT, Canada

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Introduction

Sub-aqueous sediments are particularly suited for studying arsenic cycling owing to local and seasonal variations in redox conditions that influence speciation and hence As mobility. Historical mining activity adjacent to Yellowknife Bay has resulted in sediments and porewaters with As concentrations as high as 10000 ppm and 7450 ppb respectively. Our sampling strategy centred around two distinct biogeochemical environments: i) shallow, oxic, organic-poor, arsenic-rich (1150 ppm), submerged gold mine tailings with patchy microbial populations and ii) deep, suboxic, organic-rich, mining-impacted (910 ppm As) lacustrine sediments abundant in microbes.

Results and Discussion

Synchrotron-based analyses (micro-XRF, micro-XANES and micro-XRD) of silt-size roaster-derived iron oxides with 10 micron spatial resolution, allow for detailed characterisation of these potentially unstable As-bearing phases. Micro-XRD identifies the roaster oxides as nanocrystalline assemblages of maghemite and hematite, while micro-XANES indicates they carry mixtures of AsIII and AsV in oxic conditions. Under more reducing conditions the oxides persist, but AsIII dominates species ratios. This suggests the AsIII associated with these roaster-oxides remains stable in an oxic setting but the AsV has either undergone reduction to AsIII or been liberated to porewaters.

Sediment porewaters, sampled at the millimetre scale with dialysis arrays (peepers) and speciated for As with anion exchange techniques, show seasonal differences. Late summer porewaters contain equal proportions of AsIII and AsV (16-415 ppb), but late winter porewaters are dominated by AsIII (284-947 ppb). The oxic veneer at the sediment-water interface contracts to <1 cm during the open-water season releasing As to the benthic environment, likely due to the reductive capacity of labile organic matter from increased primary productivity. After lake freeze-up and decreased organic inputs, the oxic veneer expands attenuating upwardly diffusing As onto authigenic Fe phase(s).

Arsenic mobilization in mine-impacted sediments

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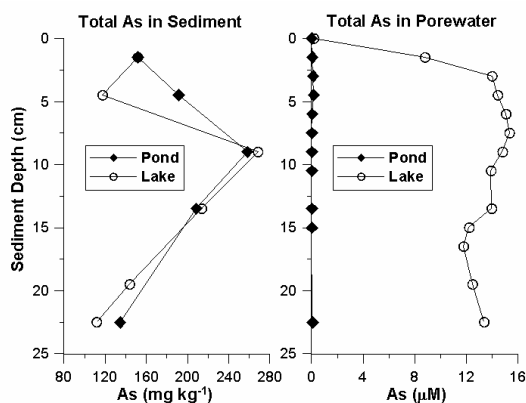
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Introduction

Lake Coeur d'Alene (CDA) and the floodplain along the CDA River, Idaho, USA are major collecting areas for metal(loids) produced during regional mining activities. Sediment geochemical properties and porewater concentrations from the lake and a nearby pond were monitored to determine the variables controlling aqueous metal(loid) concentrations. Total metals were determined by sediment digestion and aqueous concentrations were determined from porewater collected in dialysis samplers. X-ray absorption spectroscopy (XAS) was used to speciate Fe, S, and As in the solid phase.

Results

Maximum lake- and pond-sediment concentrations of As were 268 and 258 mg kg⁻¹, respectively, while maximum As in the lake porewater was 15.37 and in the pond 0.184 μM (figure below). The magnitude of the difference in available As (aqueous) in these same-source sediments indicates the importance of identifying the geochemical processes controlling As solubility.



Conclusion

Oxic conditions at the sediment-water interface in the lake promote the formation of iron oxyhydroxides and scavenging by these oxides prevents As diffusion into the overlying water column. Burial and reductive dissolution of these oxides releases As to the sediment porewater. The deficiency of sulfides in these sediments promotes high aqueous concentrations. In contrast, the anoxic interface in the pond limits oxyhydroxide formation, the subsequent scavenging of As, and negligible aqueous As concentrations.

Reductive mechanisms of arsenic mobilization from contaminated sediments

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Significant questions remain concerning the mechanism of arsenic mobilization, both in natural settings and at contaminated sites, such as the Coakley Superfund site (North Hampton, NH). During monitored natural attenuation of organic and inorganic wastes at Coakley, excessive groundwater arsenic levels have persisted. This study examines the mechanisms of arsenic mobilization at the Coakley site using field data paired with laboratory based flow experiments.

Field data tracing arsenic and other metals at the site over the past decade suggest that arsenic contamination results from reductive release from an underlying glaciomarine clay layer, where arsenic is associated with ferric species. Various pathways for iron and arsenic reduction exist. In addition to direct reduction by iron-reducing bacteria, sulfide produced by sulfate-reducing bacteria has also been tied to arsenic release [1]. Furthermore, stoichiometric analysis of site data suggests that the reduction is driven by oxidative degradation of benzene and other organic contaminants. Past studies link oxidation of organics to arsenic mobilization.[2]

Flow experiments incorporating Coakley sediments were used to evaluate abiotic and dissimilatory redox processes responsible for the arsenic mobilization. Experiments explored the roles of iron- and sulfate-reducing bacteria in consuming organic wastes and the role of sulfide as an intermediate. Stimulation of bacteria in the sediments with benzene confirmed the correlation between organic waste and increased iron reduction and arsenic mobilization. A study of the effects of sulfate concentrations also suggested that sulfate-reducing bacteria may play a major role in the mobilization of metals, as the addition of sulfate to the system was associated with increased release of iron and arsenic.

