

The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments

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Research Objective

Calcium carbonate (CaCO_3) is widely distributed through the Hanford vadose zone as a minor phase. As a result of current and past geochemical processes, CaCO_3 exists as grain coatings, intergrain fill, and distinct caliche layers in select locations. Calcium carbonate may also precipitate when high-level wastes react with naturally Ca- and Mg-saturated Hanford sediments. Calcium carbonate is a very reactive mineral phase. Sorption reactions on its surface may slow the migration of certain contaminants (Co, Sr), but its surface coatings on other mineral phases may diminish contaminant retardation (for example, Cr) by blocking surface reaction sites of the substrate.

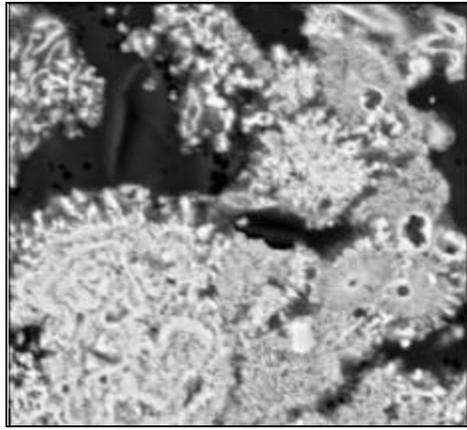
This project explores the behavior of calcium carbonate grain coatings, including how they form and dissolve, their reactivity toward key Hanford contaminants, their impact (as surface coatings) on the reactivity of other mineral substrates, and on their in-ground composition and minor element enrichment. The importance of CaCO_3 as a contaminant sorbent will be defined in all of its different manifestations in Hanford sediments: dispersed minor lithic fragments, pedogenic carbonate coatings on gravel and stringers in silt, and nodules in clay and paleosols. Mass action models will be developed that allow understanding and prediction of the geochemical effects of CaCO_3 on contaminant retardation in Hanford sediments.

Research Progress and Implications

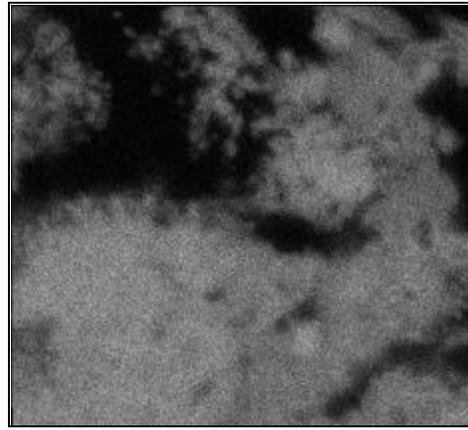
This project is in its second year of performance. Research is under way at Pacific Northwest National Laboratory (reactivity of natural CaCO_3 in Hanford sediments), Stanford University (influence of CaCO_3 grain coatings on the reduction of Cr(VI) by magnetite and biotite), and the University of Wyoming (growth and dissolution processes of calcite and magnesite in presence of contaminants). Only the results of the Pacific Northwest National Laboratory research are described here.

A series (6) of CaCO_3 -containing sediments (2% to 7%) was obtained from subsurface cores collected in the S-SX (200 West) and B-BX-BY (200 East) tank farms at Hanford. Three of these sediments contained minor, detrital lithic fragments of CaCO_3 , and two others contained pedogenic calcite. One of the 200 West sediments was paleosol caliche (calcrete) from the plio-pleistocene contact. Two other samples of bedded pedogenic caliche were also obtained from outcroppings on the Hanford Site.

The three caliche samples were thin-sectioned and analyzed by transmission electron microscopy and electron microprobe to determine the structure and minor element composition of the caliche. Results (exemplified in Figure 1) indicated the caliche exhibited complex structure and composition. The Sr and Si were common minor element impurities that seemed to be co-enriched along the most recent growth surfaces of the caliche. The native Sr concentrations were significant. All three caliche samples showed similar compositional patterns. The

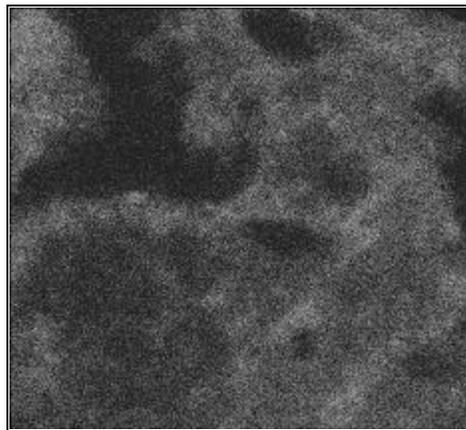


10.0 μm

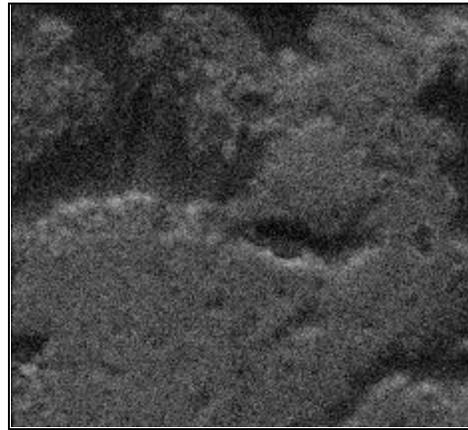


10.0 μm

A 30- μm thin section was analyzed by electron microprobe. The backscattered image (left) showed pore spaces (black) and porous radial CaCO_3 . The Ca elemental map (right) closely paralleled the backscattered image.



