

## Response to Referee #2

This article addresses CO<sub>2</sub> interaction with a clay-rich mudrock, originating from the Mont Terri Underground Lab in Switzerland. Authors have taken an imaging approach whereby the long term interaction of the mudrock with CO<sub>2</sub> is investigated and quantified.

The sample has been prepared by saturation over salt solution to obtain near-water-saturated conditions (in my understanding).

Yes, the samples have been exposed to a high relative humidity environment (98%) that is imposed by the presence of a saline solution (the samples are not in contact with the solution..)

My main points are detailed below, further comments can be found in the pdf attached.

The long-term interaction of CO<sub>2</sub> with caprocks acting as seals above CO<sub>2</sub> storage reservoirs is important for de-risking CCS in general but also allows for a deeper understanding of the coupled processes taking place in such a rock where chemistry and temperature affect mechanics and fluid transport.

Studying such coupled effects is the goal of this paper.

Mudrocks are complex rocks, especially when they contain swelling clays, like smectite. Smectite, depending on pH, water content and water composition, can swell or shrink, potentially leading to volumetric expansion or shrinkage of the rock, resulting in crack opening or closure. A careful handling of the geochemical conditions is therefore important to not come up at potentially wrong conclusions. CO<sub>2</sub> interacting with clay-rich material can do similar things. It can dehydrate the sample through water evaporation and can further swell smectite. It dissolves in water, thereby changing pH which again can trigger geochemical reactions (most likely carbonate over short time scales of weeks to months).

Separating all these effects is difficult and not straight-forward. In this study, effects mainly caused by CO<sub>2</sub> have been addressed, disregarding any other implications of water-saturation (change), pH change or other effects.

Thank you for this comment, we are discussing phenomena related desiccation, self-sealing response but maybe not enough. This is hopefully more clear in the separate Discussion section we have added:

### **5. Discussion**

#### **5.1 Long-term CO<sub>2</sub> exposure**

#### **5.2 THMC response**

#### **5.3 Implications for geological CO<sub>2</sub> storage**

This would be important in order to separate observations caused by CO<sub>2</sub> or by any other process that has nothing to do with the injection of CO<sub>2</sub> but only by handling the samples under lab conditions.

Thank you, this is what we try to demonstrate in the paper.

I have placed several comments in the text to highlight where I see this being important. I had the impression that the focus of the paper is too much on showing a CO<sub>2</sub> related effect, to confirm a

hypothesis that was potentially established before running the lab tests.

We are not sure what hypothesis does the Referee means. The objective of this work is to try to identify and focus with each test on different coupled phenomena that take place in the material (at the given THMC conditions). The fact that there is CO<sub>2</sub> – a non-wetting fluid that as shown, both here and in the literature that the Referee suggested, can dry the material and alter its chemical equilibrium – cannot be ignored for the interpretation of the results. There are indeed mechanisms that are not linked or directly linked to the presence of CO<sub>2</sub> and we think we do make this point in the manuscript. For example, self-sealing under long-duration confinement or thermal expansion due to temperature increase have nothing to do with CO<sub>2</sub>. We have also briefly addressed the topic of modified effective stress locally. The cracks due to water evaporation in the anhydrous CO<sub>2</sub> are desiccation cracks (the sample is dried out) but in this case it's the presence of CO<sub>2</sub> that launches them and we hope we have tried to make explicit that the response of the material at the scale we can observe is hydromechanical and not chemical.

This can lead to misleading conclusions, then again used by others.

This would be very unfortunate and we hope that in the revised version there is no such risk.

I appreciate the efforts that have been made in this paper to highlight coupled effects using observations in the wider sense.

Thank you for this comment.

This is a complicated topic that is difficult to address experimentally. Experiments are required to support models for upscaling to reservoir scales. Often a good understanding starts with observations and interpretations. The interpretations made in this paper might be correct but the discussion is far too linear, targeting a single goal which is to relate everything to CO<sub>2</sub>-related effects.

We have hopefully improved the discussion in the revised version – see new Discussion section.

This needs to be revisited before the paper can be further considered for publication.

We appreciate your comments and we have tried our best to revisit these aspects based on the advice and comments in the text. We hope that the discussion is now improved.

