CENTER FOR NANOSCALE CONTROL OF GEOLOGIC CO_2
An Energy Frontier Research Center (EFRC)

RESEARCH SUMMARIES

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CENTER FOR NANOSCALE CONTROL ON GEOLOGIC CO_2

INVESTIGATORS: Don DePaolo (Director), Carl Steefel (Co-Director), Jim DeYoreo (former Co-director)

OBJECTIVES To improve understanding of fluid-rock processes using a coordinated research effort focused on molecular- to pore scale phenomena, where major knowledge gaps exist for predicting macroscopic material properties and large-scale fluid-rock dynamical behavior. The unique character of the Center derives from a focus on nanoscale aspects of the behavior of supercritical CO_2 in subsurface reservoirs. The research of the Center has been organized around three Thrust Areas, which cover mineral nucleation and growth, nanopore processes, and emergent processes at pore network scale. In the final years of the project we are organizing the research around the original crosscutting themes of caprock (or seal) integrity, reservoir processes, and the issues of upscaling properties, processes and rates from nano- and pore-scale to reservoir scale for the purpose of predicting the storage security of CO_2 injected underground. Most of the work is now organized around multidisciplinary experiments.

ACCOMPLISHMENTS: Research to date has resulted in major improvements to the knowledge base for predicting the stability of carbonate mineral phases, the kinetics of carbonate precipitation in porous materials, accelerating carbonate precipitation in the presence of organic molecules, and geochemical monitoring using isotopic and trace element effects during fluid mixing, dissolution and precipitation. We have discovered that presence of microbes can accelerate the conversion of amorphous phases to crystalline carbonate, and performed experiments and modeling studies that are elucidating the effects of mineralization on pore structure and permeability. Molecular dynamics simulations provide better models for the interfacial tension between scCO2 and water, and yield insights into the controls on wetting of mineral surfaces by scCO2-water mixtures. Experimental results also show that nanopores are a major component of mineral surface area and pore volume in many rocks, and experiments and simulations indicate that confinement in nanopores changes the density and adsorption properties of CO2 as well as mineral nucleation rates. New experiments and theory provide details about the thickness of thin brine films on mineral surfaces in the presence of scCO2 and show variations in CO2 wetting on different mineral surfaces and as a consequence of reaction between mineral surfaces and scCO2 and acidified brine. Modeling studies are providing insights about the effects of mineral- and pore space distributions on fluid flow and fluid-mineral chemical interactions, and how mineral reactivity can evolve with time. We have developed direct numerical methods to simulate pore scale fluid flow and chemical reactions as a major step in developing the computational component of our upscaling efforts. Recent results are allowing us to make better long-term models for mineralization of stored CO2 and to model the geochemical effects that contribute to the sealing capacity of caprock formations, and have led as well to new fundamental models of mineral growth from aqueous solution, properties of fluids and precipitation processes in pore confinement, and molecular scale models of the mineral surface dynamical processes that control the impurity concentrations and isotopic composition of minerals.

THRUST AREA 1 OVERVIEW: CONTROLLING CARBONATE NUCLEATION AND GROWTH

TASK LEADERS: J. De Yoreo, J. Banfield, A. Navrotsky, R. Ryerson, A. Stack, G. Waychunas

OBJECTIVE:
This Thrust aims to provide an understanding of the molecular-scale mechanism and material parameters that govern processes of dissolution and precipitation in reservoir conditions, with the goal of enabling predictive modeling of reservoir-wide evolution. It also seeks to develop engineering approaches to deterministically inhibit or enhance those processes.

ACCOMPLISHMENTS:
This Thrust integrates computational and experimental tools to investigate solution structure in pores and at surfaces, the controls on nucleation, and subsequent processes of aggregation, phase transformation, and mineral growth (Fig. 1). We also explore novel biomimetic and biological approaches to enhancing rates of mineralization by utilizing bacteria and unique peptide-like polymers. This year, we (1) showed that accepted atomic potentials predict $CaCO_3$ forms at moderate concentrations through spinodal decomposition of solution rather than by conventional nucleation processes, (2) found that the enthalpies of formation for complex silicocarbonate phases (scawtite and spurrite) imply that they could form at mineral-fluid interfaces, (3) used nano- to mesoscale measurements of carbonate mineral growth rates to derive expressions capable of predicting macroscopic growth rates for inclusion in a reservoir-scale reactive transport codes, (4) discovered that subsurface fluids contain organisms of remarkable diversity, with significant representation by organisms from novel phyla with little or no prior genomic sampling, and (5) showed the capacity of microbes to enhance $CaCO_3$ nucleation scales with the membrane surface charge, which can be genetically encoded.

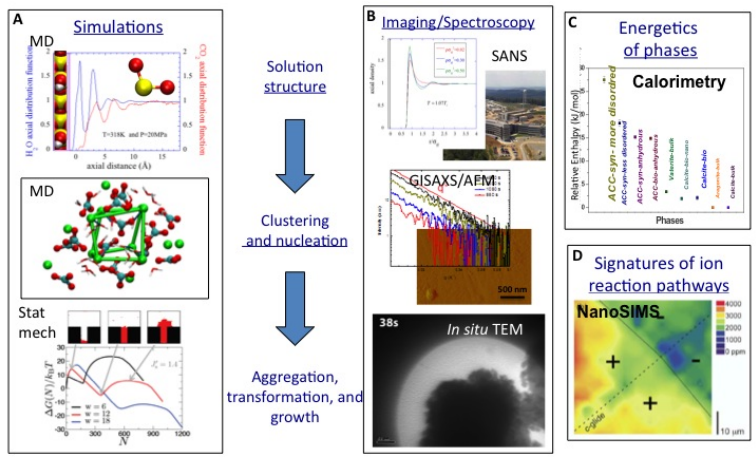


Figure 1. Thrust 1 combines simulations with imaging and spectroscopy to develop a quantitative picture of carbonate mineralization from solution structure to nucleation to mineral growth. Results are tied to carbonate-phase energetics and chemical signatures of reaction pathways to provide mechanisms and parameters for upscale modeling.

FUTURE GOALS AND EXPECTATIONS: We will determine chemical equilibria in CO_2-rich fluids of variable composition, use neutron-scattering studies of the structural properties of pure CO_2 and aqueous CO_2 solutions in rock pores, quantify the dependence of nucleation rates on pore geometry and the impact of organic films on those rates, improve our understanding of the roles of microorganisms in the subsurface, integrate nanoscale physical models of nucleation in pores into heterogeneous reservoir-scale models of carbonate formation.

Metagenomics-Based Analysis of Microbial Communities in CO_2-Rich Subsurface Environments

INVESTIGATORS: Jill Banfield, Joanne Emerson, Brian Thomas

OBJECTIVE: Explore the nature of microbial communities in the subsurface, specifically those that thrive in high CO_2 environments

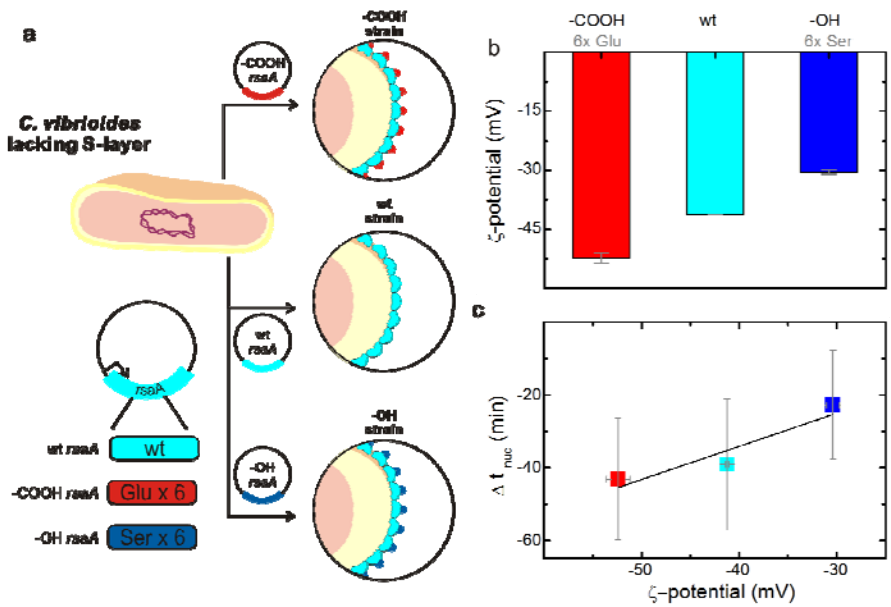
Crystal Geyser field site: a cold CO_2 geyser; the site for metagenomics-based analyses of the ecology of subsurface high CO_2 environments.

ACCOMPLISHMENTS: Research on geologic carbon sequestration raises questions about native microbiota in subsurface environments and their potential impact on stored carbon. During CO2 injection the near-well environment is flooded with CO2 and it is likely that few biota can survive in this environment. However, at more distal locations and at later times, the pore space is dominated by aqueous brine where microbes could potentially thrive. It is this type of environment where pH becomes high enough that CO2 can be transformed into carbonate minerals, and where microbes could play a significant role in controlling where and at what rate such mineralization occurs. Subsurface, high-CO_2 systems are poorly characterized biologically, due primarily to difficulty accessing suitable high-volume, uncontaminated samples. The iron-rich, CO_2-driven Crystal Geyser (Green River, Utah, USA) is an established natural analog for geologic carbon sequestration, and it provides easy access to high volumes of deep (~500 m) subsurface fluids as it erupts. We have completed field-based sampling of the erupted geyser fluids and acquired a series of samples suitable for metagenomics-based analysis of microbial consortia. DNA was extracted and sequencing undertaken for 9 distinct samples (two filter-size fractions). The first of the samples has been analyzed in detail (two sequencing allocations). The results have been obtained to date for the 0.2–3.0 µm filter-size fractions. Despite the extremely high complexity of the system, new metagenomic methods were able to achieve considerable genome-resolved insight. We find that the subsurface fluids contain a remarkable diversity of organisms, with a significant representation of organisms from novel phyla (phyla with little or no prior genomic sampling and no cultivated representatives). We assembled near-complete genomes of neutrophilic, iron-oxidizing *Mariprofundus* sp. and sulfur-oxidizing *Thiomicrospira crunogena*. Significant genomic reconstruction was also achieved for iron-oxidizing *Gallionella capsiferriformans* and *Sideroxydans* sp., for representatives of candidate bacterial phyla OP11, BD1-5, and TM7, for novel bacterial phyla, and for an archaeon distantly related to the Korarchaeota. For the first time, we saw "freshwater" and "marine" neutrophilic iron-oxidizing bacteria at similarly high abundances in the same ecosystem. We detected a variety of metabolisms, including iron, sulfur, and complex carbon oxidation, carbon and nitrogen fixation, hydrogen metabolism, and aerobic and anaerobic respiration. The dominance of chemoautotrophic Zetaproteobacteria, which have previously only been associated with marine, iron-rich environments, particularly hydrothermal systems, extends the environmental distribution of this group to the terrestrial subsurface. At least one-third of the microorganisms sampled are likely chemoautotrophs, demonstrating that microbial carbon fixation is an important component of the carbon cycle in this system.

Biological Controls on Carbonate Mineralization

INVESTIGATORS: J.A. Cappuccio, C.M. Ajo-Franklin

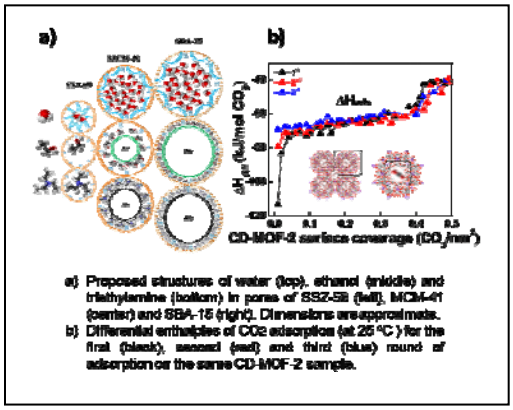
OBJECTIVES:
The objective of this work is to determine how microorganisms affect the rate of mineral precipitation under CO_2 sequestration conditions, what mechanisms underlie these changes in rate, and to develop genetic strategies to alter microbial effects on mineralization rates. By including the effects of subsurface microbes, this information will be enable a more accurate understanding of subsurface CO_2 fate and provide strategies to improve containment of CO_2 in the deep subsurface.



Genetically tuning the microbial surface charge alters the onset of $CaCO_3$ mineralization: (a) The S-layer protein RsaA was genetically modified to create microbes with different surface charge displayed on their outermost surface; (b) The ζ-potential of the –COOH and –OH strains were significantly more negative and positive, respectively, than the wt strain; (c) The change in time until the onset of calcium carbonate mineralization (Δt_{onset}) correlates to the microbial ζ-potential with a Pearson's correlation coefficient of r = 0.80. The colors of S-layers variants in (a) correspond to the measurements in (b) and (c).

