

## Short-term CO<sub>2</sub>-fluid-mineral interactions in a CO<sub>2</sub> injection experiment, Wyoming

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During geological CO<sub>2</sub> storage short-term geochemical processes will be dominated by dissolution of CO<sub>2</sub> into the formation fluid and by the reaction of this acidic fluid with soluble minerals (e.g. carbonate, oxide, sulphide and organics) in the reservoir. Modelling the progress of the fluid-mineral reactions is frustrated by uncertainties in the absolute mineral surface reaction rates [1] and the significance, in natural systems, of CO<sub>2</sub> dissolution and transport in formation fluid as an overall rate limiting step.

We present preliminary results of water chemistry from an artificial noble gas tracer study in a commercial CO<sub>2</sub>-EOR reservoir located in Wyoming, USA. In this study a noble gas spike (<sup>3</sup>He & <sup>129</sup>Xe) was introduced to a single CO<sub>2</sub> injection well [2], and fluids and gases collected from the surrounding four-point production well pattern, from September 2010 to February 2011. Preliminary results from fluid chemistry measured over this period reflect: (1) mobilization and mixing of formation water, driven by the injection of CO<sub>2</sub>; (2) the arrival of co-injected water and CO<sub>2</sub> at the production wells and; (3) dissolution of the CO<sub>2</sub> and subsequent reaction of this acidified fluid with soluble minerals in the reservoir. The spatial changes in fluid chemistry are consistent with the reservoir geology; the updip producers are dominated by processes related to the early arrival of the CO<sub>2</sub> front whereas changes in downdip fluid chemistry are dominated by the arrival of dense saline fluid from the injection well. Sigmoidal fronts in fluid chemistry are observed in the updip production wells, and correlate with changes in fluid temperature, a measure of CO<sub>2</sub> breakthrough. Elevated concentrations of divalent cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup>), in excess of the original pore fluid and injected water, are thought to represent dissolution of carbonate minerals in the reservoir which drives neutralization of fluid acidity and progressively increasing fluid alkalinity.

[1] Kampman *et al.* (2009) *Earth Planet. Sci. Lett.* **284**, 473–488. [2] Zhou *et al.* (2011) This issue.

## Multiple sulfur isotope fractionation during sulfur cycling in a warm, monomictic lake with sub-millimolar sulfate concentration

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Sub-millimolar concentrations of sulfate likely prevailed in the Archean Ocean. We studied the concentrations and quadruple isotope fractionation of sulfur species in the warm, monomictic Lake Kinneret (Tiberias), which has sulfate concentrations of <600 μM. The highest concentrations of zero-valent sulfur (ZVS), thiosulfate and sulfite occurred in the redox-transition zone (RTZ, c. a. 28 m depth), and were 5.0 μM, 1.35 μM and 0.76 μM, respectively.

In the vicinity of the RTZ, the δ<sup>34</sup>S fractionations between sulfide and sulfate are small (-17 – -21‰), with large positive Δ<sup>33</sup>S values (0.067 – 0.086 ‰), and can be attributed to sulfate reduction. ZVS is 0.1 – 4.7‰ more enriched in <sup>34</sup>S than sulfide, consistent with equilibrium isotope effects between sulfide – polysulfide – rhombic sulfur and fractionation via phototrophic sulfide oxidation.

In the deeper waters, δ<sup>34</sup>S fractionations between sulfide and sulfate are larger (-37 – -44‰), with smaller differences in Δ<sup>33</sup>S (0.009 – 0.073‰). Sulfur isotope values near the bottom of the lake can be explained by a combination of sulfate reduction and sulfur compounds disproportionation. High sulfur isotope fractionation is supported in this system even at very low sulfate concentrations by both the absence of sulfide scavenging by dissolved Fe (II) and the presence of the RTZ, where sulfide oxidation supplies zero-valent sulfur to deeper sulfidic waters.