June 14, 2018

Dear Reviewer,

We thank you for your comments. In the rebuttal letter, we addressed your comments separately. The comments are italicized, followed by our point-by-point response.

Enclosed please also find a copy of the revised manuscript with changes highlighted.

Sincerely,

Tiange Xing

Anonymous Referee #2

General comments:

This manuscript presents an experimental carbonation of olivine aggregates and the real-time observation of the reaction using in-situ dynamic X-ray microtomography and nanotomography. It builds on a previous study by the same group (Zhu et al., 2016) in which the authors reacted a cup made up of sintered fine-grained olivine (0-20 μm) and searched for dissolution, precipitation, and fracturing evidences. Here, the authors re use these data, perform more advanced investigations, and run a new experiment using coarse-grained olivine (80-100 μm). The main consequence of the olivine grain size difference is that precipitation of magnesite is spatially heterogeneous in the fine-grained experiment while it is homogeneous in the coarse-grained experiment. In the fine-grained experiment, the heterogeneous precipitation of magnesite produces a differential volume increase between the interior (maximum increase) and the nearsurface (no increase) of the cup walls so that the near-surface domains are fractured.

This leads the authors to suggest that reaction-induced fracturing occurs during carbonation and helps maintaining the reactive surfaces in olivine on short time scales.

The recognition of dissolution pits (etch pits) and channels indicates that dissolution could be the process maintaining the reaction on the long term.

Overall, the manuscript presented by Xing and coauthors is well written, presents interesting observations leading to logical conclusions, which make it a valuable contribution.

The experimental setup uses modern technics (in-situ dynamic x-ray microtomography and nanotomography) that bring novel observations on carbonation reaction. I suspect the data processing to be heavy and to require a lot of work and efforts, which makes this study even more valuable. I therefore recommend this manuscript for publication, provided the authors clarify a few points that I detail in the following.

Specific comments:

1) This study uses previous work from Zhu et al. (2016). I assume, but am not completely sure, that the authors simply used the data already acquired and did not run a new experiment using fine-grained olivine aggregate. Is that correct? In any case, Paragraph 3.2 could be slightly modified to emphasize more clearly which part of the observations and data processing is from Zhu et al. (2016) (then in theory not the best situated in a Results section but this is not a problem here) and what is completely new.

The microtomography experiment on the fine-grained olivine cup is the same as in Zhu et al. (2016) but the 3D analyses of fracture network, quantification of grain volume and porosity are new. The nanotomography experimental results (dissolution pits and tubes) on the reacted fine-grained cup are completely new.

Zhu et al. (2006) hypothesized that large grains would be preferred sites for precipitation of new crystals, Thus the loose olivine grains (100-500 μm) in the immediate vicinity of the inner cup surface (made of fined-grained, 1-20 μm, olivine) function as precipitate traps and thereby kept precipitation level at the surface of the olivine cup wall low. This led to the contrast in magnesite precipitation within the cup wall.

Because the grain size contrast played a key role in generating non-uniform volume expansion, we do need to compare the results of the fine-grained experiment (Zhu et al., 2016) to the new coarse-grained experiments. To make the points clearer, we now use abbreviations SGC (for the fine-grained experiment) and LGC (for the coarse-grained experiment) at another reviewer's suggestion.

We have edited the text and made the new results more explicit.

2) Regarding the experimental setup, I guess there was a lid of olivine aggregate on the cup as in Zhu et al. (2016)? It may be worth mention it and represent it in Figure 3. Do the authors have an idea of the fluid flow direction in the cell? Is it purely vertical or does the more porous core (loose olivine sand) involve lateral flow through the cup walls? It may be of interest to explain and understand magnesite precipitation or nonprecipitation in the different domains.

We modified Figure 3 to add the lid.

These were not flow-through experiments. A constant pore pressure of 10 MPa was kept during the experiment. The pore fluid does not flow because there was no pore pressure gradient along or across the sample. The whole sample assembly was fully-saturated.

We added this information in Section 2.1 (lines 141-143).

3) The authors report a 10% initial porosity of the cup wall (line 129). Is it identical in the two cups? I wonder what makes this porosity, is it olivine grain boundaries or fractures? How interconnected is this porosity? I would suggest adding a short paragraph describing the structure of the starting aggregate.

The initial porosities of the two aggregated are similar, estimated from the microtomographic scans (see new Figure 8). From these scans, the pores the coarse-grained aggregate are fully connected, whereas the pores in the fine-grained aggregates form different connected clusters. This might also be partly because of that some of the pore throat are beyond the resolution of the microtomographic data. Both aggregates are very permeable, indicating well-connected pore networks.

We added more descriptions of the starting materials in the text (lines 128-138).

