

## 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.

## 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?

Basically, if one considers a solid volume ( $V_s$ ) expansion of  $x$ , then the volume expansion of the solid matrix ( $\Delta V_s$ ) is a function of reaction progress ( $R$ ):  $\Delta V_s = V_s^0 \cdot R \cdot x$ . Let consider the end-member 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  $R = p^0 / (1 - p^0) \cdot x$ . 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  $\text{CO}_2$  will be limited. In a forsterite sample with 10% porosity, all the  $\text{CO}_2$  initially supplied as  $\text{NaHCO}_3$  will be consumed after 20% reaction progress.

### - 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?

- **2.3/ About the Application to Nature**

In peridotites, olivine grain size is rather large (hundreds of  $\mu\text{m}$ ). 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.

### 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 “CO<sub>2</sub> mineralization” be more appropriate here?

**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.

**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.

**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?)?

**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 !

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

**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.

**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.

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

**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?

**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.

**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.

**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?

*Comments related to the rest of the ms are included in the general comments section.*