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Transformation of As species in wetlands historically used for mine tailings disposal (Ontario, Canada)

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Background

Eighty years of silver mining in the Cobalt area (Ontario, Canada) has resulted in widespread contamination of water courses with As. The objective of this study was to determine the impact of changes in redox conditions on the stability of As in wetlands historically contaminated by mine tailings.

Methods

Under controlled laboratory conditions, tailings sampled from a wetland (~1300 mg As kg⁻¹ sediment; pH 7.4) were subjected to a 30-day reduction during which dissolved metal concentrations were monitored. The reoxidation of the samples was then accomplished by air-drying. As oxidation state in the original, reduced and reoxidized tailings samples was determined using X-ray absorption spectroscopy (XAS).

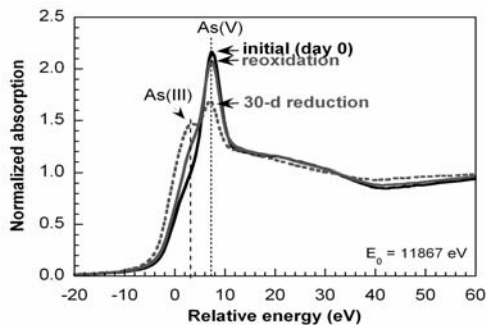


Figure 1. As K-XANES spectra for tailings subjected to 30-day reduction followed by reoxidation.

Results and Discussion

XAS analyses confirm that changes in As speciation readily occur with changes in redox conditions in the tailings sediments, resulting in rapid mobilization of As. These results will be discussed in the light of other field data suggestive of microbial sulfate reduction occurring locally in the wetland with probable co-precipitation of arsenic as a sulfide associated with framboidal pyrite.

Conclusion

This study clarifies the transformation and mobilization of As in a typical wetland area in the historic Cobalt mining camp characterized by elevated dissolved As in near-neutral drainage. The results elucidate the impact of the tailings disposal scenario on the deterioration of water quality.

Molecular speciation, mineral residence, and geochemical behavior of U in contaminated subsurface sediments

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Uranium is an important geochemical element that exhibits complex chemistry. In the hexavalent state, it is a serious groundwater contaminant at sites of U-mining/milling and nuclear materials processing. We have investigated U-contaminated sediments from different vadose and saturated zone plumes at the U.S. DOE Hanford site with the objective to develop a generalized geochemical model of U for this semiarid, mildly calcareous geochemical regime.

We describe results of spectroscopic (XAS, CLIFS, synchrotron diffraction) and microscopic (TEM, SEM, EMP, XMP) measurements to define the chemical form and spatial distribution of contaminant U(VI). Multiple techniques were required for definitive identification because of ambiguous spectroscopic signatures. A complex continuum was found between adsorption and precipitation. At one location U(VI) was found as micron-sized intragrain uranyl silicate precipitates in mm-sized granitic lithic fragments that comprised a small fraction of the sediment mass. At another location, spectroscopic measurements implied that sorbed U(VI) was present as a coprecipitate within waste-derived calcite. Deeper in this same plume, sorbed U(VI) was found within micron-thick grain coatings that were enriched with Cu(II) in the form of malachite. Batch and column desorption/dissolution experiments with these materials displayed strong and complex kinetic behavior regulated by microscopic physical and chemical factors. With the exception of the sediments containing uranyl silicates, steady state water compositions rarely conformed to the solubility of known U(VI) phases. Long-inground residence times (30-50y) have allowed significant intragrain diffusion and the formation of stable phase associations.

Speciation of uranyl adsorbed on gibbsite: A time-resolved laser-induced fluorescence spectroscopic study

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This study was carried out to identify spectroscopically-distinct species of uranyl adsorbed on gibbsite and quantify effects of pH and ionic strength variations on them. The technique of Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLIFS) was employed for that purpose. To improve the resolution of the vibronic lines of uranyl, TRLIFS measurements were carried out in cryogenic conditions. Deconvolution based on evolving factor analysis (EFA) was employed to discern the presence and contributions of non-identical emitters.

EFA showed that three main species contributed to the emission of uranyl. These included two components (referred to as Species A and B) affected by pH only, and an additional species C affected by both pH and ionic strength variations. Species A had the shortest decay time and was predominant at pH < 5.0. The emission of Species B was predominant at pH > 5.0, had a longer decay time and exhibited a red shift. This was interpreted as an indication that Species B was a deprotonated form of Species A. Species A and B were concluded to be bound via inner-sphere complexation. Species C had the longest decay time and apparently was bound via outer-sphere complexation. Because the spectrum of species C exhibited subtle changes at pHs close to the p.z.c. of gibbsite and high ionic strengths, it was concluded that it was likely to represent an envelope for several subspecies whose contributions are determined by both the surface charge and aqueous uranyl speciation.

The results show that TRLIFS of uranyl enhanced by EFA can be employed to probe the nature of uranyl species adsorbed on gibbsite and determine effects of surface and solution chemistries on their predominance. Because the emission spectra of uranyl species present on the surface of gibbsite were different from those on other representative surfaces (for instance, silica), it was concluded that detailed TRLIFS analysis for uranyl adsorbed on more complex environmentally important surfaces, notably aluminosilicates, potentially allows determination of contributions of dissimilar adsorption sites.

Reduction and retention processes within arid subsurface environments

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Introduction

Chromium and technetium are redox active metals that are significant threats to groundwater quality at U.S. Department of Energy sites. The oxidized forms of these metals, chromate [Cr(VI)] and pertechnetate [Tc(VII)], are highly soluble and mobile in the environment, while the reduced forms, Cr(III) and Tc(IV), are relatively insoluble and immobile. Chromate and pertechnetate reduction may be initiated by reduced mineral phases, dissolved Fe(II), sulfide, reduced organic matter or bacteria. Often the only potential reductant of Cr(VI) and Tc(VII) in arid subsurface environments, such as the Hanford Site in eastern Washington, is ferrous-bearing mineral phases. Beneath tank SX-108 at the Hanford Site, ⁹⁹Tc distribution was almost identical to NO₃⁻, while some retardation of Cr was observed (Zachara, 2004).

