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X-Ray CT analyses, models and numerical simulations – a comparison with common analytical methods of an experimental CO_2 study

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Abstract. An essential part of the collaborative research project H2STORE ("hydrogen to store"), which is founded by the German government, was a comparison of various analytical methods to characterize reservoir sandstones from different stratigraphic units. In this context Permian, Triassic and Tertiary reservoir sandstones were analysed. Rock core materials, provided by RWE Gasspeicher GmbH (Dortmund), GFD Suez E&P Deutschland GmbH (Lingen), E.ON Gas Storage GmbH (Essen) and RAG Rohöl-Aufsuchungs Aktiengesellschaft (Wien), was processed by different laboratory techniques; thin sections were prepared, rock fragments were crushed, cubes of 1 cm edge length and plugs of 5 cm in length were sawn from macroscopic homogenous cores. With this prepared sample material, polarized light microscopy and scanning electron microscopy - coupled with image analyses, specific surface area measurements (BET), He-porosity and N_2-permeability measurements and high resolution micro-computer-tomography (µ-CT), which were used for numerical simulations were conducted. All these methods were applied to most of the same sample material, before and after static CO_2 experiments under reservoir conditions. A major concern in comparing the results of these methods is an appraisal of the reliability of the given porosity, permeability and mineral specific reactive (inner) surface areas data. The CO_2 experiments are modifying the petrophysical as well the mineralogical/geochemical rock properties. These changes are detectable by all applied analytical methods. Nevertheless, a major outcome of the high resolution µ-CT analyses and proceeded numerical data simulations results in quite similar data sets and data interpretations maintained by the different standard methods; even regarding only CT-single scan of the rock samples. Moreover, this technique is not only time saving, but also none destructive. This is an important point, if only minor sample material is available and a detailed comparison before and after the experimental tests on micro meter, pore scale of specific rock features is envisaged.

Keywords: µ-CT, porosity, permeability, surface area, sandstone reservoir, static autoclave experiments, CCS

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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Introduction

The globally rising carbon dioxide emissions, increasing climate extremes and the "Energiewende" in Germany are keywords which are highly relevant and intensively discussed by governmental authorities, scientists, industrial representatives and the public society.

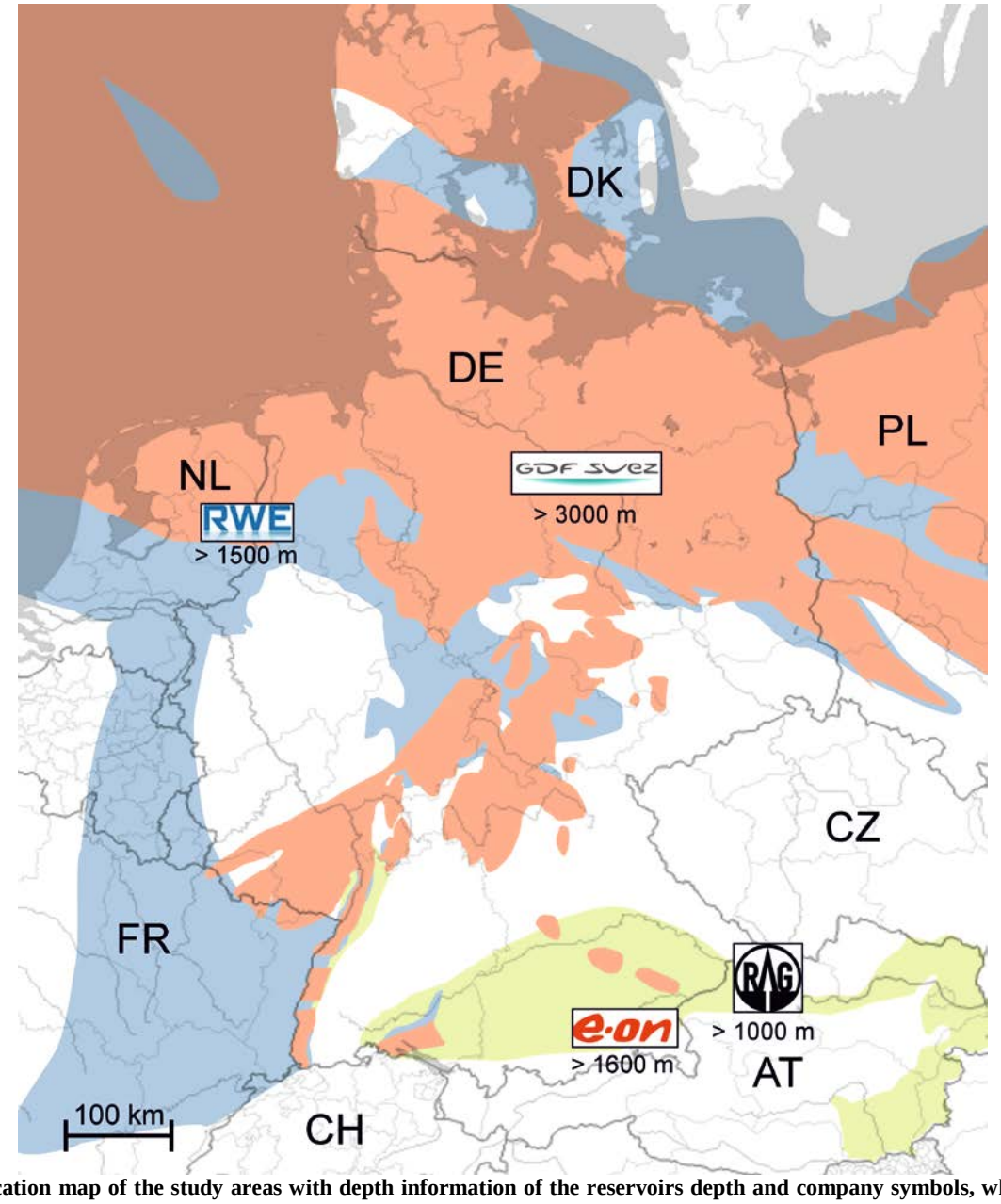

Figure 1. Location map of the study areas with depth information of the reservoirs depth and company symbols, which provided sample material. The coloured outlined areas represent the distribution of strata in the underground of the potential reservoir units. In red the Permian, in blue the Triassic and in green the Tertiary strata are shown (Modified after Henkel et al., 2013).

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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As part of these debates the BMBF founded project -Hydrogen to Store- (H2STORE) one main objective of research was to characterize mineral-, synthetic formation fluid-, microbiological- and petrophysical interactions in reservoir sandstones, induced by hydrogen and carbon dioxide autoclave batch experiments (Pudlo et al., 2013, 2015 and Henkel, 2016 submitted). Such reactions were investigated by autoclave experiments at reservoir temperatures and pressures, using none corrosive autoclaves and fluids, similar to reservoir specific formation fluids.

