

# Strontium Migration and Co-precipitation at Columbia Basin Basalt/Caliche Interfacial Regions

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## Background

Carbonate minerals (particularly calcite) are important components in the soil and vadose zone of several 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 hydroxide 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 siliclastic 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 (Slate, 1996). Where carbonate coatings exist they are likely to be more important than the substrate grains in controlling uptake of contaminants. Release of highly alkalinity 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  $^{90}\text{Sr}^{2+}$  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 (1990) and Rimstidt et al. (1998). 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; Morse and Bender, 1990). 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.

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 leaching 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.

## Microprobe Investigation of Naturally-Occurring Strontium in Caliche-coated Basalt

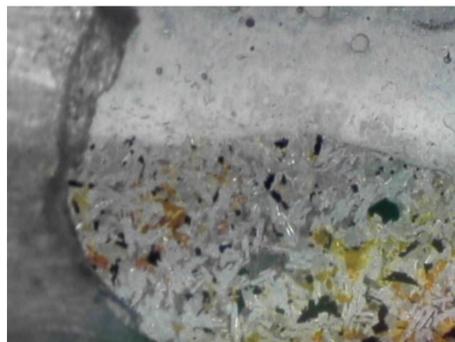


Figure 1. Thin sections – 30 microns thick – were prepared from caliche-coated samples of “Hanford formation” basalt. Microprobe imaging and analysis were conducted at sample areas where the basalt/caliche interface remained intact following mounting on high-purity silica slides. A wide-angle CCD image of the sample used in this study is pictured above, showing the regions probed.

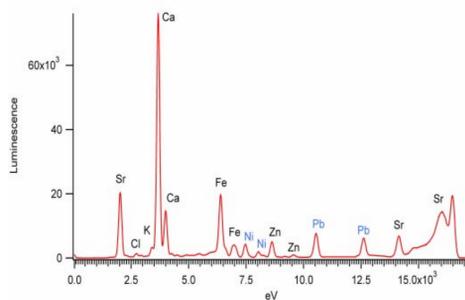


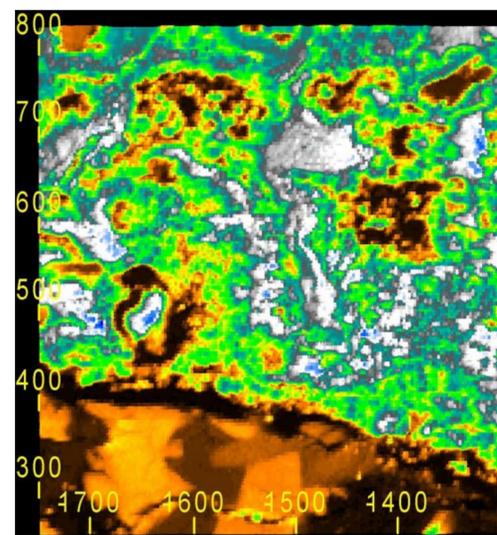
Figure 2. X-ray energy was set to the strontium absorption edge of 16.105 keV. The 13-element Ge detector located in PNC-CAT and used as a multi-channel analyzer in this study captures fluorescence from the metal constituents of the caliche layer. Blue-labelled elements represent fluorescence from components in the experimental apparatus.

## Variations in Calcite Density: Cemented Particles

Caliche is a porous material. Calcium fluorescence effectively maps the variations in calcite density within this environment. During precipitation particles of pre-formed calcite may be incorporated into the caliche matrix layers. These particles can be indistinguishable in the calcium fluorescence signal from the caliche background (Figure 4).

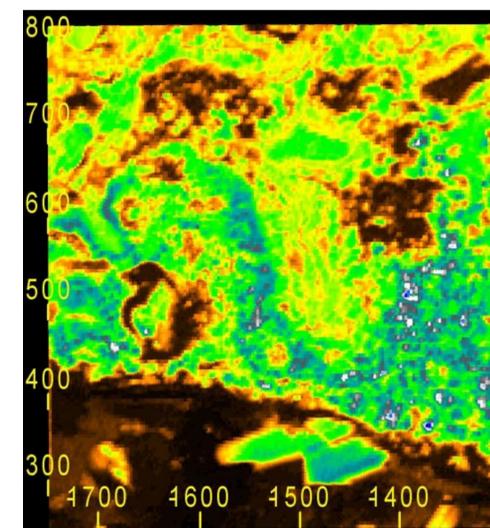


Figure 3. An optical micro-CCD image of the region in a thin section which was scanned using x-ray microprobe techniques (Figures 4-5). In the CCD images shown here, metallic iron appears black, while hematite and magnetite appear yellow/orange. Strontium-containing plagioclase crystallites appear blue.