Results and Discussion

Here we examine Cr(VI) and Tc(VII) reduction by synthetic magnetite and Hanford formation sediments under hydrodynamic conditions. The amount of Cr(VI) reduced by magnetite was dependent on influent concentration. Cr(VI) reduction was only observed when the sediments were pre-treated with 0.5 M HCl, or when the column feed solution contained 10 M NaOH. Micro-X-ray absorption spectroscopy and micro-X-ray diffraction show that Cr(III) is associated with iron rich phyllosilicates, serpentinite minerals, and magnetite. Chromate reduction by Hanford sediments is inhibited by a passivating layer; however, once this layer is removed the sediments are capable of significant chromate reduction. We expect similar results for Tc(VII) reduction by magnetite and Hanford sediments.

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Effects of monomeric silicate anion on uranyl adsorption and surface speciation at the hematite-water interface

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Widespread uranium(U)-contaminated plumes have been identified at U.S. Department of Energy sites due to uranium mining operations and nuclear weapon and energy production. Accurate assessment of environmental risks and development of optimal *in-situ* remediation strategies for vadose zones and aquifers requires fundamental knowledge of uranium reactivity and surface speciation under field simulated reaction conditions (e.g., in the presence of common groundwater ions such as bicarbonate and silicate).

As a continuation of previous studies by Bargar and co-workers (Bargar et al, 1999; 2000), we investigated the effects of monomeric silicate anion (Si) on U(VI) adsorption and surface speciation on hematite (Fe₂O₃) surfaces (suspension density = 0.3 g L⁻¹, [U(VI)]_T = 10 μM, I = 0.1 M NaClO₄, P_{CO₂} = 10^{-3.5} atm, and [Si]_T = 5-200 μM). Silicate anions are of interest in U(VI) aqueous geochemistry because dissolved Si is known to complex with U(VI)(aq) near neutral pH (e.g., Langmuir, 1978).

As known from previous work, U(VI) adsorption is pH dependent, maximizing at near neutral pH in air-equilibrated systems. Addition of [Si]_T up to 200 μM had a negligible effect on macroscopic U(VI) adsorption. However, the U L_{III} edge in XAS analyses of these samples show that the uranyl cation is coordinated with both Si and Fe atoms at 2.78 and 3.47 (±0.02-0.04) Å, respectively, suggesting the presence of mono-silicate-U(VI) ternary species with U(VI) bidentate binuclear coordination on iron octahedral structures at pH 5 and 7. These research findings add new insight to the mineral-water interfacial chemistry of U-anion (e.g., carbonate and phosphate) ternary species in predicting U(VI) transport processes in vadose zones and aquifers.

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Adsorption of neodymium onto goethite in the presence of fulvic acid at 25 °C

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Adsorption onto goethite may inhibit the migration of REE/actinides, not only in geologic repositories of nuclear waste, but also in soils and other environments that have been accidentally contaminated with nuclear materials. Trivalent lanthanides such as neodymium (Nd), are reasonable analogues of trivalent actinides such as Am³⁺, Cu³⁺, Pu³⁺. Natural organic matter such as humic and fulvic acids may be present in soils and sediments contaminated with nuclear material. This organic matter may either enhance or inhibit adsorption of lanthanides and actinides. Therefore, studies of the effect of humic substances on the adsorption of lanthanides onto goethite and other mineral substrates are required. In this investigation, the adsorption of neodymium to well-characterized goethite was studied as a function of pH and fulvic acid concentration.

Potentiometric titrations were carried out under the following conditions: 0.1M ionic strength, 25 °C and 1 atm. The pH was varied from 2 to 12 via forward titration with a NaOH solution. The pH was then lowered back to 2 via a reverse titration using an HCl solution. At each step, samples were taken for Nd analyses by ICP-AES, after filtration through a 0.2 μm membrane. Binary experiments were carried out involving the adsorption of neodymium onto goethite with total concentrations of 5 ppm neodymium. The degree of adsorption of Nd was essentially zero below pH 4.5, and then rose steeply to near 100% at pH 8 and greater, so a plot of dissolved Nd concentration vs. pH showed a classic cation adsorption edge at approximately pH 6. During the reverse titration, roughly 20% of the adsorbed Nd remained adsorbed over the time-scale (tens of minutes) of the experiments as the pH was lowered to values below 4.5.

Initial experiments in the ternary system were conducted involving the adsorption of neodymium to goethite in the presence of Suwannee River fulvic acid. Initial studies show that FA enhances the adsorption of neodymium onto goethite. There was approximately 20% adsorption at all pH values less than 4.5, and the adsorption edge was shifted to lower pH by 0.5 to 1.0 units. This observation can most likely be explained by the formation of a ternary complex between the goethite surface, Nd and fulvic acid.

Speciation of Cr and V within leached BOF steel slag

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Reuse of waste materials has become very important within the past decade because of the reinforcement of environmental legislations that force minimizing waste disposal. Basic Oxygen Furnace (BOF) steel slag is a residue from the basic oxygen converter in steel-making operations, which is partially reused as an aggregate for road constructions. Even if BOF slag is an attractive material, its long-term behaviour (and the associated environmental and human health risks) must be taken into account. BOF slag is composed essentially of calcium, silicon and iron but also contains potential toxic elements present as traces, like chromium (2600 ppm) and vanadium (690 ppm), which can be released. The present research focus on the evolution during leaching (i) of the mineral phases composing BOF slag and (ii) of the speciation of Cr and V within the carrier phase because the mobility and the toxicity of these elements strongly depend on their oxidation states.

