Insights into the interaction of a shale with CO₂

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Abstract

Caprock formations such as shales, play a key role to safe underground CO₂ storage since they serve as a hydromechanical barrier that prevents migration of the injected CO₂ to the surface. While their hydromechanical response is important to ensure their sealing capacity, interaction with the injected CO₂ involves additional thermo-chemo-mechanical (THMC) phenomena that may threaten the long-term caprock’s integrity. The low transport properties of shales make them a suitable caprock material, but at the same time challenging to study due to the very long time scales that are required for the various thermo-hydro-chemo-mechanical processes to manifest. In this work, the multiphysical interaction of the Opalinus Clay shale with CO₂ is studied with live x-ray tomography. Long-term exposure to liquid and supercritical CO₂ targets the investigation of different occurring THMC processes locally and globally in 3D that are often indistinguishable with conventional lab testing protocols. To improve spatial and temporal resolution while applying realistic pressure and temperature conditions, small size samples are studied. Long-term injection of liquid CO₂ resulted to a significant fissuring of calcite-rich zones that were for the first time visualised and quantified from the x-ray images, while a re-arrangement of the pre-existing micro-fissures in the clay matrix were observed. The volumetric response during direct exposure of an Opalinus Clay sample to supercritical CO₂ revealed an initial swelling at pre-cracked zones and initiation of new micro-fissures at areas of direct contact with the anhydrous CO₂ due to pore

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water evaporation. Advanced 3D image analysis showed an increasing CO$_2$ uptake with time the elevated value of which after pressure release suggests potential CO$_2$ trapping the material.

1 Introduction

Geological CO$_2$ Storage (GCS) is an efficient way to permanently store large volumes of captured CO$_2$ by subsurface injection at pressures higher than its critical phase point (P$_{cr} = 7.4$ MPa) where it changes from gaseous to liquid state and above a certain temperature level (T$_{cr} = 31.2^\circ$C) to supercritical. This relatively high pressure level strongly encourages the selection of deep reservoirs (min. 700-800 m depth), where the in-situ water/brine pressure equilibrates the injected CO$_2$ pressure. According to the most recent IPCC report (IPCC, 2022), Carbon Capture and Storage (CCS) is key to reaching net-zero emissions by mid-century and mitigating climate change. Besides, the need to implement CCS in a range of sectors including energy production, manufacturing and industry is underlined in the same report.

The feasibility of the technology relies on successful long-term subsurface storage which depends – at least during the first few decades – on the performance of nearly impermeable geological formations (seal/caprock) that will prevent CO$_2$ migration to the surface. Caprock formations, typically shales or tight mudrocks, are highly heterogeneous with low mass transfer properties, and their prone response to Thermo-Hydro-Chemo-Mechanical (THMC) loads remains a complex subject that deserves further inquiry.

Shales have been studied since decades by the oil and gas industry, more recently for their use as geological barriers for nuclear waste storage, but full understanding of their suitability for geological CO$_2$ storage is still somewhat limited, since CO$_2$ injection further complexities an already difficult engineering problem: (i) Unlike oil or water, CO$_2$ diffusion results in acidification of the in-situ brine that can lead to chemical interactions in the caprock and alteration of its mechanical and transport properties (Yang et al., 2022); (ii) CO$_2$ injection introduces stress state changes in both the reservoir and the overlaying caprock that can cause reactivation of pre-existing faults or creation of new fracture systems (Vilarrasa et al., 2019).

Significant progress in experimental data collection has been achieved in various scales (Armitage et al., 2010; Houben et al., 2013), related to both geomechanical response (Rutqvist, 2012; Wang and
Tokunaga, 2015; Kivi et al., 2022) and chemical interactions (Wollenweber et al., 2010; Hadian and Rezaee, 2020) during exposure to CO$_2$-rich fluids. Shales are anisotropic and highly heterogeneous at different scales (micro to macro) with strong geomechanical and geochemical couplings that often challenge our ability to distinguish the different occurring phenomena and estimate their time-scale during CO$_2$ exposure.

In recent years, the Opalinus Clay shale has been studied as a potential caprock in the context of geological CO$_2$ storage (Amann et al., 2013; Favero et al., 2016; Makhnenko et al., 2017; Sciandra et al., 2021), thanks to favourable properties such as low porosity (< 20%), low permeability (in the order of $10^{-20}$ m$^2$), high clay content (40-80%), swelling properties and high sealing capacity (Marschall et al., 2005; Crisci et al., 2019; Delage and Belmokhtar, 2022). These favourable properties of Opalinus Clay (and shales more generally) make it a challenging material to study due to the slow flow processes at resolutions that may fall within the measurement error (Minardi et al., 2021).

**Representative testing of shales remains a big issue.** Representative boundaries do not only involve applied pressure or temperature but also the spatial and temporal scale of the measurement. While large scale experiments are generally considered to be more realistic, they can be challenging to properly monitor and analyse since they involve the combination of multiple phenomena occurring under different scales, in particular in heterogeneous materials such as shales. A real scale experimental campaign has been recently completed at the Underground Research Laboratory (URL) in Mont Terri, where CO$_2$-rich brine has been injected in an existing fault in Opalinus Clay (Zappone et al., 2021). The results have not been conclusive, given the low applied pressure, the volume of injected CO$_2$ and the long time-duration required for transport phenomena to manifest in that scale.