To satisfy the demands of reducing greenhouse gas emissions given in the Kyoto protocol (1997) and most recently strengthen by the UN climate conference in Paris in 2015, intentions to capture, inject and store CO_2 into the geological underground (CCS) are even more relevant. Also the utilisation of CO_2 combined with a H_2 injection into the geological underground for "green methane" generation (Šmigiáň et al., 1990), enforced by microorganism activity (Panfilov, 2010) are options which asks for further research regarding potential CO_2-biotic-mineral-formation fluid-reactions.

Additionally, the integrity of wells, including the behaviour of e.g. bore hole casings in a highly corrosive environment of H_2/CO_2-gas mixtures is an essential point in the potential usage of the geological underground for storage options.

In this study we used rock samples provided by the industrial partners RWE Gasspeicher GmbH (Dortmund), GFD Suez E&P Deutschland GmbH (Lingen), E.ON Gas Storage GmbH (Essen) and RAG Rohöl-Aufsuchungs-Aktiengesellschaft (Wien). The high resolution computed tomography (µ-CT) data associated with numerical fluid flow simulations using the GeoDict – Math2Market® and standard petrophysical analyses, which were conducted at the Technical University Clausthal before and after the static autoclave experiments, were applied. Thus to verifying potential reactions induced by the CO_2 autoclave experiments and to compare these data with the results, achieved by the other conventional analytical methods (e.g. Pudlo, 2014).

Material

The used sandstone samples originated from areas and stratigraphic formations, which comprise the main reservoir units in Germany and Austria. The sample material originates from three different stratigraphic units, the Permian in Northeast Germany, the Triassic in Northwest Germany and the Tertiary of South Germany and Northwest Austria (Fig. 1). Therefore, the source areas, the detrital content, the depositional environment and the diagenetic evolution of these sediments are diverse, implying that the samples experienced different burial pressures, temperatures and interactions with their site specific formation fluids. The current reservoir conditions of the sample sites of interest are summarized in table 1, showing the marked differences, especially in comparing the Permian and Tertiary sample sites. The current burial depth of the Permian samples is about 3500 m with a reservoir temperature of 120-125°C. This is in contrast to the recent Tertiary reservoir conditions with a burial depth of 1600 m and reservoir temperatures of about 40°C (Tab. 1). Also the formation fluid salinities are varying from 35.22 % salinity in the Permian reservoirs to only 1.81 % salinity in the Tertiary formation fluids.

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
Manuscript under review for journal Solid Earth
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Table 1. Overview of the recent reservoir conditions of sampled locations.

Location	Stratigraphy	Recent burial depth	Recent temperature	Reservoir pressure	Salinity of formation fluid
Saxony-Anhalt	Permian	3500 m	125°C	20 MPa	35.2 %
Lower Saxony	Triassic	1700 m	100°C	10 MPa	28.8 %
Bavaria	Tertiary	1600 m	40°C	10 MPa	1.8 %
Austria	Tertiary	1100 m	40°C	10 MPa	3.5 %

In comparing the detrital rock composition due to their quartz, feldspar and rock fragment content the different locations a wide range of sandstone types is present (Fig. 2 - after McBride, 1963).

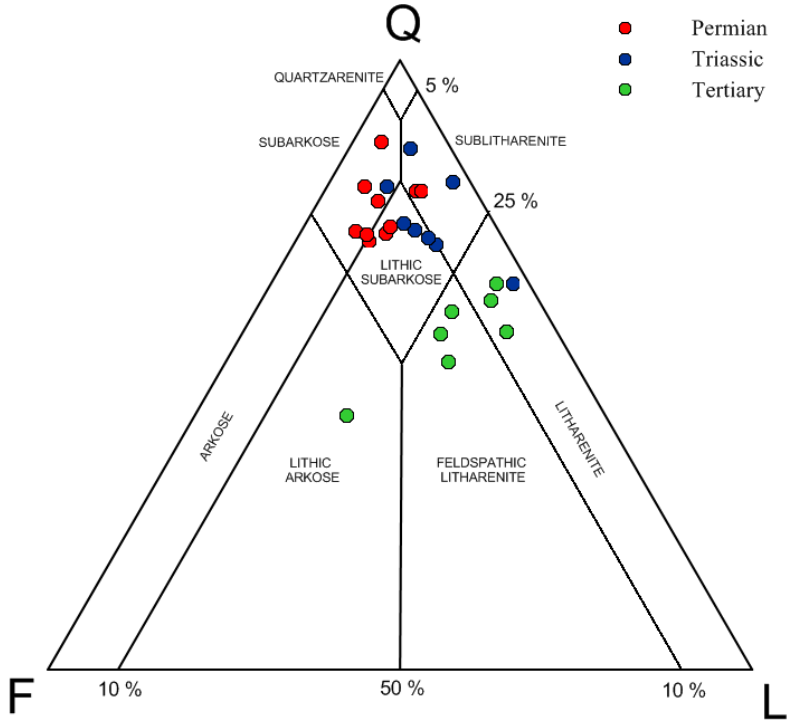

Figure 2. The petrographic sandstone classification after McBride (1963) for samples of this study with the stratigraphic classification is shown. This petrographic classification was conducted by identifying and analysing 300 minerals in thin sections of the selected samples and plotting the determined quartz (Q), feldspar (F) and lithoclast (L) content in a ternary diagram. The different colours are corresponding to the different stratigraphic units and therefore locations (cp. fig. 1).

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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The Permian samples are classified mainly as arkoses, subarkoses and quartzarenites, the Triassic sandstones vary from subarkoses, lithic subarkoses, sublitharenites to litharenites and the Tertiary samples comprise lithic subarkoses, sublitharenites, litharenites, lithic arkoses and feldspar litharenites. Moreover, the rocks contain varying amounts of pore filling, framework stabilising cements, like anhydrite, carbonate and exhibit different portions of open pore space (Fig. 3).

