

X-ray probes of the uptake of metal ions by CaCO_3

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Introduction

The mobility of metal ions through the subsurface is partly determined by the chemical reactivity of soil minerals. The rate of radionuclide and metal uptake by minerals in the soil determines the eventual environmental impact. Pollutant fate and transport are dependent on the oxidation state and chemical composition of the contaminants introduced into the subsurface.

A key element needed to model contaminant mobility is knowledge of the structure and reactivity of metals at aqueous/mineral oxide interfaces. The recent controversy over radioactive materials transport through the soils under Hanford tank farms and the beneficial role played by the “caliche” layer in immobilizing heavy metal movement, highlights the need for methods capable of analyzing and predicting metal uptake by soil minerals.

Methods and Materials

Coupling the experimental methods of laser ablation mass spectroscopy (LAMS) and x-ray photoelectron spectroscopy (XPS) was a milestone this year. The LAMS-XPS studies are multiwavelength, ongoing experiments performed at the Environmental Molecular Sciences Laboratory (EMSL). The experimental studies have begun to probe the final chemical composition of metal cations (e.g., lead, cesium, and cobalt) taken up by calcite and “caliche”. In addition, both synchrotron-radiation techniques of extended x-ray absorption spectroscopy (EXAFS) and x-ray microprobe imaging (XMI) were utilized for the analysis of the elemental composition and the mapping of metal-containing calcite single crystals and naturally occurring Columbia River Basin “caliche.” The synchrotron radiation experiments have been run at the Advanced Photon Source (APS) at the Pacific Northwest Consortium sector (PNC-CAT) located at Argonne National Laboratory.

Results and Discussion

Research into binding sites available at the mineral/water interface of CaCO_3 have recently been undertaken by geochemical researchers [1–4]. In one such study [2], Pb metal was found to sorb at surface sites in a well-ordered fashion within the 1014 cleavage plane. To further understand variations in adsorption phenomena on CaCO_3 , we conducted experimental runs at the APS to discover whether “rinding” (uniform coatings formed when metal contaminants precipitate from solution onto the surface of single-crystal calcite) are seen on geologic Columbia River Basin “caliche.” For this, XMI was employed with a spatial

resolution of 5 microns. The results are seen in Figure 1. XMI results of “rinding” show compelling evidence that the uptake of contaminants is highly nonuniform on “caliche” samples from nearby the Hanford Site. The observed “hot spots” of contaminants closely resemble those previously found in other soil samples [5], and suggest that the availability of reactive sites is less than suggested on the basis of total surface area models.

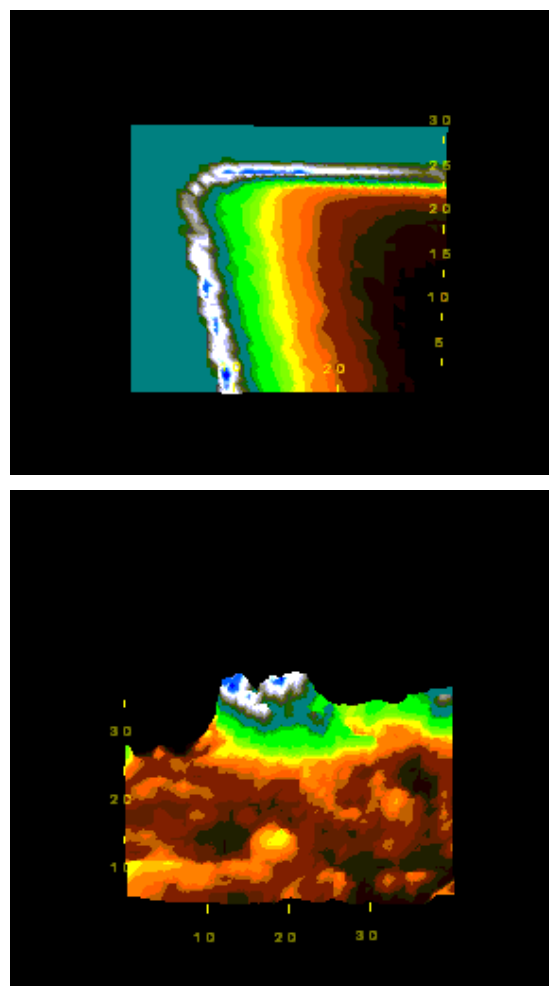


Figure 1: An XMI image of Pb^{2+} adsorption atop a 300 x 300 μm corner cross section of rhombohedral single-crystal calcite (top) and Columbia River Basin “caliche” (bottom). Concentrations in false color range from black (min.) to blue (max.). The Pb^{2+} layer is observed to be $< 20 \mu\text{m}$ in depth on the single-crystal calcite and homogenous. The “hot spot” adsorption phenomena on “caliche” is drastically different and inhomogeneous.

