

## Long-term CO<sub>2</sub>-exposure experiments – Mineralogical results and reactive geochemical modeling

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Rock core samples of the Upper Triassic Stuttgart Formation (saline aquifer) from the Ketzin pilot CO<sub>2</sub> storage site were exposed to pure CO<sub>2</sub> and synthetic reservoir brine at simulated reservoir P-T conditions (5 MPa, 40 °C). Autoclave reactors were opened and samples were taken after 15, 21, 24 and 40 months, respectively. The samples were then analysed mineralogically and geochemically and compared to baseline data of untreated samples. Rietveld refined XRD data show no significant trends for the studied intervals. On freshly broken rock fragments of the CO<sub>2</sub>-treated samples, corrosion textures were found on plagioclase, K-feldspar and anhydrite surfaces. BSE images of the respective twin samples show (intensified) alterations of feldspar minerals. EMPA data display a change in the mineral chemistry of plagioclase, namely a preferred occurrence of sodium-rich endmember compositions after CO<sub>2</sub> exposure. Inorganic fluid data show, besides others, highly increased calcium, potassium and sulfate concentrations [1]. The experimental observations were reproduced using the reactive geochemical modeling code PHREEQC.

The mineralogical-chemical measurements imply preferred dissolution of calcium out of plagioclase (albitization) next to dissolution of K-feldspar and anhydrite. Due to the heterogenic character of the Stuttgart Formation, which formed in a fluvial environment [2], it is often difficult to distinguish between natural variability and CO<sub>2</sub>-related changes. Additional profound evaluation is needed to interconnect the indicated changes during the experiments and to better understand CO<sub>2</sub>-brine-rock interaction occurring within the Ketzin reservoir.

[1] Wandrey, *et al.* (2011). Monitoring petrophysical, mineralogical, geochemical and microbiological effects of CO<sub>2</sub> exposure – Results of long-term experiments under in situ condition. *Energy Procedia* **4**, 3644-3650, doi: 10.1016/j.egypro.2011.02.295. [2] Förster *et al.* (2006). Baseline characterization of the CO<sub>2</sub>SINK geological storage site at Ketzin, Germany. *Environ Geoscience*, **13**, 3, 145-161.

## A dynamic Archean sulfur cycle

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Many aspects of the Earth's early sulfur cycle, from the origin of mass anomalous fractionations to the scale and degree of biological involvement, remain poorly understood. We have been studying the nature of multiple sulfur isotope (<sup>32</sup>S, <sup>33</sup>S, and <sup>34</sup>S) signals using a novel combination of scanning high-resolution low-temperature superconductivity SQUID microscopy and secondary ion mass spectrometry (SIMS) techniques in a suite of samples from distal slope and basinal environments adjacent to a major Late Archean-age (~2.6-2.52 Ga) carbonate platform. Coupled with petrography, these techniques allow us to interrogate, at the same microscopic scale, the complex history of mineralization in samples containing diverse sulfide-bearing mineral components. Because of a general lack of Archean sulfate minerals, we focused our analyses on early diagenetic pyrite nodules, precipitated in surface sediments. This allows us to assay fractionations by controlling for isotope mass balance.

These rocks record meaningful differences in sulfur isotopic composition at microscopic scales. We observe large gradients in  $\Delta^{33}\text{S}$  (> 5‰) over short length scales, pointing to substantial environmental heterogeneity and dynamic mixing of sulfur pools. Petrography and magnetic imaging demonstrate that these mass anomalous fractionations were clearly acquired prior to burial and compaction. We also commonly observed large radial  $\delta^{34}\text{S}$  gradients (> 20‰) in nodules, from low values near their centers, increasing to heavier values near their rims. These observations imply that microbial sulfate reduction was a conspicuous metabolism during organic diagenesis in environments with particularly high rates of organic carbon delivery.