Multiple scale structural studies (XRD, SEM-EDX, XAS) are necessary to characterize heterogeneous material as BOF slag. Synchrotron-based technique of X-ray absorption near-edge structure (XANES) spectroscopy is the most well-known method permitting direct determination of the speciation of elements present in solid sample at such low concentrations.

The linked results of chemical analysis, XRD and SEM-EDX enable to identify the main mineral phases composing BOF slag: dicalciumsilicate, dicalciumferrite, solid solutions rich in iron or calcium oxides, hydroxide and carbonate of calcium and iron metal. Then, EDX micro-analyses indicate that V and Cr are associated to dicalciumferrite. The abiotic leaching of BOF slag at a laboratory scale shows that Cr is little release (less than 0.1 % of Cr total content) while V is significantly released (3 % of V total content). Finally, XANES investigations show that chromium is present at octahedral coordination in the trivalent form, the less mobile and less toxic one, and that its speciation does not evolve during leaching. XANES spectra also indicate that V is predominantly present in the +4 oxidation state and seems to become oxidized to the pentavalent form (the most toxic form) during leaching.

Adsorption of lead on single and mixed mineral assemblages

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Thermodynamic surface complexation models (SCMs) have been successfully used to quantify metal adsorption on a wide variety of pure solids as a function of solution pH, ionic strength and metal concentration (Dzombak and Morel, 1990). However, relatively few studies have applied SCMs to complex mineral assemblages. Existing studies propose either a "component additivity" or "generalized composite" approach for modeling metal adsorption on solid assemblages (Davis et al., 1998). In this study, Pb adsorption on single and binary solid systems comprised of mixtures of HFO and silica was measured and the results compared to predictions based on the component additivity model.

Measurements of Pb adsorption as a function of pH were completed using batch reactors with total Pb concentrations of 10^{-4} , 10^{-5} and 10^{-6} M in solutions of .001, .01 and .1 M NaNO₃; samples were equilibrated for 24 hrs in a rotating shaker and supernatant Pb concentrations analyzed using ICP-MS. In all experiments, adsorption of Pb increases with increasing pH; adsorption edges are much sharper for systems containing HFO in comparison to the pure silica system. Pb adsorption is independent of ionic strength in systems containing HFO, but increases slightly with increasing ionic strength for the pure silica system.

Experimental data from the binary mineral systems is in good agreement with double layer SCM model predictions made using the equilibrium speciation code JCHESS based on the component additivity approach and data collected for the single mineral systems. Ongoing experiments will be used to assess mineral-mineral interactions in other binary and ternary systems.

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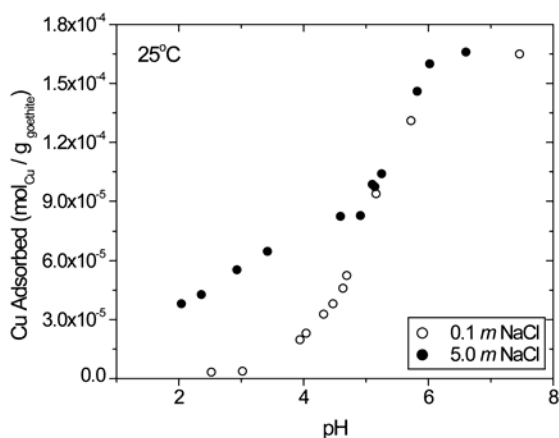
The effect of NaCl on Cu(II) sorption on goethite

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Copper mobility in water and regolith is affected by sorption; however the effect of salinity is poorly known. We determined experimentally the effect of NaNO₃ and NaCl on Cu(II) sorption onto synthetic goethite, in 16-hour experiments at 25°C, 2-8 pH, 0.1-3 m NaNO₃ and 0-5 m NaCl. Copper sorption decreased with increasing NaNO₃ concentration (0.1-1 m) at pH > 5 and is constant at higher concentrations. In contrast, copper sorption increased up to 20-fold at pH < 5 with increasing NaCl concentration (0.1-1 m) and is nearly constant at higher concentrations (Figure 1).

Figure 1: Adsorption of Cu(II)_{ads} on goethite.



Surface complexation modelling of the NaNO₃ and NaCl data indicates the presence of SOCu⁺, SOHCu²⁺, SOCuCl⁰ and SOHCuCl₂⁰. The copper chloride surface complexes enhance sorption up to 1 m NaCl, but at higher values, the presence of Cu(II) chloride aqueous complexes minimizes further increases in sorption. Higher salinity is likely to decrease the dispersion of copper during weathering and contamination.

Laser and optical chemical imaging of diagenesis in iron-oxide deposits

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Martian soils consist of iron-oxide minerals reported to include jarosite and hematite, and possibly akaganeite, goethite, schwertmannite, and ferrihydrite [1-5]. The origin of hematite is unclear, but could include direct precipitation from water or hydrothermal fluids, weathering of reduced lavas, or diagenetic alteration of soils or sediments. If Martian hematite is secondary, then it is important to determine whether phase and depositional environment signatures persists through the alteration processes. We investigate diagenetic processes that alter iron-oxide phases in layered deposits formed under acidic conditions. To search for primary signatures and document diagenetic changes, we use a combination of standard chemical and mineralogical methods, with a new method, Laser and Optical Chemical Imaging (LOCI), laser-desorption mass spectrometry coupled with fluorescence spectroscopy. Using LOCI, we are able to examine surface films as well as conduct chemical depth profiling. In a previous study, loss of some trace elements and sulfate was accompanied by a transition from schwertmannite to goethite [6]. Other trace elements appear immobile during the transition. Some chemical signatures indicative of depositional environment may be lost during diagenesis of iron-oxide deposits while other signatures persist. We use LOCI to determine at what point and under what conditions these trace element and spectroscopic signatures are lost.

