Response to the Referees

We thank both Referees for their feedback and suggestions that we consider them to be in their great majority fair and constructive. We have done our best to address and implement all remarks and we believe that the quality of the manuscript has been significantly improved. The language has been carefully revised and the methods, results and discussion have been separated in a clearer way. We have replied here below to the specific comments and to avoid confusion we refer to the line numbering of the initial manuscript. All modifications are highlighted in red in the attached files and we hope that the expectations of both Referees are now met.

Referee #1

This manuscript presents new live x-ray tomography 2D and 3D data from long-term injection tests of liquid CO2 into Opalinus Clay shale samples. The overall objective is to study the capacity of shale as caprock for CO2 storage under realistic pressure and temperature conditions. The study sets out to reveal potential chemo-mechanical processes and improve the understanding of localised Thermo-Hydro-Chemo-Mechanical (THCM) interactions in the shale under natural conditions.

The manuscript focuses on microstructural variations and kinematics of Opalinus Clay shale when exposed to CO2 in two different test modes, studied via 3D image analysis of real-time x-ray tomography. For long-term testing, liquid CO2 (8 MPa) was injected into samples and held under confined conditions (10 MPa) for 9 months under constant volume conditions in a PEEKcell. For the second line of testing, samples were exposed to supercritical CO2 (P = 10 MPa, T = 34°C) for up to 56 days. A combination of SEM-EDX mapping and x-ray tomography was used to analyse changes in mineralogical composition and structural evolution of the samples before, during, and after testing. The 3D volumetric response was analysed via digital volume correlation (DVC). Normalised grey level values (GV) x-ray imaging visualised and ultimately quantified CO2 penetration into the material.

Long-term injection of liquid CO2 resulted in re-arrangement of the pre-existing micro-fissures in the clay matrix and significant fissuring of calcite-rich zones that were for the first time visualised and quantified from x-ray images. Tests with exposure to supercritical CO2 showed initial swelling at pre-cracked zones and new micro-fissures in areas of direct contact to CO2. Advanced 3D image analysis showed an increasing CO2 uptake with time and potential CO2 trapping in the material.

The most significant findings include: successfully proving the increasing CO2 uptake and potential CO2 trapping in the Opalinus Clay shale. The method used as well as the results will need further work and will have importance for evaluating and monitoring the integrity and stability of shale caprocks in CO2 storage.

I found that the manuscript contains a variety of useful data that has the potential to add to what is known about CO2 storage regarding shaly rocks.

Thank you.

However, I also identify many issues that need to be addressed before the manuscript can be considered for publication in EGUsphere or any other Journal. My assessment is that, once the raised issues have been adequately addressed (if possible), the manuscript could be acceptable for publication. In my view, the extent of the changes required amounts to a major revision.

Thank you for this overall positive evaluation. We are addressing the different remarks/suggestions here below.

Specific Comments:

Issues range in significance and include: a lack of articulation of the significance of the study in regards of the 'big picture', sub-optimal structure of the manuscript (particularly the results and discussion), and generally poor quality of writing (See section on Technical Corrections and line-by-line comments).

1 - The study sets out to reveal potential chemo-mechanical processes and improve the understanding of localised Thermo-Hydro-Chemo-Mechanical (THCM) interactions in the shale under natural conditions. **I recommend that the author elaborates more on how the results of their study fit into the bigger context, potentially by adding a sub-section to a possible Discussion section.**

Thank you for the recommendation, we have re-organised the discussion in a separate section:

5. Discussion

5.1 Long-term CO2 exposure

5.2 THMC response

5.3 Implications for geological CO2 storage

We have added a subsection (5.3) where we address possible implications to geological CO2 storage.

