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Mineralogical responses to 9-years of interaction of a CO_2-charged brine with a sandstone aquifer: Observations from the Ketzin CO_2-storage pilot site (Germany)

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Background information

The Ketzin CO_2-storage pilot site is located 30 kilometers west of Berlin in the Northeast German Basin, a sedimentary basin containing Paleozoic to Cenozoic sediments. The reservoir for CO_2 injection is the Upper Triassic Stuttgart Formation. The site was developed in 2007 with the drilling of three boreholes (the Ktzi 200, 201, and 202 boreholes). At that time, the first drillcore was recovered from the reservoir formation prior to injection. This core material was studied for a baseline characterization of the reservoir (Förster et al., 2010). In August 2012, the Ktzi 203 borehole was drilled on the site and additional core material was retrieved. This core sampled the reservoir formation after 4 years of CO_2 injection, which started in August 2008 (Ktzi 201 borehole) and ended in August 2013. During this time, about 67,100 t of CO_2 were injected at depth of 630–700 m into the Stuttgart Formation (formerly Schilfsandstein).

Prior to the abandonment of the Ktzi 203 borehole in 2017, two sidetracks were drilled in this borehole at depths of 624.1–654.5 m and 641.5–662.7 m, and additional core was retrieved from the track drilling. The study of core material from these tracks is the major issue of this report.

The core recovered from the Ketzin drillings offered the unique possibility to study the fluid–rock interactions linked with the CO_2 injection/storage under semi in-situ conditions. The study of core material from a CO_2 storage site differs from common approaches, which base on autoclave experiments.

Introductory remarks to the report

This report compiles observations made within a time frame of two months on 24 representative thin-section samples representing the periods before and after 4- and 9-years of injection of CO_2 into the reservoir. Given this short period of time until completion of this report, some observations and conclusions drawn have to be judged preliminary. Further analytical work and in-depth interpretation of the results are underway. Information provided for the period 0–4 years after CO_2 injection include observations made by S. Bock in the framework of her not yet finished Ph.D. thesis.

Considering that drillcores for the 9-years period were not available for the entire Stuttgart Formation reservoir, comparison of results was made only for its uppermost portion below the caprock, where the sandstone/siltstone lithology was thickest (~ 30 m) and the amount of carbon dioxide penetrating the sediment largest (Fig. 1).

Analytical techniques applied encompass optical microscopy (Table 1) and (yet only on a subset of samples listed in Table 1) qualitative and quantitative electron-probe microanalysis, combined with backscatter-electron (BSE) imaging (EPMA).