ACCOMPLISHMENTS:
Previously, we observed that the presence of a diverse set of microbes accelerates the onset of carbonate mineralization. Interestingly, the time required for mineralization to begin is linearly correlated to the ζ-potential of the bacteria surface. We hypothesized that by altering nanoscale features on the surface of a given bacteria, we could tune the surface charge and thus the onset of $CaCO_3$ mineralization. To test this hypothesis, we altered the S-layer protein RsaA of *Caulobacter vibrioides* to display a protein loop rich in carboxylic acids (-COOH strain) or hydroxyl groups (-OH strain). ζ- potential measurements of these strains show that microbial surface charge is tuned by these mutations. In accordance with our hypothesis, the onset of mineralization is strongly correlated with the surface charge of these mutant strains. Thus, this work provides a quantitative framework relating the onset of carbonate mineralization and nanoscale features of microorganisms in the environment. More broadly, this work provides a scalable, genetically encoded means by which to tune carbonate mineralization rates in near-surface and subsurface environments.

Thermodynamic Properties
of Carbonates and of Nanoconfinement



a) Proposed structures of water (top), ethanol (middle) and triethylamine (bottom) in pores of SSZ-58 (left), MCM-41 (center) and SBA-15 (right). Dimensions are approximate.
b) Differential enthalpies of CO2 adsorption (at 25 °C) for the first (black), second (red) and third (blue) round of adsorption on the same CD-MOF-2 sample.

INVESTIGATORS: Alexandra Navrotsky, A.V. Radha, Di Wu (UC Davis)

OBJECTIVE: To measure thermodynamic properties by calorimetry of materials relevant to carbonate precipitation, reactions of caprock under CO_2 sequestration conditions, and confinement of CO_2, carbonate, and organics in pores.

ACCOMPLISHMENTS: We have completed and published a detailed energetic study of amorphous Mg-Ca carbonates. There is a change in properties near dolomite composition. We published the energetics of amorphous iron carbonates and finished work on amorphous manganese carbonate. These studies show that the energetic metastability of amorphous carbonate is controlled by cationic size.

Extending carbonate thermochemistry to more complex silicocarbonate phases that may form on caprock mineral surfaces, we have determined the enthalpy of formation of scawtite and spurrite and show that they might form locally at mineral-fluid interfaces when the acidity is not too high.

Di Wu has completed his Ph.D. thesis with emphasis on the confinement of organic molecules in porous silica. This is important to CO_2 sequestration and caprock interactions, because organics clearly interact strongly with mineral surfaces, changing their reactivity toward carbonate precipitation/dissolution. We find that ethanol and triethylamine bind more strongly to mesoporous silica than water, and that a medium-sized test molecule undergoes significant changes in aggregation and mobility as a function of pore size. We also find that CO_2 interacts very strongly with hydroxyl groups on a "sugar MOF," a porous metal organic framework which, in addition to its intrinsic interest for CO_2 separation, may be a model for biological molecules in the natural environment.

PUBLICATIONS 2012-13

"Energetic and Structural Studies of Amorphous $Ca_{1-x}Mg_xCO_3 \bullet nH_2O$ ($0 \leq x \leq 1$)", A.V. Radha, A. Fernandez-Martinez, Y. Hu, Y.-S. Jun, G.A. Waychunas, and A. Navrotsky, *Geochim. Cosmochim. Acta*, 90, 83-95 (2012).

"Amorphous Iron (II) Carbonate: Crystallization Energetics and Comparison to Other Carbonate Minerals Related to CO_2 Sequestration" O. Sel, A.V. Radha, K. Dideriksen and A. Navrotsky, *Geochim. Cosmochim. Acta*, 87, 61-68 (2012).

"Small Molecule – Silica Interactions in Porous Silica Structures", D. Wu and A. Navrotsky, *Geochim. Cosmochim Acta,* 109, 38-50 (2013)

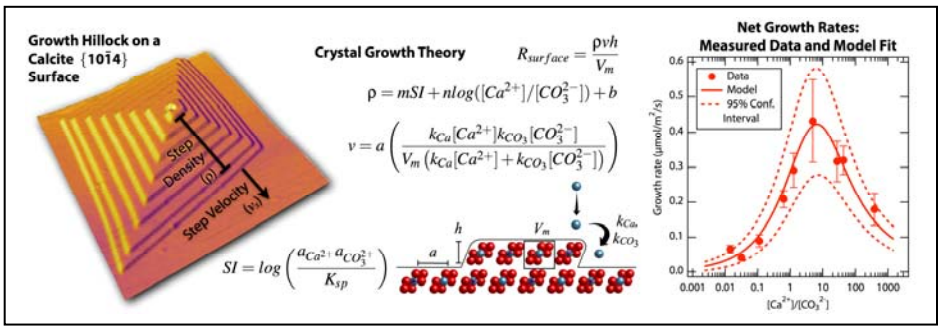
"Thermochemistry of Two Calcium Silicate Carbonate Minerals: Scawtite, $Ca_7(Si_6O_{18})(CO_3) \bullet 2H_2O$, and Spurrite, $Ca_5(SiO_4)_2(CO_3)$" Y. Zhang and A. Navrotsky, *Geochim. Cosmochim. Acta* (in press 2013)

"Direct Calorimetric Measurement of Enthalpy of Adsorption of Carbon Dioxide on CD-MOF-2, a Green Metal-Organic Framework", D. Wu, J. Gassensmith, D. Gouvea, S. Ushakov, J.F. Stoddart and A. Navrotsky, *J Am. Chem. Soc.* (in revision 2013)

Growth and Dissolution of Carbonate Minerals

INVESTIGATORS: A.G. Stack, A. Fernandez-Martinez, L.M. Anovitz, G. Rother, G.A. Waychunas, C.I. Steefel

OBJECTIVE: To determine the rates of precipitation of carbonate mineral phases, the effects of pores on precipitation and nucleation rates, and examine the dissolution of minerals that can act as a source of cations for carbonates.



ACCOMPLISHMENTS: Activity focused on understanding the growth of calcium carbonate in porous substrates, and the mechanism of dissolution of the mineral chlorite. In this period we also began worked with Thrust 3 scientists on methods to upscale mesoscale measurements of mineral growth to the macroscopic scale, and defining the directions of the Upscaling Cross-Thrust theme and the Cap-Rock theme. These activities have resulted in the following manuscripts:

1) Bracco, J. N.; Stack, A. G.; Steefel, C. I. (in review) Bridging the Gap: Upscaling AFM Results From the Meso- to Macro- Scale. *Environ. Sci. Technol.*

2) Gazzé, S. A.; Stack, A. G.; Ragnarsdottir, K. V.; McMaster, T. J. (in review) Chlorite topography and dissolution of the interlayer studied with Atomic Force Microscopy. *Am. Mineral.*

3) Stack, A. G.; Fernandez-Martinez, A.; Allard, L. F.; Anovitz, L. M.; Rother, G.; Cole, D. R.; Waychunas, G. (in prep.) The Effect of Pore Size and Composition on Precipitation of Calcium Carbonate. Environ. Sci. Technol.

In Manuscript #1, our goal was to utilize nano- or mesoscale measurements of carbonate mineral growth rates to derive expressions capable of predicting macroscopic growth rates suitable for inclusion in a reactive transport code. The rationale is that mineral trapping reactions for carbon sequestration occur at the atomic scale, but predictions must be made at the reservoir scale; therefore, expressions to upscale important atomic-level reactions must be derived. This work formed the basis for activities in the Upscaling Cross-Thrust Theme. In Manuscript #2, the goal was to understand the mechanism of etch-pit formation during leaching of magnesium from the mineral chlorite. Chlorite is important since it is a common mineral in reservoir rocks and caprocks, and its dissolution may be a major source of divalent cations that would induce carbonate mineral trapping of CO2 (Landrot et al., 2012). Our work complements the dissolution rate experiments carried out by Zhang et al. described in a separate highlight. In Manuscript #3, we have probed the ability of pores of varying sizes and composition to act as a substrate for calcium carbonate precipitation. The reason for this work is that the ability of a caprock or reservoir to self-seal fractures may depend on whether precipitation of carbonate minerals occurs in larger pores.

Nucleation at Porous Surfaces

INVESTIGATORS: J.J. Urban, A.M. Ruminski

OBJECTIVE: We hope to gain a better picture of how rock surface structure can localize the mineralization of sequestered CO_2; information that is required to understand how mineralization affects permeability. In this work, we synthesize and characterize nano- and micro- sized oxide systems arranged to create porous networks and study their interactions with dissolved carbonate phases.

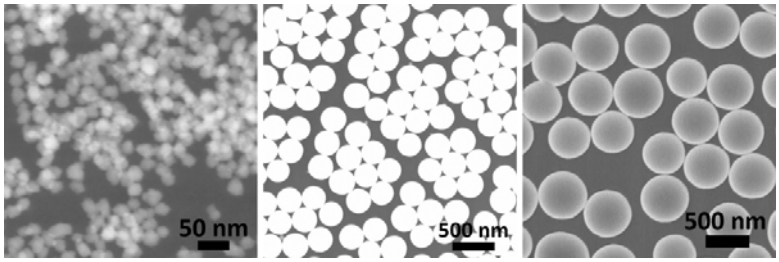


Figure 1: Scanning electron microscope (SEM) images of synthesized silica nanoparticles and resulting porous crevices. Particle diameter, left to right: 21 ± 3, 290 ± 10, 500 ± 50 nm.

ACCOMPLISHMENTS:

Thin films of silica nanoparticles were drop-cast into a well, creating pore spaces between particles (Figure 1). Samples were submerged in a solution of 21 mM $CaCl_2$. Carbonate was introduced through the diffusion method using $(NH_4)_2CO_3$. Optical microscopy was utilized to monitor calcium carbonate growth. A flat, nonporous silica surface was used as a control. Images were taken before and after 30 minutes of carbonate exposure (Figure 2). Amorphous calcium carbonate (ACC) and crystalline $CaCO_3$ growth was observed on the flat silica surface, with ACC being depleted near growing crystalline $CaCO_3$ (both calcite and vaterite). Crystalline $CaCO_3$ growth was observed on the film of nanoparticles. Overall trends showed larger $CaCO_3$ crystals grown on the layer of silica nanoparticles containing pore spaces versus the flat silica surface.

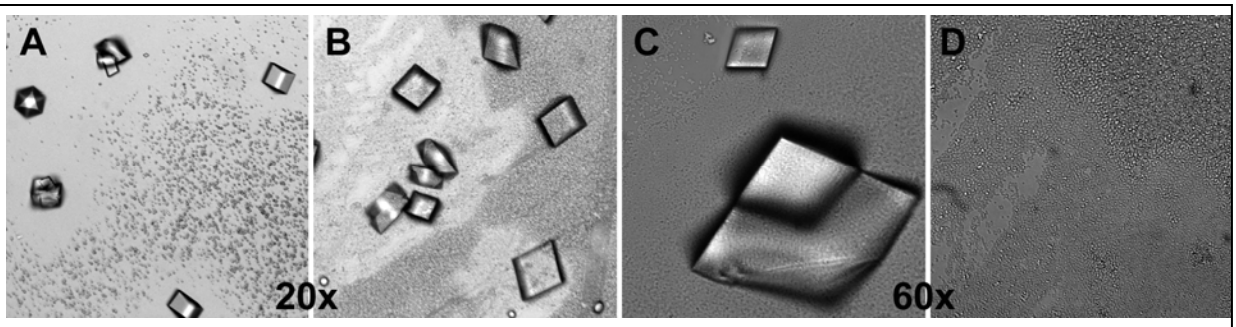


Figure 2: Optical microscope images of (A) flat silica and (B, C) a film of 500 nm silica particles after 30 minutes exposure to a solution containing dissolved calcium and carbonate. Growth of amorphous calcium carbonate, calcite and vaterite is observed. (D) Image of a film of 500 nm silica particles in a solution of $CaCl_2$ before the introduction of carbonate. Image magnifications are (A, B) 20x and (C, D) 60x.

Predicting Carbonate Nucleation and Growth Pathways

INVESTIGATORS:

A.F. Wallace, L.O. Hedges, S. Whitelam, J.J. De Yoreo, J.F. Banfield

OBJECTIVES:

This work is focused on exploring the early stages of carbonate nucleation and growth through computer simulations. Our goal is to provide a mechanistic understanding of possible crystallization pathways, both classical and nonclassical, through which mineral trapping of CO_2 may occur in storage reservoirs, and to help understand the controls on isotopic and trace element fractionation in carbonate minerals that precipitate through amorphous precursors.

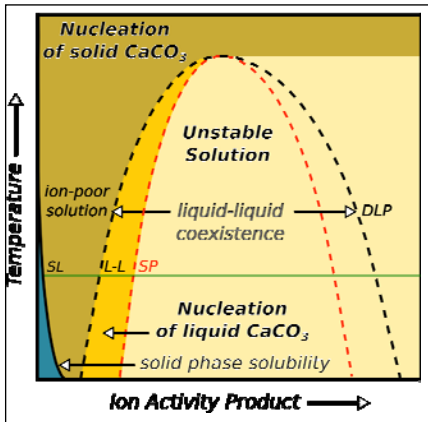


Figure 1: Schematic phase diagram to emerge from simulations.