In parallel, recent lab-scale experimental results from CO$_2$ injection tests in Opalinus samples do not show evidence of significant influence on the material’s basic properties for the given test duration (Minardi et al., 2021; Favero & Laloui, 2018); grain density, dominant entrance pore size and void ratio, as well as hydraulic conductivity do not vary in a considerable way after exposure to CO$_2$ over a **weekly time-scale**. The short duration of these tests together with the chosen sample size could be among the reasons for the absence of measurable evolution.

Representative testing conditions and duration are even more challenging when processes of geochemical nature are investigated. Indeed, the impact of chemical reactivity of shales in the presence of
of CO$_2$ remains a very challenging topic. While shales contain minerals reactive to CO$_2$, current lab measurements are not enough since they rely either on post-mortem analysis of fluid composition or mineralogy (Armitage et al., 2013; Elkady and Kovscek, 2020). The indirect interpretation of permeability results before and after CO$_2$ exposure in terms of chemical alterations (dissolution/precipitation) can be ambiguous since they may involve self-compensating mechanisms such as carbonate dissolution, mechanical crushing and inelastic compaction as shown by various authors who studied fractured caprock samples (Yasuhara et al., 2011; Hashemi and Zoback, 2021). It is thus difficult to build solid conclusions on their impact on the structural properties of the material and hence transport and mechanical response.

Taking all the above into account, there is a series of issues when testing shales in the context of CO$_2$ storage: (i) Flow is extremely slow resulting in long testing durations; (ii) Measured permeability variations are close to the measurement error; (iii) Reproduction of real site conditions is crucial since injection pressure and therefore effective stress has an important impact on properties of the material that drive flow and breakthrough, i.e. connected porosity; (iv) Chemical interactions are limited by the slow transport properties (v) The testing duration and scale that are commonly used are not enough to allow investigation in that direction.

In this work, the different coupled processes and phenomena that occur when CO$_2$ interacts with a shaly caprock material – the Opalinus Clay – are explored based on a series of measurements and observations from real time x-ray tomography. Taking full advantage of this non destructive tool, new aspects and results are targeted and demonstrated that aim to improve our understanding of the caprock’s response while under realistic testing conditions. The originality of the presented research relies on the study of smaller size samples where observation period is expected to be shorter, and most importantly the direct measurement of strain fields and structural alteration from the analysis of the 3D tomographic images. In the following, the proposed methodology, tools and analysis conventions are presented in detail. The results of two experimental campaigns where Opalinus Clay shale is exposed to either liquid or supercritical CO$_2$ are presented and discussed. These experiments target different coupled mechanisms that combined aim to contribute to a more profound understanding of the overall THMC response of shales with CO$_2$. 

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2 Methodology, Tools and Analysis Principles

Shales are highly heterogeneous and anisotropic materials, sensitive to thermo-hydro-mechanical variations and with strong multiphysical couplings and very slow transport properties (Mohajerani et al., 2014; Favero et al., 2016; Menaceur et al., 2016; Li and Laloui, 2017). Inevitably, representative testing of shales requires the employment of methods and tools that can embrace these particularities by means of controlled applied conditions and full-field measurement, i.e. a field record of a quantity (e.g., deformation, density, temperature, etc.) as opposed to point-wise data (Viggiani and Hall, 2008).

Taking into account all the above, the exploration of a new approach in testing shales with in-situ x-ray tomography is motivated. In this study, the full-field of micro-structural variations and kinematics of the Opalinus Clay shale when exposed to CO\textsubscript{2} under different boundary conditions are targeted with 3D image analysis of real-time x-ray tomographies. Long-duration exposure of Opalinus Clay to injected liquid CO\textsubscript{2} (8 MPa) under confined conditions (10 MPa) aims to reveal potential chemomechanical processes, while direct exposure of unjacketed Opalinus Clay to supercritical CO\textsubscript{2} targets the better understanding of localised THM interactions that are otherwise difficult to detect with conventional lab-testing techniques.

Despite the classic testing approaches on centimetric size shale samples in the literature, in this work very small samples (5 mm) are studied in order to first gain in temporal resolution (partly inspired by small-scale permeability testing equipment (Birmpilis et al., 2019; Birmpilis and Dijkstra, 2021), but also to optimise the quality of x-ray imaging (improved spatial resolution). This approach is challenging for the given material and the given subject; the pore size of shales is in the order of nanometres and thus impossible to visualise with x-ray micro-tomography (micrometric scale). Nonetheless, observation and quantification of microstructural modifications due to CO\textsubscript{2} can be explored with relatively high scanning resolutions (5-8 µm/px) and fast tomographies thanks to the small size of the sample.

2.1 In-situ x-ray micro-tomography and experimental protocol

A few authors have investigated the heterogeneity and anisotropic behaviour of shales pointing out the role of the microstructure by employing different imaging techniques (Wang et al., 2013; Desbois
et al., 2017; Delage & Tessier, 2021). In the case of experimental geomechanics, x-ray tomography is the most widely used technique, with a large range of results stated in literature (Viggiani et al., 2015; Bedford et al., 2017; Vego et al., 2022; Birmipilis et al., 2022). The great advantage of x-ray tomography compared to other techniques for soil characterisation (e.g. SEM microscopy), is the possibility to identify in 3D the specimen’s heterogeneity and follow its evolution in time (in-situ testing). This is a very powerful tool that allows a better interpretation of test results, such as measured permeability, fingering phenomena, localised deformation or structural modifications (Voltolini and Ajo-Franklin, 2020; Stavropoulou et al., 2020).

For this study, the dual x-ray source in PIXE platform (EPFL, Switzerland) is used. Reconstructions are performed with the XAct software provided by RX-Solutions (Annecy, France), with appropriate beam-hardening corrections applied. The PEEKcell is fixed on the rotating table, as close as possible to the x-ray source, for a maximal use of the x-ray conical beam. All scans are performed in temperature controlled environment of 21°C.

