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Budget Period covered by this Report: project up to 6/15/03

Project Title : "The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments".

A summary of key accomplishments and highlights from this project is given below. Our collaborators on the overall project are Stanford University and Pacific Northwest National Laboratory; the overall project leader is Dr. John Zachara, PNNL.

Research Objective

Our component of this project focuses on the reaction of contaminant-containing fluids with carbonate mineral surfaces in order to better understand the dissolution-growth and related solid-solution processes that ultimately affect contaminant mobility in settings containing carbonates or carbonate grain coatings. Our collaborators (Stanford, PNNL) have focused on other aspects of carbonate and carbonate mineral surfaces as part of the overall project. Because some of the sediments through which contaminants leaking from the Hanford waste have carbonate grain coatings; better understanding the chemistry of carbonate-contaminant interaction constitutes fundamental chemistry needed in order to construct better models of contaminant transport through carbonate-containing sediments.

Research Progress and Implications

In the first budget year, we made improvements to the hydrothermal atomic force microscope (HAFM) design to be used in this project. The original HAFM was built with funding from the U.S. DOE, Office of Basic Energy Sciences. Current operating limits are 70 bars and 170°C. We started studying magnesite, $MgCO_3$, because this mineral is structurally equivalent to calcite but reacts much more slowly, allowing us to study carbonate reactivity under pH conditions (i.e., low pH) that are much more problematic for the study of calcite. We found that dissolving magnesite exhibits a dramatic change in step orientation, and therefore etch pit shape, as pH is lowered through 4.2 to 3 and 2. This change in step orientation is NOT accompanied by an increase in step velocity with decreasing pH. The increase of overall dissolution rate is not caused by an increase in step velocity but rather an increase in the step density. This is, in turn, apparently caused by increases in the two-dimensional etch pit nucleation rate with decreases in pH.

We also found that, after growing magnesite on a magnesite substrate, the newly grown magnesite dissolved much more readily than the underlying substrate magnesite, and exhibited far larger etch pit densities. This effect may have been related to the rate of growth or to the presence of an Fe impurity in the growth solutions.

We studied the dissolution of magnesite and calcite (104) surfaces under a wider variety of conditions with a hydrodynamically defined AFM fluid cell, and we have observed the precipitation of a strontium-containing carbonate phase on dissolving calcite. We have applied the advection-diffusion equation coupled to proposed homogeneous and heterogeneous kinetic models to test rate laws for dissolution.

The step density, rather than step velocity, is a strong function of pH near the surface and that the step orientation is sensitive to pH. In these studies, we definitively demonstrate that diffusive mass transport is only important at very low fluid velocities for magnesite, but that studies of calcite dissolution are generally in the mixed transport-kinetics controlled regime (even at high fluid velocities) where quantitative information can only be obtained by accounting for the transport components. We also have found that alkaline earth secondary carbonate formation on calcite surfaces significantly alters the net flux of Ca^{2+} and may passivate the CaCO_3 surface from further reaction.

The image above is a backscattered electron image in which light areas indicate the presence of



heavier elements. The image is approximately 600 μm along the long axis. X-ray analysis of the light areas reveal the presence of Sr, whereas the darker area shows only Ca. The direction of solution entering the fluid cell through the HAFM inlet jet is indicated. The inlet solution was 5 mM SrNO_3 (i.e., no CO_3^{2-}). The image demonstrates the key role of transport, and both spatially and temporally variable conditions, in the study of chemical kinetics in an AFM fluid cell. The area at the arrow that is not covered by the Sr-containing phase is an area of calcite dissolution. As the fluid moves across the surface, its carbonate and calcium concentrations increase because of dissolution. Eventually, at a point indicated here by the light area encountered as the fluid moves away from the inlet jet, the fluid becomes supersaturated with respect to strontianite (probably actually an impure strontianite), and SrCO_3 begins to precipitate. We have used the HAFM to image the growth of individual crystals on this sample surface. Further downstream, the fluid approaches saturation with respect to strontianite growth, and further growth ceases. The upstream and downstream edges of the SrCO_3 precipitation zone correspond to the spatial points at which the product $[\text{Sr}^{2+}][\text{CO}_3^{2-}]$ exceeds and lags the strontianite K_{sp} , respectively. This in turn places limits on the precipitation kinetics of strontianite in the presence of Ca^{2+} impurities.