ACCOMPLISHMENTS:

Replica-Exchange Molecular Dynamics (REMD) methods were developed to conduct atomistic simulations of the early stages of carbonate formation. The resulting high-throughput sampling of the energy landscape enabled us to simulate formation of nanometer-size hydrated mineral clusters in experimentally relevant regimes. Analysis of cluster dynamics implies that they are liquid droplets, and analysis of free energy versus size shows that they form through spinodal decomposition of a mixed carbonate-water fluid. Theoretical pair distribution functions calculated following aggregation and partial dehydration of 1 to 2 nm clusters are comparable to those obtained experimentally from total x-ray scattering studies on ACC. Dynamic simulations of liquid-liquid separation based on a 2D Ising model predicts an evolution in cluster size distribution suggesting a classical explanation for reported mineral formation pathways in the $CaCO_3$ system that involve aggregation of pre-nucleation clusters and have been previously termed "nonclassical." The conversion of hydrated carbonate liquid droplets to hydrated solid amorphous carbonate could explain the large difference in Ca isotopic specificity observed for ACC precipitation in comparison to direct calcite precipitation.

PUBLICATIONS:

Wallace, A.F., et al., Liquid-liquid separation explains "non-classical" behavior during $CaCO_3$ crystallization. *Science* (Under revision).

Hedges, L.O., and S. Whitelam, Patterning a surface so as to speed nucleation from solution. *Soft Matter*, 8, 8624 (2012).

Hu, Q., et al., The thermodynamics of calcite nucleation at organic interfaces: Classical vs. non-classical pathways. *Faraday Disc.* 159, 509 (2012).

Freeman, C.L., et al., "Surface Selectivity of Calcite on Self-Assembled Monolayers" *Chem. Mater.* (In press)

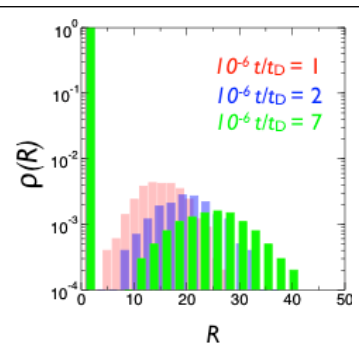


Figure 2: Predicted cluster size distributions at three time points.

BIOMIMETIC CONTROL OVER CARBONATE MINERALIZATION

INVESTIGATORS: C.-L. Chen, R. Zuckermann, J. De Yoreo

OBJECTIVES: The objective is to develop peptide-like molecules known as peptoids that mimic the capacity of proteins to control rates of carbonate formation, but exhibit stability under the conditions of subsurface-reservoirs. Using robotic synthesizers, peptoid libraries with a range of chain-lengths, sequences and side-chain chemistries were generated and screened for activity. The most active served as design points for expansion of the library. Their impact on $CaCO_3$ nucleation and growth as well as the mechanisms by which they act were explored.

ACCOMPLISHMENTS: Inspired by acidic amphiphilic proteins commonly found in natural carbonate biominerals, we designed and synthesized peptoids by using hydrophilic monomer β-alanine to mimic acidic aspartic or glutamic amino-acids, and using substituted phenethylamines to mimic hydrophobic amino-acids to tune peptoid amphiphilicity. Libraries of peptoids were built by varying the X group, percentage of acidic residues, arrangement of hydrophilic and hydrophobic monomers, and chain length. By screening of these peptoids for controlling $CaCO_3$ mineralization, we previously demonstrated that peptoids in solution were able to mimic the function of soluble matrix proteins for dramatic control over $CaCO_3$ crystal morphology and for significantly influencing $CaCO_3$ nucleation and growth kinetics. For example, one 12-mer acidic peptoid enhanced calcite growth rates by as much as 25x at 100nM levels. We have since found that some of these peptoids also influence $CaCO_3$ mineralization after being adsorbed onto mineral surfaces. Fig. 1 shows peptoid C27_4 was able to assemble into hexagonally-patterned nanofibers and formed a highly-ordered biomimetic film on mica surface. This biomimetic film was capable of directing the formation of orientated $CaCO_3$ crystals by controlling surface-templated $CaCO_3$ crystal nucleation and growth. Since leakage of injected supercritical CO_2 is an increasing issue in geological CO_2 sequestration, these results suggest that peptoids may be useful for caprock sealing after being absorbed onto caprock surfaces for enhanced $CaCO_3$ mineralization.

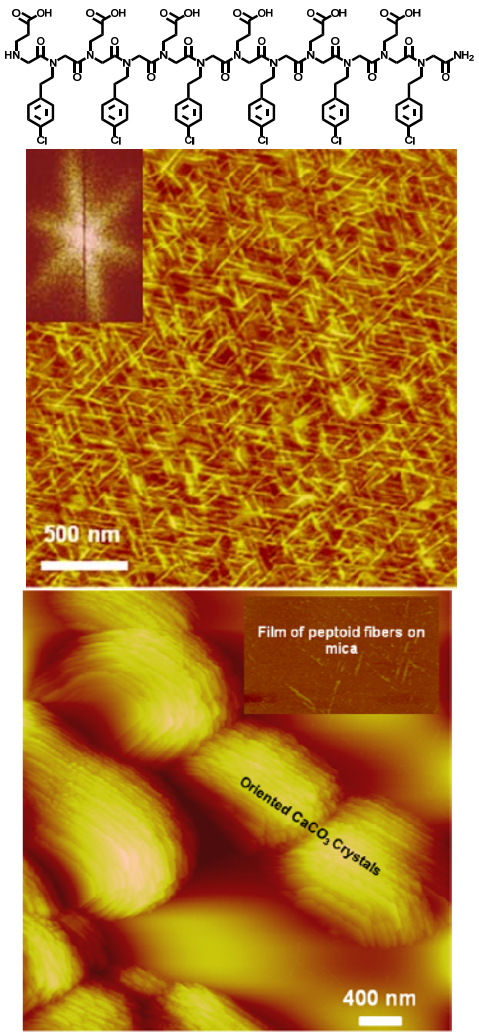


Fig. 1 - Scheme of an acidic peptoid C27_4 (Top image); Biomimetic film of hexagonally-patterned C27_4 fibers assembled from the adsorption of C27_4 onto mica surface in the presence of Ca^{2+} ions (Middle image); Oriented $CaCO_3$ crystals formed by peptoid film templated $CaCO_3$ mineralization, in which $CaCO_3$ crystal orientations are parallel to directions of C27_4 fibers assembled on mica surface (Bottom image).

Molecular Dynamics Study of Carbonate/Bicarbonate Adsorption and Dissolution on Calcite and Silica Surfaces

INVESTIGATORS: Lukas Vlcek, Ariel A. Chialvo, and David R. Cole

OBJECTIVE: Our objective is to study the effects of pH and surface morphology on CO_2 and carbonate ion adsorption, surface nucleation, and carbonate dissolution. Since mineral dissolution in one part of a porous rock combined with deposition in other parts with different local pH, chemistry, and morphology may significantly modify pore connectivity, these processes are critical in maintaining the integrity of caprock formations. From the computational perspective, they also pose a challenge in terms of upscaling results obtained from molecular modeling studies to meso- and macroscale models of precipitation [1]

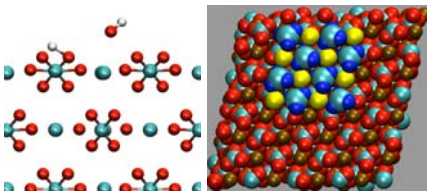


Figure 1: Left: Water dissociation on a calcite surface. Right: Terrace on a calcite surface used to study CO_3^{2-} protonation and detachment.

ACCOMPLISHMENT(S): To investigate the role of pH on carbonate dissolution, we have performed a series of reactive classical molecular dynamics simulations with our newly optimized force field (ReaxFF [2]). In these studies, carbonate ions at calcite step edges were first protonated and subsequently detached from the surface (Figure 1). We used steered molecular dynamics method to calculate the free-energy profiles of ion detachment, effectively emulating desorption of weakly bonded bicarbonate ions from calcite at low pH conditions. The preliminary results suggest relatively small differences between the desorption free energy of carbonate and bicarbonate ions. Further investigation will be needed to clarify the mechanisms driving ion detachment and incorporation into a surface.

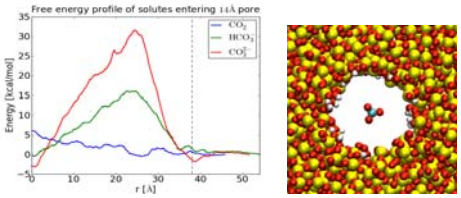


Figure 2: Left: Free-energy profiles of carbonate species moving across a silica-pore throat. Right: A corresponding pore with CO_3^{2-} ion.

Motivated by small angle neutron scattering (SANS) measurements of calcium carbonate precipitation in controlled pore glass (CPG) conducted within the NCGC project, we have performed a (non-reactive) molecular dynamics study of carbonate ion adsorption in amorphous silica pores. To explain the experimentally observed precipitation patterns, we tested the hypothesis that adsorption of carbonate ions on silica is strongly influenced by surface confinement, namely the pore diameter. We have calculated relative probabilities of carbonate and bicarbonate ions entering pores of different sizes and adsorbing on the pore walls. We have found considerable diffusion barriers at the pore throats, which are increasing with ion charge (Figure 2). The energetics of carbonate ion adsorption and nucleation at surfaces characterized by different chemical composition and morphology can be used as a molecular scale input for larger scale coarse-grained models. Nonreactive molecular dynamics studies of CO_2 and carbonate ion diffusion through narrow pores and adsorption on pore walls is relevant for caprock integrity. It also offers an opportunity for upscaling studies in which molecular simulations would provide parameters for coarser-grained models.

[1] Hedges, L.O, Whitelam, S. “Patterning a surface so as to speed nucleation from solution” Soft matter, 2012, 8, 8624. [2] Ganesh, P., Vlcek, L., Raju, M., Chialvo, A. A., Kent, P. R., van Duin, A. C. "Reactive force field for aqueous organic and inorganic carbon compounds." in preparation.

INORGANIC CONTROLS ON ISOTOPIC FRACTIONATION AND CRYSTAL GROWTH

INVESTIGATORS: F.J. Ryerson (Lead), D.J. DePaolo, P. Weber, J. Watkins, L. Nielsen, J. Hunt

OBJECTIVES: Develop an understanding of the relationship between carbonate mineral growth kinetics, trace element incorporation and the isotopic fractionation using an approach that combines experimental determinations and modeling as a function of growth rate, solution composition and influence of organic components

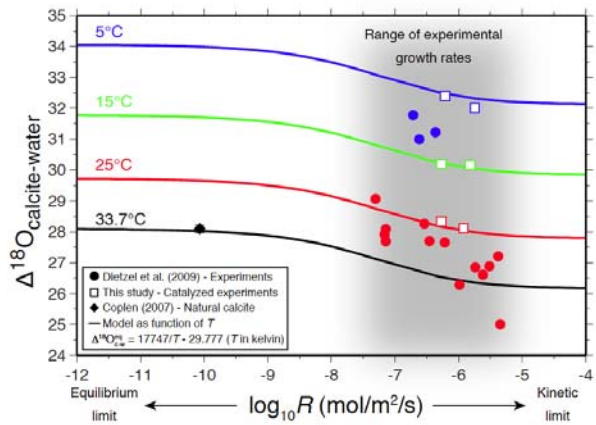


Figure 1. Calcite-water fractionation factor for oxygen, $\Delta^{18}O_{c\text{-}w}$, versus precipitation rate R. Model curves describe the rate-dependence while accommodating the equilibrium $\Delta^{18}O_{c\text{-}w}$, at 33.7°C and pH = 7.4 inferred from natural calcite. In the model, the T dependence arises solely from T-dependent partitioning of oxygen isotopes between DIC species and water. Results indicate that direct measurement of equilibrium $\Delta^{18}O_{c\text{-}w}$,by conventional methods requires experiments that last years to decades.