A cylindrical cell made out of PEEK is used for the application of the various boundary conditions, that are explained in detail in the following sections. The so called PEEKcell, is designed to host 5 mm × 5 mm cylindrical samples and can sustain a maximal pressure and temperature of 20 MPa and 80°C respectively (Stavropoulou and Laloui, 2022). An entry on each side of the cell (top and bottom) allows the application of confining pressure (top) and pore pressure on the sample (bottom). The cell is disconnected from the pressure controllers and transported under the given pressure state in the tomograph. To monitor the pressure level during the scans, a pressure transducer is placed on each side (see Figure 1).

The samples are cut to cylindrical shape of d = h = 5 mm; first sized down in rectangular pieces with a saw and then reduced to the desired size manually using fine sand paper (P240). This technique has been preferred (to a mechanical lathe for example) in order to avoid overheating the sample during preparation. The resaturation of the samples has been achieved progressively under free swelling conditions by exposing the samples in a controlled relative humidity (RH) environment with the use of an appropriate saline solution (Romero, 2001); first to RH = 75% (NaCl) and then RH = 98% (K₂SO₄) until mass stabilisation. Before testing, samples have achieved a close-to-full saturation state, corresponding to a measured water content w resat = 6.1 - 6.8 %, i.e. within the range of full
In this work, the micro-structural modifications due to long-duration CO$_2$ exposure are investigated with post-mortem measurements and analysis, i.e. after removing the applied pressures. Then, the occurring kinematics on Opalinus Clay that is exposed in direct contact (no sealing membrane) with supercritical CO$_2$ is examined with in-situ measurements, i.e. while under pressure in the cell. According to the volumetric response of the sample and the corresponding GV of the images, the CO$_2$ uptake is investigated and visualised for the first time.

When supercritical CO$_2$ is injected, a thermal jacket is used around the cell and the applied temperature is monitored with a thermal sensor that is placed between the jacket and the PEEKcell. For achieving a maximal resolution and x-rays penetration the thermal jacket is removed during the scans. Inevitably, this leads to CO$_2$ phase change from supercritical (lower density) to liquid (higher density) and consequently to pressure drop under constant volume conditions, i.e. conditions during scanning. In order to minimise this pressure drop, the cell is exposed to the scanner’s temperature (21°C) two hours in advance while maintaining the pressure at the desired level (pressure pump connected), in or-
der to avoid pressure loss due to phase change during the scan. The possible implications of this CO₂ phase transition before the scans on the given testing campaign are discussed in the corresponding section of direct exposure to supercritical CO₂.

## 2.2 Image Analysis

The result of an x-ray tomography is a 3D x-ray attenuation map of the scanned sample that is associated to the 3D density map of the material. For instance dense phases in the material (e.g. mineral inclusions) attenuate more x-rays than lower density phases (e.g. cracks, pores). The different density (attenuation) levels reflect in the grey level values (GV) of the reconstructed 3D x-ray image; higher GV corresponds to denser phases and lower GV to lower phases as indicated in Figure 1-right. Changes in the GV of a scanned sample in time or due to application of a different load allow the observation and quantification of localised micro-structural modifications (e.g. crack opening/closing, swelling/shrinking) which can subsequently be translated to 3D strain fields with Digital Volume Correlation (DVC). In this work, the open source SPAM software (Stamati et al., 2020) is used for the DVC analysis.

In DVC, two images are required; an initial (reference image) and a deformed one. In the case of local-DVC (that is used for the image analysis in this work), a grid with a given node spacing is defined and at each grid point a centred window is extracted. For each of these subvolumes a linear deformation function $\Phi$ is calculated so that $\text{im}_{\text{def}}(\Phi \cdot x) = \text{im}_{\text{ref}}(x)$. The function $\Phi$ accounts for translation, rotation and stretching and its calculation is optimised by solving an iterative problem that minimises error based on the classic sum of squared difference (SSQD). While DVC can calculate a strain field and that can then be applied it on an image, it does not take into account by definition the variations of the GV due to the corresponding strain. GV correction due to deformation is going to be applied in this work as per (Stavropoulou et al., 2020) where the aim is to investigate phase changes due to chemical reactions between the in-contact CO₂ with the same material.

All scans of each type of test are performed under the same conditions and with the same scanning parameters. Nevertheless, noise, artefacts or other external changes may be present between the different scans (that in some cases are performed in month intervals). To improve the accuracy of image analysis and minimise the GV variations due to measurement conditions rather than real changes in
the material, all images from a testing campaign are normalised based on GV of materials, the density of which is not supposed to vary between the different scans; here PEEK and aluminium. The procedure of the GVs normalisation is explained in detail in the Appendix and results in scaling the given images so that the voxels that correspond to void are set to GV = 0 and those of PEEK correspond to GV = 1.

Finally, for the strain field calculation, the occasional rigid-body transformation of the sample (translation and rotation) due to transportation and re-installation of the cell in the tomograph, is calculated based on the a single Φ function on the entire image (so called registration) and removed. DVC is then performed between the reference image and the deformed ones from which rigid body motion has been corrected. The displacement field is then calculated and translated to strain assuming small transformations (see all details in Stamati et al., 2020). The above principles and conventions are applied for the analysis of the different series of x-ray scans that are presented in the following.

