**Solid Earth
Discussions**

Interactive comment on "**Pore formation during dehydration of polycrystalline gypsum observed and quantified in a time-series synchrotron radiation based X-ray micro-tomography experiment**" *by* **F. Fusseis et al.**

F. Fusseis et al.

florianfusseis@me.com

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We would like to thank Dr Milsch for a very thorough review that certainly helped to improve the manuscript. Please find the revised manuscript and figures in the supplementary zip-archive attached to this comment.

> From my own experiences the material used is fairly homogeneous in a way that the reproducibility of an experiment performed under specific conditions is excellent. The one experiment performed should therefore be representative for the particular set of

environmental conditions (e.g. pore and confining pressures, temperature, water vapor partial pressure, drainage etc.) - a fact which should be explicitly stated in the text.

<As stated in our reply to Dr. Tripetta's comment, we are very confident that the experiment is reproducible. However, we also show that, on the scale of our sample, the material is heterogeneous. As stated in the manuscript, we consider these local heterogeneities responsible for the asymmetric advance of the reaction front. Nonetheless, we added the following paragraph to the sample description (lines 278-282):

"Gypsum dehydration has been studied in numerous experiments under a large range of boundary conditions and excellent reproducibility of experiments was demonstrated. Given the significant costs and efforts that it took to conduct the experiment reported here, we restrict ourselves to a single sample specimen. We are confident that our principal findings can be reproduced."

> In this study the assumption that bassanite is the final solid reaction product is not justi- fied by any measurement. The authors should have a look at Milsch et al (2011) where comparable dehydration experiments were performed under environmentally very similar conditions but on significantly larger samples. We show that in air and even at 388 K gypsum ultimately dehydrates to anhydrite (also cf. McAdie, 1964; Fig. 2). If your sample is still intact and available you may want to weigh it and perform the calculation of reaction progress as outlined in Milsch et al. (2011). Additionally, you can then rather precisely determine the overall sample porosity. You may want report the results in your manuscript.

<You remark correctly that we did not determine the mineralogical composition of our sample after dehydration and hence do not know whether we produced hemihydrate or γ-anhydrite. Unfortunately, it is also not possible to weigh the sample at this stage as we reported only half of the actual experiment in this paper. After the final scan at 310 minutes, we continued heating the sample to higher temperatures and acquired further datasets, which are not reported here. However, to the best of our knowledge,

the crystallographic details of the progressive dehydration of gypsum are still being debated (see Schmidt et al., 2011 for a recent discussion), and at the conditions of our experiment hemihydrate can be expected to form (Freyer and Voigt, 2009, Freyer, pers. communication). Consequently, in our experiment we investigated the breakdown of gypsum, which, at the spatial resolution we achieved, is clearly marked by the formation of porosity on the micron-scale.

> Finally, we have microstructural evidence (unpublished data) that at 398 K there is gypsum decomposition also in what you term the "inner domain".

<We assume that if gypsum were to become unstable on the bulk scale, this would ultimately result in the formation of pores of a detectable size. As we see only slightly increasing background porosity ahead of the dehydration initiation front (Fig. 4), we believe that, on the bulk scale, the dehydration of gypsum is suppressed in the 'inner domain'.

> Besides being wet, Ko et al.'s (1997) samples were dehydrated at this temperature which might explain some of the differences to the interpretations of your experiment that you claim in Section 4.1.

<Stretton (1996) conducted her experiments under very similar conditions than Ko et al., (1997) and her microstructural observations essentially match ours. Consequently we conclude that "neither the drainage configuration nor a moderate confining pressure fundamentally change the breakdown behaviour of polycrystalline gypsum." We now state this in lines 716-721.

Specific comments: >861, L. 20: check the number! The total volume change is 7% for dehydration to bassanite.

<The change in the solid volume ΔV_{solid} is – 30%, whereas the change in the amount of fluid ΔV_{fluid} is +37%. $|\Delta V_{fluid}/\Delta V_{solid}|$ should therefore be about 1.23. We corrected the number.

>861, L. 26: is this the correct Llana-Fúnez paper you are referring to?

<Yes, it is.

>861, L. 29: this depends on the (water) pore pressure relative to the pT-equilibrium curve.

<You are right, but this is already stated in lines 27(861) – 1(862).

>862, L. 17-24: this should be moved to Section 4.