Other rather major points:

English language needs to be improved. While the paper is "readable", there are many flaws in the text, like words missing, wrong syntax and partly also wrong tense. Some examples are highlighted in the pdf attached but it is absolutely necessary taking a careful look at this point before potentially re-submitting this article.

Thank you, we have tried to carefully revise the text in combination with the review of Referee 1.

Most observations are discussed in Ch 3 and 4 while Ch 5 talks about Discussion and Conclusions. In Ch 5 there is basically no discussion and mainly the image in Fig 10 is introduced to show how coupling works for the case study presented. It would be good to strictly separate results from discussions and conclusions throughout the manuscript.

Thank you, we have made a separate Discussion section and organised the text in sections 3 and 4 so that presentation of results and discussion are not mixed.

On the same note, besides the introduction (and own citation later on), there has been no inclusion of other literature sources in the "discussion" of the results. Lots of work has been done in terms of volumetric changes of (smectite-containing) mudrocks with changing water contents, pH, CO<sub>2</sub> etc. I do not think the paper can be accepted without a proper discussion including other research outputs. This again might leave to some different conclusions in this study or to a weakening of the statements made about CO<sub>2</sub>-related effects. In particular, research published by groups of Eric Ferrage, Andreas Busch, Chris Spiers, Bernhard Krooss, Richard Worden, Eugene Ilton (and others) etc can be useful in this regard.

Thank you for these references, they add indeed more gravity to the interpretation of our results. We agree that the way the manuscript was organised (mixing results and discussion) the references we had included for the interpretation of our results were a bit confusing.

We appreciate a lot the Referee's detailed comments and suggestions on the pdf of the manuscript and we have made our best to address them all. Here below are the comments from the pdf other than typing or similar suggestions that we have directly corrected/modified in the text.)

**L.39:** 'low mass transfer properties'

This is another way to say 'low transport properties'.

**L.45:** 'oil'

We have removed it

**L.82:** '...measurements are not enough since...'

Made explicit '.. not sufficient in identifying chemical interactions directly, since...'

**L.151:** 'PEEKcell'

We have named the cell 'PEEKcell' in one word which in oral pronunciation sounds similarly to pixel since it is destined for live imaging. (First presented in Stavropoulou and Laloui 2022, Evaluating CO<sub>2</sub> breakthrough in a shaly a caprock material: a multi-scale experimental approach)

**L.176:** I understand the measurements were done at 21°C, so all under subcritical temperature?

Yes, as explained in L. 174-182, during 2h45m for the x-ray scans the sample is at 21°C. We have tried to address the possible implications.??

**L.226-227:** Existing literature on smectite swelling with scCO<sub>2</sub>

Added in the new Discussion section.

**L.244:** I see differences of 11% for calcite which is much higher compared to illite in relative terms

Yes, we state this in the following sentence.

**L.246:** I am confused, where does this long-term interaction with CO<sub>2</sub> come from?

We have modified this sentence to be more clear: 'The different content values that are presented for sample A (in bold), are measured after long-term exposure to CO<sub>2</sub>'.

**L.246:** 'high clay content'

This is a typing mistake, modified to ‘high calcite content’.

**L.250:** what do you mean by inclusions

They mainly refer to ‘non-clay’ mineral inclusions

(e.g. ‘Fundamental aspects of the hydromechanical behaviour of Callovo-Oxfordian claystone: From experimental studies to model calibration and validation, Armand et al. 2017’, ‘Analysis of Local Creep Strain Field and Cracking Process in Claystone by X-Ray Micro-Tomography and Digital Volume Correlation, Shi et al. 2021’ and more.)

We have explained it in the text.