'**5.3 Implications for geological CO2 storage**

In this work, a series of coupled phenomena that take place in a shaly caprock material have been addressed and discussed based on qualitative and quantitative measurements of 3D x-ray tomography images. The various THMC mechanisms that have been demonstrated, are related to some extent to the equivalent testing conditions: stress state, CO2 pressure and time exposure, water saturation/dessication, mineral dissolution and precipitation. However, field conditions are different than these testing conditions. For instance, the levels of effective stress in a CO2 storage site are much higher, in the order of 10 to 20 MPa (depending on the storage depth). Consequently, the stress state of the material has an impact on the appearance of fissures. The fissures in the calcite-rich zones of the material have been visualised in an unconfined sample state (scan taken after pressure release). Similarly, dessication fissures due to water evaporation in the invading anhydrous CO2 might not manifest (at the given resolution) under elevated levels of effective stress. However, drying of the caprock due to interaction with undissolved CO2, is a phenomenon that might take place at the interface between the reservoir and the caprock due to the buoyant tendency of CO2. Dessication of the caprock can have implications that can threaten the caprock integrity and sealing capacity, for example, facilitate CO2 breakthrough. The exact CO2 breakthrough pathway in the caprock is not easy to predict because of the high micro-structural heterogeneity of the material. The connected

pore space (including fissures) is supposed to drive flow and breakthrough phenomena, however, the different competing mechanisms (e.g. dessication, local effective stress modification) may result in the collapse of initially conductive pathways and the creation of new ones. There has been previous evidence of such phenomena in gas migration tests (Harrington et al. 2012; Cuss et al., 2014). The results of this study and their interpretation, demonstrate the importance of considering the different localised effects for a better understanding of the long-term response of shales in the context of geological CO2 storage. Macroscopic or averaged measurements and observations that do not take into account the micro-structural heterogeneity of shales, are limited for the development representative constitutive and numerical models.

2 - Structural changes to improve readability:

a) Separate observations from interpretations and methods. Description of results is often blended with interpretations of the data, methods applied and comparisons with published literature (which should be done more often). Please could the author revise the results so that all interpretations of the data and comparisons with published literature are moved to a new, separate discussion or new sub-chapters.

b) Long sentences with lots of sub-sections make it harder to understand the precise meaning of sentences. They also divert the attention away from the main message of a sentence and distract the reader. Please could the author consider shortening sentences in order to be more precise on what they want to say.

Thank you, we have revised the text and re-organised the methods, results and discussion more clearly in different sections. We have also tried to reduce the length of the sentences in order to make the manuscript more easily readable.

Technical Corrections:

The manuscript is riddled with major writing style idiosyncrasies and needs a lot of revision. Detailed suggestions on how the text can be improved can be found in a line-by-line comment section.

Thank you for this comment. We have tried our best to apply the suggested modifications as explained below and in the text.

The following issues and others (I recommend also consulting the author guidelines) repeatedly appear throughout the text:

Thank you for taking the time to carefully address author guidelines – we are impressed by the effort of the Referee and somewhat surprised that issues related to guidelines have not been addressed during the initial editing evaluation upon submission.

1. Avoid words/expressions like ‘unveil’, ‘embrace’, thanks to’, as they are very casual.

   Thank you for the suggestion, we have at times modified or deleted such words. Not sure though why the Referee considers expressions like ‘thanks to’ to be casual – if there is a positive

impact the term ‘thanks to’ shall be used, if there is a negative impact the term ‘due to’ shall be preferred.

2. Avoid using possessive nouns (the ‘s). For example, instead of ‘the caprock’s response’, use ‘the response of the caprock material’.

   Thank you, we have eliminated apostrophes in the text.

3. Avoid ‘;’ in regular sentences, see lines 75, 187, and throughout. They are preventing the writing to be more fluid.

   Thank you, they have been modified by splitting the sentence in two or (in fewer cases) by replacing them with ‘i.e’, ‘,’ and ‘:’.

4. Commas are frequently missing or in the wrong position, see Lines 89, 91, 93 and throughout the document.

   Thank you for the comment, we have tried to better punctuate the text.

5. Italic font may be used for emphasis, although this should be used sparingly (see journal guidelines). See Lines 384, 444,...

   Removed all italics.

6. If the author’s name is part of the sentence structure only the year is put in parentheses ("As we can see in the work of Prakash et al. (2022) the precipitation has increased").

   OK.

7. If the author’s name is not part of the sentence, name and year are put in parentheses ("Precipitation increase was observed (Smith, 2009)") – per journal guidelines

   Corrected where needed.

