

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 #1

1/ Introduction

The manuscript by Xing et al. entitled “Generating porosity during olivine carbonation via dissolution channels and expansion cracks” reports on a very nice piece of experimental work on the in-situ hydrothermal carbonation of olivine aggregates. Careful attention is paid to the real-time development of microstructures to unravel reaction-induced porosity changes and fracturing. Indeed coupling and feedbacks between dissolution/crystallization and generation of new fluid pathways within mineral aggregates (synthetic rock) is still poorly known although highly relevant to metamorphic and alteration reactions which involve aqueous and carbonate fluids. The study basically confirms a reaction-transport-deformation model that has been proposed by the same authors in 2016 based on a very similar experiment using the same characterization technique. The difference with the present study mostly relies on the use of a different mineral grain size. The high similarity between the two studies makes sometimes difficult to distinguish between data that have been collected here and in the previous study. Naming samples like LGC (larger grain cup) and SGC (smaller grain cup) would potentially help.

Thank you for the suggestion! We adopted the name SGC for the fine-grained cup and LGC for coarse-grained cup in the revised manuscript.

2/ General comments

- 2.1 About Reaction progress

Estimate of the overall reaction progress in the cup is an important piece of information. In a system that is prone to porosity clogging due to volume expansion of the solid phases, it is expected that the nature, density and geometry of fluid pathways will change with reaction progress. Basically, are the features described in this study relevant to peridotites that are at the beginning of the carbonation process (< 10%) or do they apply to extensively carbonated systems?

A key finding of this study is the porosity generation mechanism that couples dissolution and precipitation during olivine carbonation. At the beginning of the reaction, it is conceivable that dissolution plays an important role in maintaining porosity. As reaction progresses, non-uniform expansion of the rock due to precipitation could lead to fractures (reaction-induced fracture). Once the host rock is fractured, accelerated reaction takes place to achieve 100% carbonation.

We added the discussion in the revised manuscript (line 453-456).

Basically, if one considers a solid volume (V_s) expansion of x , then the volume expansion of the solid matrix (ΔV_s) is a function of reaction progress (R): $\Delta V_s = V_s^0 * R * x$. Let consider the endmember case where the overall sample volume (V_r) is constant and that the expansion of the solid matrix is only compensated by porosity shrinking. Then, porosity will vanish when $\Delta V_s = V_r(p^0)$ where p^0 is the initial porosity. Finally, we end up with $R = p^0 / (1 - p^0) * x$. In the SGC cup, $p^0 = 0.1$. Assuming $x = 0.4$ (40% solid volume expansion) then $R = 0.3$. We see that for reaction progress above 30% in the cup, porosity could have potentially vanished at constant sample volume.

Obviously, the constant volume assumption does not hold in the present case but this simple calculation shows why knowledge of the reaction progress is conceptually important.

Following this idea, the knowledge of the three parameters, sample overall volume expansion, average porosity and reaction progress when the experiment is terminated would be very useful.

The knowledge of the overall reaction progress is also important if the experiment is run in a close system (technical point to be clarified) the source of CO_2 will be limited. In a forsterite sample with 10% porosity, all the CO_2 initially supplied as $NaHCO_3$ will be consumed after 20% reaction progress.

We agree that the reaction progress is an important parameter. To quantify the extent of reaction using the microtomography data, the volume increase of the reaction products (i.e., precipitation) and/or the volume decrease of the original olivine grains (i.e., dissolution) must be evaluated. Unfortunately, the phase contrast between these solid phases (i.e., precipitants vs. olivine) is very small, and at the current spatial resolution of ~ 2 micron, numerous attempts failed to segment precipitants from olivine grain (i.e., the uncertainties were larger than the volume change). 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 added a discussion to clarify this point (lines 302-303).

- 2.2/ About the Model

I see an alternative model to the stretching-induced fracturing model. The inner cup contains loose grains and the porosity is the highest there. Accordingly, most of the solution is located there, solution which, furthermore, can be partially renewed if the system is not fully close (inlet capillary open, technical point to be clarified). The dissolution activity is therefore expected to concentrate at the inner cup interface in the SGC sample. Indeed, sample cup grains may dissolve faster than loose grains due to their smaller grain size.