3 Mineralogical analysis and long-term structural modifications

In this section, the long-term chemo-mechanical interactions that can occur between CO₂ and a shaly caprock are explored. When CO₂ is placed in contact with the pore water of the shaly caprock material, it results in acidification of the pore fluid – by means of diffusion – and therefore resulting in an alteration of the chemical equilibrium. For instance, pre-existing carbonate crystals might be dissolved by the acidic fluid and enhance the material’s transport properties (Busch et al., 2008; Espinoza et al., 2011; Jia et al., 2018). On the other hand, incorporation of supercritical CO₂ in micro-structural interlayers can induce the beneficial swelling of smectitic clays (as is expected in self-sealing for nuclear storage applications), but it is not clear whether such a response would occur in situ since such tests have taken place under unconfined conditions (batch reactors) (Alemu et al., 2011).

Taking into account the small size of the samples (5 mm × 5 mm), first a mineralogical analysis of different Opalinus Clay samples is performed with x-ray diffraction (XRD) measurements, in order to evaluate the mineralogical variability. Then the mineralogical map of an Opalinus Clay sample is studied with SEM-EDX (scanning electron microscopy and energy dispersive x-ray) measurements and the identified mineral locations is directly compared and identified in the corresponding slices.
from the x-ray tomography image of the same sample. This combined analysis aims to locate and
demonstrate elements in the sample that may favour chemical interactions in the long-term presence
of CO₂ (e.g. Ca, C, Si, S, O etc.) that is here investigated with x-ray tomography by means of
occurring micro-structural modifications (fissuring, swelling, self-sealing etc.).

Table 1 shows the mineralogical composition of four sister Opalinus Clay samples from XRD
measurements. The fit was optimised on one sample and to increase comparability, the next fits were
done by keeping all refined parameters and replacing the data file on the current model. Even though
the results are quite approximate, a similar quartz and clay content is measured for all samples except
for illite that presents variations up to 8%. In the lower illite-rich samples a higher calcite content is
measured with values that vary among the different samples from 13% to 24%. The mineral content
of sample A (in bold) is measured after long-term exposure to CO₂. It presents a high clay content
that is unclear if it is affected in any way by its previous interaction with CO₂ since its overall mineral
content falls within the variability of the other three untreated samples. Sample A is used to compare
the results from all different analysis tools that are employed for this study.

<table>
<thead>
<tr>
<th>Opalinus Clay (wt%)</th>
<th>A</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>21</td>
<td>13</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>Quartz</td>
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<td>13</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Chlorite</td>
<td>15</td>
<td>15</td>
<td>13</td>
<td>17</td>
</tr>
<tr>
<td>Kaolinite</td>
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<td>2</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Illite</td>
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<td>53.5</td>
<td>52</td>
<td>45.5</td>
</tr>
<tr>
<td>Siderite</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>11.5</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1: Mineralogical composition of four sister Opalinus Clay samples based on x-ray diffraction

In order to confirm the mineralogy of the inclusions identified from x-ray tomography, sample A
has been subjected to a SEM-EDX analysis. The height of the sample is carefully reduced to the height
of the horizontal slice of Figure 2-a using again light sandpaper (the traces of which are apparent in
the SEM images). Figure 2 presents the combined information obtained both from x-ray tomography
and SEM-EDX at the same horizontal slice. In Figure 2 (a) the x-ray slice, the different GV levels
highlight the distribution of the different inclusions in the clay matrix, the mineralogy of which is
identified from the EDX analysis. In fact, there are two sets of inclusions as revealed from the GV
histogram plotted in Figure 2 (b). This is more clear when a bilateral filter is applied (red histogram)
that unveils a second peak that represents the lower GV inclusions.

Figure 2: Identification of the inclusions’ mineralogy combining x-ray tomography and SEM-EDX – (a) horizontal x-ray tomography slice, (b) histogram of GVs of the top horizontal slice, (c) SEM-EDX map corresponding to the blue window of the x-ray slice highlighting all identified elements and the areas rich in Ca and S, (d) SEM-EDX map corresponding to the red window of the x-ray slice highlighting all identified elements and the areas rich in Ca and C.

These lower GV level inclusions are rich in calcite (Ca) and carbon (C) as revealed from the EDX images (Figure 2 (c) and (d)). This type of inclusions are therefore more prone to undergo dissolution in the presence of CO₂. The denser inclusions (whiter inclusions in Figure 2 (a) at the bottom left of the sample) seem to be rich in sulphur (S) (Figure 2 (c)), a main element of pyrite (FeS₂) the density of which is very high. This supplementary EDX measurement reveals that the information from the 3D x-ray images is even richer than what has widely been used for now.

Sample A is the same sample that has been used in (Stavropoulou and Laloui, 2022); it has first been scanned in the x-ray tomograph under unconfined conditions, then after application of confinement (10 MPa) followed by CO₂ injection up to 8 MPa (pixel size 7.8 µm). After CO₂ breakthrough,
it has been let under constant volume conditions in the PEEKcell for 9 months and scanned again in the x-ray tomograph after pressure release (same pixel size and scanning parameters). It is important to mention that there has been pressure loss during these 9 months that has not been properly monitored. Nevertheless, the results present great interest that is not necessarily impacted by this pressure loss.

Figure 3: Horizontal and vertical slices of x-ray tomography on the same Opalinus Clay sample with highlighted fissures (in black) under unconfined conditions at its initial state (left) and after 9 months CO$_2$ exposure (right). The horizontal slices (top) highlight the fissuring of the carbonate phase due to dissolution and the self sealing of the clay matrix pre-existing fissures under long-term confinement; the vertical slices (bottom) highlight the fissure rearrangement and change of orientation that took place in time.

