# Geochemical effects of $CO_2$ on brine-saturated reservoir sandstones

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## Long-Term $CO_2$ Exposure Experiments

In order to investigate geochemical changes during geological $CO_2$ storage in a saline aquifer, core samples from the target horizon (Upper Triassic Stuttgart Formation) at Ketzin, Germany, have been saturated with synthetic reservoir brine and exposed to $CO_2$ at simulated *in situ* P-T-conditions of 5.5 MPa and 40°C. After 15 months, a first set of samples was removed from the high quality steel autoclaves and compared with their untreated twin samples. Supplementary core samples have been taken out after 21 and 24 months, respectively. Further core fragments will remain in the pressure vessels for longer-term experiments.

## Discussion of Results

The samples are mainly fine-grained, well to moderately-well sorted and weakly consolidated sandstones. Quartz and plagioclase are the major components, while K-feldspar, white & dark mica, hematite, chlorite and illite are present in minor and varying amounts. Cements occur as isolated, poikilitic patches and are composed of analcime, anhydrite and subordinate dolomite. The plagioclase composition determined by EMP analysis indicates preferred dissolution of the Ca-component and a trend toward Na-rich compositions up to pure albite (albitization) during the experiments. Additionally, XRD data suggest anhydrite dissolution in the course of $CO_2$ exposure. SEM micrographs show corrosion textures, such as dissolution holes, etched pits and lamellae, on mineral surfaces of e.g. plagioclase and K-feldspar. Unaltered, idiomorphic albite grains of some $CO_2$-treated samples suggest albite precipitation. The chemical evolution of the brine displays increased $Ca^{2+}$ concentrations [1] in line with the preferred dissolution of anorthitic plagioclase and anhydrite.

[1] Wandrey *et al.* (2010) 'Monitoring petrophysical, mineralogical, geochemical & microbiological effects of $CO_2$ exposure–Results of long-term experiments under *in situ* condition.' *GHGT* **10**, submitted.

# Time-resolved XRD of the siderophore-promoted dissolution of birnessite

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We used synchrotron time-resolved X-ray diffraction (TR-XRD) to track the complete dissolution of birnessite, a layered Mn (III, IV) oxide, by a siderophore. Siderophores are biogenic molecules that can significantly influence the cycling of transition metals in soils. Researchers have demonstrated that siderophores break down Mn oxide minerals through the formation of siderophore-Mn complexes in solution (*e.g.* [1]). Previously, we explored the reductive dissolution of birnessite by membranes of *Shewanella oneidensis* [2]. In the present study, we wanted to compare the crystallographic effects of membrane-mediated and siderophore-promoted dissolution. Using a flow-through reaction cell, we monitored birnessite dissolution via desferrioxamine B (DFOB) (0.01 and 0.001 M). X-ray diffraction experiments were conducted at the Advanced Photon Source beamline 13 BM-C, and diffraction patterns were collected every 70 s.

In all experiments, the loss of birnessite increased linearly with time until its complete disappearance. Rietveld analysis revealed no significant change in unit-cell parameters until ~70 wt% of the birnessite had dissolved. Beyond this point, the birnessite *c*-axis decreased by a small (~0.01 Å) amount. This contraction was an order of magnitude smaller than that associated with membrane-mediated dissolution. Based on our Scherrer particle size analysis, we postulate that the slight decrease in *c* during siderophore dissolution represents nanoscale strain rather than structural distortion due to multiple redox reactions, as occurred during membrane-mediated dissolution. Our results reveal for the first time that *in situ* crystallographic analyses of dissolving solids can distinguish among different mechanistic pathways of structural collapse.

[1] Duckworth & Sposito (2007) *Chem. Geol.* **242**, 497–508.
[2] Fischer *et al.* (2008) *Am. Min.* **93**, 1929–1932.