Could what the authors call stretching-induced fractures, be merely a localized dense network of dissolution features? Dissolution features will exhibit a different geometry in LGC sample where dissolution kinetics is expected to be smaller. According to this alternative model, reaction progress in SGC should be higher than in LGC for a given run duration, is that the case?

First, we want to clarify that the pore fluid was connected to a syringe pump at the upstream and to a pressure regulator at the downstream. A constant pore pressure of 10 MPa was maintained throughout the experiments. This experimental setup can be considered as a semi-open system. We added this information in the revised manuscript (lines 141-143)

Now, it is possible that dissolution is more rigorous at the inner cup interface of the SGC sample. However, we don't think that the observed fractures are merely a localized dense network of dissolution features because we observed intense stretching-induced fractures at the outer surface of the cup as well (see Zhu et al., 2016). The sample was jacketed by a silicone tubing (to separate the pore fluid from the confining fluid) where the porosity between the cup's outer surface and the jacket is smaller than the porosity of the cup wall. So if dissolution is the main mechanism responsible for the intense fractures observed in the SGC cup, little fracturing should be expected at the outer surface of the cup, opposite to the observations. We agree that dissolution is a contributing factor, but dissolution alone could not fully explain the fracture locations and patterns observed.

Furthermore, if dissolution is the main mechanism, one should expect fracturing to occur earlier in SGC sample because of its smaller grain size. This is not what we observed. Although it is difficult to make a rigorous comparison of the reaction progress in SGC and LGC samples, the fact that fractures in LGC appeared within 30 hours of reaction whereas no fractures were observed in the SGC sample until after ~65 hours of reaction is not consistent with the dissolution kinetics.

- 2.3/ About the Application to Nature

In peridotites, olivine grain size is rather large (hundreds of μm). Is the LGC experiment with little stretching-induced fractures the most relevant to natural settings? In nature, the high porosity zone can be the one with the smallest grain size (e.g., cataclastic fault zone) what will happen then? I generally find that the implication for natural cases is not sufficiently discussed. Consequently, the reader has sometimes the feeling that the proposed model only applies to the described experiments with their specific design.

The mechanical strength and cohesion are critical parameters in the brittle failure criteria (for example, Coulomb-Mohr criterion). There are no universal correlation between rocks' grain size and their mechanical strength and cohesion, so there is no simple extrapolation that links LGC or SGC samples to natural peridotite. Both SGC and LGC are much weaker compared to natural peridotites, and SGC is considerably stronger than LGC.

Laboratory experiments are not capable of simulating natural settings because of the vastly different length and time scales. So we focus on identifying and gaining physical understanding of the underlying mechanisms. In Zhu et al. (2016) we proposed that non-uniform expansion could be an alternative mechanism for the reaction induced fracturing in systems where crystallization force is not sufficient to break directly the host rock. In this study, our goal is to further test this idea as well as discovering other mechanisms (e.g., dissolution). Our contribution is to bring forth experimentally verified mechanisms that may operate in nature and thus help unravel the complex natural processes.

We added a brief discussion in the revised manuscript (lines 453-458).

3/ Specific comments

L48: The notion of « olivine mineralization » is unclear. I understand “formation of olivine from a fluid” whereas I believe that the authors mean “formation of carbonates from olivine”. Would not “CO₂ mineralization” be more appropriate here?

We made some literature search and found that 'olivine carbonation' appears most frequently. We now changed “olivine mineralization” to “olivine carbonation”.

Section 2.1: There are a couple of unclear issues with respect to the experimental set-up. Did the authors use a top cap made of sintered olivine as in the 2016 paper? Does the confining pressure also apply to the sample top and bottom (no deviatoric stress?)? Is the solution isolated from the inlet capillary during experiment or is the system open in order to buffer the pore pressure? This is an important issue since it defines whether the experiments have been performed in a close or (semi)open system.