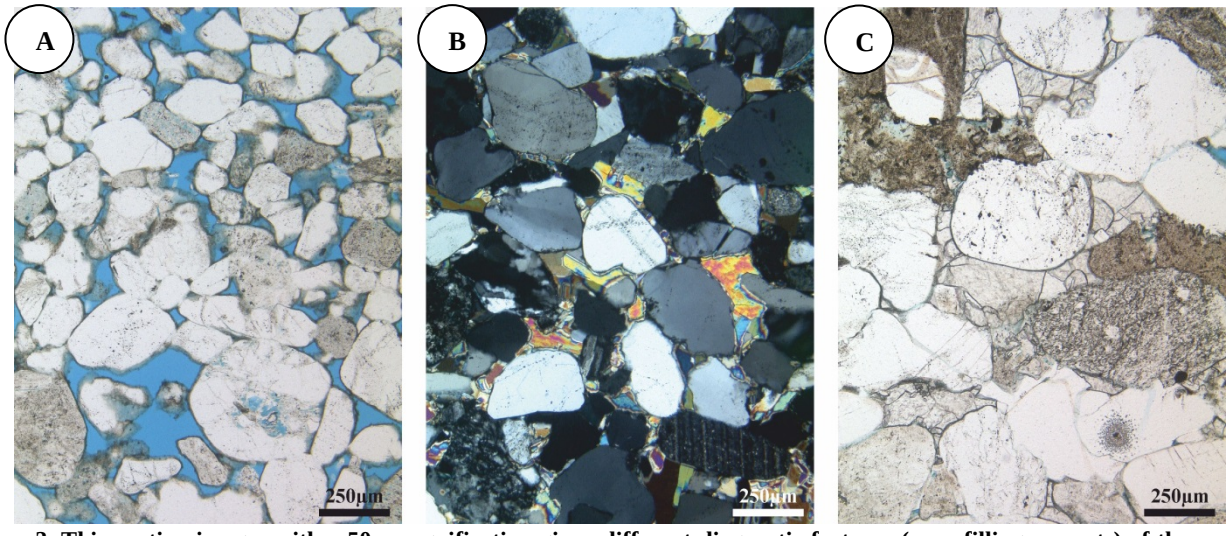

Figure 3. Thin section images with a 50x magnification given different diagenetic features (pore filling cements) of the sandstone samples. In A a transmitted light image of a sample with free pore space is shown (blue colour = open pore). In B an image of a thin section with crossed nicols is shown, highlighting pore filling anhydrite cement (rainbow colours). In C a transmitted light image of a thin section with pore filling carbonate cement is shown (arrows).

Thus a wide range of different rock compositions are available in conducting this study. Also the grain sizes of the different sandstone samples are varying from silt to coarse sand (Fig. 5) fraction after Wentworth (1922).

For the autoclave experiments and the petrophysical, mineralogical and chemical analyses the core material was prepared as given in Henkel et al. (2014). For reservoir characterisation mainly macroscopic homogeneous parts of the rocks (Fig. 4) were sampled and used for the different analytical methods and the CO_2 experiments.

Methods

Analytical methods were applied to macroscopically homogeneous sandstones from the three stratigraphic formations on identical hand specimen to compare the outcomes achieved by the different analytical methods. Additionally, the Permian samples were used for the CO_2 experiments at sample specific reservoir conditions and were analysed before and after these experiments at the same samples and marked sample positions, respectively. Therefore, a pin point comparison of different mineral reactions due to the CO_2 experiments is possible.

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
Manuscript under review for journal Solid Earth
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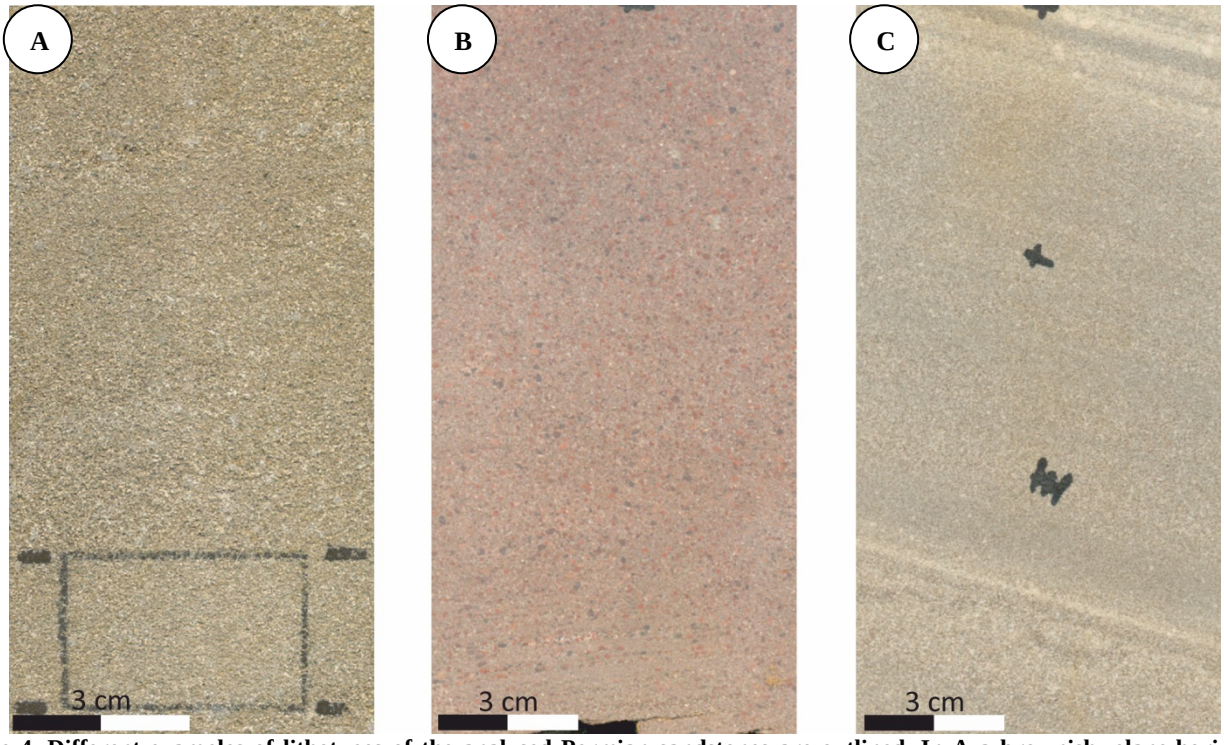

Figure 4. Different examples of lithotypes of the analysed Permian sandstones are outlined. In A a brownish, plane-horizontal stratified medium grained sandstone type is shown. In B a red, massive, medium coarse grained sandstone type is visualized and in C a greyish, obliquely bedded fine-medium grained sandstone type is presented.

The 4 to 7 week lasting CO_2 autoclave batch experiments were conducted at the Clausthal University of Technology, in rock-formation brine systems, in high pressure, high temperature (HPHT) and corrosion resistant autoclaves using selected thin sections, rock fragments and plugs (Pudlo et al., 2015 and Henkel et al., 2015). Helium porosity and nitrogen permeability measurements before and after the tests were performed on sandstoneplugs at the TU Clausthal. For porosity analysis a set-up after Torsaeter and Abtahi (2003) was used and permeability determinations were conducted with a hassler cell in an up- and downstream regime and calculated after Darcys Law equations.

