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 #3

The manuscript presents experimental results for carbonation of olivine in 4D, three spatial dimensions plus time. It is a follow-up on a previous paper from the same group (Zhu et al., 2016), and provides both some additional data on the experiment in the previous paper and results from a new experiment using a coarser-grained initial material. There is not much 4D data on such processes available in the literature, which makes this a topic that is suitable for publication, within the scope of the journal, and will attract a lot of attention. The paper is also well written and fairly easy to read, although there are some misprints.

However, in my opinion the authors are spending too much time on repeating statements and data that is already present in Zhu et al. (2016). Of course some background information from the previous paper needs to be included, but quite large parts of the text can be removed and replaced with a reference to Zhu et al., and perhaps more importantly, repeated background information should be clearly marked as being repeated, to avoid giving the fake impression of being new data presented in this manuscript. Furthermore, there is not that much information about the new coarse-grained experiment, and it would be a lot more interesting to see some more details about the differences between the fine-grained and coarse-grained experiments instead of an extended discussion of the crack patterns presented by Zhu et al. Thus, I recommend a major revision where the authors should reduce the amount of repeated data. In the following I firstly give my recommendations for what should be removed, and suggest some other data that could be included. Then I list a few major concerns, followed by some minor comments and a list of misprints.

We made a major revision in Section 3. Detailed changes are listed below.

Remove or add

- Section 3.2 is mainly repeated from Zhu et al., and should be shortened significantly.

There is no need to repeat the entire description of the formed cracks and cemented patches, since the interested reader can look up Zhu et al. instead. Figure 7 is a direct repetition from Zhu et al., but I admit that this might be useful to include as background.

The grey value distribution in figure 8 is also included in Zhu et al., although in the supplementary material and without the best fit representation. If the authors include the same type of analysis on the coarse-grained experiment, this would be interesting, but without it I don't see much value in the figure. In the end of the section the authors estimate the expansion, something Zhu et al. didn't do, apart from noting

that the material expanded. It is fine to include this number here, but it would be more interesting with a similar number from the coarse-grained experiment. The expansion might be zero in that case, but if so it should be stated clearly. Furthermore, is it possible to extract expansion as function of time from the data? That might be interesting.

We have reorganized the section 3 and to make our new result more explicit. Paragraphs and figure that might be considered a repetition have been removed from the section.

For the grey value histogram, we have now included our analysis on the LGC sample in the new Figure 7.

The expansion is not observed in the coarse-grained experiment. We have clarified this in the revised paper (lines 226-227).

- Section 3.4 would be more useful if it compared data from the fine-grained experiment with similar data from the coarse-grained experiment. As it is, this section is mainly a more verbose version of what is already written by Zhu et al., with a few additional estimates of growth rate.

This section is modified in the revised manuscript (lines 265-287)

- Section 4.2 is a large chunk of the discussion, and mainly repeats stuff from Zhu et al., and most of it can be removed. Also, figure 13 can safely be removed. Although it shows 3D data and Zhu et al. only presented a 2D plot, the data here is hard to interpret and only discussed in context of 2D porosity distribution. Thus, it has little value. A few comparisons between the two experiments might be interesting, but not much more.

We do think that it is important to visualize the 3D porosity distribution (now Figure 14). The figure provide an easy visualization that 1) the porosity reduction as a result of precipitation is non-uniform (with smaller porosity at the center); 2) there is no detectable secondary porosity generated in the region where most precipitation takes place. This is the key difference between the "crystallization pressure model" and the "volume mismatch model".

We modified the section4.2 in the revised manuscript.

Major concerns

- In figure 6, it is stated that the linear feature in the coarse-grained aggregate is caused by dissolution. It is not at all clear to me why dissolution would cause such a linear structure. In a flow-through experiment you might expect some sort of wormholing, but this can hardly be relevant here. Rather, I would assume that what is shown is a single axial crack, with secondary dissolution of the crack faces. If the authors really think the structure is just caused by dissolution, they have some explaining to do as to why this ends up being linear. Some data on formation of this crack-like structure in time and perhaps tracking of grains at each surface of the structure might help. Now this is just guessing, but I think such a structure might be caused by a crack if you have less, but non-zero, volume expansion in the coarse-grained aggregate. Higher volume change would naturally then lead to a denser crack pattern. Of course there is some dissolution going on, but I have a hard time understanding why it would organize itself as a crack.

Thanks for pointing this point.

We agree that these fractures are axial cracks, with secondary dissolution of the crack faces. They are renamed as "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."

- I do not believe that the "expansion cracks via stretching" mechanism is a reasonable full explanation of the cracks. On lines 231–233 the authors state that grains in the center of the cup wall move apart. Now, these grains were initially bonded mechanically. How can they separate if these bonds are not broken during the process?

Clearly they must be. This might be caused by some sort of dissolution-precipitation creep or by reaction induced cracking. I guess it would be difficult to tell the difference based on the available data, but to me it seems likely that these bonds are at least partly cracked, before the crack is recemented by the reaction products. Thus, there might be dense, invisible cracking in the center of the cup wall, while the effect of this cracking and expansion in the wall center is a less dense crack pattern on the outside of the cup wall. A rock simply cannot expand in a chemical process that involves dissolution of the base material and precipitation of some product unless bonds between the initial grains are broken. Uneven heating of a rock would cause something like the situation presented in figure 14, with the yellow part being warmer than the green, but in a chemical process there has to be some deformation in the reacted part.

