Does reservoir rock integrity change during geological CO_2 storage in a saline aquifer?

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At Ketzin in the federal state of Brandenburg, Germany, CO_2 is injected into a saline aquifer of the Upper Triassic Stuttgart Formation, since June 2008. Ketzin is the first European onshore pilot site for the geological storage of CO_2. To evaluate CO_2-fluid-rock interactions, two sets of long-term CO_2-exposure experiments were carried out. One set on reservoir rock (described here), the other on cap rock (data in process). Core samples of Ketzin reservoir sandstone were exposed to pure CO_2 and synthetic reservoir brine at simulated in-situ P-T conditions of 5 MPa and 40 °C. Mineralogical and geochemical analyses were performed on rock and fluid samples taken after 15, 21, 24, and 40 months, respectively. Over time, XRD data with Rietveld refinement show decreasing proportions of analcime, chlorite, hematite and illite, and increasing proportions of quartz. On freshly broken rock fragments, CO_2-treated samples display corrosion textures on plagioclase, K-feldspar and anhydrite surfaces. EMPA data exhibit a change in plagioclase composition from intermediate to Na-rich and albite endmember compositions. Compared to the synthetic reservoir brine, Na^+, Mg^{2+} and Cl^- concentrations increased slightly, while K^+, Ca^{2+} and SO_4^{2-} concentrations increased significantly. Reactive geochemical modeling using PHREEQC-2 code was performed to reproduce experimental observations.

The mineralogical and geochemical measurements imply preferred dissolution of Ca^{2+} out of plagioclase next to dissolution of K-feldspar and anhydrite. Petrophysical data show tendentially increasing porosities and permeabilities [1] also suggesting mineral dissolution during the experiments. Due to the heterogeneous character of the Stuttgart Formation, which formed in a fluvial environment [2], it is often difficult to distinguish between natural, lithostratigraphic variability and CO_2-related changes. Assuming thermodynamic equilibrium, preliminary reactive geochemical modeling of the observed CO_2-fluid-rock interactions shows that the measured evolution of fluid composition is consistent with precipitation of albite and dissolution of anhydrite and illite, respectively. Based on experimental data, the integrity of the Ketzin reservoir is not significantly affected by CO_2.

[1] Zemke et al. (2010) *Petrophysical analysis to investigate the effects of carbon dioxide storage in a saline aquifer at Ketzin, Germany (CO_2SINK).* Int J Greenhouse Gas Control; doi: 10.1016/j.ijggc.2010.04.008.
[2] Förster et al. (2006) *Baseline characterization of the CO_2SINK geological storage site at Ketzin, Germany.* Environ Geoscience, 13, 3, 145-161; doi:10.1306/eg.02080605016.

Ru isotope anomalies in meteorites

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Nucleosynthetic isotope anomalies in bulk meteorites have been documented for some siderophile elements (e.g., Ni, Ru, Mo) [1-4] but seem to be absent for others (e.g. Os) [5]. The contrasting isotope systematics of these chemically similar elements may place important constraints on the extent and efficiency of mixing processes as well as pathways of material transport within the early solar nebula. So far, only a limited number of samples have been investigated for Ru and nucleosynthetic anomalies have been mainly reported for magmatic iron meteorites [3]. These Ru isotope anomalies correlate with those in Mo exactly as predicted from s-process nucleosynthesis, supporting evidence for a heterogeneous distribution of s-process carrier phases [1,4]. To further investigate the extent of Ru isotope anomalies in meteorites and to evaluate the significance of the cosmic Mo-Ru correlation we developed new analytical techniques for precise Ru isotope measurements by multicollector inductively coupled mass spectrometry (MC-ICPMS). We present new Ru isotope data for IVB iron meteorites, the ungrouped iron Chinga, and the CB chondrite Gujba. Ruthenium isotope compositions were measured using the ThermoScientific Neptune Plus at the University of Münster and are reported in ε^iRu-deviation from terrestrial Ru. For mass bias correction relative to ^{99}Ru/^{101}Ru all samples show a well resolved negative anomaly in ε^{100}Ru, consistent with previous data for IVB irons [3]. There are also hints for positive anomalies in ε^{96}Ru and ε^{98}Ru and negative anomlies in ε^{102}Ru but these are not yet clearly resolved. When normalized to ^{99}Ru/^{100}Ru all samples show resolvable deficits in ε^{96}Ru and large enrichments in ε^{101}Ru, ε^{102}Ru and ε^{104}Ru. Small deficits in ε^{98}Ru seem to be present as well but are currently not well resolved. The observed Ru isotope patterns are in excellent agreement with anomalies predicted for a deficit in s-process isotopes according to the stellar model of nucleosynthesis [6], consistent with previuosly reported data [3]. The CB chondrite Gujba plots on the Mo-Ru correlation line for a s-process deficit, indicating that the cosmic Mo-Ru correlation also extends to relatively young carbonaceous chondrites. However, more high-precision Ru isotope data for chondrites are needed to further evaluate the correlated behaviour of Mo and Ru anomalies in case of carbonaceous chondrites. A companion study on the same IVB irons did not find evidence for nucleosynthetic Pt isotope anomalies [7], indicating that in contrast to Ru and Mo, the solar nebula was well mixed with regard to Pt (and Os [5]) isotopes. The contrasting isotope systematics of Os, Ru and Pt may thus be related to thermal processes within the nebula, rather than reflecting a primordial heterogeneity in the distribution of presolar dust.

[1] Dauphas et al. (2002) *ApJ* **565**, 640-644. [2] Regelous et al. (2008) *EPSL* **272**, 330-338. [3] Chen et al. (2010) *GCA* **74**, 3851-3862. [4] Burkhardt et al. (2011) *EPSL* **312**, 390-400. [5] Yokoyama et al. (2007) *EPSL* **259**, 567-580. [6] Arlandini et al. (1999) *ApJ* **525**, 886-900. [7] Kruijer et al. (2012) *LPSC* **XLIII**, #1529.