The fluid samples of the formation fluids used in the autoclave experiments (5-10 ml) were taken before, during and after the tests at the TU Clausthal and chemically analysed in regard of their major, minor and trace element contents at the Friedrich Schiller University Jena. For the analyses, with an error of about 1 %, an inductively coupled plasma spectroscope with optical emission (Varian 725 ES) and a mass spectroscope (Thermo Fischer scientific X Series II) were used (ICP-OES/MS). Also the physico-chemical characterisation of the formation fluid was conducted in the laboratories of the Institute of Geoscience in Jena. With the software PHREEQC 3.3 (Parkhurst & Appelo, 2013) and the database for highly saline fluids (Pitzer et al., 1984) the saturation indices of the fluids for the pore filling minerals (carbonate and anhydrite) were calculated. Polarized light microscopy and field emission scanning electron microscopy (FE-SEM) were used at the FSU Jena for the mineralogical investigations. Thereby a Zeiss Axioplan II petrological microscope, equipped with an ocular of 10x magnification and objectives of 2.5x, 5x, 10x, 20x, 40x magnifications were applied, which was combined with a mounted

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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Hitachi HV-C20 digital camera for the light microscope. For the field emission scanning electron microscopy (FE-SEM) and the energy dispersive X-ray spectroscopy (EDX) a SMT ULTRA plus field emission scanning electron microscope of Carl Zeiss enterprises, coupled with an EDX-detector and the analytical software of Bruker AXS Microanalysis GmbH was used for mineral documentation and identification.

For the high resolution computer tomography, a Procon CT Alpha 160 device at the Johannes Gutenberg University Mainz was used. The detector resolution was about 2048x2048 pixels. The used parameters for the measurements are 100 kV of voltage and a current of 80 µA. Scans were performed at 0.45° steps over a total rotation range of 360°. The achieved resolution for the different sample material is between 7.6 µm and 8.6 µm per voxel. The reconstruction of the scans was performed with the software Octopus 7.0®. The µ-CT image adaption with anisotropic diffusion filtering and pore space segmentation was performed with the software Avizo® fire 7.1. Intense distinct beam hardening was corrected with the software MATLAB® and the approaches after Jovanovic et al. (2013). For the calculations of porosity, surface area, fluid flow and deduced permeability the corresponding modules of the software package GeoDict from the company Math2Market® were used (Wiegmann, 2007 and Wiegmann et al., 2013). The Navier Stokes-Brinkmann flow solver in the module FlowDict with the density properties of water at 20 °C were used for the fluid flow simulation and permeability calculations.

The specific surface area (BET) measurements on crushed rock fragments were determined after Brunauer et al. (1938) at the Technical University Munich before and after the experimental runs at exactly the same sample material.

Results

The initial state of the statistical porosity, permeability and specific surface area data determined by the different methods from all the analysed sample material of this study is shown in figure 5. The measured helium porosity and nitrogen permeability values for the Permian plug samples ranges from 5.64-14.73 % in porosity (mean:10.96 %) and 2.61-161.32 mD (mean: 96.27 mD) in permeability. For the measured Triassic samples, the helium porosity data are between 11.02-29.95 % (mean: 21.01 %) and for nitrogen permeability data between 251.93 and 1609.43 mD (mean: 521.26 mD). The measured Tertiary plug samples represent porosity values of 19.14-26.62 % (mean: 25.67 %) and permeability values from 25.80-388.00 mD (mean: 188.82 mD). The corresponding parameters calculated from the µ-CT data with the Software GeoDict and the implemented Navier Stokes-Brinkmann solver for the permeability results in the Permian samples in porosity values of 2.55-15.36 % (mean: 9.74 %) and permeability values of 8.56-570.28 mD (mean: 222.64 mD). For the Triassic samples porosities of 9.79-22.57 % (mean: 15.85 %) and permeability values range from 18.41-449.09 mD (mean: 280.16 mD). The Tertiary samples have calculated porosities of 0.52-10.41 % (mean: 6.24 %); due to no existing flow connectivity in the samples (no detectably connected pore networks) modelling of permeability from CT-data was not possible.

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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The measured specific surface area by the BET-method after Brunauer et al. (1938) on crushed rock fragments of the Permian samples reveal values of 0.64-2.34 m²/g (mean: 1.18 m²/g) and for the Triassic samples values ranging from 0.45-1.72 m²/g (mean: 1.05 m²/g). The calculated surface areas from the CT-data sets for the Permian sandstones range from 0.0018-0.0033 m² (mean: 0.0024 m²) and from 0.0006-0.0038 m² (mean: 0.0023 m²) in the Triassic samples.