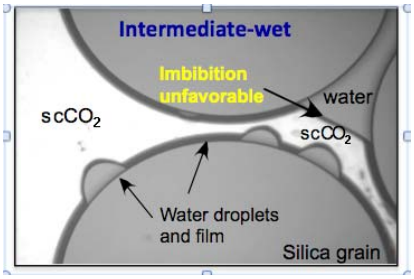
ACCOMPLISHMENTS: Oxygen isotopic variations in fluid derived from pilot-scale CO_2 storage demonstration project and EOR operations have been used to infer the extent of mineral dissolution and mixing in the fluid reservoir. Although oxygen isotope separation is expected on theoretical grounds, the temperature-dependence remains uncertain because other factors, such as slow exchange of isotopes between dissolved CO_2-species and water, can obscure the temperature signal. This is problematic for crystal growth experiments on laboratory timescales and for interpreting the oxygen isotope composition of crystals formed in natural settings. We performed experiments in which inorganic calcite is precipitated in the presence of 0.25 µM dissolved bovine carbonic anhydrase (CA). The presence of dissolved CA accelerates oxygen isotope equilibration between the dissolved carbon species CO_2, H_2CO_3, HCO_3^-, CO_3^{2-} and water, eliminating this source of isotopic disequilibrium during calcite growth. The experimental results allow us to isolate kinetic oxygen isotope effects occurring at the calcite-water interface during mineral growth. The $\delta^{18}O$ of precipitated calcite is lower than dissolved HCO_3^- yet heavier than CO_3^{2-} at pH = 8.3. ^{18}O uptake into calcite varies with precipitation rate, but the observed rate-dependence is lower than in previous studies where calcite is not precipitated in the presence of dissolved CA. The non-equilibrium effects can be explained in terms of isotopologue-specific reaction rate coefficients. We have developed a framework of ion-by-ion growth of calcite that reconciles our new measurements with measurements of natural cave calcites that are the best candidate for having precipitated under near- equilibrium conditions. Our findings suggest that isotopic equilibrium between calcite and water is unlikely to have been established in laboratory experiments or in many natural settings. The use of CA in carbonate precipitation experiments offers new opportunities to refine oxygen isotope-based geothermometers and to interrogate environmental variables other than temperature that influence calcite growth rates.

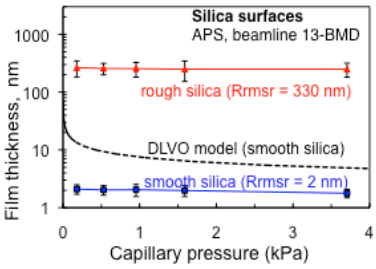
THRUST AREA 2 OVERVIEW

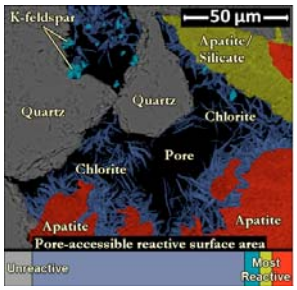
INVESTIGATOR: Ian Bourg, Thrust Area 2 lead

OBJECTIVE:
This Thrust aims to probe the structure, dynamics, and transport of fluids in nanopores and thin films in conditions relevant to geological carbon sequestration (GCS) to determine, how the properties of confined fluids differ from those of bulk fluids, how mineral wetting phenomena arise from molecular scale properties, and whether there are changes in wetting properties to chemical interactions between CO_2, acidified brine and mineral surfaces.

ACCOMPLISHMENTS:
We completed the first ever measurement of the ionization of water in scCO2 in conditions relevant to GCS. Our results show that this ionization is negligible; therefore, the reactivity of humid scCO2 with mineral surfaces requires the mediating presence of adsorbed water films at the mineral-CO2 interface (Capobianco et al., in review). We confirmed our recent finding that the adsorption of CO2 on silica surfaces has a non-monotonic pressure-dependence (CO2 is positively adsorbed at low P, negatively adsorbed at high P) and is quite long-ranged (Rother et al., 2012). We demonstrated for the first time that CO2 solubility in nanopore water is either enhanced or inhibited depending on the hydrophilicity of the pore walls (Chialvo et al., 2012). Mudstone and shale caprocks commonly have a bimodal distribution of pore sizes, with 3 to 50 nm wide nanopores and 25 to 100 µm wide macropores (Cole et al, in review), that the reactive surface area of caprocks tends to be dominated by clays (illite, chlorite) at the nanoscale, and that the type of surface coatings formed during weathering depends strongly on porosity distribution (Navarre-Sitchler et al., 2013). We carried out the first ever characterization (with resolution better than 2 nm) of the thickness of adsorbed water films on silica and mica surfaces at low capillary pressures in GCS conditions (Kim et al., 2012, in review). Finally, we demonstrated for the first time that the hydrophilicity of mineral surfaces (quartz, mica) can decrease sharply in the presence of scCO2, with important implications for the capacity and capillary trapping efficiency of reservoir rocks and the sealing capacity of caprocks (Jung and Wan, 2012; Kim et al., 2012).



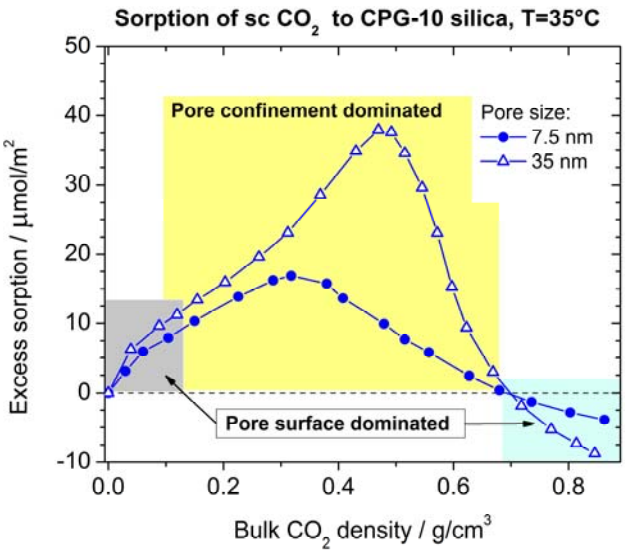




Pore Size Dependence of Supercritical CO_2 Adsorption in Nanoporous Silicas Serving as Sandstone Proxies

INVESTIGATORS: Gernot Rother, David R. Cole

OBJECTIVE: Geologic carbon storage (GCS) in porous rock requires that large quantities of supercritical carbon dioxide are pressed into storage rock formations, where the fluid occupies pore spaces that were previously filled with brine. Some of the most important potential storage sites in the U.S. utilize sandstone formations at depths of 500–3000 m. For storage-site selection, knowledge about the storage capacity of sandstone and other quartz-rich reservoir rocks as a function of temperature, pressure, and pore size is essential.



ACCOMPLISHMENTS:

Using a gravimetric high-pressure sorption apparatus, we have measured the excess sorption and mean pore density of pure supercritical CO_2 in amorphous silica with cylindrical interconnected pores and 7.5 nm and 35 nm mean pore size. The data show pore densification of the fluid for densities of up to ~ 0.7 g/cm^3, followed by a transition to pore depletion at higher pore densities. It is found that the position of the excess sorption maximum shifts to higher bulk density with increasing pore width. The surface-normalized excess sorption (see Figure 1) is higher for the silica with the larger pores, indicating multilayer adsorption of supercritical CO_2 under GCS conditions. Pore density of CO_2 in silica pores is higher at lower temperature and in narrower pores, and high storage efficiency is achieved at moderate pressures of ~ 100 bar, indicating that shallow sandstone rock formations with fine-grained morphology offer significant storage capacity. In coarse sandstones and at greater depth, CO_2 can be stored with near bulk density. This research constrains the storage capacity of rock formations near the injection well, where a plume of supercritical CO_2 will form. Adsorptive and capillary trapping are the dominating short-term storage mechanisms, and remain dominant for long-term storage in unreactive rocks. The NCGC project studies these problems in the reservoir rock capacity research theme. Future work on this topic will involve neutron-scattering studies of the structural properties of pure CO_2 and aqueous CO_2 solutions in rock pores.

G. Rother, E. G. Krukowski, D. Wallacher, N. Grimm, R. J. Bodnar, and D. R. Cole (2012): Pore Size Effects on the Sorption of Supercritical CO_2 in Mesoporous CPG-10 Silica, J. Phys. Chem. C 116, 917-922.

Ionization in H_2O-Bearing Carbon Dioxide Determined by Conductivity Measurements

INVESTIGATORS: M. Gruszkiewicz , R. Capobianco, R. Bodnar

OBJECTIVES: The goal of this initial investigation is to determine whether significant ionization occurs in supercritical CO_2 saturated or nearly saturated with water. Recent studies report rapid corrosion of metals and carbonation of minerals in contact with "wet CO_2". The observed rates of these processes even exceeded those involving CO_2-saturated aqueous phase at the same *PT* conditions. One explanation for this behavior is that addition of small amounts of H_2O to CO_2 leads to significant ionization within the fluid (analogous to corrosion in aqueous fluids). The homogeneous ionization equilibria in CO_2-rich fluids and the mechanisms of chemical interactions between these fluids and minerals or metals are essential to predicting reservoir storage capacity, caprock integrity, and equipment corrosion.

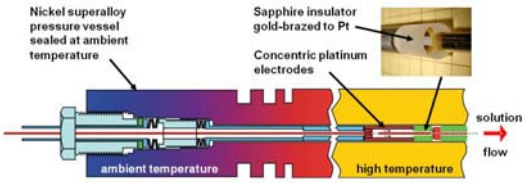


Fig. 1. The ORNL conductivity cell designed or measuring conductivities of very dilute solutions.

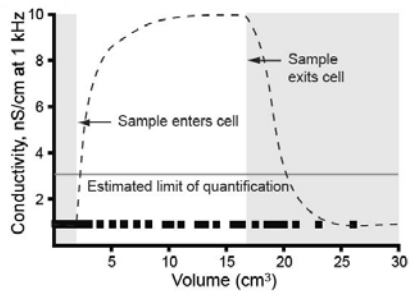


Fig. 2. Typical results shown as full square symbols compared with results expected in the case of detectable ionization (curve).

ACCOMPLISHMENTS: Very sensitive detection of electrolytic conductivity is possible by means of the new ORNL flow-through conductivity cell (Fig. 1). Experiments were conducted at temperatures between 25 and 200°C and pressures to 200 bar with H_2O mass fractions up to ~1650 ppm corresponding to the solubility of water in CO_2 at 25°C. In all experiments, conductivities below the detection limit of the instrument were obtained (at least one to two orders of magnitude less than the conductivity of water due to auto-ionization), (Fig. 2) indicating that the solution is essentially ion-free. No trends of conductivity as a function of water content were detected. This suggests that the observed corrosion and carbonation reactions are not the result of ionization in the bulk fluid, but possibly proceed via CO_2-saturated adsorbed aqueous films. This mechanism would strongly depend on the amount of available water and the rate of its diffusion to the interface.

Capobianco, R.; Gruszkiewicz, M. S.; Bodnar, R., Rimstidt, J. D. "Ionization in H_2O-bearing carbon dioxide determined by conductivity measurements" *submitted to Geochimica et Cosmochimica Acta*.

CO_2-Rich Environments under Significant Silica Confinement

INVESTIGATORS: Ariel A. Chialvo, Lukas Vlcek, and David R. Cole (OSU)

OBJECTIVE: We targeted the molecular-based characterization of the interfacial fluid behavior of CO_2-rich phases under extreme confinement between silica surfaces at CCS conditions, in the presence of common CO_2 contaminants such as SO_2, H_2S, NO_2, and H_2O. This effort aims at providing new and crucially needed insights into the significant interactions between highly dilute contaminant species (including water), CO_2, and the mineral surfaces, a behavior not currently accounted for in the interpretation of experiments involving caprock-fluid interactions and corresponding reactive-transport modeling.

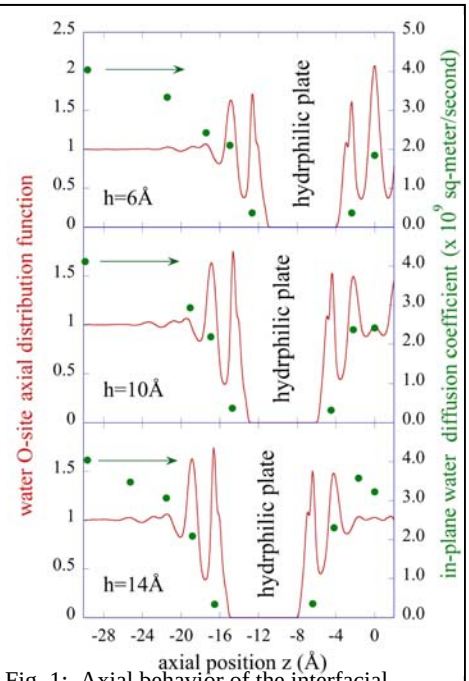


Fig. 1: Axial behavior of the interfacial structure of aqueous CO_2 environments confined between hydrophilic silica surfaces, separated by a distance "h", and its strong impact on water translational diffusivity

ACCOMPLISHMENTS: We studied, by isobaric-isothermal/grand-canonical simulation, the interfacial behavior of species in H_2O-rich and CO_2-rich phases in contact with and under confinement of silica surfaces with varying surface polarity. The polarity scheme was used to represent hydrophilic, hydrophobic, and mismatched surface configurations typically found during the formation of new fractures and cracks in mineral formations and caprocks, as well as during the drying out of wet surfaces in contact with supercritical CO_2 environments. The implications of found behavior are manifold: (a) the slit-pore fluid environment (i.e., density and composition) bears no resemblance to that of a bulk counterpart at the prevailing state conditions (e.g., cannot be described by equations of state when either interpreting or modeling the process at a macroscopic level), (b) the fluid environment in contact with the mineral surface can be considerably different from either that a few molecular diameters away or that of the corresponding bulk, consequently (c) transport phenomena and chemical processes occurring in these nanopore aqueous environments become strongly affected by the nature of the mineral surfaces and the resulting confined environments, i.e., they cannot be modeled as "well-stirred" homogeneous systems.