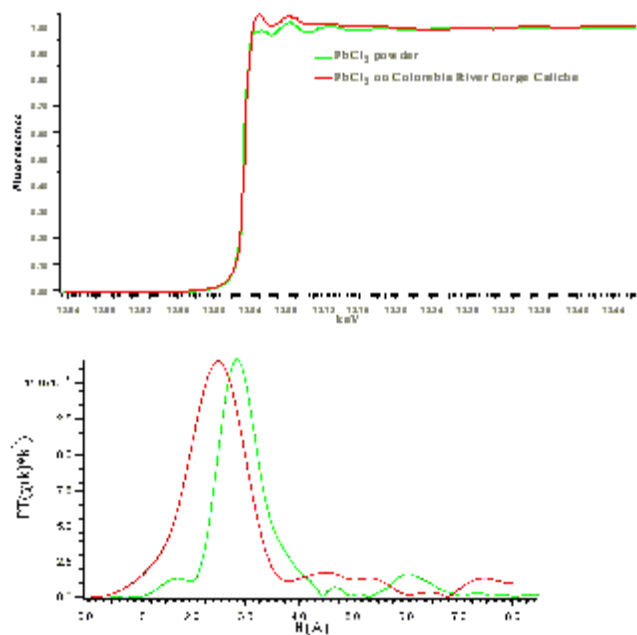


Figure 2: EXAFS and a FEFF8 fit of the first scatter peak bond distances of Pb-X in the powder PbCl_2 standard compared to the “hot spot” formation on the “caliche” sample in Figure 1. The bond distance of Pb on “caliche” is associated with a Pb-O bond distance of 2.51 angstrom and that of PbCl_2 is associated with a Pb-Cl bond distance of 2.874 angstrom. Lead has been incorporated into the lattice structure of the “caliche” polycrystal.

Additional runs at the APS were undertaken to initiate a study of coprecipitation effects on Columbia River “caliche.” Samples of “caliche” were prepared in a solution of metal chlorides at < 0.00001 M and subsequently rinsed. XMI was conducted on the samples for native impurities of Fe and Cu, as well as the metal compounds added from solution. The results are shown in Figure 3. XMI results show Pb formations tend to abut Ca formations that display dramatic concentration variations. Initial analysis also indicates that a relationship exists between native Cu deposit sites and Pb uptake.

Acknowledgments

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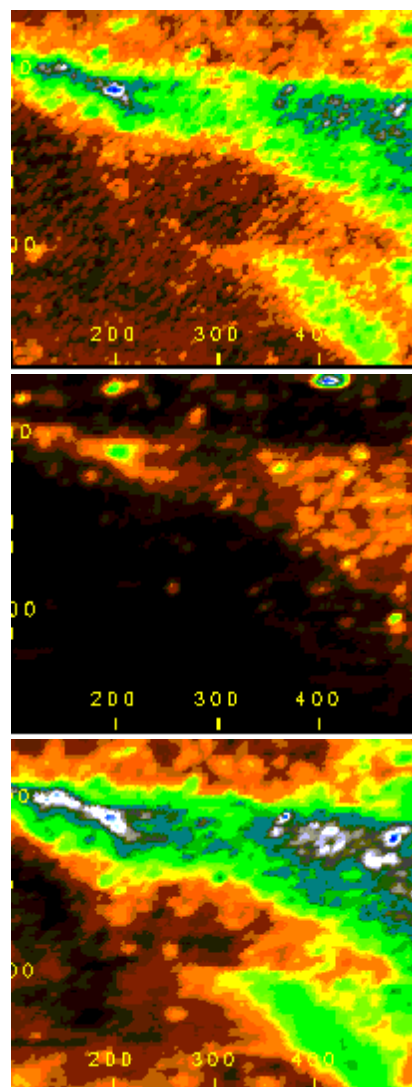


Figure 3: XMI images of (top to bottom) Pb, Cu, and Fe on a sample of Columbia River Basin “caliche.” The spatial resolution is $\sim 1 \mu$ throughout. Significantly, Pb^{2+} precipitate is associated with native impurity sites of Cu deposition. Coprecipitation is an important area of ongoing research into the dynamics of metal uptake in CaCO_3 .

References

- [1] R.P. Chiarello, and N.C. Sturchio *Mater. Res. Soc.*, **337**, 181–186 (1996).
- [2] Y. Qian, N.C. Sturchio, R.P. Chiarello, P.F. Lyman, T.-L. Lee, and M.J. Bedzyk *Science*, **265**(5178), 1555 (1994).
- [3] L. Cheng, P.F. Lyman, N.C. Sturchio, and M.J. Bedzyk, *Surface Science*, **382**(1–3), 690–695 (1997).
- [4] R.J. Reeder, *10th Symposium of PNW Chapter of the AVS, June 16–19*, (1998).
- [5] R.J. Reeder, G.M. Lamble, and P.A. Northrup, *American Mineralogist*, **84**, 1049 (1999).