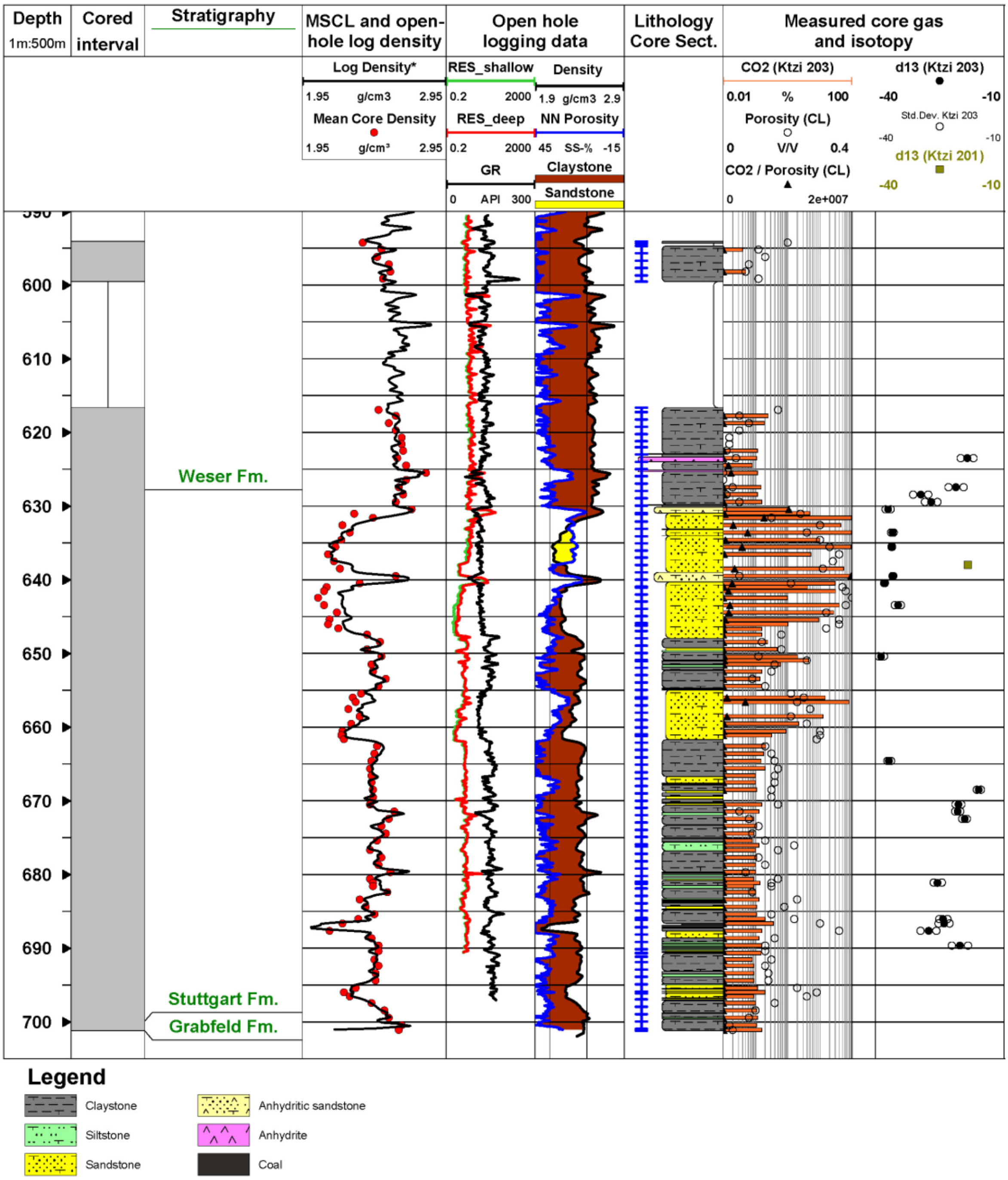


Figure 1. Lithological profile of the CO2 Ktzi 203 borehole

Table 1. Samples from CO2 Ktz203 borehole studied by optical microscopy

Before injection	After 4 years	After 9 years
A-12-1a (633.16 m)	F-5-5/1 iK (630.54 m)	
A-12-1a (633.16 m)	F-5-6 iK (630.98 m)	KM 8-2-11_16 (631.33 m)
A-13-1aP (635.75 m)	F-6-5 iK (635.37 m)	KM 11-1-9_71 (635.71 m)
A-13-1aP (635.75 m)/ A-13-3	F-7-3b iK (638.74 m)	KM 12-2-8_37 (637.55 m)
A-15-3 (644 m)	F-8-4 iK (644.69 m)	KM 16-2-7_72 (644.78 m)
-	F-9-2 KR (647.67 m)	KM 2-1-5 (648.74 m)
-	F-9-2 KR (647.67 m)	KM 7-1-4 (648.84 m)
-	F-10-4 red & gray (654.84 m & 654.99 m)	KM 13-1-3 (655.42 m)
-	F-11-1 iK (656.15 m)	KM 15-1_2 (657.19 m)
-	F-11-5b (660.76 m)	KM 19-1-1 (661.19 m)

Results

The most important observations obtained by optical microscopy of the thin sections listed in Table 1 are compiled below (Table 2). Note that not all of these observations have yet been verified by electron-microprobe imaging and analysis. They were used in conjunction with the results of earlier studies on the reservoir rock before and after 4 years of CO_2 interaction to describe the mineralogy of the CO_2-flooded sandstone unit and the recognized changes as function of time.

Table 2. Microscopic observations on pore-filling mineralogy as function of time

cap rock	before injection	after 4 years of CO_2 injection	after 9 years of CO_2 contact
Schilfsandstein reservoir	A-12-1a (633.16 m) Pore-filling minerals: analcime and anhydrite.	F-5-5/1 iK (630.54 m) Unchanged. F-5-6 iK (630.98 m) Unchanged.	KM 8-2-11_16 (631.33 m) Mostly unchanged. Increased number of Fe-coating on detrital minerals.
	A-13-1aP (635.75 m) Pore-filling minerals: analcime and anhydrite.	F-6-5 iK (635.37 m) Analcime and anhydrite. Formation of Calcite-I. F-7-3b iK (638.74 m) Analcime and anhydrite. Formation of siderite-I and calcite-I.	KM 11-1-9_71 (635.71 m) No anhydrite. Abundant newly formed calcite-II. KM 12-2-8_37 (637.55 m) Minor anhydrite. Pore-filling calcite-II.
	A-15-3 (644 m) Pore-filling minerals: analcime and anhydrite.	F-8-4 iK (644.69 m) Analcime and anhydrite. Formation of calcite-I. F-9-2 KR (647.67 m) Analcime and anhydrite. Formation of calcite-I.	KM 16-2-7_72 (644.78 m) Minor anhydrite. Calcite-II rimming clasts. KM 2-1-5 (648.74 m) No anhydrite. Tiny calcite crystals. Formation of a yet undefined Fe-Ca-phase. KM 7-1-4 (648.84 m) No newly formed minerals because of strong cementation.
		F-10-4 (654.84 m, 654.99 m) Pore filling minerals visible. NaCl and KCl present.	KM 13-1-3 (655.42 m) No newly formed minerals.
		F-11-1 iK (656.15 m) Pore filling minerals visible. Formation of a Fe-Ca phase.	KM 15-1_2 (657.19 m) Formation of larger calcite crystals.
		F-11-5b (660.76 m) No anhydrite. More open pores. Formation of Ca-phases.	KM 19-1-1 (661.19 m) No anhydrite. No newly formed minerals.

Baseline situation

The lithology of the Stuttgart Formation at Ketzin, situated at a depth of about 630–700 m, is well known from core material and well logs (Förster et al., 2010; Norden et al., 2010). The formation is lithologically heterogeneous and made up by fluvial sandstones and siltstones interbedded with mudstones, all displaying remarkable variations in porosity. The thickest sandstone units, which are the target of the present report, are associated with channel sandstone and considerably vary in thickness over short lateral distance (9–20 m).

