Interactive comment on “Syn-kinematic hydration reactions, dissolution-precipitation creep and grain boundary sliding in experimentally deformed plagioclase-pyroxene mixtures” by Sina Marti et al.

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Author’s response to comments from Reviewer 1 (J.W.)

General comments

Rev.1: This paper discusses experiments on deforming pyroxene plagioclase mixtures in the presence of water, a common scenario during metamorphism in the Earth. The work aims to elucidate deformation mechanisms when there are ongoing reactions, by means of mechanical and microstructural observations. The work is of good quality and in general the conclusions are justified but the paper would benefit from some “scene setting”. It is not always obvious in advance why various measurements were made, although the interpretations are interesting afterwards. For example coronas have thickness anisotropy but was that a particular focus of the work, and were there hypotheses to be tested prior to the observations? In terms of results, a bit more discussion would be beneficial. For example two stress exponents, n, are obtained using constant strain rate data and strain rate stepping experiments, but it is not explained why they are different. The observations on porosity are interesting – it is difficult to envisage open pores at 1.5 GPa, but there they are. Is there a chance they formed on sample unloading? The initial powders were highly porous presumably. I can’t tell if they were more or less fully compacted prior to deformation. Other points are made below.

Authors: We would like to thank you for your revisions and greatly appreciate your comments and suggestions. We agree that the manuscript would benefit from some more “scene setting” and tried to incorporate such especially in the sections on EBSD and amphibole corona analyses. Concerning the pores discussed in our manuscript – they were also commented by Reviewer 2 – this discussion point was added to the specific comments, see below. Samples were almost fully compacted prior to sample deformation (revised manuscript lines 169-170)

Specific comments
1. Abstract first line is vague – what exactly is poorly constrained?

Authors: Text altered to “It is widely observed that mafic rocks are able to accommodate high strains by viscous flow. Yet, a number of questions concerning the exact nature of the involved deformation mechanisms continue to be debated.” (Revised manuscript lines 1 - 2).

37. diffusion creep always involves GBS; see also 6, 288, and Raj and Ashby (1971) p. 1120. Title: “Syn-kinematic hydration reactions, dissolution-precipitation creep and grain boundary sliding in experimentally deformed plagioclase-pyroxene mixtures” does not really need reference to GBS as it is implicit.

Authors: Thank you for pointing this out. We are not unaware of the relationship between diffusion creep and GBS. In the original manuscript, we listed both of them separately, as either diffusion creep or GBS could be the dominant strain accommodating mechanism, while the other is merely accommodating (diffusion creep accommodated by GBS vs. GBS accommodated by diffusion creep, e.g. correlating to Lifshitz and Rachinger sliding after Langdon, 2006, respectively). The manuscript text lines have been modified, see revised manuscript lines 16-22. The title has been altered in response to this comment as well.

43. “diffusion is expected to be faster along phase boundaries compared to grain boundaries”. Wheeler (1992) does not say this, instead he shows that coupled diffusion and reaction may enhance strain along heterophase boundaries even if diffusion coefficients are the same as along single phase boundaries. I think that work has been misquoted previously. I do not know if the other cited works are explicit that diffusion is expected to be faster along phase boundaries compared to grain boundaries.

Authors: True, in the cited literature (Hickman and Evans, 1991; Wheeler, 1992; Sundberg and Cooper, 2008) it is not referred to the diffusion coefficient (i.e. no statement about higher diffusion coefficient along phase- compared to grain- boundaries), but it is observed or suggested that convergence/divergence between two different mineral phases appears faster than between two grains of the same mineral phase. The respective manuscript text passage has been modified, see revised manuscript lines 48 – 51. Do you agree with this reformulation?

95. overestimates – how?

Authors: The way in which \( \gamma_a \) is calculated is an incremental approach where the increments are determined by the sampling frequency of the displacement transducer. The end-value of \( \gamma_a \) then is a function of the increment size. Comparison of \( \gamma_a \) with the simple shear component \( (\gamma_s) \) calculated after Fossen & Tikoff, (1993) (Figure attached, from Marti et al., 2017) show that \( \gamma_a \) is always a bit higher and is considered to overestimate the simple shear component in the general shear progressive deformation. The text passages have also been criticized by reviewer 2 and were modified, see revised manuscript lines 108 - 114.