8. Use metaphoric terms instead of clear objective terms (‘opening the door’ instead of ‘possibly’, ‘on the other hand’ instead of ‘conversely’)

   Thank you for the suggestion, we have tried to modify where judged appropriate or necessary.

9. Avoid incorporation of superfluous words/phrases (e.g., ‘indeed’, ‘will be discussed in section xx’, ‘as discussed above’)

   Thank you for the suggestion, we have tried to eliminate such parts to the maximum.

10. Avoid erroneous usage of temporal terms instead of comparative terms where no time frame is implied (e.g., ‘while’ instead of ‘whereas’, ‘occasionally’ or ‘sometimes’ instead of ‘rarely’ or ‘less commonly’, ‘often’ instead of ‘commonly’)

    Thank you for your comment, even though we do not entirely agree with the term ‘erroneous’ in the usage of the indicated terms, we have tried to be more literal.

11. Use precise or quantifiable language instead of vague and/or relative terms (e.g., ‘relatively high/low’, ‘a very long time’, ...)

    Thank you, we have tried to eliminate such terms.

12. As per the journal guidelines on capitalization: only the first word is capitalized in headers (in addition to proper nouns) – per journal guidelines

    Thank you, headers have been corrected.

13. From the journal guidelines: The abbreviation "Fig." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence, e.g.: "The results are depicted in Fig. 5. Figure 9 reveals that...".

    Thank you, this has been corrected, as well as the citation style where needed in the text (according to the guidlines).

14. Be consistent throughout the manuscript. For example:

    - Opalinus samples, Opalinus Clay shale, Opalinus Clay samples

      Thank you, corrected ‘Opalinus Clay’ where missing. Did not modify ‘Opalinus Clay shale’ in some places in order to stretch out the fact that this material is a shale.

    - 8% and 8% (spaces must be included between number and unit, e.g., 1%, 1 m)

      Corrected.

    - In situ and in-situ (Latin phrases should not be hyphenated (e.g., "in situ", not "in-situ")

      Thank you, corrected.

Figures:

Figure 1: This figure is very self-explanatory. Caption: please use ‘grey values’ instead of ‘grey-values’.

Corrected ‘grey values’. Not sure whether the Referee uses the term ‘self-explanatory’ as a negative aspect of the figure and how to improve it.

Figure 3: Visually separate the columns and/or separate the headlines by a different font or boldness to make it clear at first view that the bottom sections are also from the initial / after 9 months material.

Done.

Figure 6: Please add to the caption explanations: what type of sections, what type of imaging, what the red dotted lines are marking, ... also consider adding (a), (b), (c), (d) to mark the panels.

Thank you, modified accordingly.

Figure 7: Name the columns and describe them in the figure caption. What type of imaging was used? Named panels make it easier to highlight significant features throughout the text. Add arrows to show there is a progression.

OK. Caption modified to: 'Volumetric response of the Opalinus Clay sample in time after exposure to supercritical CO_2 – left: middlde vertical slice of the x-ray CT image, right: corresponding map of volumetric strain from DVC analysis'

Figure 8: Consider naming the panels (a), (b), (c), (d), (e). An arrow or several arrows would indicate to the reader that there is a progression. Add a scale and legend. Mark the significant areas in some way to make it easier for the reader to know what you are discussing specifically.

Thank you, modified accordingly.

Figure 9: Please consider naming the rows (panels), add arrow(s), mark the most significant feature(s), and consider making the images of the second row larger, as it is difficult to see features.

Modified accordingly.

Figure 10: Overall, this figure presents a great summary of the work. I suggest making the subsets larger, as the current size makes it difficult to see what is going on.

Thank you, tried to enlarge the insets as well as possible.

Line-by-line:

Line 11: ... the long-term integrity of the caprock.

Done.

Line 12: Please be more specific, what is a 'very long time'? Compared to what?

Done.

Lines 15-16: Please revise/split this sentence for better understanding.

Done.

Line 19: ...resulted in significant fissuring ...

Done.