Recently, we have completed studies of calcite dissolution, step velocity, and growth of Sr-containing secondary phases at a range of initial Sr concentrations (0.2, 0.4, 1.0, and 2.0 SrNO_3). In addition, much additional SEM and AFM imaging have been accomplished. In the subsurface Hanford setting, diffusive transport is likely to often be a rate-controlling factor. At lower Sr concentrations, Sr-containing carbonate crystals with crystal habits identical to strontianite or aragonite grow, but not over an entire band of the surface as in the above illustration; rather, crystals only grow at macrosteps on the calcite surface and other locations where the dissolution flux of carbonate is likely to be high and for which the partly diffusion-controlled reaction leads to higher aqueous carbonate concentrations near the surface and thence to favored strontianite nucleation and growth.

Planned Activities

We are currently continuing with studies similar to those described in this report using Co^{2+} and CO_4^{2-} instead of Sr^{2+} . These projects are nearing completion as the end of the project nears in

September, 2003. The graduate student working on the project, Ms. Briana Deeds, has moved away from UW in the past project year for family reasons, which has slowed progress.

Information Access:

Publications

- Jordan, G., Higgins, S.R., Eggleston, C.M., Knauss, K.G. and Schmal, W.W. (2001) Dissolution kinetics of magnesite in acidic aqueous solution, a hydrothermal atomic force microscopy (HAFM) study: Step orientation and kink dynamics. *Geochimica et Cosmochimica Acta* 65(23), 4257-4266.
- Higgins S. R., Jordan G., and Eggleston C. M. (2002) Dissolution kinetics of magnesite in acidic aqueous solution, a hydrothermal atomic force microscopy (HAFM) study: Step kinetics and dissolution flux. *Geochimica et Cosmochimica Acta* 66(18), 3201-3210.
- Higgins S. R., Boram L. H., Eggleston C. M., Coles B. A., Compton R. G. and Knauss K. G. (2002) Dissolution kinetics, step and surface morphology of magnesite (104) surfaces in acidic aqueous solution at 60 oC by atomic force microscopy under defined hydrodynamic conditions, *Journal of Physical Chemistry B* 106, 6696-6705.

Abstracts submitted for conference presentations:

- Greer B., Higgins S. R., Eggleston C. M., Boram L. H., Knauss K. G. (2002) Study of heterogeneous kinetics at calcite surfaces in the presence of strontium using atomic force microscopy, contributed talk at the ACS National Meeting, April 2002, Orlando, FL.
- Higgins, S. R., Greer, B., Boram, L. H., Eggleston, C. M., Jordan, G., Knauss, K. G. (2001) Study of heterogeneous kinetics at carbonate mineral surfaces using hydrothermal atomic force microscopy. ACS National Meeting, August 2001, Chicago, IL.
- Higgins, S. R., Greer B., Boram L. H., Eggleston C. M., and Knauss K. G. (2001) Hydrothermal Scanning Probe Microscopy and its Application to Problems in Heterogeneous Kinetics: Adventures (and Misadventures) at Mineral Surfaces. Invited speaker at the 11th Annual V. M. Goldschmidt Conference, Hot Springs, VA, May 2001.
- Higgins, S. R., Boram, L. H., Greer, B., Coles, B. A., Compton, R. G., Eggleston, C. M., Knauss, K. G. (2001) Hydrodynamic atomic force microscopy and its applications to carbonate mineral dissolution. Materials Research Society Meeting, San Francisco, CA, April, 2001.
- Eggleston, C.M. and Higgins, S.R. (2001) In-Situ Observation of Crystal Growth Processes by Atomic Force Microscopy: New Methods in Hydrothermal Surface Science. Invited presentation at the Geophysical Laboratory, Carnegie Institute of Washington, Feb. 2001.
- Higgins, S., Jordan, G., Coles, B., Compton, R., Eggleston, C., Knauss, K., Boro, C. (2000) Studies of the dissolution of magnesite(104) in acidic aqueous solutions: A new approach using hydrothermal scanning probe microscopy under controlled hydrodynamic conditions. Contributed talk at the 10th Annual V. M. Goldschmidt Conference, Oxford, UK. *Journal of Conference Abstracts*, 5(2), 513.