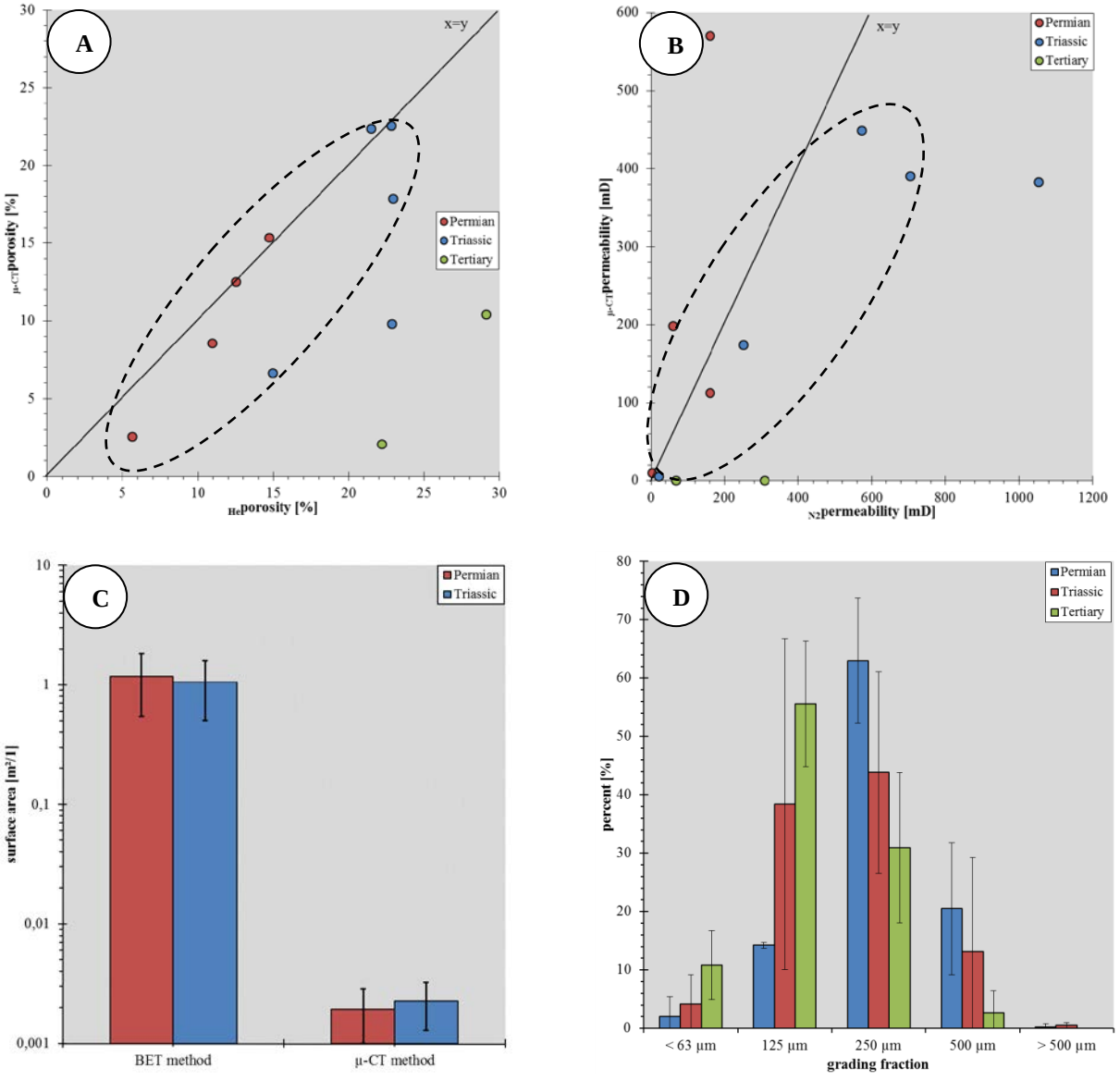

Figure 5. In A the porosity results of the same eleven µ-CT and He-porosity analysed samples are shown for three different stratigraphic units. The ellipse marks the sandstone samples with coarse sand (2.00-0.63 mm) and medium sand (0.63-0.20 mm) grain sizes. In B the permeability data of the same sample set as shown in A is presented. Again the ellipse is outlining the grain sizes of the different samples. In C the comparison of the mean specific surface area data for the BET and µ-CT method is outlined. In D the mean grain fraction sizes (after Wentworth, 1922) analyzed on thin section with the corresponding standard deviation of the samples in this study are shown.

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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PHREEQC numerical simulations confirm that due to the very high concentrations in Na^+, Ca^{2+} and Cl^- (Tab. 2) the used formation fluids are very close to saturation with respect to NaCl and $CaCO_3$ (Tab. 3). In contrast this modelling suggests that anhydrite ($CaSO_4$) can be dissolved in these fluids, because of their slight undersaturation of sulphur (S). Due to the high ion concentrations in the synthetic brine a very high electrical conductivity was measured (cp. Tab. 2 and Tab. 3).

Table 2. Results of formation fluid analyses (ICP-MS/OES) of selected ions and the corresponding physico-chemical data of two Permian samples, before and after CO_2 experiments under static reservoir conditions. Due to the common stratigraphic origin the initial formation brine composition is similar for both samples.

	Before CO_2 experiment						After CO_2 experiments					
	Na^+ [g/l]	Ca^{2+} [g/l]	Cl^- [g/l]	S^{total} [mg/l]	pH	elec.cond. [µS/cm]	Na^+ [g/l]	Ca^{2+} [g/l]	Cl^- [g/l]	S^{total} [mg/l]	pH	elec.cond. [µS/cm]
S 1	65.53	54.27	203.80	7.50	9.45	45700	7.05	6.15	22.24	247.00	6.71	6790
S 2	65.53	54.27	203.80	7.50	9.45	45700	5.53	4.77	17.54	54.00	6.77	5370

Table 3. PHREEQC modelling, showing saturation results of the interaction of the synthetic formation fluid used before, during and after the CO_2 experiments exposed to the Permian sandstones (n.a. = not analysed, SI = saturation index, pE = negative logarithm of electron concentration - directly proportional to the redox potential).

	P [MPa]	T [°C]	pH	pE	SI $CaCO_3$	SI $CaSO_4$	SI NaCl
Laboratory standard conditions before CO_2 experiment	0.1	20	9.54	6.7	0.48	-3.27	-1.35
Reservoir conditions during CO_2 experiment	25.0	120	3.23	6.7	-3.19	-4.09	-1.70
Laboratory standard conditions after CO_2 experiment	0.1	20	6.71	n. a.	-3.39	-4.93	-3.10

For the CO_2 experiments only sample material from Permian sandstones was used. The measured petrophysical data after the 4-7 weeks lasting CO_2 experiments (Fig. 6) under sample specific reservoir conditions from the selected 16 sandstone plugs range from 3.25-19.24 % (mean: 13.11 %) in porosity and from 0.01-419.60 mD (mean: 918.99 mD) in permeability. The calculated petrophysical data from the two cube samples by µ-CT scans resulted in 10.43 % and 17.93 % in porosity and 247.58 mD and 1909.05 mD in permeability.

For the determination of the specific surface area in these 16 Permian samples the BET method was used and revealed values of 0.51-2.75 m^2/g (mean: 1.31 m^2/g). In contrast calculated surface areas by the µ-CT-data from the two sample cubes are lower with 0.17 cm^2 and 0.24 cm^2, respectively.