Figure 3, shows a horizontal and vertical slice of two x-ray scans of sample A, initially and after 9 months of CO$_2$ exposure, both in unconfined conditions. The micro-fissures have been manually highlighted in black for more clarity, but the entire volumes can be found at their original form in the supplementary material. The initial image of the sample reveals a vertical bedding orientation according to the orientation of the pre-existing fissures in the clay matrix. After 9 months of CO$_2$ exposure there are two important observations to be pointed out. First, clear fissures in the carbonate
phases have been formed revealing the calcite dissolution for the first time from x-ray images and under non-extreme (if not realistic) testing conditions. In addition to the fissuring of the carbonate inclusions, a disappearance of the initially pre-existing fissures in the clay matrix is observed. This can be explained first by means of self-sealing behaviour of the material under long-duration application of confinement and then by precipitation of Si-reach zones that are not distinguishable from the x-ray images, since they have similar density with the clay minerals. Indeed, (Prakash et al., 2022) pointed out a more pronounced precipitation activity in zones parallel to the direction of the bedding plane.

For a better understanding of the micro-structural modification of the sample after long-term CO$_2$ exposure, the orientation of the minimum eigenvectors (longest axis) of the inclusions and micro-fissures have been plotted in 3D together with their projection in the 2D plane, as shown in Figure 4. Both types of orientation plots are presented for a better demonstration of the result of each studied phase – the 3D histogram is more comprehensible for the cracks’ orientation and the 2D projection for the inclusions. For this analysis, a bilateral filter has been applied on the two images to reduce noise and to smoothen the edges between the different phases (clay/cracks, clay/inclusions). In this way a better segmentation of the phases of interest (cracks and inclusions) can be achieved. It is known that segmentation of shale images remains a difficult task due to the heterogeneity and the contrast of the different phase interfaces. Even though these results could be optimised from a quantitative point of view, the overall shape modification of the two segmented phases is realistic.

The 2D projection of the min. eigenvectors of the inclusions reveals a preferential orientation along the vertical axis – axis parallel to the bedding plane – both initially and after 9 months exposure (Figure 4). The vertical axis of the 2D plots is parallel to the Y axis of the spherical histograms that are plotted in this view to demonstrate the vectors’ orientation on the ZY plane. After 9 months exposure to CO$_2$ the population of inclusions is increased as demonstrated by both plots on the right of Figure 4. This increase in the number of inclusions is a clear indication of carbonate dissolution that resulted in inclusion fissuring and consequently identification of more numerous inclusion particles. The main orientation axis after dissolution remains vertical, suggesting that fissuring due to dissolution has mainly occurred along the shortest axis of the inclusions and therefore perpendicularly to the bedding plane.

In a similar way, the spherical histograms of the minimum eigenvector of the sample’s identified
cracks and their 2D projection are plotted in Figure 5; initially and after 9 months of CO₂ exposure. The shape of the 3D histogram initially reveals the sample’s anisotropy with a preferential orientation parallel to the bedding plane. This is confirmed by the high number of vectors projected on the vertical axis of the 2D plot – even though the low number of cracks make it harder to evaluate. Interestingly, the shape of the cracks’ 3D histogram on the right is very different, confirming the observations and assumptions discussed from Figure 3. First, the number of cracks is reduced, validating the self-sealing (or precipitation) response of the sample after long-duration confinement. Then, most importantly, the orientation of the main cracks has been totally modified and is no more parallel to the bedding. It is not clear whether these new fissures are the result of alteration of the pore fluid’s pH that enhances further chemical reactions between minerals that are not detectable from x-rays and CO₂, or whether they are related to mechanical impact from CO₂ breakthrough (see 3D volumetric response after breakthrough in Stavropoulou and Laloui, 2022). In either case, this result points out a potential rearrangement of the fissure network after long-term CO₂ exposure that has not...
Figure 5: Spherical histogram of the minimum eigenvector of the inclusions and the cracks in sample A, initially and after 9 months exposure to CO\textsubscript{2} (colour represents the number of projected points per bin divided by the median number of points in all bins).

been previously discussed. Most importantly, these results show how little we still know regarding the coupled long-term THMC response of the caprock/CO\textsubscript{2} interaction at the micro-scale and their implications to the large scale response. Longer-duration testing under realistic boundary conditions are required for a better understanding of the complex mechanisms that occur.

Finally, in the aim of a better visualisation of the texture of the carbonic inclusions, the SEM image of the same (unpolished) slice with Figure 2 is presented in Figure 6. For the SEM images, two detectors have been used; (top) a secondary elements detector that basically illustrates the surface topography; and (bottom) a backscattered electrons detector that shows a Z contrast, \textit{i.e.} lighter elements (such as Si, Al, O, K) are darker and heavier elements (here Ca or C) are brighter. The secondary elements detector does not reveal any information regarding the targeted inclusion other than the fewer sandpaper traces that are very obvious on the softer clay matrix. On the other hand, the backscattered electrons detector provides a better distinction between the two phases. The higher
Figure 6: Opalinus Clay core sample

The resolution of SEM allows a better visualisation and understanding of the interface between the carbonate inclusion and the clay matrix that is otherwise not visible with x-rays. While the resolution is still in the micrometric scale and no nanometric pores can be detected in either types of images, a distinct calcite/clay interface of increased porosity is revealed in the zoomed area of the bottom SEM image (blue window). Indeed, this is a good confirmation of what is reported in (Minardi et al., 2021) carbonate-rich Opalinus Clay; the pore size distribution is bimodal with a second dominant pore size between 50-100 μm corresponding to the interface of carbonate/clay particles. This high inter-particle porosity can serve as a preferential CO₂ pathway and eventually enhance geochemical interactions; in this case carbonate dissolution.
### 4 Direct exposure to supercritical CO$_2$