The dominantly fine-grained and well to moderately-well sorted, immature sandstones classify as feldspathic litharenites and lithic arkoses. Quartz (22–43 wt.%), plagioclase (19–32 wt.%), and K-feldspar (5–13 wt.%) predominate mineralogically. Muscovite plus illite and mixed-layer minerals are omnipresent (4–13 wt.%). Quartz, feldspar, as well as meta-sedimentary and volcanic rock fragments comprise the most abundant detrital components, which often are rimmed by thin, early diagenetic coatings of ferric oxides, and locally of clay minerals. Feldspar grains may be unaltered and optically clear, partially to completely dissolved, partially altered to sheet silicates (mainly illite), or albitized (Fig. 2). Analcime and anhydrite constitute the most widespread and often spatially associated pore-filling cement minerals. Authigenic dolomite, barite, and coelestine are subordinate. The percentage of cements ranges in total from about 5 vol.% to 32 vol.%. Except of samples intensely cemented by anhydrite and analcime, total porosities of the sandstones range from 13% to 26%. The fraction of intergranular porosity varies between 12% and 21%. About 1–5% porosity has been generated by dissolution of detrital plagioclase, K-feldspar, and volcanic rock fragments. Conclusively, these sandstones are comparatively rich in minerals that may potentially react with the injected CO_2.

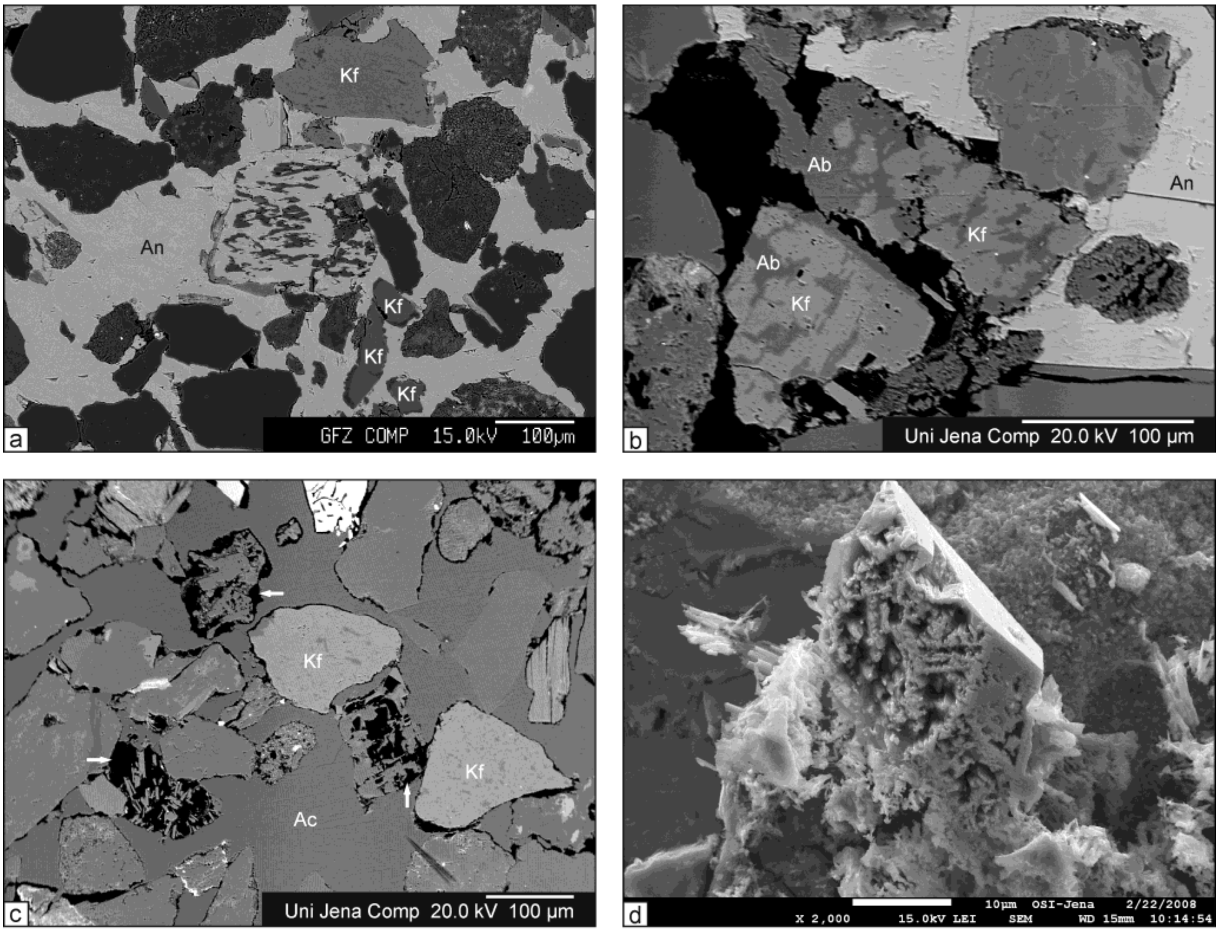


Figure 2. **Baseline situation:** BSE images of thin section (a-c) and a SE image (d) of broken rock surface of sandstones of the Stuttgart Formation at Ketzin as baseline observations prior to CO_2 contact. (a) K-feldspar grain replaced during diagenesis by anhydrite (An) cement. Albite lamellae in the detrital grain (dark gray) remained largely unaffected. Other K-feldspar grains (Kf), partly with albite rims (dark grey), were not affected by replacement. (b) Replacement of detrital K-feldspar (Kf) by albite (Ab). (c) Intensely dissolved plagioclase grains or plagioclase-rich volcanic rock fragments (white) arrows; pore-filling analcime (Ac) cement. K-feldspars (Kf) grains remained unaffected by dissolution. (d) Partially dissolved detrital plagioclase