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Zinc sorption on hydroxyapatite: Systematic uptake and EXAFS studies

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The systematics and mechanisms of Zn sorption on hydroxyapatite (HAP) in pre-equilibrated suspensions open to air were characterized using a combination of batch sorption experiments, X-ray diffraction (XRD), and extended X-ray absorption fine-structure spectroscopy (EXAFS). Experiments were conducted over a range of pH values and Zn concentrations to assess the dominant Zn sorption mechanisms. Sorption isotherms of Zn(II) on HAP at pH 5.0 and 7.3 show an initial steep slope, followed by a plateau up to $[Zn] \leq \sim 750 \mu\text{M}$, whereas at $[Zn] > 750 \mu\text{M}$ a sharp rise in the pH 5.0 isotherm suggests precipitation, and slight continued uptake in the pH 7.3 isotherm is suggestive of an additional uptake mechanism. At pH 9.0, the isotherm shows a steep uptake step at $[Zn] \leq 0.8 \mu\text{M}$, followed by an increasing linear trend up to $[Zn] = 5 \mu\text{M}$, without any indication of a maximum, suggesting that precipitation is an important uptake process at this pH.

Zn K-edge EXAFS results show a first oxygen shell at $1.96\text{-}1.98 \pm 0.02 \text{ \AA}$ in sorption samples with $[Zn]_{\text{tot}} \leq 250 \mu\text{M}$ at pH 5.0, 7.3, and 9.0, consistent with tetrahedral coordination of Zn. EXAFS results reveal additional P and Ca backscatters, supporting formation of an inner-sphere Zn surface complex. In contrast, EXAFS and XRD data indicate that precipitation of $Zn_3(PO_4)_2 \cdot 4H_2O$ (hopeite) dominates the mode of Zn uptake at $[Zn]_{\text{tot}} \geq 3 \text{ mM}$ at pH 5.0. Linear combination fits of EXAFS data reveal a mixture of inner-sphere Zn surface complexation and precipitation of $Zn_5(OH)_6(CO_3)_2$ (hydrozincite) in sorption samples for $[Zn]_{\text{tot}} = 5 \text{ mM}$ at pH 7.3, and for $[Zn]_{\text{tot}} = 1 \text{ mM}$ at pH 9.0. The different mechanisms of Zn uptake by HAP suggest that immobilization of Zn, as well as the potential for remobilization, depends sensitively on solution conditions, including pH, Zn concentration, and the presence of dissolved CO_2 .

Determination of cation exchange rates in synthetic birnessite using time-resolved synchrotron X-ray diffraction

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Birnessite is the most abundant and chemically important layer-structure Mn-oxide phase found in soils, desert varnishes, and ocean nodules. For this work, we measured changes in unit cell parameters over time to quantify the degree of cation exchange as a function of concentration. Aqueous K^+ , Cs^+ , and Ba^{2+} cations at varying concentrations at pH 7 were exchanged for interlayer Na^+ in synthetic birnessite using a simple flow-through cell, and the exchange products were monitored via time-resolved X-ray powder diffraction at the National Synchrotron Light Source. Powder X-ray diffraction patterns were collected every 2-3 minutes.

Rietveld analyses (using the GSAS program) of X-ray diffraction patterns for K- and Ba-exchanged birnessite revealed a decrease in unit cell volume over time; in contrast, Cs substitution increased cell volume. For all three cations, the exchange occurred in two stages. A rapid and dramatic change in unit cell volume was followed by a modest adjustment over longer timescales. Fourier electron difference syntheses revealed that the rapid, initial stage of exchange was marked by major re-configurations of the interlayer species, whereas the second, protracted phase of substitution represented ordering into the newly established interlayer positions. We calculated normalized volume contraction (or expansion) coefficients for the period of rapid initial exchange for each cation solution concentration. Specifically K-exchange at 0.05M, 0.01M, and 0.001M resulted in volume contraction coefficients of $1.51E^{-3} \text{ min}^{-1}$, $4.68E^{-4} \text{ min}^{-1}$, and $1.69E^{-4} \text{ min}^{-1}$ respectively. These values yield the following rate equation that corresponds to the rate of cation exchange:

$$\log [\text{Rate Volume Contraction}] = 0.5524 \log [KCl] - 2.1469.$$

Further refinements of the Ba^{2+} and Cs^+ exchange results will result in a comparison of the rate of exchange for different cations.

Arsenic speciation and mobility in contaminated soils: Comparison of column and batch extraction experiments

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Aims

The chemical behavior of arsenic (As) in soils is dependant on a variety factors. These involve soil characteristics as well as its chemistry (e.g. pH, Eh, phosphate concentration, etc). The aims of this study are to understand the behaviour of As and the precise mechanisms involve in its mobility within two historically polluted industrial sites. To this end, an overall methodological approach was constructed: (1) a highly detailed characterization in arsenic pollution determined by an arsenic speciation made by a variety of techniques (2) mobility tests with static studies (single batch extractions) and dynamic studies (columns experiments). These leaching experiments were done by varying the pH and phosphate concentrations. The remobilization kinetics of As, inherent to column experiments, were also investigated in a series of single batch tests with varying extraction times.

Results and discussion

In the three soils studied, As was mainly present as arsenate (between 92 to 100% of total As) and arsenite was the other As species detected. No arsenic crystalline phases were identified. SEM-EDS investigations showed an arsenic/iron association; this was confirmed by the sequential extractions experiments which also suggested an As association with amorphous iron oxides. This pollution characterization shows As as being potentially labile by reductive dissolution of iron oxides.