"Aqueous Carbon Dioxide Environments under Silica Nano Confinement" Annual AICHE Meeting (Pittsburgh. Oct. 28-Nov. 2, 2012), A. A. Chialvo, L. Vlcek, and D.R. Cole

"CO_2 rich environments under silica confinement" 22nd Annual VM Goldschmidt Geochemical Conference (Montreal, Canada. June 29, 2012), A. A. Chialvo, L. Vlcek, and D.R. Cole.

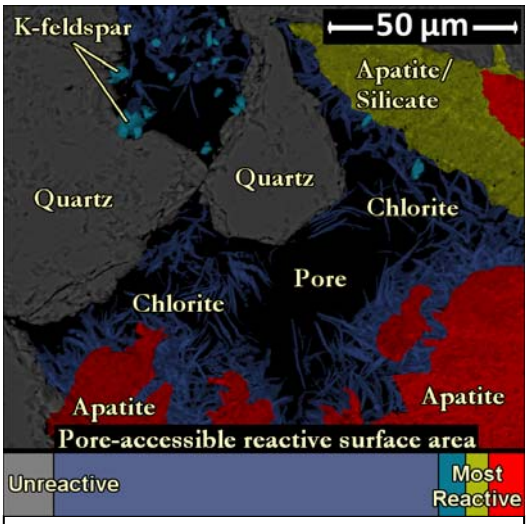
"Aqueous CO_2 Solutions at Silica Surfaces and within Nanopore Environments. Insights from isobaric-isothermal molecular dynamics" A. A. Chialvo, L. Vlcek, and D.R. Cole, *Journal of Physical Chemistry C,* 13904-13916 (2012)

"Acid gases in CO_2-rich subsurface geological environments" A. A. Chialvo, L. Vlcek, and D.R. Cole, In submission to *Reviews in Mineralogy and Geochemistry* (April, 2013)

Characterization of Nanoporosity and Reactive Surface Area in Caprocks and Reservoir Rocks

INVESTIGATORS: D. Cole, A. Swift, L. Anovitz, G. Rother, J. Ajo-Franklin, J. Sheets, C. Steefel

OBJECTIVE: The overarching goal is to characterize pore and fracture features, determine how nanoporosity evolves in reactive systems, and quantify reactive surface area. Specific goals for the recent work period are to determine how porosity and permeability vary spatially within representative caprock and reservoir formations; describe the nano- to microporosity in both rock types; quantify the reactive surface areas in both pore and fracture networks; and examine how pore and fracture mineralogy change as a consequence of interaction with CO_2-bearing fluids at elevated P and T.



Backscattered electron image showing the relative proportion of pore-accessible minerals, ordered by reactivity with a CO_2-saturated brine.

ACCOMPLISHMENT(S): We have used an array of complementary methods—scanning and transmission electron microscopy, small and ultra-small neutron scattering, dual-beam focused ion beam, mercury porosimetry and BET—to characterize a number of rocks that have experienced different extents of weathering or diagenesis. The rock types vary from classic sedimentary basin lithologies (sandstone, mudstone, and shale) to basalt, diabase, and granite. This wide variability in composition, texture, and geologic context afforded us the opportunity to quantify how pore size, shape, distribution, connectivity, and reactive surface area in pore and/or fracture networks have evolved as a function of the extent of alteration. In our studies of mudstone and shale caprocks, we commonly observe a bimodal distribution of total porosity and a sympathetic bimodal distribution of connected pores between 3 and 50 nm and 25 to 100 microns (Cole et al., in review). Reactive surface area in these rocks tends to be dominated by illitic-clay and/or chlorite at the smaller length scale, and by intimate contact of clay with carbonates, feldspar, or quartz at the coarser length scale. In sandstone formations, especially those comprised of facies containing more reactive phases such as carbonates, feldspar, and phosphates, we tend to observe late-stage pore fillings dominated by layered silicates (chlorite, illite) or by iron-oxyhydroxides, carbonate and feldspar (Swift et al., in prep). The former, as illustrated in the figure above, are less reactive and tend to armor potentially more reactive phases, whereas the latter more readily participate in reactions with CO_2-bearing brines. The different patterns in porosity development of granite and basalt are attributed to advective infiltration, plus diffusion in granite that has spheroidal fractures versus diffusion only in basalt that does not. Fracturing apparently diminishes the size of the diffusion-limited parts of the spheroidally weathering rock system to promote infiltration of reactive fluids, therefore explaining the faster alteration advance rate into that rock (Navarre-Sitchler et al., 2013).

Brine Film Thicknesses and Capillary Pressure Relations Under Supercritical CO_2 Confinement

INVESTIGATORS: **T.K. Tokunaga, T.W. Kim, S. Sutton, M. Newville, A. Lanzirotti, J. Bargar, M. Latimer, S. Webb, J. Wan, J.W. Jung, Y. Kim, W. Dong**

OBJECTIVES: As the wetting fluid phase, brine films are expected to remain on mineral surfaces following injection of supercritical (sc) CO_2 into deep reservoirs, and strongly influence multiphase flow, reactions, and transport. Despite the importance of aqueous films confined by $scCO_2$, understanding of how these films depend on mineral substrates, $scCO_2$ pressure, and capillary (disjoining) pressure was previously lacking.

These gaps in understanding are being addressed through the following subtasks.

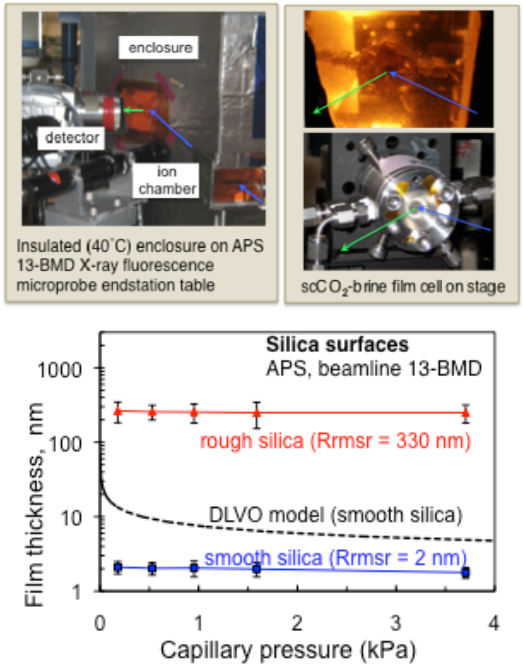
1. Predict adsorbed brine film thickness dependence on properties of mineral surfaces, brines, $scCO_2$, and disjoining (capillary) pressure, based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) model.

2. Develop an experimental system that allows control of capillary pressure with high resolution (10 Pa) while operated at high total pressure (~10 MPa $scCO_2$).

3. Develop a high pressure film chamber for X-ray fluorescence measurements of tracer ions in brine films, over wide ranges of film thicknesses (~2 nm to ~2 µm), with $scCO_2$ as the confining fluid.

4. Measure brine film thicknesses on silica surfaces (smooth and rough), under $scCO_2$ confinement, over a range of low disjoining pressures typical of permeable reservoirs.

5. Measure brine film thicknesses on mica (smooth and rough), under $scCO_2$ confinement, over a range of low disjoining pressures.



Capillary pressure-dependent thicknesses of brine films on silica.

ACCOMPLISHMENTS:

All subtasks listed above were successfully completed, leading to two publications and two manuscripts in review. This work developed the conceptual and experimental basis for investigating films under capillary equilibrium with $scCO_2$, and provides the motivation for the new NCGC research theme on capillary pressure-saturation relations.

Publications:

Tokunaga, T.K., 2012, DLVO-based estimates of adsorbed water film thicknesses in geologic CO_2 reservoirs. Langmuir, 28, 8001-8009.

Kim, T.K., T.K. Tokunaga, D.B. Shuman, S.R. Sutton, M. Newville, A. Lanzirotti, 2012, Thickness measurements of nanoscale brine films on silica surfaces under geologic CO2 sequestration conditions using synchrotron X-ray fluorescence. Water Resour. Res. 48, W09558.

Tokunaga, T.K., J. Wan, J.W. Jung, T.W. Kim, Y. Kim, W. Dong, Capillary pressure and saturation relations for supercritical CO_2 and brine in sand. Water Resour. Res. (in review).

Kim, T.K., T.K. Tokunaga, J.R. Bargar, M.J. Latimer, S.M. Webb, Brine film thicknesses on mica surfaces under geologic CO2 sequestration conditions. Water Resour. Res. (in review).

Wettability Alteration and its Impacts on CO_2 Storage in Deep Reservoirs

INVESTIGATORS: J. Wan, Y. Kim, J, Jung, and T.K. Tokunaga

OBJECTIVES: Currently, the degree and mechanism of CO_2 trapping in reservoir rocks are knowledge gaps in geologic carbon sequestration, but we know that wettability plays an important role. This task is designed to address critical questions concerning rock/mineral wettability under deep reservoir carbon sequestration conditions, and its impacts on CO_2 storage. The main questions being addressed include:

(1) Does wettability change upon reaction with supercritical CO_2 ($scCO_2$), and to what degree for different minerals? What are the controlling factors?
(2) Does wettability alteration impact CO_2 saturation and residual trapping, and to what degree?

ACCOMPLISHMENTS: Using a high-pressure micromodel-microscopy technique, we observed/recorded the dewetting process on silica surfaces (water film thinning, water droplet formation, and water contact-angle increase) upon reactions with scCO2 at pore scale for the first time. Contact angles increased from near 0° to 80°, with larger increases under higher ionic strength conditions.

Using a high-pressure sessile drop technique, we measured equilibrium contact angles on silica surfaces in CO2-brine systems under wide ranges of pressures and ionic strength conditions. We found that the contact angles increased sharply with increased pressure within a narrow pressure range of 7 to 10 MPa, and remained practically constant at higher pressures. We found that contact angles increased progressively as ionic strength increases. Furthermore, these two effects are not significantly coupled, so their net effects are approximately additive. This feature provides a basis for potentially predicting contact angles under reservoir conditions.

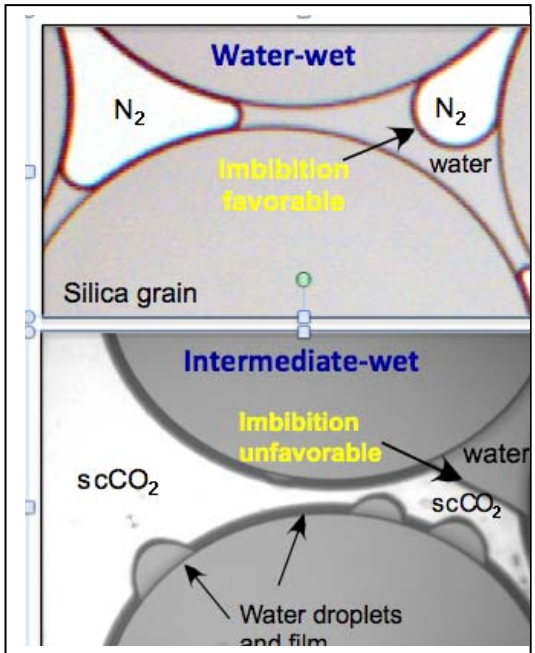


Figure 1. Microscopic images of a single silica pore at the late stage of a drainage process. (a) In a gas N_2-brine system, the silica surface remained water-wet; (b) but in $scCO_2$-brine system the silica surface became intermediate-wet, indicated by the curvatures of two fluid interfaces. The experiments were conducted at 85 bar, 45˚C.

Jung, J. and J. Wan, Supercritical CO_2 and ionic strength effects on wettability of silica surfaces: Equilibrium contact angle measurements, Energy & Fuels, 26, 6053-59, 2012.

Kim, Y., J. Wan, T. J. Kneafsey, and T.K. Tokunaga, Dewetting of silica surfaces upon reactions with supercritical CO_2 and brine: Pore-scale studies in micromodels, Environ. Sci. Technol., *46* (7), 4228–4235, 2012.

We hypothesized that spontaneous imbibition becomes energetically unfavorable due to dewetting, so that increased residual CO2 trapping at the post-injection stage can be expected (this is not an obvious hypothesis; there are different opinions in the literature). We are testing this hypothesis at both core and pore-network scales, and our preliminary results from both scales support this hypothesis.

In the next phase of NCGC research, we will shift our focus from silica/quartz to carbonate reservoirs.

THRUST AREA 3: EMERGENT PROCESSES ASSOCIATED WITH CO2 INJECTION AND SEQUESTRATION

THRUST LEAD: C. Steefel

OBJECTIVES: The objective of this Thrust Area has been to improve our understanding of how pore scale processes and effects can lead to emergent behavior associated with the far from equilibrium CO2 injection and sequestration systems, including evolving geochemical reactivity, reaction-induced porosity and permeability changes, and supercritical CO_2 distributions in naturally heterogeneous subsurface formations. An addition objective is to upscale pore scale results from modeling and characterization to the continuum reservoir scale.

