Solubility of carbon dioxide in rock-buffered aqueous fluids

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Modelling of CO₂ behavior in geological storage reservoirs suggests that significant amounts of CO₂ will dissolve in the formation water within periods of years to hundreds of years and that ‘solubility trapping’ will be important in the overall trapping of CO₂. However, the interactions between the fluid phase and the surrounding rock, and their influence on CO₂ solubility, are not well constrained. Most potential CO₂ storage reservoirs involve formation waters with considerable concentrations of Ca²⁺, and the addition of acidity will result in enhanced dissolution of reactive minerals within the rock, potentially leading to even higher Ca²⁺ concentrations. This will significantly affect the solubility of CO₂ (c. f. [1]). At the same time, dissolution of the rock will neutralize some of the added acidity, and this pH-shift will also affect the solubility.

We perform solubility measurements in rock-buffered fluids, at both supercritical and subcritical CO₂ pressures. These experiments have been conducted using a number of pure mineral phases, as well as crushed North Sea sandstones. Intermittent sampling of the fluid phase (in lower-pressure experiments coupled with pH measurements) also allow us to follow the evolution of the system with time.

At constant pCO₂, mineral reactions result in elevated pH relative to the pure fluid system, but different minerals respond at different rates. For typical sandstone formations, the initial dissolution of calcite in response to CO₂ injection will be followed by Ca-Na exchange with clays and further reaction with feldspars. Exchange experiments with Na-exchanged SWy-2 montmorillonite indicate that the Ca:Na ratio of the fluid will adjust on a timescale of days. The results also indicate that while the presence of divalent cations lower the solubility of CO₂, the difference in pH between rock-buffered fluids and unbuffered fluids might actually lead to an increased solubility in rock-buffered fluids.


Redox-dependent, diffusion-driven fractionation of Fe isotopes in silicate melts and its structural controls


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Chemical diffusion of cations and atoms in silicates and metals can promote large isotopic fractionation [1]. Iron isotopes can be used, therefore, to probe various differentiation processes. Here, we evaluate experimentally the effect of the redox state of Fe on diffusion-driven isotopic fractionation.

Diffusion couples were prepared from CaMgSi₂O₆ and Fe-bearing CaMgSi₂O₆ glasses. Experiments were done in a piston-cylinder apparatus at 1 GPa and 1630°C. Samples were either loaded in C capsules to produce melts with all Fe reduced to Fe²⁺ or in a double Pt capsules with PtO₂ buffers to produce melts with oxidized iron (high Fe³⁺/Fe²⁺) and to avoid isotopic fractionation during diffusion of Fe into Pt capsules [2].

There is a significant difference between diffusion coefficients of ferrous and ferric ions - Fe²⁺ diffuses faster than Fe³⁺ by a factor of 1.5. Also, Fe isotopes appear more fractionated by diffusion in reduced melts than in oxidized melts. Relating the diffusion coefficients of ⁵₆Fe and ⁵⁴Fe to their mass ratios through an empirical coefficient, β to model our data, we find that βFe²⁺>βFe³⁺. Because Fe²⁺ and Fe³⁺ do not have the same structural roles in molten silicates [3], our data allows us to provide an interpretative framework to understand and predict variations of β values for a broad range of elements in various materials