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Reservoir rock integrity of the Ketzin pilot storage site (Germany) during long-term CO_2-exposure experiments - Mineralogical, petrophysical and geochemical modeling results

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In order to investigate CO_2-brine-rock interactions occurring at the Ketzin pilot storage site, core samples of the siliciclastic reservoir rock were exposed to pure CO_2 and synthetic reservoir brine at simulated in-situ P-T conditions of 5 MPa and 40 °C. Autoclaves were opened and rock and fluid samples taken after 15, 21, 24 and 40 months, respectively. The samples were analysed for mineralogical and chemical composition and compared to baseline data of untreated samples. XRD data with Rietveld refinement show decreasing weight percentages for analcime, chlorite, hematite and illite. While plagioclase as well as K-feldspar both do not reveal a coherent trend over time, quartz exhibits increasing weight percentages in the same interval. On freshly broken rock fragments corrosion textures were found on plagioclase, K-feldspar and anhydrite surfaces of CO_2-treated samples. BSE images of the respective samples indicate (intensified) alterations of feldspar minerals. EMPA data display a change in plagioclase composition from intermediate to sodium-rich and albite endmember compositions during CO_2 exposure. Compared to the synthetic brine used for the experiments, sodium, magnesium and chloride concentrations increased slightly, while potassium, calcium and sulfate concentrations significantly increased. Potassium and calcium even exceed reservoir brine concentration levels. Experimental observations were reproduced using the reactive geochemical modeling code Phreeqc-2.

The mineralogical and geochemical measurements imply preferred dissolution of calcium out of plagioclase next to dissolution of K-feldspar and anhydrite. Petrophysical data show tendentially increasing porosities and permeabilities that also suggest mineral dissolution during the experiments. Due to the heterogeneous character of the Stuttgart Formation 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. In a next step, kinetic data have to be included into the model to determine changes over time. Based on experimental data, the integrity of the Ketzin reservoir is not significantly affected by CO_2.