105. Corona thickness is an interesting property – but, to be clear, why was it measured? What hypothesis was being tested?
**Authors:** Some introduction to why the amphibole coronas were measured has been added in the revised manuscript lines 267 – 270, and in lines 349 – 352.

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**Rev.1:** 107. “separated manually” needs further explanation.

**Authors:** Some more information/explanation to this has been added in lines 122 – 124.

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**Rev.1:** 133. “Strain rate stepping tests” – why, what is their role?

**Authors:** to test the sensitivity of shear stress on strain rate.” Revised manuscript line 155.

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**Rev.1:** 141. Reaction R1 is not easily balanced, and will be different for Opx and Cpx. Any comments?

**Authors:** Reaction balancing has been attempted and yes, for hornblende as a reaction product needs both Opx and Cpx. These phases are present in the Maryland diabase starting material. As both the measured pyroxene and the resulting amphibole chemistry show some variations, reaction balancing did not yield a single solution and only the schematic reaction (without exact balancing) is listed in the manuscript.

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**Rev.1:** 178. “increased amount of reaction products at higher Pc”. Any idea why?

**Authors:** Probably due to the fact that zoisite and albite are favored over intermediate Plagioclase at the higher Pc of 1.5 GPa. From thermodynamic modeling, plagioclase in the Maryland Diabase experiments should, for the most part, disappear by reaction. However, the mineral assemblage of the calculated pseudosections shows some deviation from the observed assemblage in the samples. It is therefore difficult to make assumptions based on these pseudosections.

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**Rev.1:** 287. Why are stress exponents different?

**Authors:** With the database we have, this question is difficult to answer. Explanations could be:

(i) The microstructure in the samples is heterogeneous due to the strain localization. The stress exponents are determined from mechanical data that only measures bulk sample response. Small differences in microstructures such as shear band orientation and shear band interconnectivity might lead to different bulk determined stress exponents.

(ii) A potential switch from interface to transport control of the dissolution-precipitation creep (DPC) rate could potentially explain the difference in stress exponent. The intermediate plagioclase in 1.0 GPa Pc experiments is largely stable, whereas it is highly metastable in the 1.5 GPa Pc experiments. The driving force for dissolution of the intermediate plagioclase and growth of a more stable phase in the 1.5 GPa Pc experiment thus could be expected to be much higher compared to the 1.0 GPa Pc experiments. DPC at 1.5 GPa Pc could be transport controlled, whereas DPC at 1.0
GPa P_c could be interface controlled.

(iii) The data set from which the stress exponents are determined is relatively small. It cannot be fully ruled out, that the small difference in stress exponent is an artifact from too small sampling size (not enough data points to cover the variability between individual experiments)

Rev.1: 296. Why does cation ordering affect strength (give reference)?

Authors: The part has been deleted from the sentence. See revised manuscript line 377 - 379.

Rev.1: 314. “Furthermore, a CPO can form due to interfacial energy, e.g., via host-controlled nucleation (e.g., ..” (Jiang et al. 2000)). This is a rather confusing phrase. What does “due to” interfacial energy mean? Nucleation rate is certainly influenced by interfacial energy, but surely nucleation is “due to” (in this case) a chemical driving force, namely to change plagioclase to albite.

Authors: Whereas the dominant driving force for nucleation is likely to be a chemical driving force, the crystal orientation of the growing nucleus could be determined by the neighboring crystals. That is, the grain boundary energy between nuclei and the neighboring grains may favour a specific orientation, if a certain orientation between matrix grain and nucleus has a particularly low energy. If the matrix grains show a CPO, this could then cause a CPO of the newly nucleating grains.

The manuscript text has been slightly altered regarding this, see revised manuscript lines 394 - 396.

Rev.1: 326. Or could the coronas have been squeezed out somehow? Move line 343 up here to answer.