4) This is of importance because I do not completely get the distinction between the fracture and the dissolution planes, particularly the lines 239-243 and the Figures 5 and 6. For the reaction-induced fractures, do they cut across the olivine grains (i.e., breaking them in two) or do they use the grain boundaries? I have the same question for the dissolution planes. I also wonder why dissolution would form a single flat plane and not an anastomosing network. What causes the dissolution plane to have this geometry? Can we imagine that the size of the olivine grains plays a role, favoring large-scale, single *structures (e.g., what is described as a single dissolution plane) in the coarse-grained experiment and small-scale, network-like structures (e.g., what is described as a crack pattern) in the fine-grained experiment?*

The reaction-induced fractures cut through cluster of grains. Because the spatial resolution in the microtomography experiments is ~2 micron, and the reaction-induced fractures occur only in the fine-grained sample (0-20 micron), we are not able to resolve whether the grains were broken in two , most fractures developed using grain boundaries. Nanotomography data show that some fractures also cut though the olivine grains.

The Figure 9 (now Figure 10 in the revised manuscript) shows that the dissolution plane is primarily a single feature with a few small branches. Development of such secondary features are probably limited by the reaction duration (30 hours).

We think these fractures are dissolution-assisted fractures under tri-axial extension. We explained the formation of the planar features in the text:

"Under a constant confining pressure, volume reduction in olivine grains (i.e., dissolution) likely shortened the LGC sample length as reaction proceeded. Because the axial piston was kept at a fixed position during the experiment, this shortening in sample length resulted a decrease in axial stress. Because the LGC sample is mechanically weak (less cohesion), even though the reduction in axial stress is small, it could be sufficient to cause fracture LGC in the manner of dilation bands under triaxial extension (e.g., Zhu et al., 1997). Detailed examination of the 3D images revealed the disappearance of small grains along the plane which is clear evidence of dissolution. Thus we refer to these planar cracks as dissolution-assisted fractures under triaxial extension. The dissolution-assisted fractures were not observed in the SGC sample because it is much stronger owing to its fine grain size (e.g. Eberhardt et al., 1999; Singh, 1988). The triaxial extension stress condition would be no longer present once precipitation started (after ~36 hours) and sample volume expansion took place."

5) The last part of the discussion focuses on the application of the findings to natural systems. I think this could be improved by discussing more how the results compare with observations made on natural samples. For instance, in the last paragraph, the authors state that reaction-induced fracturing helps maintaining the reaction on the short term while dissolution does it on the long term. There is one study on natural samples that could reinforce these conclusions. Reaction-induced fracturing has been recognized in peridotites serpentinized at mid-ocean ridges by Rouméjon and Cannat (2014, G3). The hydration leading to the replacement of the olivine by serpentine occurs along a network of fractures (forming the so-called mesh texture). These fractures develop in two steps: 1) conjugate fracture planes of combined tectonic and thermal contraction origin that crosscut the olivine before hydration; 2) reaction-induced fractures associated to the volume increase consecutive to serpentinization while hydration occurs. It is shown (see their Figure 8c) that the reaction-induced fracturing occurs in the early stages of serpentinization (probably before 20% of serpentinization) while the rest of the volume increase is accommodated by the serpentine itself and dissolution processes dominate until completion of the reaction.

Many thanks for the suggestion and we also really appreciate the reference. This could be an important direction for the future work.

We added new discussion on the relevance of the laboratory experiments and field studies (lines 450-458).

6) Another question to develop concerns the typical length scale of the dissolution and fracturing processes. In this study, such processes occur at nano- to micrometer scales (Lines 291-2923: "micro-meter scale in the case of the coarse-grained aggregate and at nano-meter scale in the case of fine-grained aggregate, and reaction-induced fracturing in the case of the fine-grained aggregate."). These scales are rather small for natural samples and would correspond to a second order permeability. Much larger permeability pathways (e.g., mm to cm cracks) are required to efficiently channel fluids and provoke carbonation of significant volumes at rapid time scales. Do the authors think their results are transposable at such larger scales? And if so, could they make suggestions on what would it require for actual CO2 sequestration? (e.g., system dimensions, typical grain size, . . .)

In this study, we focus on understanding the underlying mechanism of porosity generation during olivine carbonation reaction. The physics of the porosity generation mechanism is scale independent. While the grain size used in laboratory settings are much smaller, the time scale using is also much shorter. It is conceivable that given enough time, the nano- to micrometer scale cracks could grow to centimeter fractures.

We do however, recognize that upscaling is always challenging for laboratory investigation. We added new discussion on the relevance of the laboratory experiments and field studies (lines 450-458).

7) Finally, I find Figure 12 intriguing and full of potential for further studies. This is a nice example of advances made posible by X-ray tomography in the comprehension of mineralogical reactions. I think there is still a lot of microstructural work possible using such technics.

We agree.

Technical corrections:

Lines 19-20: "dissolution fractures developed". I guess the authors mean dissolution planes?

Corrected.

Line 24: I would rephrase the end of this sentence: "by the volume mismatch in the cup walls, between the expanding interior and the near-surface that keeps a nearly constant volume"?

We have modified the sentence to clarify.