**L.271:** Any idea about total pressure loss and what was the temperature? Can you exclude sample dehydration?

The temperature was ambient (and controlled) for this test (25°C). We unfortunately do not have an idea that we can state in the paper about the pressure loss. There was no pressure loss during at least the first 4 months, and after 9 months the pressure was down to half from initially 10 MPa. We discuss in the first part of the Discussion section why we believe sample dehydration is not likely to have affected the results given the observed response of the material (mainly fissure closure) after long term confinement:

‘Possible desaturation of the sample is not likely to explain the creation of these localised fissures, since dessication cracks in shales appear mainly within the clay matrix or at the interface of the clay matrix with other inclusions (calcite, pyrite etc.). Fissuring in the clay matrix is however not observed even after total pressure release (unconfined conditions). On the contrary, the number of pre-existing fissures initially in the sample is reduced. This is additionally ensuring for the potential impact of progressive pressure loss during these 9 months of exposure. Pressure loss may result in desaturation and fissuring of the sample (usually parallel to the bedding orientation) that have not been observed at the given resolution of this study.’

**L.271:** A fissure is not necessarily a sign of dissolution

We have modified this statement to be less absolute ‘suggesting calcite dissolution’.

We discuss in new Section 5.1 why we believe that these fissures are related to dissolution:

‘In this study, the identified cracks in the calcite zones of Opalinus Clay after long-term interaction with CO<sub>2</sub> are associated to dissolution effects. Even though calcite dissolution has not been previously observed to result in fissuring, the fissures in the calcite zones of the material reveal a localised activity within these zones. Calcite dissolution in shales is mainly identified indirectly by post-mortem analysis either of injected fluids or solid samples. In this work, the visualisation of large calcite inclusions allow the observation of micro-structural modifications that occur locally, within the area of interest (i.e. the calcite zones).’

**L.271:** ‘..under non-extreme (if not realistic) testing conditions’.

Modified to ‘under realistic pressure and temperature conditions’.

**L.283:** Any evidence for precipitation of Si-rich zones based on SEM?

Unfortunately not – we have made it explicit in the text.

**L.304:** Fissuring due to dissolution suggests a preferential dissolution of a carbonate grain. Is this correct?

There seems to be a preferential fissuring orientation in the calcite inclusions due to dissolution (as we assume): the fissures are perpendicular to the long axis of the inclusion. We have modified the text: ‘The main orientation axis after dissolution remains vertical, suggesting that fissuring in the carbonate particles has mainly occurred along their shortest axis and therefore perpendicularly to the bedding plane’.

**L.310:** What is "harder"? For the authors, the reader, in general?

We have removed this sentence because it is unnecessarily confusing.

**L.314:** if you argue precipitation, then you should also speculate on the type of precipitation

We have removed this discussion and interpretation of these results from this section to Section 5.2

**L.320:** it seems to me that something has been observed in XCT scans over 9 months of interactions (where temperature and pressure are not very well known). Some fissures developed and some disappeared; sometimes they are preferentially oriented with the bedding, sometimes not. The resolution of the XCT scans is rather low considering the grain sizes of a mudrock. So actually what is happening is unclear but it is the first time (as mentioned a couple of times) that this has been observed from XCT. Correct?

The ‘non well monitored’ pressure conditions are explained in a comment above and added in the text: there was 5 MPa pressure loss during the past 5 months. Temperature is controlled at 25°C. We have done our best to explain that the fissures that appear in the calcite zones are too localised to be dissociated from geochemical interactions with CO<sub>2</sub> (see Section 5.1). The other fissures that pre-existed in the clay matrix are parallel to the bedding orientation and have been most probably created during saturation of the sample. The fact that they do not reappear (we are unfortunately limited by the resolution) after pressure release but rather fissures of perpendicular orientation show up is commented. As explained (hopefully better now) in the sentence above, these new perpendicular fissures may be just due to the mechanical boundaries from previous hydromechanical testing of the sample.

We have chosen not to be absolute for the interpretation of the results but it is maybe a mistake. Yes, it is the first time we can identify such effects in 3D and in localised regions of the material rather globally from averaged measurements. We are sorry to sense some irony in the way the Referee’s comment is articulated.

**L.337-341:** I do not think that this is very useful. We know that Opalinus Clay has a low diffusion coefficient which is mainly because of low pore connectivity, so small pore throats. Accessibility should be via diffusion in fully water-saturated pore space. If this is not the case, it is not representative of carbon storage. If water saturation is >1, then there is potential for advective flow (which

would not be representative for CCS or only when the cap pressure is exceeded). So the argument that just because a larger pore is identified is insufficient in providing an explanation of accessibility to the pore space for CO<sub>2</sub>.