Line 21: 'a re-arrangement ... was observed'

Done.

Lines 24-25: The meaning of this sentence is not clear. Please revise.

Done.

Line 30: Please be more specific. Relatively high compared to what?

Done.

Line 50: Replace 'in' with 'on'

Done.

Line 53: Please specify what type of anisotropy. Mechanic, seismic, acoustic, ...? Heterogeneous in terms of what? Mineral composition, fabrics, ...?

Done.

Line 59: Consider replacing 'thanks to' with 'because of' OR: ... due to the fundamental mechanical/physical properties of the material, such as ...

replaced with 'because of' – 'due to' is related to something negative which contradicts the 'favourable properties' that motivated the usage of 'thanks to'.

Line 64: Please explain what is meant by 'representative boundaries'. Critical limitations for testing, perhaps?

As explained in the following words of the sentence, boundaries refer to the applied testing conditions such as applied pressure, temperature but also duration and size of the tested sample. Modified to 'Field-representative testing conditions' and is hopefully more clear now.

Line 66: What are 'large scale experiments?

We believe that the term 'large scale experiments' can stay without explicit precision given the introduction of this paragraph; this refers to a wide range of scales between the lab and the field, i.e. from the higher centimetric scale to a pilot scale (a few meters) scale.

Line 71: Please consider revising this sentence.

Done.

Line 72: ... on that scale.

Done.

Line 74: ... on the fundamental material properties ...; Consider what properties: i.e., physical, mechanical, ...

Modified to 'fundamental material properties'. The kind of properties we refer to with 'fundamental' are explained after the colon ':'.

Line 75: Replace ';' with ',' and consider moving the citated authors: ... injection tests in Opalinus samples (references) do not show evidence ...; The references could be moved to the end of the sentence.

Moved citations at the end of the sentence and replaced ';' with ':' for better clarity and splitting of the sentence, *i.e.* avoid s too long sentence.

Lines 77-78: Please clarify what this statement is based on.

When the transport properties of the material are so slow, limited amount of testing duration and/or big sample sizes may be the reason why not much is observed. Waiting longer and/or testing smaller samples may lead to more interesting observations.

Line 82: This sentence could be improved by making clear in what regard the measurements not enough. Also: consider replacing 'not enough' with 'not sufficient' or something similar.

Explained: 'not sufficient in identifying chemical interactions'

Line 88: Consider replacing 'on' with 'about': ... conclusions about their impact on the structural properties ...

We have modified the sentence to be more clear 'It is thus difficult to build solid conclusions on the impact of chemical interactions on the structural properties of the material, and consequently on its transport and mechanical response'.

Line 89: Add a comma: ... and hence, transport and mechanical response.

Modified sentence.

Line 91: Add a comma: Flow is extremely slow, resulting in ...

Done.

Line 93: Add commas: ... since injection pressure, and therefore effective stress, has an important ...

Done.

Line 95: Please state what has slow transport properties and add ';' before (v) to be consistent. Done. Consider revising (v), as it does not seem to fit into the context of (i-iv). Give more details about the scale? Modified 'scale' to sample size – this last point (v) refers to the testing limitations that are related to the previous points.

Line 99: non-destructive

Done.

Lines 101-104: Commas?

Modified the structure of the sentence to be easier to read.

Line 109: Please change the headline to: ... Analytical Principles

Modified to 'Principles of Analysis'.

Line 117: Consider using another term instead of 'exploration'. For example: 'development'.

Thank you for the suggestion, even though we believe that the term 'exploration' is more representative of the reality we modified to 'development'.

Line 126: Please consider: ... in order to improve the temporal resolution ... OR ... in order to increase the temporal resolution ...

Done.

This could be split into two sentences instead of using ()

Line 129: ...subject. The pore size...

Done.

Line 131: Be more specific, for example CO2 injection / exposure / ...

Thank you, we have corrected this typing mistake: '... due to interaction with CO_2 ...'

Line 135: Please specify what type of heterogeneity and anisotropy

Sepcified: 'mineralogical heterogeneity' and 'THM anisotropy'.

Line 136: Microstructures

Not sure what the comment is about – microstructure in singular is more appropriate to our understanding.