Concerning mobility tests; despite the given extraction conditions (pH or phosphates concentrations), dynamic tests led to an arsenic remobilization which was much more important than the semi-equilibrium leaching test batches; this remobilization could reach, in the alkaline medium (pH 11), 78% of total As, by the end of the experimentation. These mobility experiments also provided information about As release mechanisms in such specific conditions.

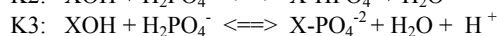
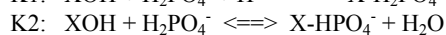
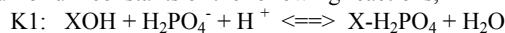
Improved thermodynamic equilibrium constants of phosphate adsorption onto HFO

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Phosphate released via fertilizer overuse and sewage disposal causes widespread eutrofication of freshwater systems and may promote desorption and release of other oxyanions (arsenate, chromate) adsorbed onto sedimentary hydrous ferric oxide (HFO) and other minerals. Understanding these processes requires accurate data that quantify the pertinent equilibrium surface complexation reactions.

In this study we have carried out batch experiments measuring phosphate adsorption onto HFO as a function of pH, phosphate concentration, ambient CO₂ and ionic strength in NaNO₃ electrolyte at 25° C. The results were used to constrain mass law and mass action parameters for PO₄³⁻, HPO₄²⁻, and H₂PO₄⁻ adsorption onto HFO according to a double-layer model formulation. Our optimal values for equilibrium constants of the following reactions,



where XOH denotes the hydroxyl group on HFO, are listed below:

	DM90	1 σ unc.	This study	1 σ unc.
Log K1	18.981	-	19.0	0.33
Log K2	13.081	0.044	14.1	0.75
Log K3	5.411	0.101	8.3	0.39

These improved values principally differ from those of DM90 in the K3 reaction, which our results constrain as three orders of magnitude more stable. Our values were constrained using a larger dataset than that used by DM90 and therefore should better describe phosphate-HFO adsorption over a wider range of systems compositions.

Reference

DM90: Dzombak D. A. and Morel F. M. M. (1990) Surface Complexation Modeling: Hydrous Ferric Oxide, Wiley-Interscience, New York.

Investigating Ni partitioning in a contaminated aquifer

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Improved prediction of the transport and bioavailability of transition metals in contaminated soils and sediments demands a better quantitative understanding of how metals partition between aqueous solutions and mineral phases. In this study, five-step Tessier sequential extractions (Tessier et al., 1979, *Analytical Chemistry* **51**, 844-851) and adsorption experiments were performed on sediments from uncontaminated and nearby Ni contaminated shallow aquifer sediments from a site located near Monroe, MI USA.

Measurable Fe and Ni concentrations were obtained only from the sequential extraction step designed to extract particulate Fe/Mn phases and associated metals. This suggests that Ni partitions primarily into Fe or Mn oxide phases in this aquifer. Based on similar observations, models used to guide remediation efforts at the contaminated site have relied primarily on predicted behavior for Ni adsorption onto ferrihydrite.

However, Ni adsorption experiments performed on whole sediments over a wide range of pH (2-12) are not in agreement with results predicted based on the assumption that Ni adsorption is primarily controlled by ferrihydrite. In particular, there is more sorption of the Ni at low pH than is predicted for a system composed only of ferrihydrite. This suggests that other phases present in the aquifer, such as clay minerals, may significantly affect Ni speciation in this contaminated aquifer.

Chemical speciation study of amphibolite weathering under different climatic setup of Mysore plateau, southern India

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Chemical speciation of elements during weathering of amphibolites has been studied to understand their elemental mobility and redistribution in the weathering products developed under different climatic conditions. The bioavailability of any nutrient element depends on the form in which the element exists in weathered products or soils. Saprolite and soil samples developed on profiles and rinds were collected from semiarid (annual rainfall 70-80 cms) and humid (300-400 cms) regions of Mysore plateau, Southern India. The humid regions of Mysore plateau, the Western Ghats constitute an ecological hotspot in the country. Chemical speciation on the weathered rock samples was performed using the standard methods. We have found that Al and transition metals analyzed (V, Cr, Mn, Fe, Co, Ni, Cu, Zn) are mostly associated with the organic fraction, crystalline iron, amorphous iron and Mn oxide fraction in the listed order. Carbonate fraction is also important for Cu, Zn and Ni. Organic fraction and exchangeable forms are significantly important for Na, K, Mg, Ca, Sr & Ba. For obvious reasons Mn occurs in the Mn oxide and Ca in the carbonate form. We note that despite the differences in climate (semi-arid Vs humid) and mode of weathering (rinds Vs profile), the organic fraction plays an important role in sequestering the mobilized elements during weathering, which could be available to the plants under certain favourable conditions. We also observe that there is a general similarity in the chemical speciation of elements studied here in weathered products of amphibolites irrespective of the nature and extent of chemical weathering. Therefore, we suggest that the chemical speciation of the elements in weathering products was not constrained by varied climatic setups and bulk geochemistry of the weathered products of amphibolites in the study area.

Changes in Zn speciation in the rhizosphere of graminaceous plants induced by phytostabilization of a contaminated sediment

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The maintenance of waterways generates large amounts of dredged sediments, which are often rich in metal contaminants. Understanding how the metals are speciated at the molecular level is critical for formulating effective metal containment strategies, such as phytoremediation. The mineralogical transformations of Zn-containing phases induced by the graminaceous plants, *Agrostis tenuis* and *Festuca rubra*, in a contaminated sediment ($[Zn] = 4700 \text{ mg kg}^{-1}$, $[P_2O_5] = 7000 \text{ mg kg}^{-1}$, $pH = 7.8$), untreated or amended with hydroxylapatite (AP) or Thomas basic slag (TS), were investigated after two years of pot experiment by SEM-EDS, μ -SXRF, and powder- and μ -EXAFS.