The microtomographic images clearly show a volume expansion in the center of the cup wall where there is no evidence of cracking or porosity increase. So we think that the expansion is more likely resulted from a dissolution assisted creep process, not by fracturing caused by crystallization pressure.

The main point of Figure 15 is that in a system where the crystallization force is not large enough to directly fracture the host rock, if the volume expansion (by creep) is heterogeneous within the sample, reaction-induced fracturing and porosity increase can still occur as a result of stretching caused by the volume mis-match.

We modified the text to clarify this point (lines 444-450).

Minor comments

Generally, please state more clearly in figure captions whether results are from the fine-grained or coarse-grained experiment.

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

Line 179: A description of the color scale used would be helpful, e.g. something like "... where X represents black, and Y is white".

This is a statement of the binarization process. We convert the image into the phase of interest (assigned value 1) and the matrix (assigned value 0).

In our data, the black to dark grey colors represent pores, and white to light grey colors represent olivine (illustrated in Figure 7).

Lines 264–266: Here, it is noted that there is evidence for hierarchical fracturing within the olivine grains. Later, it is peculiarly written on lines 333–335 that there is no evidence of cracks in olivine grains. This is at best sloppy. Furthermore, why are these cracks forming, if not by the very reaction induced cracking that the authors claim is not observed?

Thanks for pointing this out. The sentence (lines 333-335 in the original version) was modified:

"Indeed, the nanotomography data show only dissolution features such as etch pits and worm holes, with no evidence of crystallization pressure induced cracks (Figure 11)" (lines 368-370)

Lines 278–288, and figure 12: It would be interesting to see plotted the individual volume change of the olivine grain and the formed precipitates. I would also suggest changing the figure a bit, it is hard to see the structure of the precipitated material. Something closer to figure 5 in Zhu et al. would be better.

We made diligent attempts to segment the different solid phases (i.e., olivine vs. precipitates). Unfortunately, the phase contrast between the precipitants and olivine grains is very small, and at the current spatial resolution of ~2 microns, we could not segment precipitants from olivine grains with acceptable uncertainties. Even at the sites where large orthorhombic crystals are present, it is difficult to determine the phase boundaries between olivine and orthorhombic crystals. Improved imaging techniques and perhaps different experimental designs are needed to quantify the reaction progress.

We modified the figure (now Figure 13) to increase the contrast between olivine and precipitates.

Figure 1: The text "Reacted" is extremely hard to see, please consider changing the color.

Thanks for pointing this out. We have changed the color in the revised Figure 15.

Figure 5: Why is the dissolution or crack always in the lower right corner?

This is a mere coincidence. Dissolution features and cracks are also observe in other part of the sample. Figures below shows that this dissolution is also observed in other places rather than just the lower right corner.

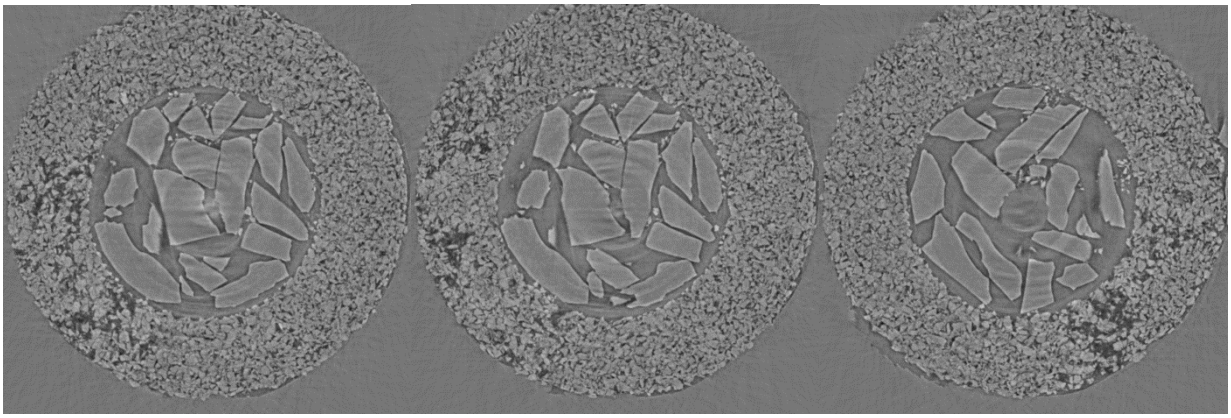

Figure 9a: I'm unable to interpret the fracture network, please consider reworking the figure a bit and perhaps include a view from different angles.

We have changed a viewing angle of the fracture network in Figure 9 (now Figure 10 in the new version of manuscript). We also partly changed the opacity of the fracture to better illustrate the structure.

Misprints

Line 38: reaction -> reactions

Corrected.

Line 92: system -> systems

Corrected.

Line 131 (and other places): x-ray -> X-ray

Corrected.

Line 154: images -> image

Corrected.

Line 206: shown -> shows

Corrected.

Line 232: gains -> grains

Corrected.

Line 242: alone -> along

Corrected.

Line 251: appeared -> appearing

Corrected.

Line 255 and figure 14 caption: none-uniform -> non-uniform

Corrected.

Figure 1: crystalization -> crystallization

Corrected.