2.2.P09

Ion concentration profile near rock pore wall as revealed by centrifugation

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When a porous media is saturated with an aqueous solution, surface charges emerge at the pore wall due to dissociation and adsorption of proton, anion/cation, etc. If the pore wall is negatively charged, cation (or anion) concentration gradually increases (or decreases) as approaching the pore wall. The ion concentration profiles near water-solid interface should reflect an electric double layer. Since a water-solid interface is the place where dissolution and precipitation occur, the ion concentrations near the solid surface provide information on dissolution and precipitation. However, the thickness of an electric double layer is as thin as less than 1 micrometer depending on solution composition, and direct observation of the ion concentration profiles in such a thin water layer is quite difficult.

In this study the composition of pore water in a glass-dominated porous rhyolite (porosity: 21%; pore radius: about 4 nm - 0.5 mm) was studied. To evaluate the composition of pore water, a water-saturated rhyolite block was immersed in an aqueous solution of 50 micromole/L of lithium iodide for a week, and the pore waters were centrifugally extracted with increasing centrifugal force in incremental steps. The analyses of the pore waters revealed that the concentrations of cations (Li^+, Na^+, and Ca^{2+}) increase and those of I^- and Si decrease with increasing centrifugal force. Of these elements, Na^+, Ca^{2+}, and Si dissolved from the rhyolite during one week's immersion. As increasing centrifugal force, it is presumed that water comes out in the order of larger pores to smaller pores or that the thickness of water near pore wall gradually decreases. In either case, the composition of extracted water gradually shifts to those at the water-solid interface (note that the volume fraction of the electric double layer is larger for smaller pore). The increases in the cation concentrations at higher centrifugal force show that the cations are concentrated at the negatively charged pore wall. The decreases in Si and I^- concentrations at higher centrifugal force imply that some Si is in the form of anions such as $SiO(OH)_3^-$ and $Si_4O_6(OH)_6^{2-}$. This is contrast to the presence of electrically neutral $Si(OH)_4$ as a dominant aqueous Si species which is thermodynamically equilibrated with bulk pore water (pH=6-7). These results indicate that the centrifugation technique provide useful information on the composition of the solution near water-solid interface.

2.2.P10

# Experimental study of oxygen isotope exchange between calcite and water

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Calcite is a common phase in many geological environments, as primary particles in soils and sediments and as coatings or cement between grains and as secondary minerals in fractures and veins. The oxygen isotope ratio ($^{18}O/^{16}O$) is a well-known indicator of calcite origin and precipitation temperature. Considerable information about oxygen isotope fractionation between calcite and water already exists in the literature but there is still no consensus on equilibrium fractionation magnitude and on the role of calcite precipitation rate. The aim of this work was to study oxygen isotope fractionation between water and calcite precipitated from electrolyte solutions under well-defined and strictly controlled experimental conditions. Precipitation experiments were carried out using the constant addition technique at 25° C. We used a two-approach method where two companion runs are designed to be identical in every respect, except in the isotopic composition of the starting waters. Results show that the two values of $\Delta_{calcite-water}$ (=$10^3 ln\alpha$) determined for "total" calcite (starting material + overgrowth) approach each other as calcite grows. The average value for each two companion runs are close to 28‰, the average equilibrium value at 25° C published by Kim and O'Neil (1999). Delta values are independent of calcite precipitation rate over the range of
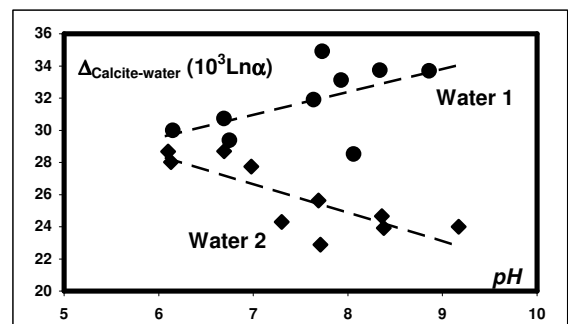
2.8e-10 to 2.3e-8 mol min^{-1} mg^{-1}. However, fractionation does depend on pH. The plot above shows $\Delta_{calcite-water}$ determined for runs with different starting water. Water that was heavier or lighter with respect to expected equilibrium values produced trends that were opposite in slope. These results show that the lower pH is, the closer the measured $\Delta_{calcite-water}$ is to its equilibrium value. This is probably affected by very different rates of $^{18}O/^{16}O$ equilibration between HCO_3^- and CO_3^{2-} and water.