Line 141: ...to identify the heterogeneity of the specimen in 3D ... What type of heterogeneity?

Modified to: '...the mineralogical heterogeneity of the specimen in 3D...'

Line 142: To be more specific you could change the beginning of this sentence: X-ray Tomography is a very ...

Thank you, modified.

Line 145: Please consider specifying what type of platform this is?

Added: '...platform for X-ray micro-tomography...'

Line 149: Replace 'of' with 'at'

Done.

Line 150: Explain what PEEK is / stands for

Done.

Line 157: ... is placed on both ends (). OR 'Two pressure transducers are in position at the top and the bottom of the cell to monitor pressure levels during the scans.' Sides are also left, right, front, back.

Done.

Line 158: This sentence could be improved by not using a ';'. For example: The samples ... mm by cutting rectangular pieces with a saw, followed by ...

Done.

Line 177: 'a pressure drop' OR specify how it drops: successive/constant/rapid at the end/beginning/middle, ...

Done.

Line 187: ... are reflected ...

Done.

Line 187: Replace ';' with '.' and start a new sentence.

Done.

Line 197: Make sure all variables are explained.

Modified to $im_{deformed}\ (\Phi \cdot x) = im_{refrerence}(x)$

Line 202: Please take a look at the citation style / grammar of this sentence and amend accordingly. ...

Modified to: 'Deformation based GV correction as per Stavropoulou *et al.*, (2020) is going to be applied in this work, aiming to investigate phase changes due to chemical reactions between the in-contact CO_2 with the same material'

Line 206: ... monthly ... ALSO consider revising this sentence and/or split it into two.

Removed the content of the parenthesis.

Line 215: Please check the grammar of this sentence. ... based on a single ... for the entire image ...

Corrected.

Line 226: Consider using 'Furthermore' or something similar instead of 'On the other hand'.

Done.

Line 235: Please replace 'is' with 'are'

Done.

Line 237: What is meant by 'demonstrate elements'? Show the presence of elements perhaps?

Thank you, modified.

Line 238: Consider replacing 'by means' with 'by studying'

Modified to: 'and evaluate their response based on the occurring micro-structural modifications that are identified from x-ray tomography (fissuring, swelling, self-sealing *etc.*)'

Line 243: Consider putting the evaluation at the end of the sentence / section. 'quite approximate' is vague, be more specific, for example by citing numbers.

Deleted the first part of the sentence.

Line 247: The meaning of this sentence is unclear due to grammatical and structural issues. Please revise.

Modified to: 'Even after long-term CO_2 exposure, its mineralogical composition does not vary in a significant way compared to the other three untreated samples.'

Line 248: Consider moving this before presenting the Sample A results.

Line 249: analytical

Done.

Line 252: ... Figure 2-a, using sandpaper.

Done.

Line 254: Be consistent: Figure 2-a OR Figure 2 (a).

Done.

Line 256: Consider starting the sentence like this: There are two sets of ...

Done.

Line 257: Consider rewriting this sentence, for example: 'This becomes more significant by taking into account that a second peak representing the lower GB inclusions is visible when a bilateral filter is applied (Figure 2 (b)).'

Thank you, modified accordingly.

Line 261: 'lighter' instead of 'whiter'

Modified to ''brighter'.

Line 263: The meaning of this sentence is not clear. Please revise.

We removed this sentence.

Line 268: Replace 'let' with 'held' or 'subjected to' or similar.

Done.

Line 271: Please be more specific about the significance of this! How significant was the pressure loss? What is the time scale, etc.?

We have explained: 'during the last 5 months the confining pressure has been reduced to half and the CO_2 pressure to 1 MPa'. We discuss possible implications at the end of paragraph 2 in new Section 5.1:

' 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.'

Line 271: Why is there no significant impact? What leads to this statement? If this is based on the results from this study, it should be moved to the discussion.

Please see our previous reply.

Line 282: Please clarify: is the explanation self-sealing followed by precipitation or are both explanations independent from each other?