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 least-squares fitting 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 % sphalerite, ~40 % Zn-ferrihydrite, and ~10-20 % (Zn,Al)-hydrotalcite plus Zn-phyllosilicate. In unvegetated but amended sediments (AP and TS), ZnS and Zn-ferrihydrite 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 heterogeneous precipitation on mineral surface.

Coprecipitation of As(III) with synthesized phyllosilicates and hydrotalcite-like phases

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We have previously reported the existence of As(III)-bearing smectites from the geothermal environment. Synthesis experiments were conducted to understand the possible mechanisms how trace metals are incorporated into the layered structure of smectites and hydrotalcite-like phases. In all experiments, arsenic uptake was observed through initial uptake by precursory phases. Further uptake occurred by ageing the precursory phases into their final mineral forms. The mechanism of uptake involves complexation of As(III) with dissolved species (e.g. Al) prior to the formation of the solid precursory phase (i.e. X-ray amorphous solids). The stabilization of the As(III) in the final mineral phase (e.g. phyllosilicate or hydrotalcite-like phases) occurs during ageing. The observed uptake of As(III) depends on the initial complexation reactions and timing of the precursory phase precipitation. If these synthesized materials show the stabilization of As(III) similar to the natural sample previously reported, they can be effectively used in demobilizing dissolved As(III) in contaminated natural waters.

Temperature-resolved synchrotron X-ray diffraction study of dehydration of birnessite-like phases

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Manganese oxide minerals having the birnessite-type layer structure occur in a wide variety of geological settings, including soils, sediments, Mn crusts and nodules, and rock varnish. They readily participate in cation-exchange and oxidation-reduction reactions, and synthetic birnessite-like phases are extensively being studied as possible catalysts and cation-exchange agents. The interlayer region is occupied by H₂O molecules and various cations such as Na⁺, Ca²⁺, K⁺, etc; synthetic birnessite phases have been synthesized having a wide assortment of other interlayer cations. The chemical activity exhibited by birnessite is, at least in part, due to the apparent ease with which the structure adjusts to accommodate a range of interlayer water and cation compositions.

In situ, temperature-resolved synchrotron X-ray diffraction and the Rietveld method were used to investigate the dehydration behaviors of synthetic Na-, Mg-, H-, Ba- and K-birnessites as they were heated from room temperature to ~300 °C. The X-ray diffraction data were collected in air at beam line X7B of the National Synchrotron Light Source, Brookhaven National Laboratory, using a wavelength of 0.9370 Å and a MAR345 full imaging plate detector.

Na- and K-birnessite exhibit complex dehydration behaviors when heated from room temperature to 300 °C, accompanied by three distinct structural changes: at 70-80 °C, 100 °C, and 140-150 °C. The unit-cell volume decreases at each dehydration step but most dramatically above 140 °C. At ~175 °C K-birnessite transforms to an anhydrous layer structure with a layer spacing of 6.69 Å, that persists to at least 300 °C. Upon cooling in air this phase rehydrates. Ba- and Mg- birnessites exhibit only minor volume decreases up to 150 °C. Above this temperature, the Ba-birnessite structure breaks down abruptly, and the unit-cell volume of the Mg phase gradually decreases up to ~350 °C.

Interaction of U(VI) with birnessite: A solution chemistry and EXAFS study

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Radionuclide migration in natural aqueous environment is an ongoing concern in environmental research. Because layer Mn oxides are widespread, have a large surface area and a high density of binding sites, they control the fate of many important metals, including radionuclides. This work investigates the mechanism and kinetic of the uranyl interaction with birnessite, the predominant layer-type MnO₂ mineral at the Earth's surface. The sorption of U(VI) on synthetic birnessite was studied macroscopically with experiments performed under various conditions of pH (ranging from 4 to 6), dissolved U(VI) concentrations ($[U^{VI}] = 3.10^{-7}$ to 7.10^{-4} M), and ionic strength (0.01M to 0.1M, in NaClO₄ or Na₂CO₃ media). Under these conditions, the speciation of U(VI) in solution was contrasted, being dominated either by hydrolyzed species, uranyl-carbonato complexes, or polynuclear species. Sorption kinetic depended on the concentration of dissolved U(VI). The amount of sorbed U(VI) per specific surface area largely exceeded the coverages previously reported on related environmental minerals, such as montmorillonite and ferrihydrite, under similar experimental conditions, thus confirming the strong affinity of U(VI) for the birnessite surface. Sorption isotherms exhibited a complex form, and was indicative of, at least, two types of sorption sites. EXAFS data revealed the presence of two equatorial O shells at ca. 2.31 Å and 2.42- 2.51 Å (in addition to the two axial oxygens at about 1.80 Å), and a Mn shell (except in the Na₂CO₃ media) at 3.4 Å in the pH 4 sorption samples. The average number of Mn atoms decreased and the distance of the second equatorial O shell increased to 2.51 Å with increasing aqueous U(VI) concentration. At pH 6, the equatorial oxygens remained split into two distinct shells, but no nearest Mn was detected. No C shell was detected for any samples, even in the Na₂CO₃ media, nor U-U pair, despite the prevailing presence of polynuclear dissolved species in some of the samples.