4 years after CO_2 injection

Although the sandstone/siltstone reservoir has experienced continuous CO_2 injection since a couple of years, substantial changes of its mineralogical composition and petrophysical properties (porosity, permeability) could not yet be recognized neither macroscopically nor microscopically. Preexisting detrital species and authigenic minerals remained virtually unaltered and miss signs of noticeable corrosion and dissolution. Hematite ± clay-mineral (preferentially illite) coatings on mineral surfaces appear neither chemically affected nor mechanically destructed. The only yet established consequence of reaction with CO_2 is the precipitation of minor amounts (< 1 vol.%) of carbonates comprising Ca-rich siderite-I postdated by S-bearing calcite-I or monohydrocalcite (Fig. 3). Even more subordinate is a second generation of calcite characterized by being not associated with siderite (not shown here). Eventually, nucleation of all these species was supported by microbial activity.

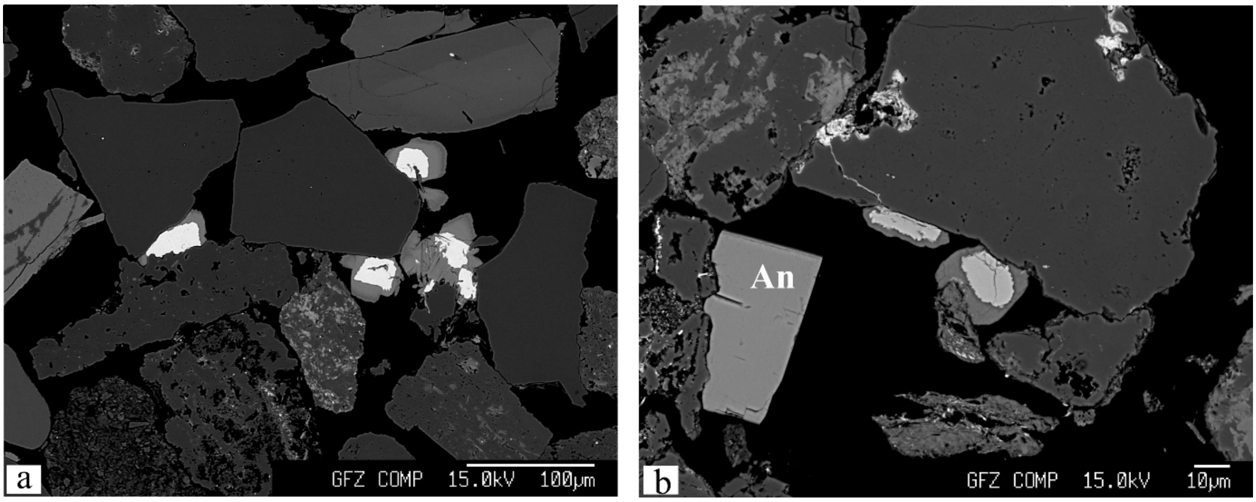
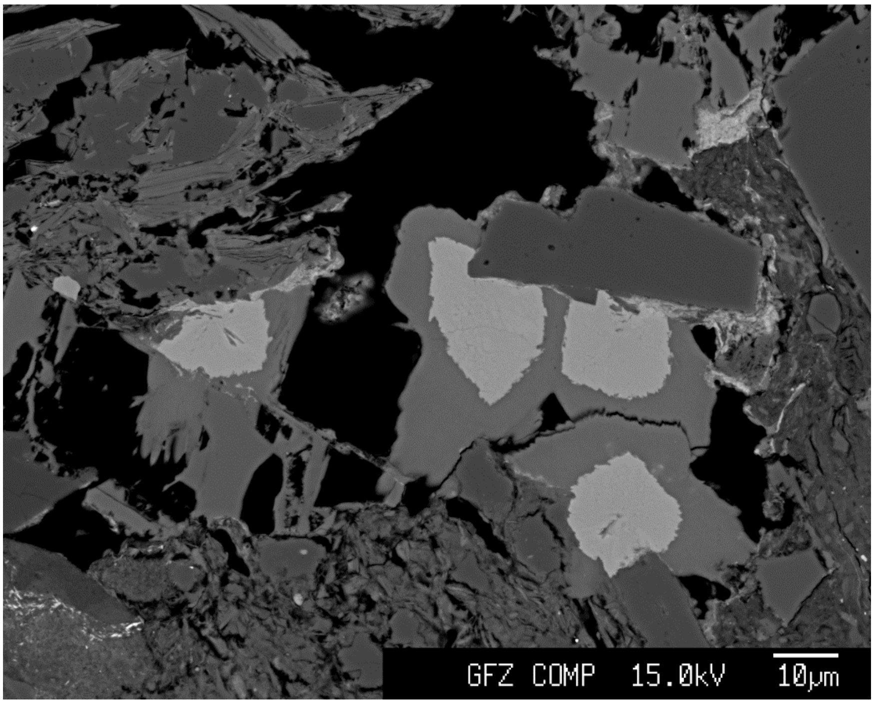


Figure 3. **After 4 years:** BSE images of (a) several small grains of siderite-I (bright) mantled by calcite-I or hydrocalcite (dark) and (b) two grains of these carbonate species associated with an almost euhedral grain of pre-existing authigenic anhydrite (An) devoid of chemical alteration and surface corrosion



