Strontium Migration and Co-Precipitation at Columbia Basin Basalt/Caliche Interfaces

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Introduction

Carbonate minerals are components in the soil and vadose zone of several Department of Energy (DOE) sites (e.g., Hanford Site). Because they can form rapidly and are highly reactive, carbonates may be extremely effective in attenuating transport of toxic metals and radionuclides by several uptake mechanisms, including co-precipitation and adsorption. In contrast to the sorptive behavior shown by many hydr/oxide and clay minerals, sorptive uptake of dissolved metals onto calcite usually results in co-precipitation. This has important implications for the long-term retention of contaminants, since metal species are incorporated into the bulk, rather than solely at the surface of the crystal, and bulk dissolution is necessary for their re-release to fluids.

Throughout the vadose zone of the Hanford Site, which is dominated by siliciclastic sediments, pedogenic calcification has resulted in the extensive occurrence of carbonate as coatings on grains, as disseminated particles and as thick and extensive, buried caliche layers.[1] Where carbonate coatings exist they are likely to be more important than the substrate grains in controlling uptake of contaminants. Release of highly alkaline tank waste into the vadose zone, combined with a generally low soil moisture content, is expected to promote periodic precipitation of calcium carbonate, and high pH conditions should also favor sorption on existing calcite. Preliminary characterization of the caliche underlying a tank waste location at the Hanford Site indicates that ^{90}Sr^{2+} radionuclides are strongly associated with calcite.

A variety of co-precipitation studies have been conducted for divalent metal species with calcite and aragonite, with many corresponding to seawater chemistry conditions. Principal trends have been reviewed by Mucci and Morse[2] and Rimstidt et al.[3] A significant observation is that transition and post-transition metals (divalent Co, Zn, Mn, Fe, Cd) typically show highly compatible incorporation behavior for calcite (i.e., K>1), whereas alkaline earth metals (divalent Mg, Sr, Ba) are incompatible (K<1). There is, however, a very significant finding among the co-precipitation studies that have assessed the influence of crystallization rate on uptake behavior; specifically, incompatibility diminishes with increasing growth rate (e.g., Lorens, 1981[4]; Morse and Bender, 1990[5]). Consequently, under conditions of rapid growth, such as might be expected in the soil and vadose zone as a result of periodic wetting and drying, uptake of incompatible contaminant species by co-precipitation (as well as compatible species) may be significant for calcite.

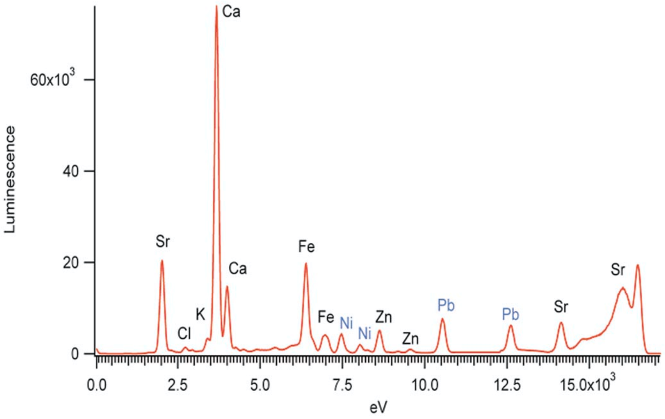
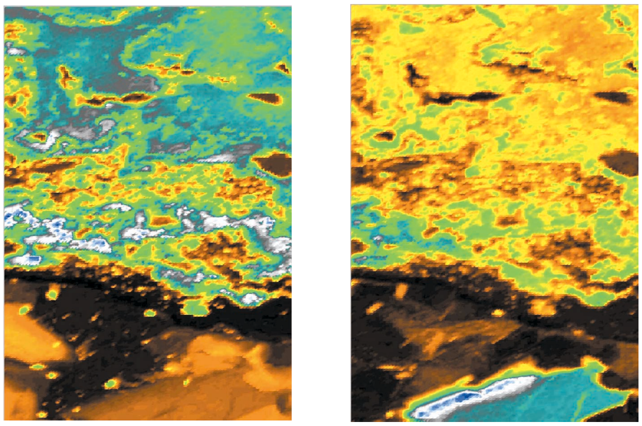


FIG. 1. X-ray energy was set to the strontium absorption edge of 16.105 keV. The 13-element Ge detector located in PNC-CAT and used as a multichannel analyzer in this study captures fluorescence from the metal constituents of the caliche layer. Blue-labelled elements represent fluorescence from components in the experimental apparatus.



(a) *(b)*

FIG. 2. (a) The x-ray microprobe technique used here allows the direct fluorescence mapping of Ca^{2+} constituents at the basalt/caliche interface over the 820 x 350 micron region above. (b) The fluorescence signal of Sr^{2+} was gathered simultaneously over the same region as in a). The heterogeneous nature of the calcium and strontium fluorescence signals apparent in these extensive images may be evidence of co-precipitation. Concentrations in false color range from black (min.) to blue/white (max.) Sample stepping size was maintained at 2.0 microns over this +19 hour scan.

Methods and Materials

The companion synchrotron-based techniques micro x-ray fluorescence (sometimes called x-ray microprobe) and micro-XAS (x-ray absorption spectroscopy), which offer micron-scale element mapping combined with x-ray absorption spectroscopy, are ideally suited for determining spatial heterogeneity of contaminants on natural samples with various levels of information about speciation. Naturally occurring strontium near the basalt/caliche interfacial region affords an opportunity to investigate how divalent metal leeching and co-precipitation may occur within the caliche layer. Our primary focus is the heterogeneity of contaminant uptake and retention on natural caliche and coatings from Hanford Site samples.

Results

Extensive fluorescence mapping has indicated (e.g., Fig. 2) that the primary characteristic found in the caliche overlayer is a heterogeneous strontium content with calcium. A co-precipitation process that could account for natural strontium migration and incorporation in "Hanford formation" basalt deposits is consistent with these findings.

Discussion

Carbonate minerals (particularly calcite) are important components in the soil. In contrast to the sorptive behavior shown by many oxide and clay minerals, sorptive uptake of dissolved metals onto calcite usually results in co-precipitation. Extensive mapping of natural strontium deposits near the basalt/caliche interface via x-ray microprobe indicates heterogeneous calcium and strontium concentrations – "where there is calcium, there is strontium." This implies a co-precipitation mechanism for natural strontium migration and incorporation in caliche.

Since metal species are incorporated into the bulk, rather than solely at the surface of the crystal, this has important implications for the long-term retention of contaminants. Uptake of incompatible divalent contaminant species by co-precipitation appears to be significant for calcite.

Acknowledgments

This work was supported by the U.S. Department of Energy's Office of Biological and Environmental Research, and partially performed at the William R. Wiley Environmental Molecular Science Laboratory located at Pacific Northwest National Laboratory. Pacific Northwest National Laboratory is operated for the DOE by Battelle under contract DE-AC06-76RLO 1830. Use of the Advanced Photon Source (APS) was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Work was performed at the APS through the Pacific Northwest Consortium, PNC-CAT.

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