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
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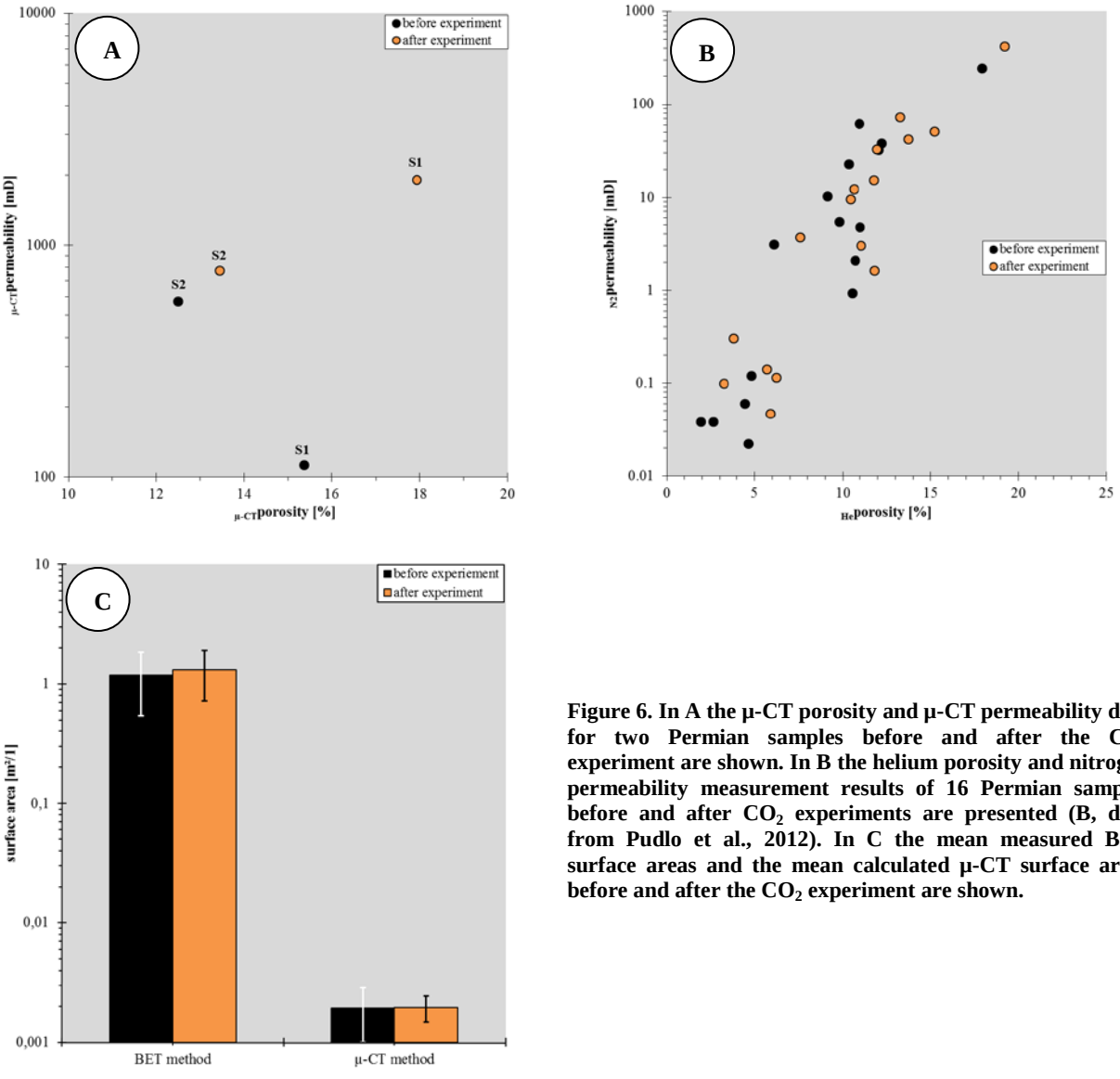

Figure 6. In A the μ-CT porosity and μ-CT permeability data for two Permian samples before and after the CO_2 experiment are shown. In B the helium porosity and nitrogen permeability measurement results of 16 Permian samples before and after CO_2 experiments are presented (B, data from Pudlo et al., 2012). In C the mean measured BET surface areas and the mean calculated μ-CT surface areas before and after the CO_2 experiment are shown.

By comparing the calculated fluid flow fields before and after the CO_2 experiments (cp. Fig. 7 A-B and Fig. 8 A-B) an increase of fluid pathways related to enhanced porosity and permeability are developed after the CO_2 tests. Regarding the FE-SEM and EDX results on thin sections a dissolution of pore filling anhydrite and carbonate cements is recognized when comparing identical sample position before and after the CO_2 experiments (Fig. 9). The fluid chemical analyses after the CO_2 experiments indicate an increase of sulphur and a depletion of Na^+, Ca^{2+} and Cl^- (Tab. 2) in the formation fluid. Also the pH and the electrical conductivity values are decreased in the formation fluid after the CO_2 experiments (cp. Tab. 2 and Tab. 3).

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
Manuscript under review for journal Solid Earth
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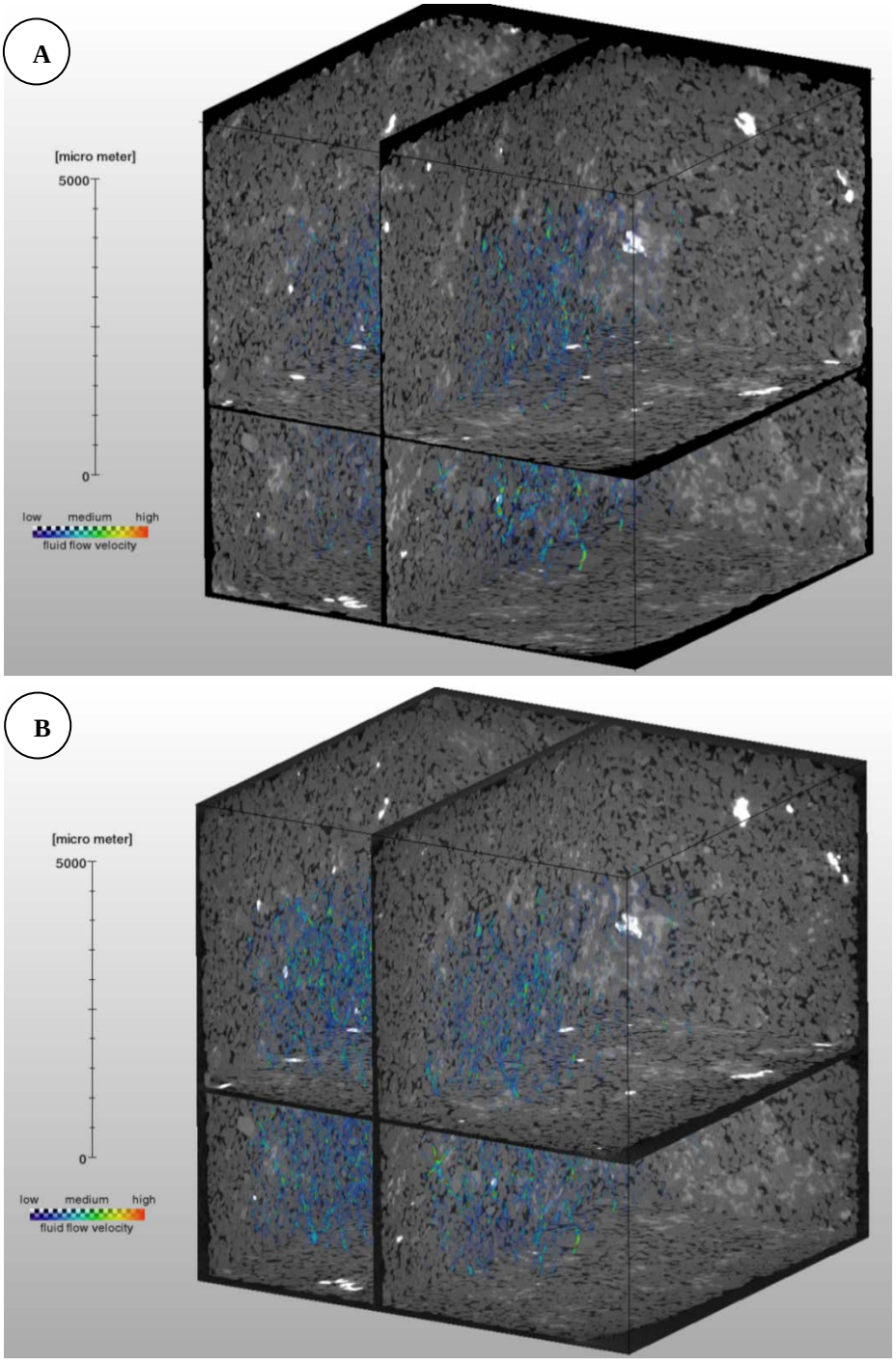

Figure 7. In A and B the details of the same Permian sandstone sample before (A) and after (B) the seven weeks lasting CO_2 experiments under reservoir conditions is shown. Note the reduction of the blocky cements (light grey) and the fluid flow field with increased fluid migration pathways after the experiments (blue-red colours).