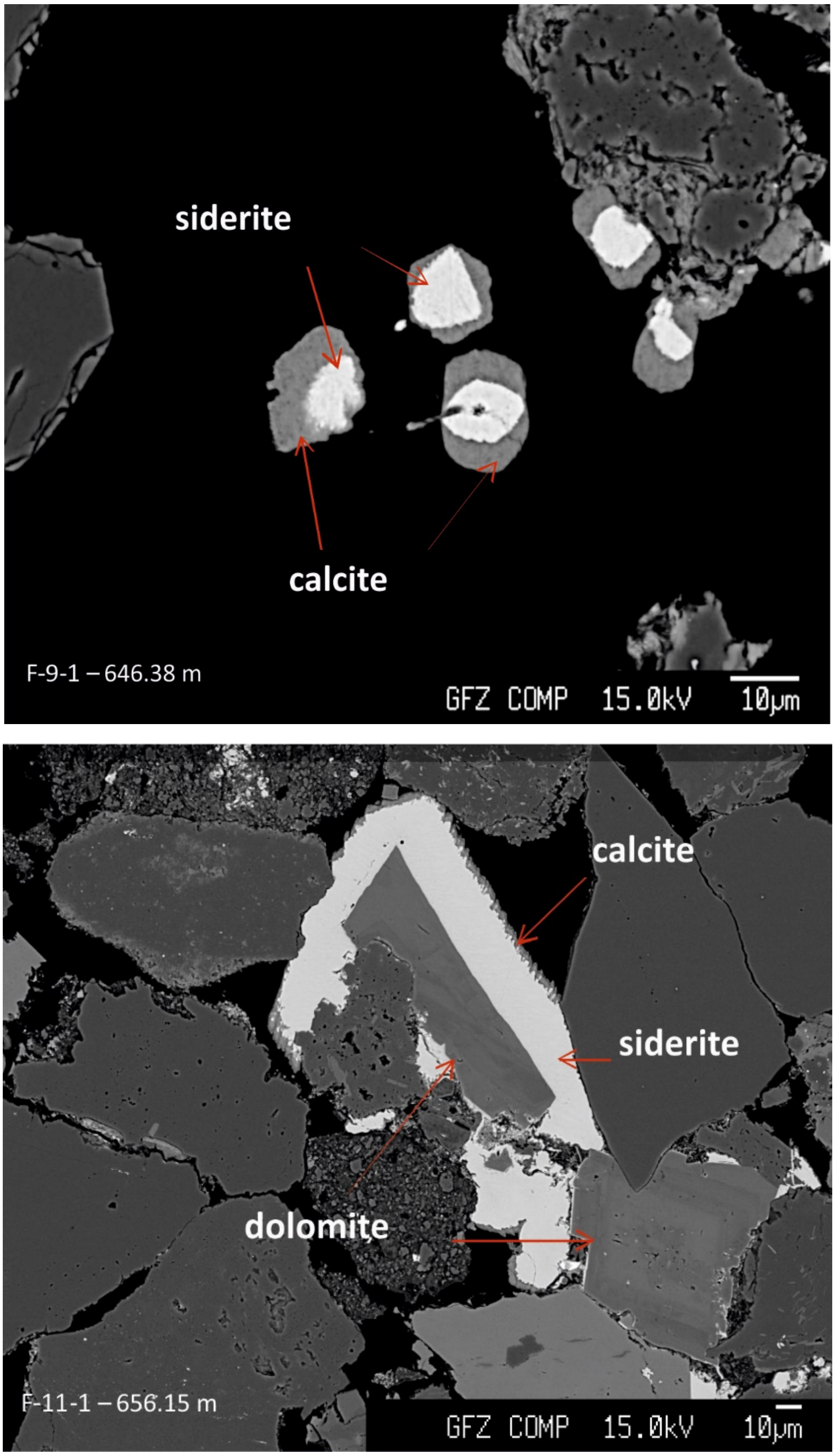


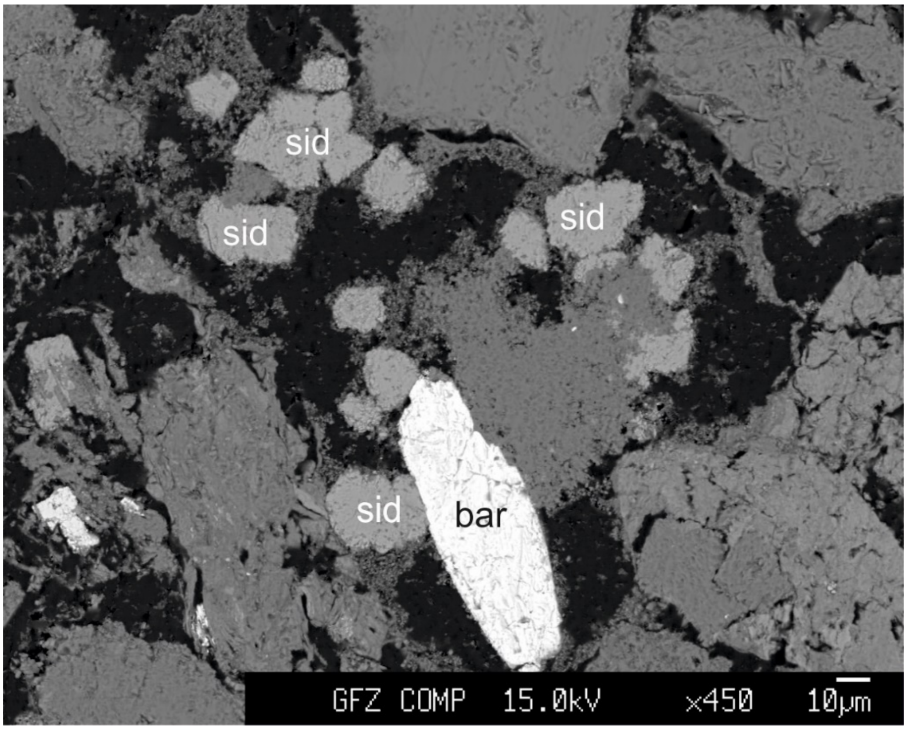
Figure 4. **After 4-years:** Siderite-I (bright) nucleating on detrital grains (upper, 632 m), precipitating in open spaces (middle, 646 m), and overgrowing relics of pre-existing dolomite (lower, 656 m)