We have moved this part to the new Discussion section, where hydromechanical self-sealing and self-sealing due to mineral precipitation are more clearly dissociated.

'Fissure closure can be explained by means of hydromechanical self-sealing behaviour of the material under long-term confinement. The self-sealing response of shales is one of the main properties for which this material is studied as a potential sealing material in a broader context of underground storage, such as radioactive waste, CO2 or hydrogen storage (Bossart et al., 2019; Di Donna et al., 2022, Yu et al., 2022). Hou et al., (2022) discussed the self-sealing response of caprock materials in terms of mineral precipitation. They showed that in illite-rich shale precipitation took place in quartz, i.e. Si-rich zones. In the current study, Si-rich zones are unfortunately not distinguishable from the either SEM or x-ray images. Prakash et al., (2022) pointed out a more pronounced precipitation activity in zones parallel to the direction of the bedding plane. This is in line with the identified orientation of fissures in the sample before and after confinement and CO2 exposure. The pre-existing fissures that were parallel to the bedding orientation disappear, and the fewer fissures after long-term confinement and CO2 exposure are in their majority no longer parallel to the bedding. Other works have shown that incorporation of supercritical CO2 in micro-structural interlayers can induce the beneficial swelling of smectitic clays (Alemu et al., 2011; Busch et al., 2016).'

Line 284: See comment Line 202: a better start of this sentence would be: Prakash et al. (2022) ...

Done.

Line 295: Elaborate – what is the basis for this statement?

Segmentation in a material like shale that is composed by many different phases (not like concrete for example where there are 3 main phases: aggregates, cement/sand and pores), is very sensitive to the user. Accurate image segmentation is an entire research filed by itseld and since more recently is apporached with very sophisticated methods including neural networks and machine learning algorithms. So here we wanted to indirectly acknowledge that the precision of segmentation has not been a topic where we invested our effort to use complex and sophisticated tools for the analysis of our images, but a standard thresholding approach.

We have removed this sentence and rearranged the previous ones to avoid confusion.

Line 297: minimum instead of min.

Done.

Line 309: Please clarify – does this refer to the initial sample?

Yes, modified to 'The initial shape of the 3D histogram' and it is is hopefully more clear.

Line 337: Citation style: These results confirm the findings of Minardi et al. (2021) from carbonate rich Opalinus Clay shale.

OK.

Line 338: Please clarify if these are results from this study or from Minardi et al. (2021).

Modified to: 'These results confirm the findings of Minardi et al. (2021) on carbonate rich Opal-

inus Clay shale that identified a bimodal pore size distribution, with a second dominant pore size between 50-100 μm corresponding to the interface of carbonate/clay particles.

Line 349: ... are applied. CO2 is introduced into the PEEKcell when the P-T conditions are stable.

Modified to: 'CO_2 is then introduced in the cell in direct contact with the sample. The target pressure and temperature are applied and maintained stable over a period of 56 days.'

Line 351: ... 56 days (scan 03) of CO2 exposure. A final scan is performed after the release of pressure and temperature (scan 04).

Modified, thank you.

Line 359: These ... with an initial maximum aperture of ...

Done.

Line 362: Name the middle slice in the figure to make it easier for the reader to connect what you describe to what it is you see. In this instance, it is not clear at once what part of the figure is referred to.

Added in Figure 7.

Line 376:. A distinct pattern is absent in the rest of the material, but the calculated volumetric ...

OK.

Line 384: Consider regular, not italic

Done.

Line 387: ... suggests that the sample is not completely saturated.

Done.

Line 390: ... at full saturation, which means a decrease of free water and increase in CO2. Is this correct? Please be more specific here

Line 395: ... has been discussed little in the ...

Done.

Line 395: Add references

Done – see added references at the end of this document

Line 403: Whose calculation?

Modified: '...the volumetric evolution of the fissures in the different scans is calculated and presented in Figure. For this calculation...'

Line 410: Please elaborate what mechanisms may be active and discuss why these mechanisms.

Done.

Line 417: Consider deleting the first sentence of this section. Start with: Analysis of the evolution of GV from x-ray images after correction for volumetric strain (Stavropoulou et al., 2020) is used to visualise and quantify the CO2 penetration into the material.