ACCOMPLISHMENTS: The first reconciliation of pore and continuum scale reaction rates (calcite precipitation) were carried out as part of the NCGC and published in Noiriel et al (2012). This work was complemented by another first of its kind study in which atomic scale calcite precipitation rates were compared with bulk rates (Bracco et al., in review). A study of the hydrologically accessible reactive surface area in the Cranfield Formation, a CO_2 injection site in Mississippi, was able to achieve unprecedented new resolution down to 100 nm using a hybrid 2D and 3D mapping approach (Landrot et al., 2012). Microcapillary tube experiments in which the mineral forsterite dissolved under $scCO_2$ conditions demonstrated that diffusion-controlled "immobile" zones could be favorable sites for carbonate (magnesite) precipitation because of the lack of flushing with acidic waters, allowing for the increase in pH and alkalinity necessary for precipitation to take place. These micro-capillary tube experiments made use of Raman spectroscopy to quantify the accumulation of magnesite along the diffusion path bordering a brine-$scCO_2$ flow path. Imaging of both mineral precipitates (Noiriel et al., 2012), pore structure (Landrot et al., 2012), and CO_2 distributions (Ajo-Franklin and Voltolini, in prep.) using X-ray microtomography at the Advanced Light Source and neutron tomography/radiography (Anovitz, in prep.) demonstrated the power of these approaches for mapping pore scale geochemistry, mineralogy, and physical properties.

Innovations in modeling and simulation were equally important to the NCGC Thrust III effort over the past year. It can be argued that a new paradigm for high resolution pore scale modeling was established with the successful coupling of the SCIDAC-developed Chombo platform for direct numerical simulation of flow and transport to the multicomponent geochemical routines in CrunchFlow (Molins et al., 2012). This high performance computing approach has made it possible to investigate how geochemical reaction processes upscale from the pore to continuum scale, since subsurface aquifer texture affecting flow, transport, and reaction can be explicitly introduced into the pore scale model, with full resolution of all interfaces at the micron scale. Now underway is a simulation of an experiment in which crushed calcite is introduced into a capillary tube and reacted under flow conditions with a high pCO_2 (acidic) solution. X-ray microtomography at the Advanced Light Source was used to map the pore geometry within the capillary tube and these 3D maps have been converted to digital numerical representations for the pore scale model. These simulations, almost certainly the largest and most highly resolved pore scale reactive transport simulations ever undertaken, demonstrate a distinct "pore scale" effect due the heterogeneity of flow and reaction rate within the porous grain pack. The pore scale results (experiment and modeling) show a systematically lower reactivity than the equivalent continuum reactive transport models, as expected, despite the use of the same reaction rate laws in both models.

Pore to pore network to micro-continuum scale modeling has also been used to investigate the controls on CO_2 invasion and post-injection distributions and geochemical reactivity. A highly efficient

invasion percolation model has been used to predict $scCO_2$ distributions in naturally heterogeneous aquifer materials and compared with microtomographic and radiographic images (Ajo-Franklin and Pride, in prep.). A new lattice Boltzmann model for pore scale $scCO_2$ invasion treats the partial miscibility of brine and CO_2 for the first time (Aursjoe and Pride, in review). Cohen and Rothman (in prep.) have developed a new pore scale model that demonstrates that mineral precipitation depends strongly on the size and the shape of trapped bubbles of CO_2. In addition, they identified a typical length scale in which most of the precipitation of calcium carbonate occurs, finding that precipitation on a small boundary layer at the interface between CO_2 and brine may lead to lowered diffusivities, slower kinetics, and mechanical trapping of CO_2. Micro-continuum (mm to cm) scale reactive transport modeling of an initially heterogeneous CO_2 distribution (from the invasion percolation model mentioned above) within a sand containing the reactive phases plagioclase and/or chlorite demonstrate that the lifetime of a residually-trapped CO_2 bubble may be as short as about 25 years in some cases, contradicting the conclusions of earlier studies that suggested a 10,000 year time scale over which mineral sequestration of CO_2 is important (Steefel and Pride, in prep.).

Neutron Tomography/Radiography of Flow in Porous and Fractured Media

INVESTIGATORS: L.M. Anovitz

OBJECTIVES: The goals of this initial investigation are (1) to develop equipment and techniques to utilize neutron radiography and tomography to quantify flow and precipitation in fractures and porous media at the meso-scale, (2) to obtain real-time, 3-D data on progression of infiltration and dissolution fronts at pore-to-core scales of H_2O/CO_2 fluids, (3) to analyze fracture/pore interactions, and to quantify Infiltration of CO_2-rich fluids and propagation of dissolution.

Fig. 1. The ORNL neutron radiography/ tomography flow cell (partially disassembled).

ACCOMPLISHMENTS: While similar in application to standard core flooding cells, the cell designed for this project had to be suitable for neutron applications (high neutron transmission, low activation) at conditions suitable for this study (confining P to 10,000 psi, flow P to 5000 psi, T to 350°C). As shown in Figure 1, this cell has now been designed, built, and tested, and a paper is being prepared for *Review of Scientific Instruments*. Prior to completion of the cell, experiments were conducted on capillary flow in porous sandstones, and CO_2 dryout in a "fractured" (cut) sandstone. Experiments with the cell have been conducted to: (1) measure neutron transmission for cold and thermal neutrons (at HFIR and NIST), (2) observe water/air flow fronts in a "fracture" over a range of flow rates at high images rates (Figure 2), and (3) observe and obtain 3D data on precipitation in a fracture (Figure 3).

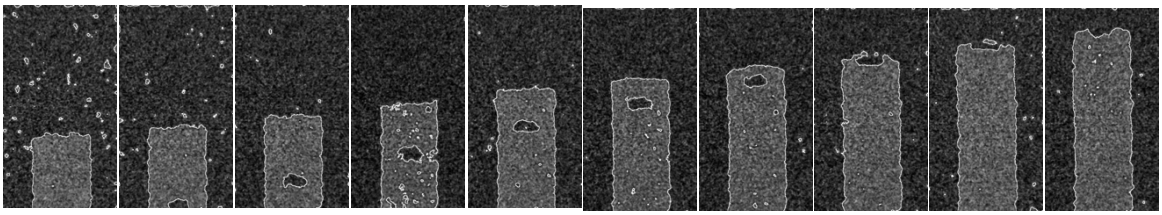


Fig. 2. Neutron radiographic image of water flowing at 1L/min in a 1.5" x 1/6" fracture in granite. Front velocity ~10.8 inches/sec, 10 ms exposures, 14 frames/sec. Air bubble captured migrating through front. Edge detection applied to quantify interface characteristics

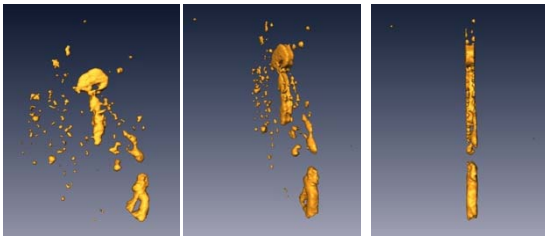


Fig. 3. Isosurface of boric acid precipitate in a fracture.

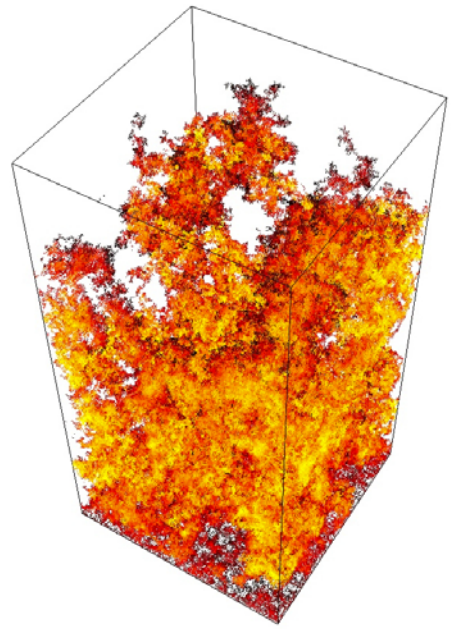
Emergent Post-Invasion CO_2 Structure in Porous Rock and Its Relation to Dissolution of Silicate Minerals and Precipitation of Carbonate

INVESTIGATORS: S. Pride (lead)

OBJECTIVES:

(1) To use Lattice-Boltzmann (LB) methods to numerically model the way one fluid invades a pore space occupied by another when there is partial diffusive mixing between the two fluids. Modeling the partial miscibility of CO_2 and water while maintaining a well-defined interface with a controllable surface tension requires novel LB algorithms.

(2) To apply a variant of the invasion-percolation algorithm to numerically determine the CO_2 distribution in pore-space images obtained from X-ray CT at the ALS. The diffusion-length algorithm can then be applied to the brine distributions so determined. This modeling obviates the need to perform invasion experiments under pressure at the ALS, although it will be tested against such experiments. Work is in collaboration with Jonathan Ajo-Franklin.



Example of the fast Invasion Percolation algorithm. A 256 x 256 x 512 invasion structure (invasion from bottom) generated in 0.1 sec CPU time. Invading fluid shown in orange, the grains and defending fluid are transparent.

ACCOMPLISHMENTS :

(1) Two articles were written on a new way to perform LB modeling of CO_2 invading a porous material saturated with brine. In the first article *("Lattice Boltzmann modeling of binary mixtures: I. Miscible fluids in a gravitational field", Aursjoe and Pride, to be submitted to Phys. Rev. E*), the method for modeling how two fluids miscibly diffuse into one another is developed (no menisci are allowed for). In particular, existing LB models are not able to allow accurately for the force driving the flow to be spatially variable. In the miscible fluid problem, the density of the fluid is changing as they mix, and thus the gravitational force acting on the fluids is spatially variable. A method was developed to treat this situation that overcomes the errors of previous models. This novel LB algorithm is the first to be able to model the problems of natural convection (e.g., the Earth's mantle) or solutal convection (what happens in the pores of a rock as CO_2 and water mix). In a second article *("Lattice Boltzmann modeling of binary mixtures: II. Partially immiscible fluids, Aursjoe and Pride, to be submitted to Phys. Rev. E*), the interface between the two fluids is included in such a way that particles can pass through the interface up to a solubility limit. The width of the interface is controlled through a parameter. Final numerical examples are being generated prior to submitting these two otherwise complete articles. This work will help in our understanding of the emergent pore-scale saturation states that occur after a CO_2 flood.

(2) An extremely efficient Invasion Percolation (IP) algorithm was written that uses binary trees to search for what pore to invade next. CPU time for the new algorithm scales with the number of sites N in the system as $N^{0.9}$, as opposed to $N^{1.8}$ in the standard algorithm. Modeling an X-ray monitored CO_2 invasion experiment in the lab now takes only seconds. This model is being submitted as *"A fast algorithm for invasion percolation", Masson and Pride, J. Comp. Phys.*

Long-time Geochemical Evolution of Sequestered CO_2

INVESTIGATORS: D. Rothman (lead), Y. Cohen

OBJECTIVES:

We seek to understand and predict how the kinetics of the carbonate system influence the spatio-temporal evolution of sequestered CO_2 at long time scales. Our approach is complementary to that of Steefel, Pride and others (following page) in that we are investigating simpler chemical systems to define the important first order effects that can occur in systems with the general properties of CO_2+brine+minerals. By combining theory and numerical simulation, we study:

(1) Pattern formation of the injected $scCO_2$ in the fluid-rock system;
(2) The coupling of transport, chemical reactions, and intricate microgeometry of the rock; and the implications of this coupling for the mobility of the carbonate species;
(3) Chemical and mechanical separation of phases at long time scales.

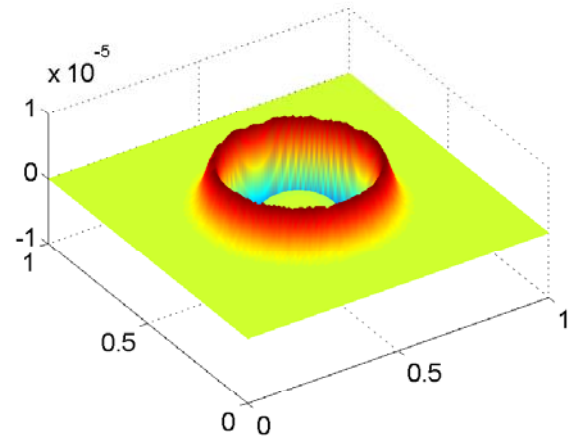


Figure 1: Minerals accumulation at the interface of a circular domain of high CO_2 concentration surrounded by a brine phase. The carbonate crust created in a small boundary layer can lead to a mechanical separation of the two phases.

ACCOMPLISHMENTS :

1. Demonstrated the irregular shaped pockets of the CO_2 bubbles, by using an invasion percolation model.
2. Developed a numerical solver for the reaction-diffusion equations that includes the nonlinear reaction rates of the carbonate system and mineral dissolution and precipitation.
3. Demonstrated that mineral precipitation strongly depends on the size and the shape of trapped bubbles of CO_2.
4. Identified a typical length scale in which most of the precipitation of calcium carbonate occurs. Mineral precipitation on a small boundary layer at the interface between CO_2 and brine may lead to lowered diffusivities, slower kinetics, and mechanical trapping of CO_2.