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
Manuscript under review for journal Solid Earth
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The PHREEQC calculations (Tab. 3) using the data sets of ICP-MS/OES analyses after the CO_2 experiment suggest a supersaturation with respect to $CaCO_3$ in the formation fluids. The slight undersaturation of $CaSO_4$ (anhydrite) in the fluids gets even further depressed during the CO_2 experiments.

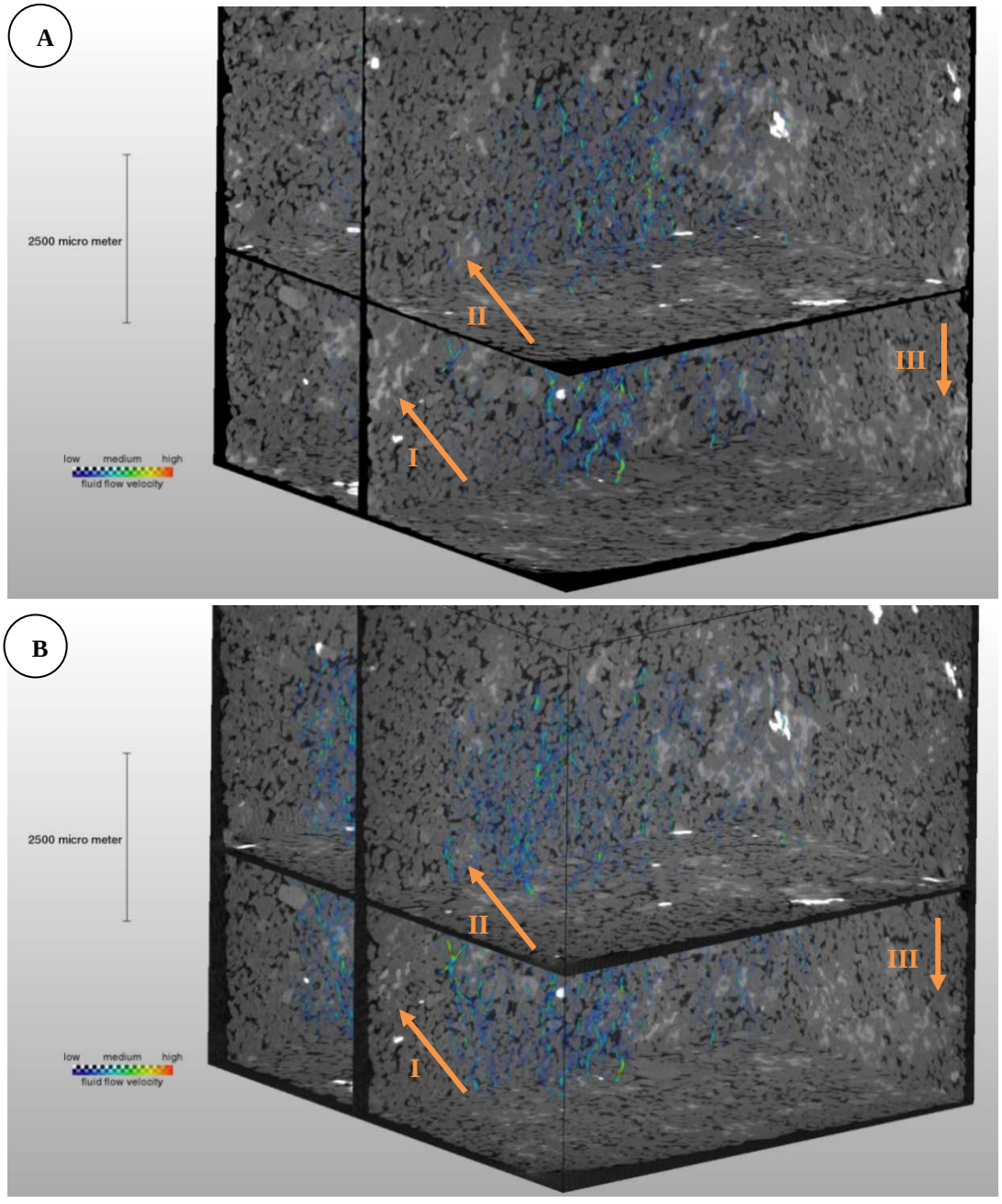

Figure 8. In A and B the identical Permian sandstone sample is presented before (A) and after (B) CO_2 experiments under reservoir conditions. The images are enhanced section from fig. 7 and verifying the dissolution of the blocky pore filling cements (arrows) and the enhanced fluid flow field and fluid flow velocities after the experiments resulting from the dissolution events.

Solid Earth Discuss., doi:10.5194/se-2016-36, 2016
Manuscript under review for journal Solid Earth
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Conclusions

The given comparison of the porosity data deduced high resolution computer tomography scans and measurements by helium porosity confirm that both methods achieve most similar results. Nevertheless, grain sizes of sandstones (cp. fig. 5 A-D) and therefore the distinct required resolution rate of the µ-CT Scans will influence the quality of the calculated porosity data. Results from the fine and very fine grained sandstones samples from the Tertiary and Triassic imply that the data of helium porosity measurements are more precisely due to the helium intrusion even into micro pores (< 7.6 µm resolution of µ-CT) and thus the capability of helium migration even through very narrow pore throats. In contrast, because of the limited resolution of µ-CT scans (7.6-8.6 µm/voxel), such micro pores are not detectable and calculated porosities are less than revealed by helium porosity measurements. Most likely these differences in regarding micro pores led to distinct porosity data in fine to very fine grained rocks, whereas porosity determinations on coarse and medium grained sandstone samples are most similar. By comparing the results of both methods from identical samples after the CO_2 experiments, both methods confirm the same increase in porosity. The mean helium porosity measurements reveal an increase of total porosity by 16.0 % and the calculated µ-CT data one of 12.6 % due to the CO_2 experiments. Thus, an effect on porosity characteristic after the 4-7 weeks lasting CO_2 experiments under reservoir specific conditions are verified by both methods.