From the combination of solution chemistry and EXAFS results, a structural model for the sorption of U(VI) at low pH is proposed, in which the oxygens from the equatorial plane of uranium form two types of surface complexes with edge sites from the birnessite layers. At low aqueous U concentration, adsorption occurred via a bidentate complexation. When the U(VI) concentration increased, the saturation of the previous sites led to the formation of a second type of surface complex, involving monodentate binding to the mineral surface.

Bioaccessibility of As(V) and Pb(II) from mimetite

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Arsenic and lead contamination is prevalent problem throughout the world. One of the method suggested for their removal from wastewaters is based on precipitation of lead chloroarsenate - mimetite $Pb_3(AsO_4)_3Cl$ (Twidwell at all., 1994). In this process, mimetite quickly forms crystalline precipitate of relatively low solubility, suitable for separation and storage.

In this study, a bath equilibrium technique was adopted to quantitatively evaluate bioaccessibility of As(V) and Pb(II) released by dissolution of synthetic mimetite. EDTA (pH 7), acetate buffer (pH 5), and H_2SO_4 (pH 2 and 4) leaching fluids were used to simulate the presence of organic materials in soils and landfills and the effects of acid rains.

The highest solubility of mimetite was observed in the presence of EDTA. Dissolution in both, EDTA and acetate buffer is congruent and results in stoichiometric Pb/As ratio. Mimetite dissolves relatively fast and within first week the solution becomes saturated. In contrast, dissolution of mimetite in H_2SO_4 is incongruent and results in formation of anglesite $PbSO_4$ while As(V) remains in solution.

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Interaction between arsenic oxyanions and iron-sulfide minerals

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Introduction

Elevated arsenic (As) concentrations are frequently encountered in groundwater extracted from 30-50 m depth on the Indian sub-continent. Mineralogical studies in these aquifer strata suggest the importance of Fe-S minerals in this As mobilization process. In this project, we study the molecular mechanisms of As interaction with Fe-S minerals (both natural and synthetic pyrite FeS_2 and pyrrhotite FeS) under different redox conditions.

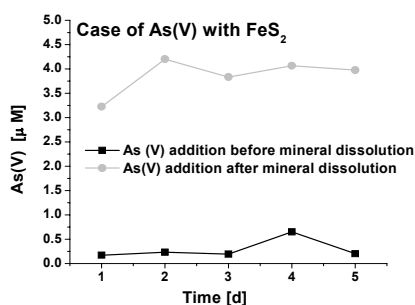
Methods

Fe-S minerals were equilibrated in batch experiments with solutions containing various concentrations of either As(III) or As(V). The redox state in solution was controlled by purging with N_2 , air or H_2S , and anoxic experiments were conducted in a glove box. Subsamples were withdrawn at different time intervals, filtered and analyzed for pH, total Fe, S and As by ICP-MS and for As speciation by AEC-ICP-MS.

First results

Arsenate adsorbed stronger to the Fe-S minerals than arsenite, and FeS adsorbed the As species stronger than FeS_2 . Surprisingly, results suggest that sub-stoichiometric levels of As species influence the solubility of the Fe-S minerals. Also, the mobility of the As species increased as the Fe-S mineral began to dissolve slightly (Fig. 1), i.e. As adsorption was reduced by Fe and/or S released from the mineral.

Figure1: As concentration in solution with and without pre-equilibration between Fe-S mineral and solution



Effects of brucite on ozonation treatment of dye wastewater

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Dye wastewater, also other organic polluted water, can be treated with ozonation technics. Before the organic pollutants translate to CO_2 and H_2O during ozonatin, it undergoes a periods of stable state in low carbon acids. During this statement, the pH of the wastewater lower value, the COD (Chemical Oxygen Demand) decreased rate almost does not increase with O_3 adding. United technics of O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{O}_3/\text{catalyst}$ are commonly used before.

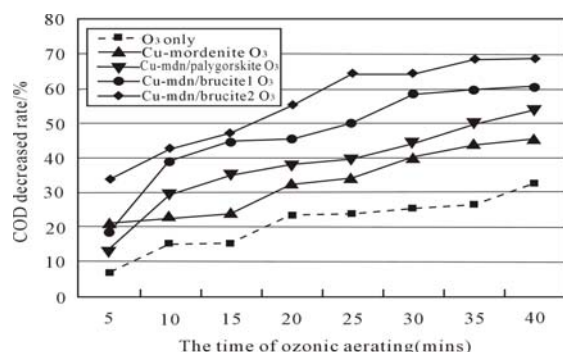


Figure 1: Correlativities of COD decreased rates with catalytic minerals added.

This study proves that zeolite and palygorskite play an efficient role when those minerals are added to the ozonic system. Furthermore, brucite increase the effects of ozonation sharply as illustrating in Figure 1. The $500\text{mg}\cdot\text{L}^{-1}$ wastewater, the COD equal to $279.9\text{ mg}\cdot\text{L}^{-1}$, synthesizes by active-Brilliant Red dyes. Mixed air and 17.2mg/h O_3 in 1.1L/min flux flow through 900mm high glass aerating reactor filled in 50ml dye wastewater. COD decreased rates increase with minerals joine to the system form O_3 only to Cu modified mordenite+ O_3 , mordenite plus palygorskite, until brucite+ O_3 get the highest value.

Brucite enhancemrnt ozonation efficiency is attributed, firstly, to the O_3 decomposition initial reaction, $\text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2 \cdot + \text{O}_2^-$, occurs in alkali environment. The generation and oxidation ability of hydroxyl radical are stronger in alkali condition. The dissolubility of brucite is good for a solid alkali buffer in water treatment. Secondly, reaction of Mg^{2+} dissolved from brucite with organic acid radical precipitates magnesium salts from wastewater.

Acknowledgement

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