Thank you for your comment. We have removed the last sentence.

**L.344:** define unjacketed. Is this unconfined?

Added 'no membrane'

**L.344:** so, this time it is 100% water-saturation and not saturated via salt solutions at near 100%?

We do not mention 100% saturation in the text. The same saturation protocol has been applied for all samples, i.e. progressive increase of applied RH using saline solutions. This is explained in the 3rd paragraph of Section 2.1, not sure why it is not clear to the Referee.

**L.349:** what is "in-contact"? Does that mean the CO<sub>2</sub> is in direct contact with the outside of the sample rather than through the aqueous phase?

We have made it explicit 'unjacketed' means '(no membrane)' around the sample. So the injected CO<sub>2</sub> is in direct contact with the material from all sides.

**L.351:** that is after how long?

Right after scan 03, i.e. 56 days. We have explained this in the text and is also highlighted in Figure 7.

**L.396-398:** I think this has been addressed in the literature already. It would be good to come up with a little calculation of how big this effect can be, so how much water could, in theory, evaporate from the sample into the gaseous phase. Water dissolution in CO<sub>2</sub> is known as a function of p,T and if you know your gas volume and the porosity such a calculation can be done. If there is desiccation, I would assume this to happen at the outside of the sample, not the centre where most fractures are visible.

Thank you for the comment. We have added some references that mention this interaction – not necessarily in the same type of material. What the Referee suggests is happening is in line with our observation: desiccation cracks appear at the bottom of the sample which then propagate upwards. The fact that there are pre-existing fissures, make this phenomenon more pronounced in these zones too, starting from the sides inwards – there is no membrane, the CO<sub>2</sub> is provided from all sides, top, bottom, right, left.

**L.409-410:** this is quite a quick interpretation. How about delayed stress-relaxation cracking? How about smectite swelling/shrinkage due to pH changes?

We are discussing this in Section 5 and our reasoning is hopefully better elaborated.

**L.458:** when comparing the density decrease compared to the increase, there seems to be a balance between the two of 0.210?

Not sure what the Referee means with this comment. The stated GV changes are relative to the initial state of the sample (00). During the first month (00-01 and 00-02) the GVs have decreased in a stable way  $\approx -0.110$ . A month later (00-03) the density has increased compared to the initial state of

the sample.

**L.464:** there has been much of a discussion in previous sections already but not really by taking into account other literature sources

This issue is hopefully resolved in the new discussion Section 5.

**L.472:** I think it should be noted that these fissures would not exist under reservoir conditions because there we can expect close due to high effective stresses.

We have added: 'In the field, fissures in the caprock formation could found around the injection wellbore or fault zones'

**L.477:** maybe better to quantify the conditions. Non-extreme sounds like not upper mantle

Thank you, made it explicit in the text.

**L.478-479:** I still dont see why fissuring would be a sign of dissolution. Dissolution will not occur in the form of a fissure but rather through dissolution of the outer rim of the grain(s)

We have modified the text in a less absolute way: 'Fissuring of calcite-rich zones after 9 months of CO<sub>2</sub> exposure is associated to dissolution-related effects'

**L.484-487:** can have multiple reasons like impact of water, stress-cycling etc on a previously dehydrated sample

We have modified this statement in line with the corresponding discussion in Section 5: 'This result demonstrates the self-sealing response of Opalinus Clay that can be attributed to a series of mechanisms: long-term hydromechanical loading (HM coupling), expansive smectitic response, mineral precipitation of Si-rich zones (CM couplings).

Not sure where reasoning related to stress-cycling or sample dehydration arised from. Pressure loss does not involve stress cycles and 'previously' dehydrated sample does not apply to the initial state of the studied sample (i.e. with a fissure network that we have characterised).

**L.490-492:** what could be a mechanical reason for this to happen?

We are reasoning on the potential breakthrough pathways: 'The preferential pathway of CO<sub>2</sub> breakthrough is not yet well understood in such heterogeneous microstructures and may induce fissuring of different orientation than the in-situ bedding.' Also see end of new section 5.3.

### **Added references:**

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