Solubility of carbon dioxide in rock-buffered aqueous fluids

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Modelling of CO_2 behavior in geological storage reservoirs suggests that significant amounts of CO_2 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 CO_2. However, the interactions between the fluid phase and the surrounding rock, and their influence on CO_2 solubility, are not well constrained. Most potential CO_2 storage reservoirs involve formation waters with considerable concentrations of Ca^{2+}, and the addition of acidity will result in enhanced dissolution of reactive minerals within the rock, potentially leading to even higher Ca^{2+} concentrations. This will significantly affect the solubility of CO_2 (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 CO_2 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 pCO_2, 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 CO_2 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 CO_2, the difference in pH between rock-buffered fluids and unbuffered fluids might actually lead to an increased solubility in rock-buffered fluids.

[1] Duan & Sun (2003), *Chemical Geology* **193**, 257-271.

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 $CaMgSi_2O_6$ and Fe–bearing $CaMgSi_2O_6$ 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 Fe^{2+} or in a double Pt capsules with PtO_2 buffers to produce melts with oxidized iron (high Fe^{3+}/Fe^{2+}) 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 - Fe^{2+} diffuses faster than Fe^{3+} 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 ^{56}Fe and ^{54}Fe to their mass ratios through an empirical coefficient, β to model our data, we find that $\beta Fe^{2+} > \beta Fe^{3+}$. Because Fe^{2+} and Fe^{3+} 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

[1] Richter *et al.* (2009) *Chem. Geol.* **258**, 92-103. [2] Roskosz *et al.* (2006) *Earth Planet. Sci. Lett.* **248**, 851–867. [3] Mysen *et al.* (1985) *Am. Min.* **70**, 317-322.