10.0 μm



10.0 μm

The CaCO_3 contained Si, with accumulation in porous surface regions (left). Sr (right) also concentrated in Si-rich, porous regions.

Figure 1. Electron Microprobe Analysis of Caliche

hypothesis underlying this project is that most contaminant sorption to caliche will occur in regions of Si enrichment, and that ^{90}Sr will be preferentially adsorbed to areas of Sr accumulation by isotopic exchange.

Four of the sediments with different $\text{CaCO}_{3(s)}$ contents were equilibrated in $\text{CaCO}_{3(aq)}$ solutions that differed in pH (7.2 to 9.8) and Ca concentration ($10^{-3.7}$ to $10^{-1.7}$ mol/L). All of the $\text{CaCO}_{3(aq)}$ solutions had been pre-equilibrated with $\text{CaCO}_{3(s)}$. The total normality of all the solutions was adjusted using NaHCO_3 , NaClO_4 , and/or NaOH . The ion composition of the solutions took an additional 2 weeks to stabilize with respect to Mg^{2+} , Sr^{2+} , and $\text{Si}(\text{OH})_4^-$. The aqueous concentrations of Sr^{2+} arising from dissolution from the sediment ranged from 10^{-5} to 10^{-6} mol/L. Following stabilization, the suspensions were spiked with ^{90}Sr (10^{-8} mol/L), and its distribution followed with time. The adsorption of ^{90}Sr occurred rapidly without significant kinetic behavior. The distribution coefficient [$K_d = (\text{mol/g-sorbed})/(\text{mol/L-solution})$; a measure of sorption strength] varied by two orders of magnitude (Figure 2), depending on aqueous Ca^{2+} concentration.

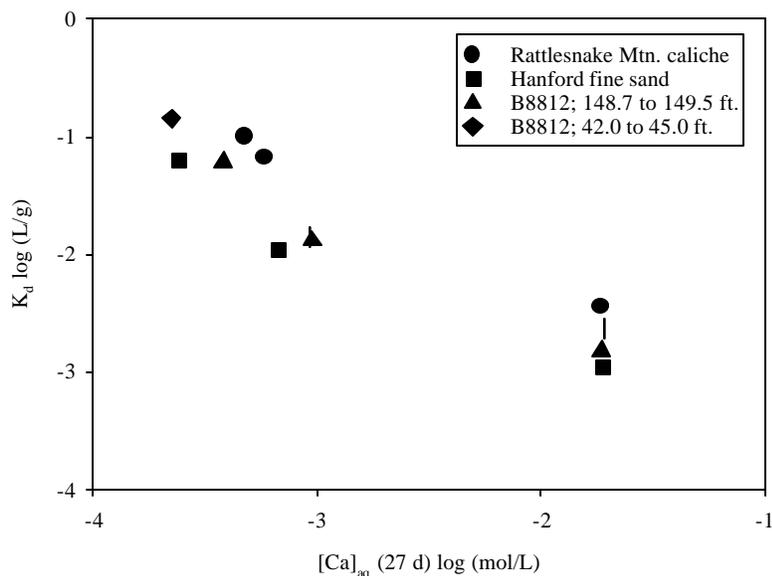


Figure 2. Distribution Coefficient (K_d) of Sr^{2+} with Selected Caliche-Bearing Materials

To date, our results indicate that ^{90}Sr is retained by Hanford sediment by a complex isotopic exchange process. The ^{90}Sr exchanges with the native $^{86/88}\text{Sr}$ pool, and the extent of sorption is dependent on the surface concentration of $^{86/88}\text{Sr}$ and the mineral phases with which it is associated. Calcium plays a major role in controlling the distribution of the native Sr through ion exchange and surface exchange processes on layer silicates and $\text{CaCO}_{3(s)}$.

Planned Activities

- Phosphor imaging study of locations of ^{90}Sr adsorption in caliche to the resolution scale of 25 μm . Does ^{90}Sr accumulate with native Sr in different types of caliche from Hanford?
- Ion exchange isotherms of Sr^{2+} in Na^+ and Ca^{2+} electrolytes to define factors/reactions controlling the surface excess of native Sr^{2+} in Hanford sediments. Is the ion exchange behavior of Sr^{2+} affected by the presence of $\text{CaCO}_{3(s)}$?
- Kinetic isotopic exchange studies of ^{90}Sr in Hanford sediments with different concentrations and mineral distributions of native Sr. Is the adsorption process of ^{90}Sr driven by isotopic exchange to carbonates or layer silicates?
- Development of a reaction-based isotopic exchange model for ^{90}Sr adsorption to Hanford sediment.

Information Access

Zachara JM, SC Smith, JP McKinley, and C Liu. 2001. "Sorption of ^{90}Sr in Calcareous Hanford Sediments: The Role of Isotopic Exchange and $\text{CaCO}_{3(s)}$." *Geochimica et Cosmochimica Acta* (Submitted).