9 years after CO_2 injection

The most prominent observations comprise (**a**) the disappearance resp. almost total decomposition of calcite-I that predominantly overgrew siderite-I in the sandstone samples recovered after 4 years (*cf.* Figures 3 and 4, lower), (**b**) the survival of siderite-I (*cf.* Figures 4, upper, and 5, lower) , (c) the massive precipitation of newly formed calcite-II in the uppermost meters of the sandstone (635–645 m depth), (**c**) the significant reduction of the percentage of anhydrite cement in sandstone intervals distinguished by calcite-II precipitation (*cf.* Figure 6, upper), and (**d**) the likely formation of small amounts of new Fe-bearing phases (oxides and/or hydroxides) implying an increase of Fe mobility with time.

Our study provides the ultimate proof that calcite-II formed at the expense of anhydrite (*cf.* Figure 6, upper), thereby enriching the brine in sulfur. Interestingly, no S-trapping mineral has been formed until 9 years after CO_2 injection terminated. Moreover, calcite-II is chemically distinct from calcite-I (lower in Na and Cl), indicating that it likely precipitated from a less saline brine compared to the fluid that governed crystallization of calcite after 4 years. That implication is in line with the circumstance that NaCl crystals are relatively rare in the reservoir sandstone collected after 9 years.

There is as well a depth zonation of the mineralogical responses to CO_2 injection. The most intense nucleation of calcite (calcite-II) occurred within permeable zones of the upper part of the reservoir, between roughly 635 and 645 m. Calcite-II precipitation did not take place in the lower sandstone package (between 655 and 663 m). Here, the only mineralogical response is the apparent dissolution of calcite-I rimming siderite-I. The implication would be that the brine was relatively more concentrated in dissolved CO_2 at the top of the Stuttgart Formation, where calcite-II crystallized. This supposition is well in line with the results of CO2-gas concentration measurements in the Ktzi203 well performed in 2017 (Zimmer et al., 2018).



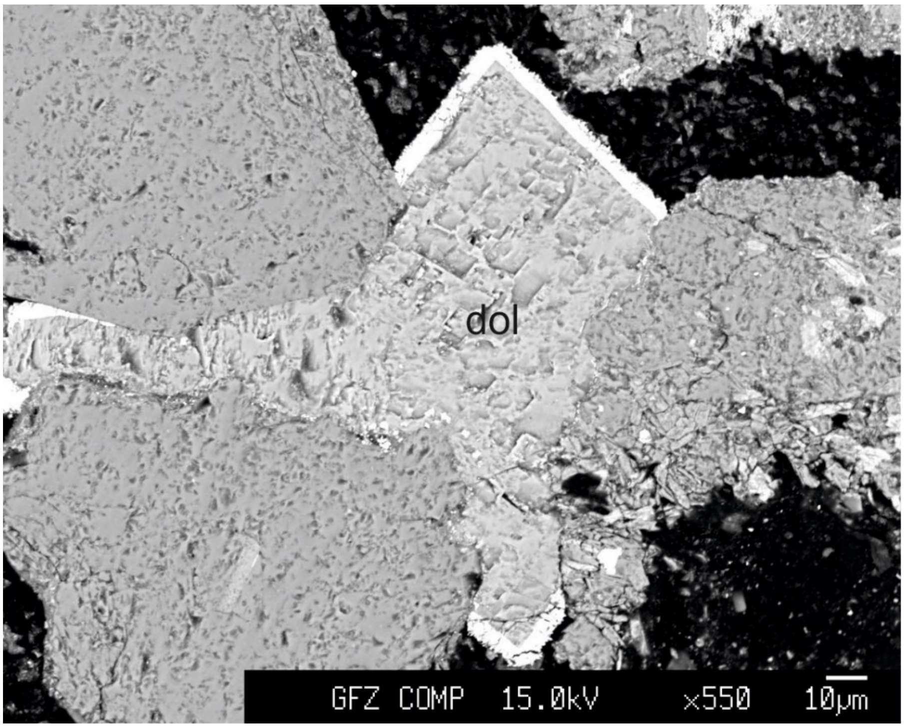
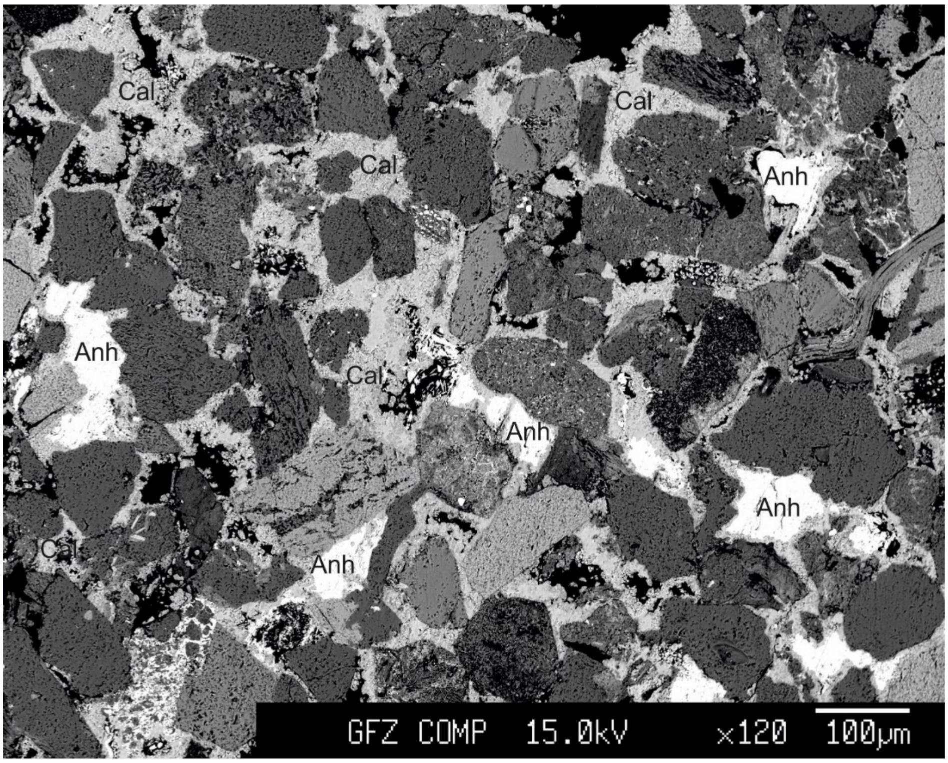