Calcium

Figure 4. The x-ray microprobe technique utilized here allows the direct fluorescence mapping of  $\text{Ca}^{2+}$  constituents at the basalt/caliche interface over this 575 x 460 micron region. A Kirkpatrick-Baez mirror assembly was utilized to obtain a resolution of 1.5 microns. Concentrations in false color range from black (min.) to blue/white (max.).



Strontium

Figure 5. The fluorescence signal of  $\text{Sr}^{2+}$  was gathered simultaneously over the same region as in Figure 4. The heterogeneous nature of strontium fluorescence is apparent in this image. Large, intact particles of calcite - impervious to later strontium uptake - are present (left and center image). Electron microprobe experiments on this caliche sample point to a varied distribution of apparently pre-formed calcite particles within the caliche matrix. Again, concentrations in false color range from black (min.) to blue/white (max.).

## Uptake of $\text{Sr}^{2+}$ By Columbia River Gorge Caliche

X-ray microprobe has been applied to other regions of the basalt/caliche interface in which electron microprobe and other techniques have not found abundant particle inhomogeneities. Extensive fluorescence mapping has indicated (e.g., Figure 7-8) that the primary characteristic found in the caliche overlayer is a strontium content homogeneous 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.

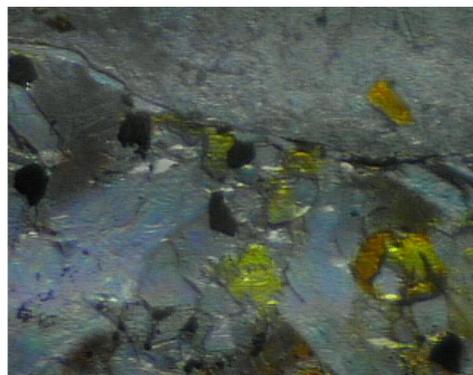
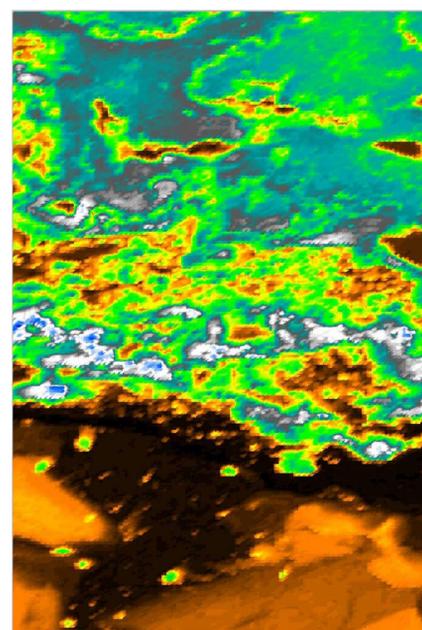
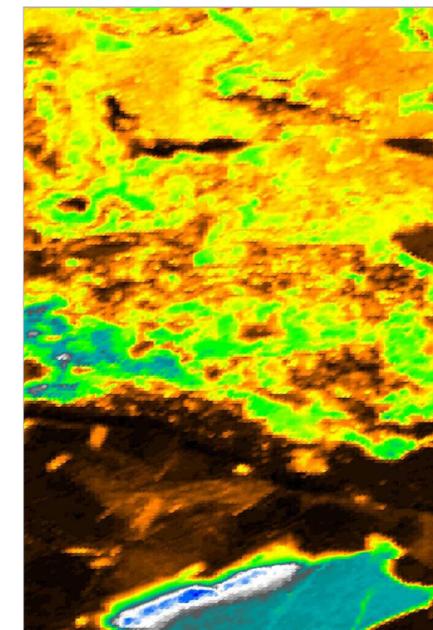


Figure 6. The optical micro-CCD image near the thin section region scanned using x-ray microprobe techniques (Figures 7-8). Again, metallic iron appears black, while hematite and magnetite appear yellow/orange. Plagioclase appears blue.



Calcium

Figure 7. The x-ray microprobe technique utilized here allows the direct fluorescence mapping of  $\text{Ca}^{2+}$  constituents at the basalt/caliche interface over the 820 x 350 micron region above. Sample stepping size was maintained at 2.0 microns over this +19 hour scan. Concentrations in false color range from black (min.) to blue/white (max.).



Strontium

Figure 8. The fluorescence signal of  $\text{Sr}^{2+}$  was gathered simultaneously over the same region as in Figure 7. The homogeneous nature of the calcium and strontium fluorescence signals apparent in these extensive images may be evidence of co-precipitation. Again, concentrations in false color range from black (min.) to blue/white (max.).

## Conclusions

Carbonate minerals (particularly calcite) are important components in the soil. In contrast to the sorptive behavior shown by many hydroxide 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. 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.

Extensive mapping of natural strontium deposits near the basalt/caliche interface via x-ray microprobe indicates homogeneous calcium and strontium concentrations. This implies a co-precipitation mechanism for natural strontium migration and incorporation in caliche.

## Acknowledgements

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