Also, the calculation of the surface areas by µ-CT data is limited due to the restricted resolution of the µ-CT scans. However, the software GeoDict calculations can offer reference values. However, the results of the specific surface area measurements after Brunauer et al. (1938) are more realistic, if compared with sandstone data from the literature (see e.g. Pudlo et al., 2015). Most likely, by including additional parameters like e.g. rock/mineral densities, the volume and the compositional as well as the morphological features of the pore space exposed mineral phases to the GeoDict approach, more reliable data are achieved. An important outcome in comparing data sets compiled before and after the CO_2 experiments is that both methods confirm an increase in surface areas; by µ-CT investigations and calculations this enhancement in the surface area is about 14.3 %, which is most similar to the 10.4 % maintained by the BET-method. The measured nitrogen permeability data and the results from the µ-CT calculations by Geodict are in the same order. However again, the quality of calculated permeabilities from the µ-CT data sets of the segmented pore space (pixel resolution: 7.6-8.6 µm) depends on the grain size of the samples. Whereas for coarse and medium grained sandstones the results are most similar to the nitrogen permeability measurements, these resemblances are minimized with decreasing grain sizes. Nevertheless, by comparing the permeability data after the CO_2 experiments with the results before the experiments, both methods confirm a marked increase in permeability induced by the tests. This increase is about 1.75 times higher in the calculations than in the nitrogen permeability measurements.

This study confirms that high resolution computer tomography is a suitable method to verify the alteration of various mineral phases of sandstone samples induced during CO_2 batch experiments. The dissolution of carbonates and anhydrite, present as pore filling cements before the tests, is increasing rock porosity and the surface areas. The gain in surface areas is caused by

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an enhanced exposure of small grain rimming clay minerals to the pore space, which were covered by the pore filling cements before the experiments.

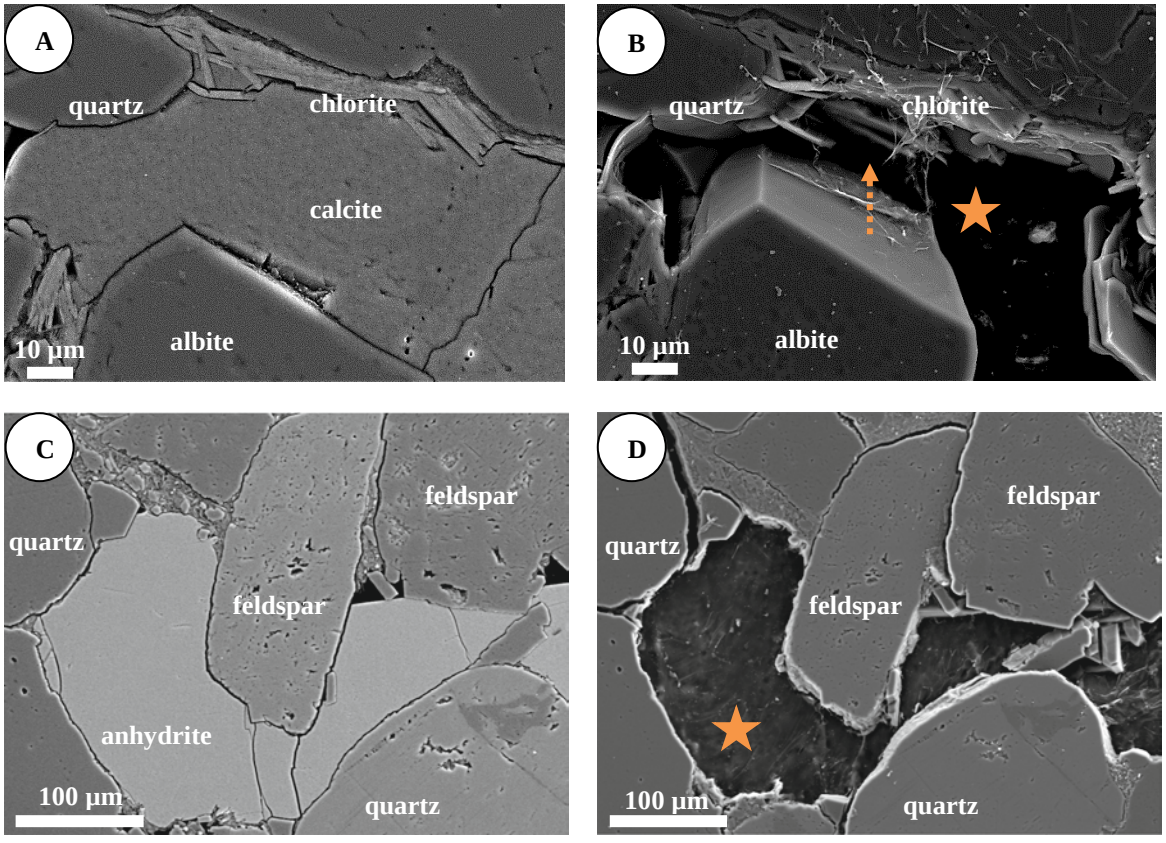

Figure 9. Secondary electron FE-SEM images of the same section of a Permian sandstone sample before (A + C) and after (B + D) CO_2 experiments under reservoir specific conditions for seven weeks. The dissolution of pore filling calcite cement (star in B) and the exposure of grain rimming clay minerals (arrow in B) leading to the increasing porosity outcomes after the CO_2 experiments and the increase of the specific surface area (modiefied after Henkel et al., 2014). In C and D the dissolution of pore filling anhydrite cement (star in D) is shown at exactly the same thin section position before (C) and after (D) the CO_2 experiment also leading to increasing porosity values after the experiments.

These results from µ-CT analyses and numerical simulations are in accordance to helium porosity and nitrogen permeability measurements, the determination of specific surfaces by BET after Brunauer et al. (1938) and findings by scanning electron microscopy as well as hydro-, mineral- and geochemical analyses on similar sandstones (e.g. Pudlo et al., 2012, 2013, 2015 and Henkel, 2016 submitted) confirming marked modifications in rock composition induced by CO_2 autoclave experiments, which are most relevant in evaluating the suitability and quality of potential underground reservoirs.

In the future, the discussed deviations of data reliability related to grain size with very good in coarse and medium grained and minimized accordance in fine to very fined grained sandstones can be precluded by applying higher scan resolutions and/or smaller sample sizes, following the approach of Nordahl and Ringrose (2008) in determining an appropriate

representative elementary volume (REV) for each sample. This complexity is one of the major topics of the ongoing work by the authors in the collaborative research project "HyINTEGER".

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