Figure 5. **After 9-years:** Siderite-I (sid) (upper, 649 m) missing the rimming calcite-I noticed after 4 years (*cf.* Fig. 4 upper and middle). It has yet to be clarified whether the plethora of nm-sized tiniest crystallites surrounding the siderite-I grains represents decomposing calcite-I. The lower image displays small rims of siderite-I overgrowing old dolomite (dol) in a sandstone sample taken from 656 m depth. Note that the tiny rims of calcite-I, that overgrew siderite-I on dolomite in the sandstone after 4 years (*cf.* Fig. 4, lower image), got apparently dissolved. bar = old barite cement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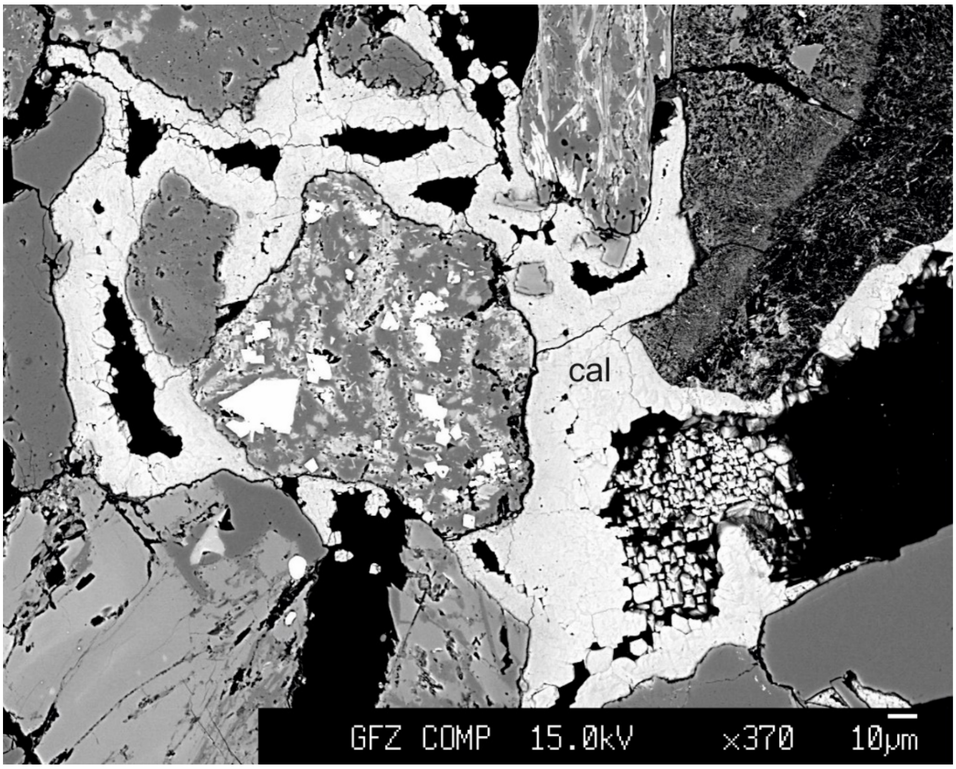
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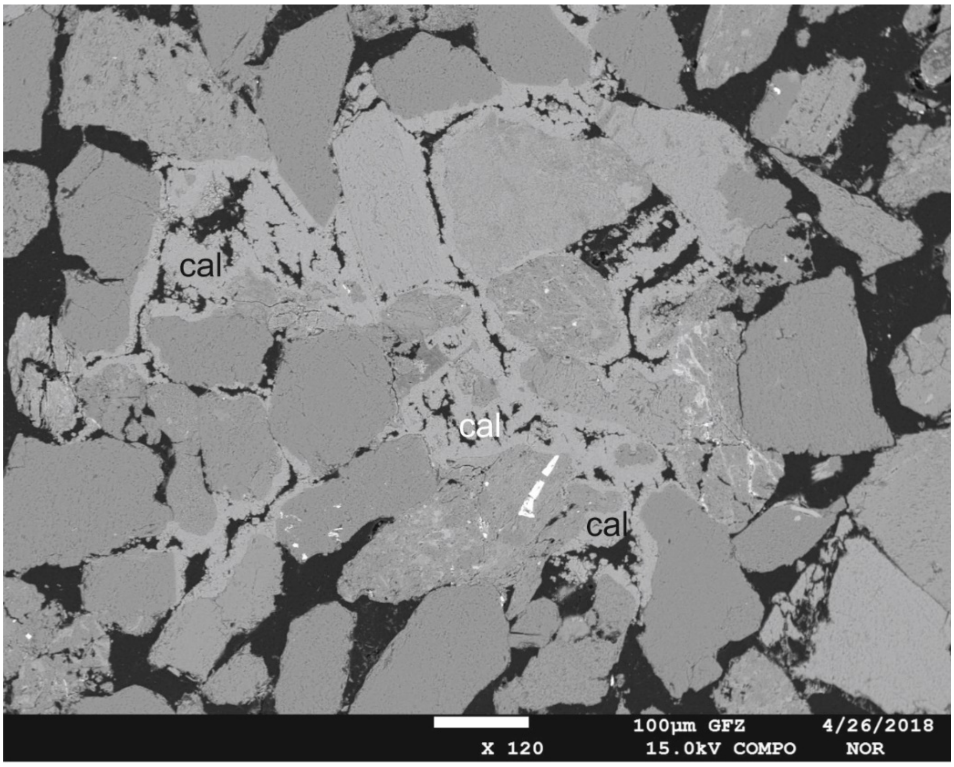

