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**Dissertation Title:**

Mineralogical-geochemical effects during geological storage of CO<sub>2</sub> – Experimental investigations and geochemical modeling

**Abstract:**

In order to analyze mineralogical-geochemical changes occurring in whole rock reservoir samples (Stuttgart Formation) from the Ketzin pilot CO<sub>2</sub> storage site, Brandenburg/Germany as well as to investigate single fluid-mineral reactions laboratory experiments and geochemical modeling were performed. The whole rock core samples of the Stuttgart Formation were exposed to synthetic brine and pure CO<sub>2</sub> at experimental P-T conditions and run durations of 5.5 MPa/40 °C/40 months for sandstone and 7.5 MPa/40 °C/6 months for siltstone, respectively. Mineralogical changes in both sets of experiments are generally minor making it difficult to differentiate the natural variability of the whole rock samples from CO<sub>2</sub>-induced alterations. Results of sandstone experiments suggest dissolution of analcime, anhydrite, the anorthite component of plagioclase, chlorite + biotite, hematite and K-feldspar. Dissolution of anhydrite, the anorthite component of plagioclase and K-feldspar is also observed in siltstone experiments.

During equilibrium simulations best matching models were ranked based on a mathematical-statistical dispersion relation. The best matching model comprises a mineral combination of the albite component of plagioclase, anhydrite, dolomite, hematite, and illite. The equilibrium modeling showed that it is difficult to match K<sup>+</sup>, Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> brine concentrations simultaneously. The best matching subsets of the equilibrium models were finally run including kinetic rate laws. These kinetic simulations reveal that experimentally determined brine data was well matched, but reactions involving K<sup>+</sup> and Fe<sup>2+</sup> were not completely covered. Generally larger mismatches for dissolved Al<sup>3+</sup> and Si<sup>4+</sup> in all the completed simulations are most likely related to the sampling strategy and respective inaccuracies in the measured concentrations of dissolved Al<sup>3+</sup> and Si<sup>4+</sup>. The kinetic simulation suppressing mineral precipitation yields best matches with experimental observations. The modeling shows acceptably well matches with measured brine ion concentrations, and the modeling results identified primary minerals as well as key chemical processes. It was also shown that the modeling approach is not capable of completely covering complex natural systems.

Experiments on mineral separates were conducted with 2 M NaCl brine and pure CO<sub>2</sub> using siderite, illite and labradorite samples. Experimental P-T conditions were 20 (30) MPa and 80 °C; run durations were one (siderite), two (illite) and three weeks (labradorite), respectively. Based on the acquired set of mineralogical-geochemical data the distinct experiments show: (i) dissolution of ankerite and stable siderite, which is therefore interpreted to be a potential CO<sub>2</sub> trapping phase, (ii) preferred dissolution of the Ca-smectite component out of the illite-smectite mixed-layer mineral and (iii) dissolution of labradorite, respectively.

No mineral precipitates (e.g. carbonate phases) were detected in any of the conducted laboratory experiments, and only one single kinetic simulation predicts the formation of minute amounts of dolomite.

Based on the data acquired during this dissertation the mineralogical-geochemical effects of CO<sub>2</sub> are minor, and the (chemical) integrity of the Ketzin reservoir system is not significantly affected by injected CO<sub>2</sub>.