In this part, the interaction of an Opalinus Clay sample with supercritical CO$_2$ is evaluated in time by means of quantitative 3D x-ray image analysis. The unjacketed caprock sample is exposed from all sides (equilaterally) to direct contact with supercritical CO$_2$ (p = 10 MPa and T = 34°C) and regular x-ray scans (resolution 5.38 µm) are performed for the study of its volumetric and micro-structural response. The water saturated sample is mounted in the PEEKcell and a first scan (00) is performed under initial ambient unconfined conditions. Then, the target pressure and temperature are applied and the sample is let to interact with the in-contact CO$_2$. Further scans of the sample are performed while under pressure in the PEEKcell after 13 days (scan 01), 30 days (scan 02) and 56 days (scan 03), as well as after release of pressure and temperature (scan 04).

#### 4.1 Volumetric response

The 3D volumetric response of the caprock material under the above mentioned conditions are evaluated and quantified by means of DVC analysis. As explained earlier, to properly compare and analyse the acquired images, the occasional rigid-body transformation (translation and rotation) is removed so that the images are well aligned as shown in the left column of Figure 7. The middle vertical slice of the tested sample reveals the pre-existence of 3 principal fissures parallel to each other and parallel to the bedding orientation of the sample, i.e. perpendicular to the vertical axis of the sample. These micro-fissures of initial max. aperture $\approx 30$ µm may have been induced during sample preparation and/or during resaturation under free swelling conditions. Their existence is not necessarily an issue for the given study; on the contrary they can provide important insight into the impact of their presence upon interaction with CO$_2$. Looking more closely at the microstructure of the middle slice in Figure 7 an increase of the bottom principal pre-existing fissure can be observed, as well as the creation and propagation of additional new micro-fissures at the bottom of the sample; between the bottom left inclusion structure and the lower principal fissure.

For a more quantitative analysis of the localised response of the sample, the volumetric strain is calculated in 3D between each scan and the initial state of the sample (scan 00) that is used as reference. For the DVC analysis, the chosen parameters (half window size, node spacing etc.) are detailed with the additional provided data online. The map of the calculated volumetric strain of each...
Figure 7: Volumetric response of the middle vertical slice of the Opalinus Clay sample in time after exposure to supercritical CO$_2$.

- It must be noted that the values of measured volumetric strain, total ($\varepsilon_{\text{vol}}$) and maximum ($\varepsilon_{\text{vol,max}}$) correspond to the entire 3D volume. In all scans a more pronounced expansion is measured on the location of the lowest pre-existing micro-fissure ($\varepsilon_{\text{vol,max}}$). Only after 2 months of CO$_2$ exposure (scan 03) a slight expansive activity may be measured around the other two pre-existing ones. The overall...
expansive response of the sample (positive $\varepsilon_{\text{vol}}$) is clearly dominated by the expansion of the fissures that remains mostly constant in time. For the rest of the material it is hard to observe a clear pattern, nevertheless the calculated volumetric strain reveals an initial expansion ($\varepsilon_{\text{vol},01} = +0.041$) that in time reduces ($\varepsilon_{\text{vol},01} = +0.027$) and stabilises ($\varepsilon_{\text{vol},01} = +0.024$). Finally, upon pressure decrease, the material expands in a pronounced way ($\varepsilon_{\text{vol},01} = +0.090$) not only at the lower crack zone but everywhere in the sample due to stress relaxation, as explained in the following.

The interpretation of this response is not straightforward since the sample is subjected to complex THMC boundary conditions. In theory, the application of constant pressure equilaterally and directly in contact with a fully water saturated sample is not supposed to affect the applied effective stress that should remain zero. In other words, since CO$_2$ is injected equilaterally in the unjacketed sample, the concept of effective stress is not valid, neither is the concept of hydraulic fracturing with the increase of pore pressure as it is the same with the applied skeleton pressure. However, the presence of pre-existent fissures suggests that the sample cannot be realistically fully saturated and there matric suction must be present locally in the fissured and partially saturated zones. Upon high pressure CO$_2$ exposure suction breakdown occurs locally (decrease of effective stress) and the sample swells until stabilisation at full saturation – water + CO$_2$. This interpretation can confirm the initial volumetric activity that eventual stabilises in time.

Local modification of the effective stress is not the only mechanism that may take place upon exposure of a shale sample to supercritical CO$_2$. Temperature increase (34°C) induces thermal expansion to the sample that can indeed justify the rather isotropic expansion measured in scan 01. Another important aspect that has been little discussed in the literature is the dessication of the material when in contact with CO$_2$. Indeed, the pore water of the material evaporates in the anhydrous CO$_2$ resulting desaturation which can result to further crack opening (expansion) and pore collapse in the clay matrix. This dessication effect could explain the lower volumetric expansion in time until eventual equilibrium. This little discussed interaction can occur in real field conditions at the bottom of the caprock formation in contact with the buoyant CO$_2$, leading to partial desaturation of the caprock and threaten its mechanical integrity and sealing capacity.