Authors: Lines 343f (original manuscript) were moved up to revised manuscript lines 354 - 357. It is stated there that based on the microstructure, squeezing out or shearing off is not seen as a likely cause for the amphibole corona thickness decrease in high stress sites.

Rev.1: 334. “The geometry of deformation by diffusion creep is irrotational” – please explain. Grains DO rotate during diffusion creep, surely, which is one way it weakens a prior CPO.

Authors: True, the sentence needs rewording (see revised manuscript lines 366 - 369). What we wanted to point out is that the instantaneous grain shape change expected to result from DPC would be orthorhombic, as a grain gets dissolved and grows with respect to the orthogonal stress field (i.e. dissolving towards sigma1 and growing towards sigma3). As soon as any grain boundary sliding is involved (i.e. during progressive deformation), grains are very likely to rotate, which will likely also cause grain shape to deviate from an orthogonal shape. We think that this is nicely shown in the corona evolution, where at very low strains (at peak stress, gamma smaller equal 1) the average corona shape shows this orthogonal shape, where at high strains, this shape fabric changed to a monoclinic/sigmoidal shape.
Rev.1: 399. This seems reasonable but is not entirely logical. Of course finer grain sizes are more prone to DPC but microstructures are always hard to interpret. The best evidence is the low stress exponents.

Authors: The sentence has been deleted from the text.

Rev.1: 404. “the chemical driving potential for attaining a lower energy assemblage partially controls the reaction rate”. Broadly yes except there is no unique driving force (no Gibbs free energy defined) in a stressed system (Wheeler 2014, 2018).

Authors: We agree, thank you for pointing this out, the text has been modified and citations added, see revised manuscript lines 457-458.

Rev.1: The observations on porosity are interesting – it is difficult to envisage open pores at 1.5 GPa, but there they are. Is there a chance they formed on sample unloading? The initial powders were highly porous presumably. I can’t tell if they were more or less fully compacted prior to deformation.

Authors: We disagree that the presence of pores is contradicting with the experimental conditions. Surely the high confining pressures and the activation of viscous deformation in the material will suppress large amounts of pore space opening, however this should not mean that no porosity at all is able to exist. In fact, the observation of (small amounts of) porosity in experiments performed at high Pc & T conditions (with flow stresses below the Goetze criterion) has previously been observed in a number of studies, e.g. Tullis & Yund (1991); Dimanov et al. (2007); Rybacki & Dresen (2010); Precigout & Stünitz (2016). And is as well proposed for natural shear zones, e.g. Fusseis et al. (2009); Menegon et al. (2015).

A reason why porosity in experiments is not that uncommon to observe might be the high strain rates – in natural rocks, dilatant sites during grain boundary sliding can be filled by precipitating phases (e.g. Kruse & Stünitz, 1999; Kilian et al., 2011) or closed by plastic deformation of adjacent grains. However, as the displacement rate in experiments is high, pores might be more frequent to form as reaction rate and plastic deformation are not able to keep up with pore space formation. The pores in our experiments are not very frequent and are also small, with sizes on the 10x nm scale. We don’t know how long they are open but it is likely that their occurrence time is short. Decompression porosity commonly is easily recognized by its location and orientation in cracks normal to the shortening direction – such features are different from what is described here. The samples are almost fully compacted after the lead run-in (hydrostatic part of the experiment, see Appendix Figure 1c, prior to sample deformation)

Technical corrections

Authors: Thank you for pointing this out, the text has been corrected accordingly

Rev.1: 373. What is t in $\Delta G_t$?
Authors: $\Delta G_t$ has been removed as it is not further used in the text.
Rev.1: Fig 1. What is CCL?
Authors: CCL is a typo, is now corrected and replaced with “counter clockwise”

Rev.1: Table 1, 3. Poor quality – reformat?
Authors: Table 1 and 3 are reformatted

Rev.1: Fig. 5k Make colours a bit stronger?
Authors: Colours in Figure 5k have been enhanced.

Rev.1: Fig 7b) In colour, like others?
Authors: Colours have been modified


Fig. 1. Appendix Fig. 3 (Marti et al., 2017)