Carbon sequestration geochemistry

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It is widely recognized that geologic sequestration of CO_2, when combined with economical means of capture, may be critical to reducing net CO_2 emissions to the atmosphere over the next century while maintaining energy supply for a rapidly developing world. But what does it have to do with geochemistry? Many expect that the trapping of CO_2 in subsurface rock formations (mainly sandstones) will be accomplished primarily by physical means such as low permeability capping formations (shales) or pore scale trapping due to surface tension effects. Geochemistry is viewed as secondary, but actually is important to ensuring efficient and safe long-term storage.

To achieve the full potential of subsurface CO_2 storage, it will be necessary to use as much of the available subsurface pore space in sedimentary formations as possible, and a wide range of sedimentary rock formations, most of which have not been previously characterized, are not entirely composed of large quartz grains, and which have pore space filled with salt-rich aqueous fluid. Injection of CO_2 into saline geologic formations involves forcing a buoyant, low-viscosity fluid into a more dense, higher viscosity fluid. The difference in wetting properties of the two fluids, their partial miscibility, the fact that CO_2 and H_2O form an acid, and the heterogeneity of geologic formations combine to make the flow and transport details fascinating but difficult to characterize and predict. A major question is whether the flow of CO_2 into subsurface formations, the efficiency of pore space filling, and the trapping efficiency can be not only predicted but enhanced over the decades of injection that might be associated with the life of a power plant, and the millenia of storage needed thereafter. There is plenty of geochemistry in this - the effects of nanoscale and microscale confinement on material properties, flow and chemical reactions, the effects of nanoparticles, mineral surface dynamics, and microbiota on mineral dissolution/precipitation and fluid flow, and the dynamics of fluid-fluid and fluid-mineral interfaces. The Holy Grail of fully coupled reactive transport models including thermal, hydrological and mechanical effects may be essential; and isotopic and trace element tracers valuable. Many of the salient geochemical questions revolve around rates of chemical reactions, which remain uncertain for natural systems and a focus of much geochemical research.

Kinetic theory of isotopic and trace element partitioning between calcite and aqueous solution

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Kinetic theory is used to develop a formulation describing how Ca and O isotope fractionation and Sr/Ca ratios of calcite vary as a function of rate of precipitation from aqueous solution. Proximity to equilibrium conditions is determined by the ratio of the net precipitation rate (Rp) to the gross (forward) rate of precipitation (Rf) when transport to the crystal surface is not limiting. Whereas Rp can be measured, Rf requires assumptions. To first order Rf can be deduced from the bulk dissolution rate of calcite into an infinitely undersaturated solution, (Rb). It is posited that $Rf = Rp + Rb$, and hence that equilibrium precipitation takes place only when Rp ($= Rf - Rb$) $<< Rb$. For precipitation rates high enough that $Rp >> Rb$, both the isotopic and trace element partitioning is controlled entirely by the kinetics of ion dehydration and attachment to the mineral surface. For isotopic partitioning, a transition region between kinetic control and equilibrium conditions exists near where $Rp \approx Rb$. The transition region for trace element partitioning is shifted away from $Rp = Rb$ depending on the ratio of the equilibrium to kinetic partition coefficients. For excluded elements like Sr the transition is shifted to higher Rp values. This theory accounts for most of the experimental data in the literature on the dependence of $^{44}Ca/^{40}Ca$ and Sr/Ca fractionation in calcite as a function of precipitation rate, and also accounts for $^{18}O/^{16}O$ variations with some assumptions. The apparent temperature dependence of Ca isotope fractionation in calcite is a result of the dependence of Rb on temperature; there should be analogous pH dependence as well. The theory may be valuable for understanding the fractionation behavior of a range of elements of interest in low-temperature geochemistry. The proposed theory involves 'growth entrapment,' but obviates the need for a model like that of Watson (2004), which requires a fictitious solid-state diffusivity. There is evidence that the mineral-fluid molecular exchange rate, assumed to be equal to a constant Rb (a function of T) in the simplest form of the theory, is in fact dependent on the saturation state and chemical composition of the solution.