Thank you for the suggestion, modified accordingly.

Line 420: Consider using 'difficult' instead of 'ambitious'.

Changed to 'challenging'

OR say something like the method is not particularly sensitive for the small scale of density variations due to supercritical CO2 invasion. Also, give details why this statement is made. Are there other studies that show the 'slight density variations'? Are these results from this study? Give more details.

When sc-CO2 invades the open porosity sample, the density of the sample is not going to change in a striking way. That would be the case if we were injecting a dense fluid, e.g. Mercury. This is where the challenge comes from.

Line 423: This whole section describes a method and should be moved. Thank you moved to the end of section 2.2.

Line 430: After Stavropoulou et al. (2020) the attenuation ...

Done.

Line 432: Explain $\Delta\mu$ as well.

Done.

Line 439: Move the explanation of the legend to the figure caption.

OK.

Line 444: Consider using regular instead of italic

Done.

Line 448: Please clarify: ... around and in crack locations or either around or in crack locations.

Done.

Line 451: ... fissures. Therefore, the density will always be decreased in the direct vicinity of the fissures.

Done.

Line 452: Please consider: ... of the material increases homogeneously ... otherwise words like 'eventually' and 'relatively' are vague terms that make the statement highly speculative.

Done.

Line 461: 'the' instead of 'their'

Done.

Line 465: For this work... Please mention briefly why the interaction (...) was studied.

Line 476: ... of a shaly material ... OR ... of Opalinus Clay shale

Done.

Line 477: What are those conditions? Give numbers.

Done.

Line 478: ... that develop fissures after 9 months of exposure.

Done.

Line 486: ... as shown in Stavropoulou and Laloui (2022) but do not re-appear 9 months later, after pressure release.

Done.

Line 488: Capacity; ..., the x-ray scan after 9 months of CO2 exposure shows new micro-fissures in the ...

Done.

Line 498: It is significant that after CO2 release....

Done.

Line 501: Consider replacing 'sums up' with 'highlights'.

Done.

Line 504: Non-destructive

Done.

Line 506: Please consider naming the phenomena here to underline the significance of the contribution.

These phenomena include the volumetric reponse and water evaporation during exposure to supercritical CO_2, the localised chemo-mechanical interactions in calcite-rich zones, the CO_2 uptake and the role of micro-fissures in the material, and the volumetric response upon CO_2 breakthrough.

Referee #2

This article addresses CO2 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 mdrock with CO2 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 CO2 with caprocks acting as seals above CO2 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 shrimkage 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. CO2 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 chaging 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 CO2 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 dessication, self-sealing response but maybe not enough. This is hopefully more clear in the seperate Discussion section we have added:

5. Discussion

5.1 Long-term CO2 exposure

5.2 THMC response

5.3 Implications for geological CO2 storage

This would be important in order to separate observations caused by CO2 or by any other process that has nothing to do with the injection of CO2 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 CO2 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 CO2 – a non-wetting fluid that as shown, both here and in the literature that the Referee suggested, can dry the material and alter it's chemical equilibrium – cannot be ignored for the interpetation of the results. There are indeed mechanisms that are not linked or directly linked to the presence of CO2 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 CO2. We have also briefly addressed the topic of modified effective stress locally. The cracks due to water evaporation in the anhydrous CO2 are dessication cracks (the sample is dried out) but in this case it's the presence of CO2 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 ovbservations 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 CO2-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:

Englisch 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, CO2 etc. I do not think the paper can be accepted without a proper discussion inclusing other research outputs. This again might leave to some different conclusions in this study or to a weakening of the statements made about CO2-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 pronounciation sounds similarly to pixel since it is destined for live imaging. (First presented in Stavropoulou and Laloui 2022, Evaluating CO2 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 scCO2

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 CO2 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_2'.

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 CO2 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 inlusion. 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 unecessarily 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: its 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 dessociated from geochemical interactions with CO2 (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 been 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 CO2.

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 CO2 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_2 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 CO2 is know 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: dessication 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 CO2 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 it 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_2 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_2 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.

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