Figure 6. **After 9-years:** Formation of new pore-filling calcite (calcite-II) between 4 and 9 years of CO_2 exposure. Upper: at 636 m depth, middle: at 638 m, lower: at 645 m

Conclusions and implications

Any interpretation of the observations must take into consideration that the sandstone units of the Stuttgart formation are largely heterogeneous with respect to mineral modal composition down to the thin-section scale. For instance, modal abundance of the most prominent pore-cementing minerals analcime and anhydrite varies between roughly 5 and 25%. Moreover, many detrital components experienced alteration and corrosion prior to CO_2 injection, thus it cannot be unambiguously decided to which process(es) such phenomena are related. Conclusively, inferences on the rates of dissolution of a specific component or the participation of one other in providing elements for the precipitation of new species are tricky.

In spite of these complications, a number of important observations and conclusions could be drawn:

- CO_2 immobilization by mineral trapping apparently starts immediately after injection finished
- Newly formed carbonates are heterogeneously distributed within the reservoir, as are the minerals that provided components (mainly Ca and Fe) for their formation.
- The percentage of CO_2-sequestring minerals increased over time and maximized to ~ 7 percent at the thin-section scale.
- Siderite constitutes the first-formed carbonate, succeeded by calcite.
- The first-precipitated calcite became again unstable and dissolved almost totally.
- Early grown siderite was stable within the 9-years of exposure to the CO_2-doped brine.
- Major trapping carbonate species may change in geologically extremely short time; precipitation and dissolution processes of the same carbonate species may alternate within at least years.
- Although problematic to quantify exactly, dissolution of minerals appears to be approximately counterbalanced by mineral trapping, thus porosity and permeability were not significantly affected within the time period of observation.

It is important to establish that what happened in reality at Ketzin is only partly in accordance with predictions from experimental studies and reactive geochemical modeling relevant to the reservoir sandstones (Fischer et al., 2010, 2011, 2013; Wilke et al., 2012; Klein et al., 2013). Correspondence exists in that dolomite and anhydrite dissolution will contribute to the precipitation of carbonates. On the contrary, hard evidence for forecasted dissolution of calcic plagioclase, K-feldspar, analcime, hematite, chlorite, and biotite does not exist at Ketzin for the 9-year time period. Alteration of Illite and smectite (or dissolution of Fe-oxide coatings, *cf.* Kampman et al., 2014) could have facilitated availability for Fe to form siderite (*cf.* Wilke et al., 2012; Kasina et al., 2017), however, an ultimate proof for operation of these processes could not be provided. Notably are the differences with regard to the time of onset of carbonate trapping and both the type and sequence of carbonate precipitation (Klein et al., 2013). For instance, siderite formed very early, and not several 1000 years after CO_2 injection. And calcite is not subordinate relative to siderite, but instead constitutes a significant trapping phase already from the very beginning.

The most essential implication from this study is that reality is only imperfectly reproduced by experimental approaches or numerical modelling. Notwithstanding, such exercises are important in supporting understanding of processes associated with CO_2 storage, but any inferences derived from them for reservoir assessment in space and time treated be used with caution.

Finally, for the sake of honesty, from the here reported short-term observations, mid- or long-term inferences on reservoir integrity could not be made with sufficient confidence. CO_2-trapping carbonates formed with the time period of 9 years may again dissolve at some later time. Vice versa, yet not attacked detrital and authigenic species may become unstable if time proceeds. Even more complicated to predict is the impact that microbial activity may exert on the reservoir over time.

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