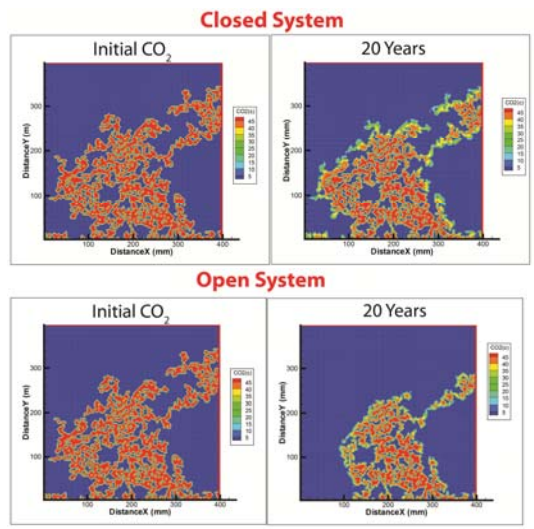
The Effect of Heterogeneity on Carbonate Precipitation Rates With a CO_2 Plume

INVESTIGATORS: C. Steefel, S. Pride

OBJECTIVES: The primary objective of this study is to use numerical modeling and simulation to determine the effects of physical and geochemical heterogeneities on the rates of carbonate precipitation within a subsurface CO_2 plume.

ACCOMPLISHMENTS: Continuum models assume that all constituents within a modeling voxel are in well-mixed contact. In reality, when CO_2 invades brine-saturated porous media, a complex fractal distribution of residual water patches emerges between the branching fingers of CO_2. The CO_2 will gradually diffuse into the local aqueous phase, acidifying the water and thus driving dissolution of carbonate and silicate mineral phases. These silicate phases (feldspar, micas) can provide the metal cations and alkalinity needed to precipitate carbonate mineral phases, thus sequestering CO_2 in a stable mineral form potentially over geologic time scales. However, the homogeneous continuum models, which are in wide use in the estimation of carbonate mineral trapping, do not capture the millimeter-to-centimeter-scale gradients in concentration and pH, making the estimates of the rates of precipitation suspect.

In the present work, we perform 1D and 2D numerical modeling of the reactions and diffusion described above over mesoscopic length scales between pore sizes and continuum voxel sizes. In 1D systems involving a single feldspar grain at one end of a tube and a pure CO_2 bubble at the other, we observe that when the ends of the tube are closed, the calcite rates begin to drop when the tube is sufficiently long that diffusion begins to limit the dissolution (and therefore precipitation) rates. In the closed system case, which is likely applicable to the center of the CO_2 plume, the system eventually homogenizes, while in the open system (close to the edge of the plume), steady-state gradients in pH, alkalinity, and cation concentrations may be maintained, and there is a critical tube length at which calcite rates are a maximum. In 2D systems having complex distribution of the minerals and CO_2, we observe local maximums in the calcite rate far above the predicted well-mixed rates. For systems in which plagioclase dissolves, significant consumption of CO_2 can occur through the combination of solubility and mineral trapping within 10–25 years.

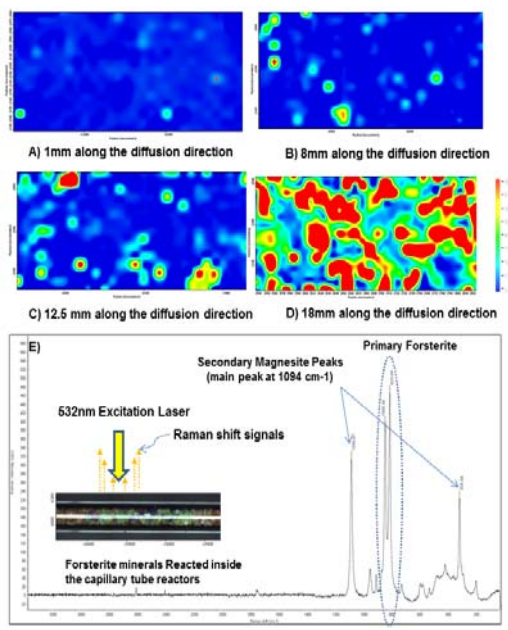


Comparison of closed and open system behavior for a CO_2 distribution reacting with a plagioclase-rich sand. The closed system (center of plume) eventually homogenizes, while the open system maintains gradients that accelerate the rate of carbonate precipitation and solubility trapping, thus attenuating the CO_2 bubbles at a higher rate.

Coupled Kinetics of Secondary Carbonates Formation from Primary Silicate Mineral Dissolution under Geological CO_2 Sequestration Conditions

INVESTIGATORS: C. Steefel (lead), L. Yang, H. Bechtel

OBJECTIVES: The primary focus of this study is to understand the kinetic processes of secondary carbonate formation resulting from primary bedrock mineral dissolution under geological carbon-sequestration conditions. A key objective is to determine the primary controls on the precipitation of secondary carbonates and the kinetics of their formation, so as to provide critical rate parameters needed for geochemical modeling of mineral dissolution and precipitation associated with CO_2 injection during geological carbon sequestration.



RAMAN map of the secondary carbonate precipitates (upper) and corresponding Raman spectroscopy

ACCOMPLISHMENTS: Building upon the previous findings from single pore microfluidic experiments, we have engineered a custom-designed high pressure/temperature, microcapillary tube reactor to study geochemical reactions between primary minerals and CO_2-containing brines within subsurface media, under conditions relevant to geological carbon sequestration. The design of the microcapillary tube reactors enables the isolation of complex coupled flow and diffusion-controlled geochemical processes in subsurface media into well-defined, separate regimes for close study. The design also enables identification of the dominant controls on the potential formation of secondary carbonates associated with geological carbon sequestration. The experiment setup is configured to closely integrate with reactive transport modeling, to more accurately determine the coupled kinetics of primary mineral dissolution-secondary carbonate precipitation. Coupled flow and diffusion experiments have been successfully performed using mineral forsterite grains packed inside T-shaped, 200 µm I.D. microcapillary tube reactors. The experimental devices have been injected with high concentrations of CO_2 brines to examine their reactions under various flow- or diffusion-controlled regimes in a microporous media environment. Our results showed that magnesite was the only secondary carbonate mineral identified by RAMAN spectroscopy analysis. Although the pore fluids in the flow-cell samples have reached oversaturation with respect to magnesite, no carbonate precipitation was detected. The secondary magnesite predominantly formed in the diffusion-controlled samples where the pH, alkalinity, and Mg^{2+} concentration have risen to be much more supersaturated and more favorable for secondary-phase formation. Based on the profile of the magnesite precipitation in the diffusion cell, we carried out multicomponent diffusion-reaction modeling to obtain the important interfacial energy parameter for magnesite heterogeneous nucleation. This study revealed the importance of diffusion-controlled processes and the local heterogeneity of geological microporous media in controlling subsurface mineral carbonation reactions during geological carbon sequestration.

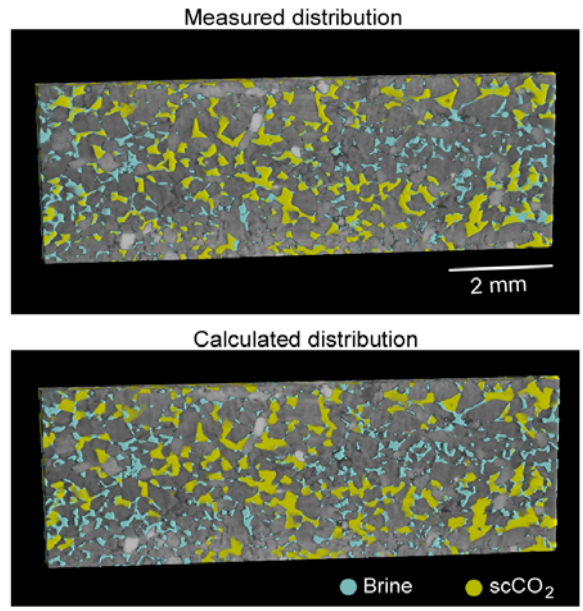
Pore-Scale Imaging of $scCO_2$ Distribution and Pore Structure Alteration in Reservoir Materials Using Synchrotron Micro-Tomography

INVESTIGATORS:

Jonathan Ajo-Franklin and Marco Voltolini

OBJECTIVE:

Pore morphology, topology, and surface properties directly control $scCO_2$ distribution within porous materials. The distribution of $scCO_2$ in the pore space controls a variety of processes including diffusion rates, capillary trapping, and effective reaction rates. This task strives to develop the experimental systems required to allow observation of multi-phase flow of $scCO_2$ & pore-structure alteration in the context of synchrotron micro-tomography (microCT) and provide concrete observations of 3D $scCO_2$/brine distribution in a variety of reservoir sandstone samples, as well as characterize feedbacks between reactive flow, pore structure, and permeability.



Dynamic synchrotron radiography image of $scCO_2$ invasion into a reservoir sandstone acquired at ALS BL 8.3.2.

ACCOMPLISHMENTS : During this period of NCGC support, we have continued our dynamic tomographic imaging experiments using the high-pressure triaxial cell that we developed during the prior year. Experiments were also conducted in a flexible mid-pressure cell that has allowed for controlled examination of pore-scale CO_2 distribution during a more varied set of flow conditions. All imaging experiments were conducted at Beamline 8.3.2 of the Advanced Light Source. During these experiments, we have successfully imaged supercritical and gas-phase CO_2 during imbibition and exsolution, as well as drainage at resolutions down to 1.89 microns. Our investigations have also been also been extended to a wider variety of sandstones, including the previously studied Domenging Fm (Sacramento Basin), the Starkey and Mokelumne Sandstones (Sacramento Basin), and several standard petrophysical test formations (Bentheimer, Berea, and Boise Sandstones). Several technical advances were made this year, including improvements in our reconstruction and segmentation approaches—advances that have made quantitative extraction of $scCO_2$/brine phase distribution possible.

Most importantly, we have initiated an effort to compare the $scCO_2$ distributions imaged using synchrotron micro-CT to model predictions based on invasion-percolation (IP) theory and network analysis. An efficient code was written to calculate $scCO_2$ distribution based on thickness maps and medial axis analysis; the resulting $scCO_2$ distributions were compared to imaged distributions for the drainage phase of $scCO_2$ invasion (see figure). The results showed an excellent match, suggesting that over short time periods, $scCO_2$ drainage in clean sandstones is largely dictated by pore dimensions and network properties, in accordance with classical models of capillary fingering described by IP theory. An important caveat is that the experiments conducted occurred over relatively short time durations (hours); in these situations, dynamic changes in surface wettability such as those observed by Jung and Wan (2012) may not yet be critical mechanisms in predicting CO_2 distribution. We anticipate that the manuscript describing these experiments and the recent analysis will be submitted this spring,

Experimental Determination of Chlorite Dissolution Rates in CO_2 Saturated Saline Water at Elevated Temperature and Pressure Conditions

INVESTIGATORS: S. Zhang, L. Yang, C. Steefel (lead)

OBJECTIVES: Our principal objective is to determine the kinetics of chlorite mineral dissolution when reacted with CO_2-containing brines under geological carbon sequestration conditions. This study combines with the work of Landrot et al. (2012) on reactive mineral surface areas in geological subsurface media, and would enable predictions of the amount of CO_2 sequestered in potential CO_2 storage reservoirs, such as Cranfield sandstones using the measured pore space geometry and reactive surface area.

ACCOMPLISHMENTS: A series of experiments were performed by reacting chlorite with brines saturated with CO_2 under different pressures (0 bar, 20 bar, and 60 bar) and different flow rates (0.25 ml/min, 0.05 ml/min and 0.01 ml/min) in a flow-through high-pressure reactor at an elevated temperature. Dissolution rates of chlorite were determined as a function of pH and Gibbs free energy, as shown in Figs. 1 and 2. The measured dissolution rate of chlorite in this study is on the order of $5x10^{-11}$ mole/m^2/sec at reservoir conditions when minerals are reacted far from equilibrium. This rate, when considered in light of the relatively high surface area of chlorite ($11.62x10^{-2}m^2/g$ according to Landrot et al., 2012), is sufficient to allow 575 moles of CO_2 mineralization in 1 m^3 of chlorite-bearing sandstones, on a time scale of 1000 years, given that the rock density is 2800 kg/m^3, 8.3% of the rock is chlorite, and 31.8% of chlorite is accessible (Landrot et al., 2012). On the other hand, if we assume only 10% of the rock volume is filled with supercritical CO_2, which has a density of 600 kg/m^3, the total amount of CO_2 in 1 m^3 rock would be 1364 moles, which means that the Mg and Fe released from chlorite in such sandstones is still sufficient to mineralize about half of the stored CO_2 in 1000 years.