Line 32: Not sure Escartin et al. (1997) is the most relevant here. Maybe you could cite review papers such as Deschamps et al. (2013, Lithos) or Guillot et al. (2015, Tectonophysics) that list and discuss peridotite exposures

We have added the citation of Deschamps et al. (2013) in the introduction.

Line 78: "olivine mineralization" is unclear, needs clarification

We have modified this to olivine carbonation.

Lines 104-105: I suggest reformulation: "with larger grain size (80-100 μm) compared to the previous experiment reported by Zhu et al. (2016; 0-20 μm).

Modified.

Line 129: I guess the 10% porosity refers to the coarse-grained olivine aggregate. Is it comparable to the fine-grained olivine aggregate?

Both samples have an initial porosity of 10%. Also shown in the Figure 8, initial porosity of the two samples are comparable.

Line 133: I do not think the authors clearly mention the duration of their experiment. I suppose this is 36h for the coarse-grained experiment and 7 days for the fine-grained experiment (from lines 149 and 150)? In the abstract they mention "until the olivine aggregates became disintegrated". Is it really the case? It should be described here.

The clarification has been added.

Line 164: "simplified analyses" is a bit odd. I think I understand what the authors mean but that can be rephrased.

This phrasing has been modified.

Lines 168-169: "both the cup wall (surface?) and the cup (wall?) interior"

The sentence has been modified to clarify this.

Lines 187-189: Not sure this paragraph is really useful

We have modified the paragraph and also the structure of the section 3.

Line 191: "is not observed to be dominated by stress-generated fracturing" is a though formulation, needs rephrasing

Modified.

Lines 192-193: this should go in the discussion

We have incorporate that into the discussion.

Lines 193-195: Needs rephrasing, the sentence about the loose grains seems to be in the middle of two sentences talking about the cup walls. "precipitation-caused nonuniform stretching" is hard to follow.

Modified.

Line 195: "in the sample". I guess the authors refer to inside the olivine aggregate as opposed to the surface. Throughout the manuscript, it is sometimes hard to follow what the authors are referring to due to the changes in the terminology (e.g., interior is also used to refer to the inside of the cup wall)

Modified.

Line 199: "as a single plane" instead of "along a main plane"?

Corrected.

Line 202: "disintegration of the cup's wall"

Modified.

Lines 203-204: Maybe I am wrong, but "fragile" and "cohesion-less" seem to say the same thing here, so I suggest rephrasing

Modified.

Line 205: "after 68 hours of reaction". "exhibits a hierarchical manner" is a bit odd, needs rephrasing.

Modified.

Lines 206-207: "Figure 5b shows that the fractures first occurred in areas close to the surface and propagated inwards. "The fracture first developed as a single. . .".

Modified.

Line 209: "systematic" can be deleted

Modified.

Lines 210-212: The end of the sentence is not clear and would need rephrasing. But it also looks like discussion and should be removed (as well as line 213).

This is a description of the fractures network pattern. Its morphology is similar to the 'mud desccication crack'.

Line 215: "their", not really clear what it refers to

We have modified the sentence to clarify.

Line 216: cite Figure 8 here instead of at the end of the next sentence?

Added the citation.

Line 231: "a volume expansion"

Modified.

Line 241: "It's obvious". . .not really

A citation to Figure has been added here.

Line 242: "along"

Corrected.

Line 251: "exhibits a hierarchical geometry in which the fractures that appeared first are now the largest"

Line 252: "domains" instead of "patches"

Modified.

Line 262: Is there a way to have typical sizes (e.g., diameters) or it is too variable?

The typical radius of the ~6 pixels (360 nm). We discussed the radius in the estimation of the permeability in discussion. Statement on the inner diameter of the tubes has been added here.

Line 326: I would add a reference here, as in the introduction (line 51)

Line 360: "should still be in a range"

Corrected.

Line 422: "and the resulting contrast in the expansion" is unclear, needs rephrasing

The statement has be modified to clarify.

Figure 1: "reacted" and "unreacted" are not clearly visible, change the color Lines 579-580: the sentence is complicated, needs reformulation

Modified.

Figure 4: It took me a while before understanding where the subvolume 2 was exactly positioned. It gives the impression that the subvolume 2 was outside of the cup. Perhaps a 2D sketch would be more efficient.

We changed the shading to better illustrate the cubes. The 2D representation of subvolumes 1&2 could be found in Zhu et al. (2016).

Figure 9: If possible, add the orientation of these volumes

We have added annotation to indicate the cup's outer and inner surface (now Figure 10).

Figure 10: To which experiment and time does this figure correspond? Also, I could understand that the dashed line polygon corresponds to the upper half of the photos but it was not straightforward. I suggest indicating that differently (e.g., annotate the upper half of the photos or modify the orientation picture).

We have added in the figure captions the names SGC for the fine-grained sample and LGC for the coarse-grained sample.

We modified figure capture to better describe the dashed lines (new Figure 11).