To better understand the impact of the afore mentioned coupled THM mechanisms, the evolution of the fissures’ volume in the different scans is presented in Figure 8. For their calculation the same
GV threshold has been used for all the normalised scans. Once again, segmentation of shale images is a difficult exercise, the optimisation of which is out of the scope of this study. The obtained results are considered sufficient to demonstrate the overall behaviour of the material. While the volumetric increase of the pre-existing fissures has already been identified from the calculated volumetric maps of the entire sample, Figure 8 clearly demonstrates the creation and propagation of a new family of fissures at the bottom of the sample. These new fissures demonstrate in a very clear way the dessication effect of anhydrous CO₂ explained above. Additional chemo-mechanical mechanisms may contribute to the initiation of these micro-fissures that are impressively localised in a calcite-rich area at the bottom of the sample (see x-ray images in Figure 7). Eventual dissolution aspects are hard to interpret since preferential fissuring patterns in calcite-rich zones may primarily be due to increased porosity between the calcite and the clay mineral interface (as shown in Figure 6).

4.2 CO₂ uptake

After the in-depth analysis of the microstructural response of the caprock material during direct contact with supercritical CO₂, an attempt to visualise and quantify the CO₂ penetration in the material is attempted in this part of the study. The analysis is based on the evolution of the x-ray images’ GVs after correction due to volumetric strain as per (Stavropoulou et al., 2020). This approach is quite ambitious in the context of CO₂ uptake, since the density variations due to supercritical CO₂ invasion are very slight. This is why normalisation of the images’ GVs is imperative for this kind of analysis (see Appendix).
Taking into account the measured strain field from the DVC analysis, the variation of the x-ray attenuation coefficient ($\mu_x$) in time is corrected and measured. Volumetric strain results in density variation (and therefore $\mu_x$ variation) that is manifested in the GVs level of the deformed image via a linear relationship. A simple example to better understand this reasoning is the case of thermal expansion with no mass transfer, where the density of the material is expected to reduce, and consequently the attenuation field $\mu_x$ or GVs to decrease proportionally to the change in density. Any additional GV variation is therefore assumed to be due to additional mass transfer (gain or loss); in this work due to CO$_2$ uptake. According to (Stavropoulou et al., 2020), the attenuation variation of a sample is calculated as a function of the mechanical volumetric strain assuming mass conservation:

$$\Delta \mu = -\varepsilon_v \cdot \mu_0$$ (1)

where $\varepsilon_v$ is the measured volumetric strain of the sample and $\mu_0$ is the initial attenuation of the image (before loading).

In order to measure the additional changes of GVs due to mass transfer, the calculated strain field is applied on the reference image (scan 00), while taking into account the corresponding GV correction. Then, simple subtraction of the deformed image (with corrected GVs due to volumetric variation) from the corresponding original image (e.g. 01 minus 00_def_to_01) results in the uptake or loss of mass. The result of this analysis is presented in Figure 9, where the chosen colourbar represents density (in terms of GV) increase (red) or decrease (blue).

The maps of the GV variation show a density decrease overall during the first month of exposure (00-01 and 00-02). This response can be supported by the sample’s desaturation discussed earlier; in fact, invasion of anhydrous CO$_2$ in the material partially occurs through water evaporation, therefore the material is filled up with a fluid of lower density. While these results are somewhat noisy for precise conclusions, nevertheless a more pronounced density decrease is obtained during the first month at the lower part of the sample where crack initiation occurs. On the other hand, around the zones of the pre-existing fissures a density increase is measured; in this case the non saturated zones around these fissures might have been filled in with CO$_2$. It has to be noted that this approach is even less accurate around in-the crack locations. This is because the obtained fields are the result of the subtraction between the initial least fissured image (00) with a future deformed image (e.g. 02) that has more fissures – the application of the calculated deformation field on 00 cannot create these new...
Two months after CO$_2$ exposure, the overall density of the material eventually increases in a relatively homogeneous way, if not with more noticeably around the lower pre-existing fissure. It is interesting to notice that between scans 02 and 03 the volumetric activity that was measured is almost negligible. This density increase under constant volume reveals the saturation of the material with CO$_2$. Indeed, unlike the previous two fields, here the material seems to be in equilibrium indicating that CO$_2$ has invaded it in its entity. Final CO$_2$ pressure release (00-04) leaves the sample with an overall increased density, in particular at the zones around the fissures and at the bottom. This final result may indicate chemo-mechanical or CO$_2$ trapping phenomena that may occurred during the two month exposure. This is a first attempt to visualise CO$_2$ invasion in a caprock material and even though it is quantitative in terms of GV levels, their physical interpretation in terms of e.g. actual CO$_2$ volume increase or water decrease requires further studies and measurement for the calibration of the different phases’ GVs.
5 Discussion and Conclusions

In this work the interaction between the Opalinus Clay, a caprock representative material, with CO₂ is studied with x-ray tomography imaging. The different results and observations reveal the complex response of this material due to multiple coupled phenomena that occur in parallel. Exposure to supercritical CO₂ implies temperature increase of the material that results in thermal expansion (TM coupling). This expansion leads to inevitable desaturation of the material (TH coupling). At the same time, the live observation of the caprock material in time revealed another important aspect when anhydrous CO₂ is in contact with the water saturated sample; the pore water evaporates in the anhydrous CO₂ causing further dessication of the material that starts fissuring. Fissures, whether pre-existing in the material or new ones, play an important role on the CO₂/caprock interaction. They drive most of the volumetric and hydraulic phenomena; swelling, desaturation, uptake, breakthrough. Their impact is still not well understood, in particular under realistic field conditions.