Yes, sintered olivine lids made from the same material as the cup were used in both SGC and LGC experiments. A small axial end load is applied independently from the confining pressure by locking the axial piston at a fixed position. Changes in the sample length during reaction could lead to some variations in the axial stress. The planar fractures observed in LGC, for example, could be affected by the reduction of axial load due to may be The fractures in SGC are unlikely to be associated with the differential stress because the fracture pattern is not consistent with stress-induced cracks.

The upstream was connected to a syringe pump to keep a constant pore pressure of 10 MPa. The downstream was regulated by a pressure regulator. So the experiments can be considered semi-open. We added the information in the revised manuscript (lines 141-143).

Section 2.1: The authors mention that they use forsterite. Is that San Carlos olivine, please clarify, since it would define the amount of ferrous iron that is present in the system.

We used pulverized San Carlos olivine as the starting material to synthesize the olivine cups. The loose olivine grains are also San Carlos olivine. This has been clarified in the revised manuscript (lines 128-129).

Section 2.1: Can the authors exclude that drilling the aggregate to fill it with olivine sand grains may induce micro-cracks in the inner cup wall that will further localize dissolution features? Does cooling of the aggregate after sintering can induce thermal micro-cracks (nano-tomography characterization of the cup before running the sample?)?

Yes, we are certain that the fractures observed are not from the mechanical (drilling) or thermal (cooling) manipulation during sample preparation. For both sample, we performed several 3D scans, 1) before confining and pore pressure was applied, 2) after pressures were applied but at room temperature; 3) during temperature increase from 23-200C; 4) immediately after reaching the desired pressure and temperature conditions. No micro-cracks or fractures were observed in any of these scans in both SGC and LGS experiments.

L125: The present experiment only differs from the 2016 one by the change in the grain size of the sintered olivine poly-crystal that forms the cup. The importance of increasing the grain size of the cup olivine grains to approach the grain size of those located inside the cup should be more emphasized in the introduction section since it justifies writing a new paper !

We modified the text to emphasis the grain size investigation using LGS (lines 105-112).

L234: "Edge", I suppose the authors mean inner edge of the cup according to Fig. 6 in the 2016 paper. Please clarify.

"Edge" here refers to the near surface of the cup wall. We have modified the sentence (line 387)

Section 3.3 and 3.4: It is not always clear in these two sections whether the authors are describing features belonging to LGC, SGC sample or both? Please clarify.

We adopted the names SGC and LGC and modified the text to clarify.

Section 3.3b: Dissolution features occur to be planar and perpendicular to the vertical z-axis (Fig. 6b & 9b). Is that related to the sample geometry, stress distribution? Are they expected to develop as such in rocks? This geometry of the dissolution features is not really discussed in the manuscript although they are the only macroscopic features that generate porosity in the sample (LGS) produced in the present study.

The LGC sample is mechanically weak, so it is conceivable that the dissolution of olivine could break the weak bonding and initiate the fracture. The planar nature of the fracture suggest that the propagation of the fracture is likely caused by mechanical load (in contrast to chemical load). It is possible that the axial compressive stress is lower than the radial stress in the LGS experiment. We also could not rule out the possibility that this planar fracture is dictated by the defect in the sintered sample. It is clear that this planar fracture in LGC is NOT induced by the non-uniform expansion. The grain size contrast is necessary for causing the non-uniform expansion.

We modified the text to clarify these points (See sections 3.1 and 3.4).