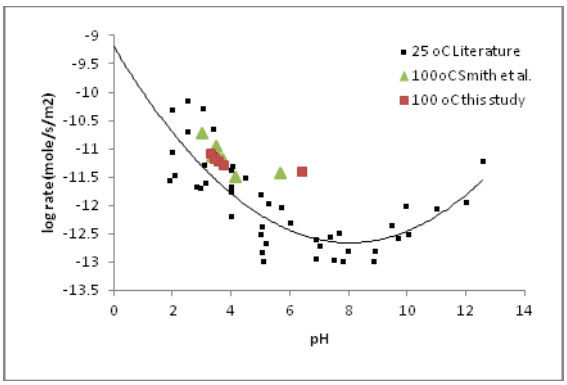


Figure 1: Relationship between delta G normalized dissolution rates and pH from current study compared with literature

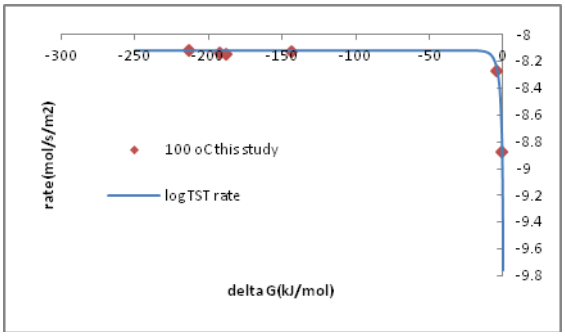


Figure 2. Relationship between pH normalized dissolution rates and delta G determined from current study compared with linear TST kinetic law

High-Performance Pore-Scale Simulations of Calcite Dissolution in a Capillary-Tube Experiment Using Microtomographic Image Data

INVESTIGATORS: S. Molins, D. Trebotich, L. Yang, J. Ajo-Franklin, T. Ligocki, C. Shen, C. Steefel

OBJECTIVE: To explore pore-scale processes, especially those involving mass-transport limitations to reactive surfaces which result in continuum-scale rates that depart from those predicted by laboratory studies, we performed a flow-through capillary tube experiment. The capillary tube (L=0.7 cm, D=500 µm) is packed with crushed calcite (Iceland spar). The 3D pore structure is imaged by x-ray computed microtomography (µCT) at Berkeley Lab's Advanced Light Source at 0.9 µm resolution. A solution in equilibrium with a partial pressure of CO_2 of 4 bar is injected into the capillary, and the effluent concentrations of calcium are measured over 2.5 hours. We use this experiment to validate a pore-scale reactive transport model comprised of high-performance simulation tools and algorithms for incompressible flow, transport and multicomponent geochemical reactions, using a direct numerical simulation approach (Molins et al., 2012).

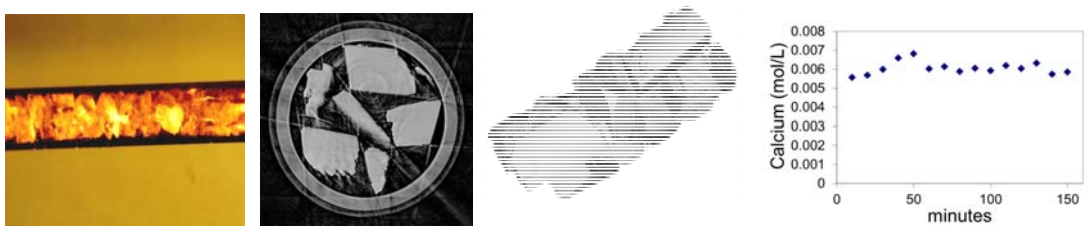


Fig 1. Capillary experiment µCT image computational domain measured effluent Ca

ACCOMPLISHMENT(S): The simulation domain was constructed from the µCT image using implicit functions to represent the mineral surface locally on a grid. Simulations are performed using up to 100,000 processors on NERSC's Cray XE6 Hopper to achieve grid resolutions of 1.16 µm to 2.32 µm. Figure 2 is a plot of simulation results to date. The 2.32 µm resolution run is about 10 times faster than the 1.16 µm resolution run. Equivalent continuum-scale simulation results show significantly higher calcium effluent concentration than pore-scale results. This difference can be attributed to pore-scale effects. These effects are quantified once steady state is reached (> 9 s).

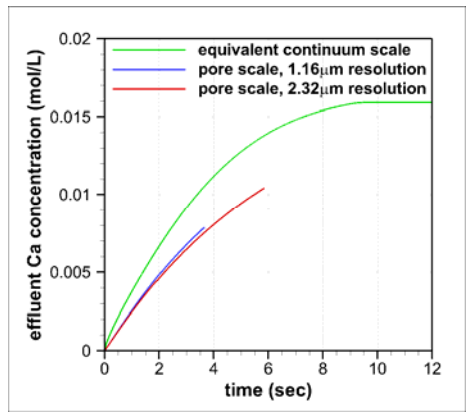


Fig 2. Simulated effluent Ca concentrations

A manuscript that summarizes this effort is in preparation. This work is the first-ever large-scale simulation of reactive transport pore-scale processes on real-pore-space geometry as obtained from experimental data. Pore-scale modeling will be used as a tool for direct upscaling of reaction rates to the continuum scale.

Molins, S., D. Trebotich, C. I. Steefel, and C. Shen (2012), An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation, Water Resour. Res., doi:10.1029/2011WR011404.

Modeling Subsurface Reactive Transport Processes from Mineral to Pore to Continuum

INVESTIGATORS: David Trebotich, Sergi Molins, Carl Steefel

OBJECTIVE: The overall objective is to develop new upscaling approaches for representing chemical kinetics and interfacial dynamics in Darcy-scale numerical models. We hypothesize that a quantitative, mechanistic understanding of coupled physical and chemical processes at the pore-and-grain scale is possible, and that such an understanding can form a rational basis for upscaling fluid dynamics and geochemical kinetics to the field scale.

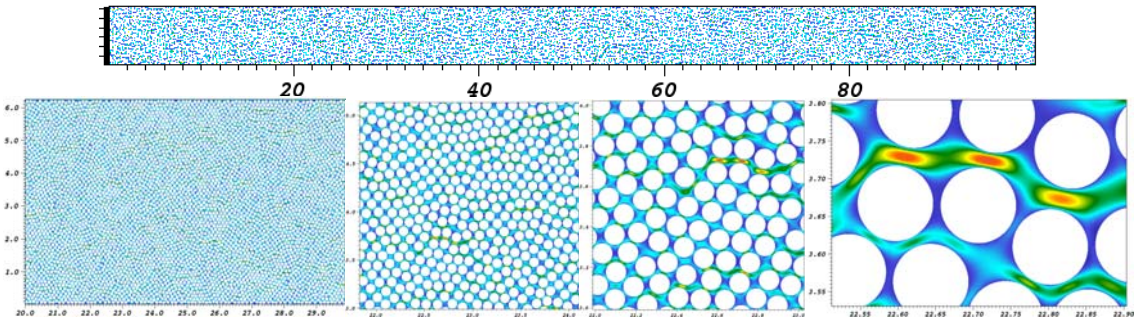
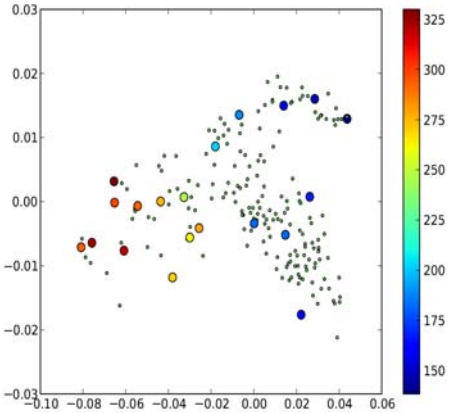


Figure 1: (top) Fluid velocity (red=fast, blue=slow) in 100 cm packed channel; (bot) magnifications of channel: 10cm×6cm, 2cm×2cm, 1cm×1cm, and microscopic pore space. Resolution is 65536×4096 cells (15 micron grid spacing). Porosity is 0.355. Units in cm. Flow is left to right.

ACCOMPLISHMENT(S): Using direct numerical simulation at the pore scale, we are able to completely resolve (to 15 microns) a Darcy-scale domain (1 m) without the use of an effective medium. This capability provides a powerful tool for building a basis for upscaling using both deterministic and stochastic multiscale techniques. In a deterministic approach, we are developing an adaptive model based on the framework in our pore-scale reactive transport code, Chombo-Crunch. At the coarse level, the Darcy equations are solved; at local Darcy gridblocks, the pore-scale equations are solved when model refinement criteria are met. Heterogeneous values of permeability and reaction rates can be derived for the continuum scale. We have validated this capability by comparing results from equivalent continuum and pore-scale solvers for a homogeneous medium. The ability to directly define pore-scale heterogeneity will be used to evaluate the pore scale effects on Darcy-scale phenomena, e.g., scale dependence of reaction rates. Another novel approach is to make use of the topology of the pore space to statistically characterize the pore space. Using an ensemble of pore-scale packings and sample simulations, we have derived a single material descriptor curve that can be sampled to determine the likelihood of permeability with a given packing (porosity and heterogeneity). This work was presented at the February 2013 SIAM Conference for Computational Science and Engineering in Boston.



Permeability derived from topology. Simulated points are enlarged with permeability value in color, demonstrating coverage of entire ensemble by the approach.

CONTROLS ON MINERALIZATION IN VOLCANOGENIC RESERVOIR ROCKS

INVESTIGATORS: Don DePaolo (lead), Carl Steefel, Shuo Zhang

OBJECTIVES: The principal objective is to determine the extent to which CO_2 can be mineralized in sandstone formations for $scCO_2$ sequestration. Volcanogenic sandstones with a relatively high percentage of volcanic rock fragments (VRF) could be a promising target for CO_2 sequestration in that they have a sufficient percentage of reactive minerals to allow substantial mineralization of injected $scCO_2$, which provides the most secure form of CO_2 storage, but can be porous and permeable enough to allow injection at acceptable rates.

ACCOMPLISHMENTS: The limitation in using volcanogenic sandstones as CO_2 reservoir rocks is that porosity and permeability tend to decrease with increase of volcanic rock fragments (VRF) and with the length and complexity of the diagenetic history. Decreased porosity limits the rate at which CO_2 can be injected. We evaluated these tradeoffs to assess the feasibility of using volcanogenic sandstone to achieve highly secure CO_2 storage. Using relationships between VRF percent, porosity and permeability from available geological data, the reactive transport code TOUGHREACT was used to estimate the rate and extent of CO_2 mineralization over 1000 years, and the trade-off between higher reactivity and lower porosity and permeability. The results show that in rocks with 10 to 20% reactive VRF, as much as 80% CO_2 mineralization could occur in 1000 years and still allow sufficient injectivity so that ca. 1 megaton of CO_2 can be injected per year per well. With increasing VRF percentage, the amount of injected CO_2 decreases although the percent of CO_2 mineralized increases. For the parameter set that we believe is defensible, the optimal VRF percent for the amount of mineralized CO_2 is around 15-20%. The key to estimating how much CO_2 can be injected and mineralized is the relationship between permeability (or injectivity) and reactive mineral content. The overall relationships can be reduced to a simple equation that relates the fraction of injected CO2 that becomes mineralized in 1000 years to the volume fraction of reactive minerals. To better quantify the porosity-permeability-reactivity relationships we have sampled examples of volcanogenic sandstones from central California and we are characterizing characterized their mineralogy and permeability. Core flooding experiments are also in progress to obtain realistic reactivity estimates.

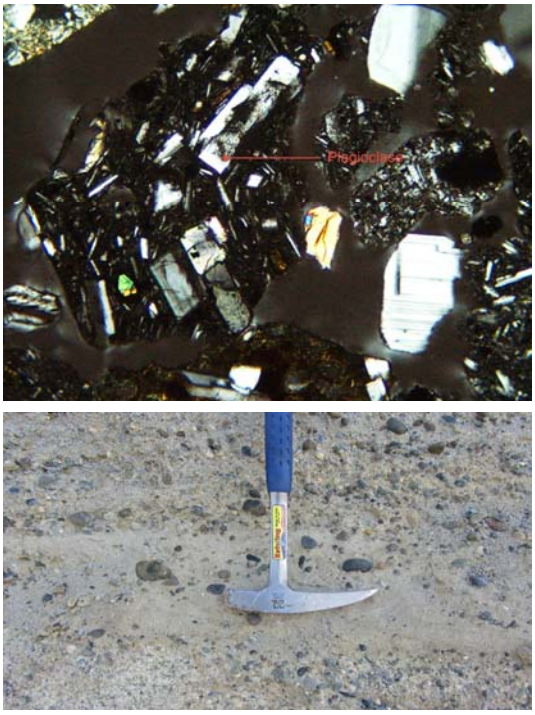


Figure 1: (top) Photomicrograph showing volcanic mineralogy and abundant pore space (bottom) outcrop photo. Miocene Etchegoin Formation, central California

Zhang, S., DePaolo, D.J., Xu, T-F, Zheng, L. (2013) Mineralization of carbon dioxide sequestered in volcanogenic sandstone reservoir rocks. *Greenhouse Gas Technologies* (in press)