The long-term impact of CO₂ on the micro-structure of the shaly material is for the first time visualised with x-ray tomography on a solid sample and under non-extreme temperature and pressure conditions. Calcite dissolution is identified in carbonate-rich zones that after 9 months of exposure they were fissured (CM coupling). The mineralogical composition of these denser (white) inclusions in the x-ray images has been confirmed from SEM-EDX measurements. Segmentation and labelling the inclusions before and after long-duration CO₂ exposure confirmed an increased number of inclusions due to breakage (dissolution) the mean orientation of which did not significantly evolve. A similar analysis has been made on the fissure network in the clay matrix of the sample before and after long-term exposure. The principal crack orientation in the sample is initially parallel to the bedding orientation of the shaly material. These fissures close with the application of confinement as shown in (Stavropoulou and Laloui, 2022) but very interestingly they do not re-appear 9 months later after pressure release. This result demonstrates the self-sealing response of Opalinus Clay (HM coupling). In addition to the closure of pre-existing fissures, the 9 months x-ray scan revealed the appearance of some new micro-fissures in the clay matrix (other than the fissures in the calcite zones) surprisingly in a perpendicular direction to the bedding. This aspect of potential re-arrangement of the fissure network of the material is demonstrated for the first time and could be due to additional chemo-mechanical mechanisms within the clay matrix or related to CO₂ breakthrough that due to
self-sealing of the initial micro-fissures initiated a new optimal pathway throughout the sample.

Finally, the CO₂ uptake in the caprock material has been investigated by combining the calculated strain fields and the GV variation of the acquired x-ray images. CO₂ penetration in the sample has been identified two months after initial exposure. It is hard to interpret the multi-phase fluid interaction in the porous space of the material prior to two months due to the multiple THMC phenomena that take place simultaneously and often counteract each other. It is interesting to note that after CO₂ release the density of the sample remained increased compared to the initial two months earlier, revealing potential CO₂ trapping in the material.

Figure 10: Coupled THMC mechanisms studied with in-situ x-ray imaging on small size shale samples.

Figure 10 sums up the different coupled mechanisms that have been identified in this work to occur during the CO₂/caprock interaction. These topics require undoubtedly further investigation with long-term experiments under continuously monitored conditions. Analysis of the response using
a non destructive tool, i.e. x-ray tomography allows the study of the material while under realistic conditions. The study of small shale samples has significantly contributed to the better understanding of the various coupled phenomena, first by achieving better time resolutions under non extreme temperature and pressure conditions, and then by studying the material’s response under high spatial resolutions in 3D that revealed mechanisms previously undetectable with conventional testing methods and resolutions.

6 Data availability

The 3D x-ray images that have been used in this paper are provided online in Zenodo [link TBC]. Additional data or results can be provided by the Authors upon reasonable request.

7 Acknowledgements

This study has taken place in the frame of the Spark SNSF CRSK-2_196559 project. The Authors wish to thank the PIXE platform (EPFL) for the assistance during the x-ray tomography scans, as well as the Mont Terri laboratory and SwissTopo for providing the tested Opalinus Clay material.
Appendix A: Normalisation of x-ray tomographies

For the analysis of the attenuation evolution of the images, the different scans are normalised using always as reference scan 00. The objective of this normalisation is to set to zero the voxels that correspond to void in order to be able to more reliably detect density variations. The normalisation is performed considering the parts of the image that are not supposed to vary in density with time; PEEK and Aluminium. Since the void attenuation is changing with the introduction of CO$_2$, the ratio of the greyvalues (GV) between Aluminium, PEEK and air is considered constant as shown in Figure A1.

![Figure A1: Measured greyvalues as a function of corresponding density in scan 00](https://doi.org/10.5194/egusphere-2022-824)

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<th>Aluminium</th>
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Table A1: Measured (normal font) and calculated (bold font) mean greyvalues (and standard deviation/error in the parenthesis) of the parts of the scan that are not expected to vary in density with time for the normalisation of the images

This ratio is calculated from the reference scan 00 (first row of Table A1) and considered constant.
in order to deduce the air greyvalue of the rest of the scans. The computed GV of air (first column of Table A1) is then subtracted from each scan, which is then divided by the corresponding PEEK value so that PEEK average value is 1 for the sake of simplicity. The histogram of scan 00 after normalisation is shown in Figure A2-a, while the histogram after CO$_2$ introduction (scan 003) is changed to that in Figure A2-b. The GV normalisation of the different scans can improve the volumetric analysis (DVC) and it is indispensable for the detection of density variations.

A2: Greyvalues histogram of normalised (a) scan 00 (no CO$_2$) and (b) scan 01 (with CO$_2$)

Appendix B: Segmentation of the x-ray images

The different steps for the segmentation for the different types of phases are illustrated in Figure B1. First, a bilateral filter is applied on the original image in order to smoothen the zones of similar phases and sharpen the edges between different phases (Figure B1-a).

The distributions of the GV levels before and after the application of this filter are plotted in Figure B2; a more narrow distribution is obtained after the bilateral filter, providing more precision for the selection of each GV range for the segmentation of the different phases. The resulted segmented slices of the inclusions and the micro-fissures after the application of a threshold GV range are shown in Figure B1-b and c, respectively. In the case of the inclusions, a double cycle of dilation and erosion of the binary image has been applied in order to reduce noise. This is not possible for a further reduction of the noise of the fissures’ segmented image due to their 1 pixel thickness.
Figure B1: Horizontal slices after the (a) application of a bilateral filter, (b) segmentation of the two types of inclusions (calcite and denser inclusions), (c) micro-fissures

B2: Greyvalues histogram of the original horizontal x-ray slice and after the application of bilateral filter of Figure B2 (a)

References