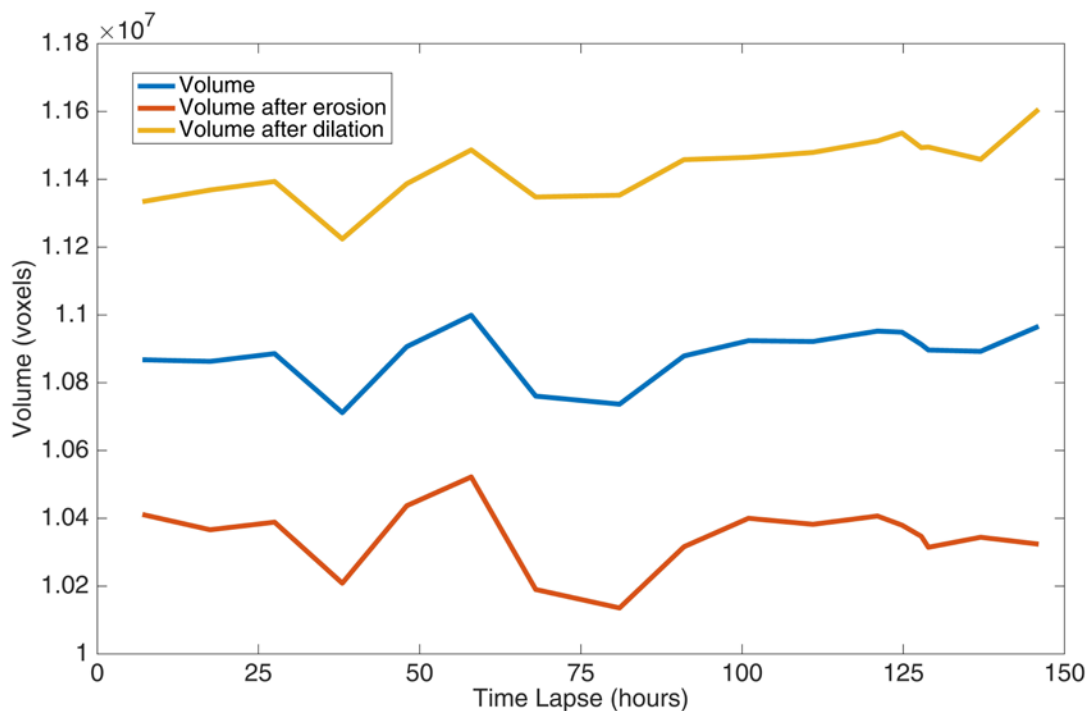
L287: “became dominate” should be “became dominant”?

Corrected.

L277-288: The grain size fluctuations described in this paragraph are fascinating. If I understand correctly, the size evolution of several grains has been monitored although only the size variation of a selected grain is displayed in Fig. 12. The possible link between local grain dissolution after 68h and development of fracturing in the cup is highly interesting. It would however be useful to see the size evolution of more than a single grain (what seems to be possible according to the available dataset?) to strengthen the inference. Would it also be possible to give error bars on the volume data to emphasize the significance of the observed variations?

We only selected the single olivine grain presented in Zhu et al. (2016) on which changes of the volume of magnesites are significant since segmenting one relatively large grain from the image is a process that require time and intensive work.

The volume of the grain is directly measured from the segmented olivine grain from inside the cup. The error of the volume measurement would only come from touching of other grains which is insignificant amount. We used the “erosion and dilation method” commonly used in image analysis to investigate the error that could be induced by spatial resolution. Results from the erosion and dilation does not change the trend of volume change presented here.



Section 4.1: It is unclear to me what data from this study supports the notion that the tubes pierce through the whole grains (holes), could not they just remain pits.

From the 3D analysis of the nanotomographic data, some tubes have clear bottoms inside the grains, but others form through-going holes across the whole grains. Since we do not see any precipitation filling or clogging the tubes, it is reasonable to think that these features represent different stages of tube formation. They started as the etch-pits. At the pits site, enhanced dissolution takes place, and the pits grow deeper and eventually become the through-going tubes.

We clarified this point in the text (lines 290-293)

L331: “Our quantitative estimates indicate that in these experiments, crystallization pressure can lead to maximum ~5% volume expansion”. Is not that estimate an average value of the volume expansion over the whole sample whereas reaction crystallization-pressure induced fracturing should be regarded as a volume expansion at the local scale? Please clarify.

Here the “crystallization pressure” means the mechanical force produced by the chemical reaction. We modify the sentence to clarify this point: “Our quantitative estimates indicate that in these experiments, the maximum volume expansion is ~5%.”

L331: I suppose that this assertion relates to the LGC, what is the volume expansion estimate for the SGC experiments where crystallization-pressure induced fracturing is also ruled out by the authors?

This above volume expansion estimate is for the SGC experiment. For the LGC experiment, no detectable volume expansion is observed.