<Done.

>865, L. 9: where is the "length scale" in the equation (L. 10)?

<The length scale is given through the thermal diffusivity of the material, which, for the case of gypsum is 0.285 m2s-1. We replaced 'thermal diffusion length scale' by 'thermal diffusivity and the dimension of the sample'.

>865, L. 23-25: this should be moved to Section 4.

<Done.

>866, L. 28: the difference in density is rather significant.

<Removed 'slightly'.

>867, L. 21-23: this should be moved to Section 4.

<This is a minor detail; we find that it is easier to integrate it here than write an entire new paragraph in the discussion.

>868, L. 15: you only used one sample.

<Obviously a typo, which we corrected.

>869, L. 9-27: this is very hard to understand and also should be moved to Section 2 as it is a purely technical description.

<As you pointed out earlier, this manuscript has a highly pioneering character. We developed a large number of new procedures to analyze the data. We are aware that they should be primarily described in section 2, however, being isolated there would render them highly abstract for the reader. We therefore prefer to include them in the 'results' part but certainly try to integrate them as smoothly as possible.

>870, Eq. 1: there is something wrong with this formula. Check the nomenclature and the units; what is r in L. 9; how does D obtained compare to potentially available literature data?

<There was a (previously undetected) formatting error, we corrected the formula. 'r2' is the correlation coefficient.

>870, L. 26-29: dry gypsum is brittle at ambient pressure and moderate temperatures (Milsch and Scholz, 2005)!

<We included the reference. Nonetheless, based on our observations, which are supported by further findings reported in paper in preparation (Karrech et al., in prep), we do not believe that the pressure in the inner domain is ambient but rather expect it to be at least 26 MPa. The lack of confining pressure certainly results in ambient pressure on the sample boundaries. However, the large anisotropy of gypsum's thermal expansivity and elasticity generates significant internal stresses in the sample interior since the grains are, to first order, orientated randomly. It is those internal stresses that suppress the reaction in the sample center. Nevertheless, on the scale of bulk sample, these internal stresses are balanced.

>871, L. 3: explain what you mean by "the outer domain".

<We changed 'outer domain' to 'dehydrating domain'.

>871, L. 10: this is a natural rock!

<We added 'and minor local variations in porosity'.

>872, Fig. 9: how important is this figure? Replace it by Fig. 5 in the supplement?

<Good point, we replaced the two figures.

>Also, [872] L. 17 "Fig. 4" refers to Fig. 5?

<This is a reference to supplementary figure 4, which, in the submitted manuscript was 'Suppl. Figure 4' but was reformatted by Copernicus.

>872, L. 18-23: the paragraph should be moved to Section 2 as it is a purely technical description.

<As you pointed out earlier, this manuscript has a highly pioneering character. We developed a large number of new procedures to analyze the data. We are aware that they should be primarily described in section 2, however, being isolated there would render them highly abstract for the reader. We therefore prefer to include them in the 'results' part but certainly try to integrate them as 'smoothly' as possible.

>872, L. 25: what is the "raster effect"?

<We changed the sentence to: "For this analysis we only consider pores larger than 50 voxel to minimize shape artefacts resulting from the limited possibilities to approximate the shape of small pores by a small number of (cubic) voxels."

>873, L. 4-28: consider moving technical parts of these two paragraphs to Section 2.

<See comment above.

>873, L. 20: what do you mean by "migrated through a volume".

<We clarified this to: "The cumulative pore size frequency distribution indicates that soon after the dehydration front has passed, pores interconnect."

>874, L. 19-25: again, you should emphasize that this study deals with unconfined and dry conditions.

<We added '[on drainage] at atmospheric pressures'

>875, L. 11: at unconfined conditions gypsum will evidently fail at these internal pore pressures, relaxing them immediately! Also see comment above (861, L. 29).

<See our explanation in the comment above.

>875, L. 21: what do you mean by "run-away".

<This refers to a scenario where the reaction initiates instantly throughout the sample and pores interconnect rapidly as opposed to the slow and stable advancement of the dehydration front that separates an unreacted domain from a reacted domain that we observe. The former scenario is advocated by e.g. Ko et al. (1997) and Miller et al., (2003). We clarified the sentence to: "However, our data also indicate that any pores that form remain largely below the resolution limit of about 1 micron, and that they to not initiate drainage".

>876, L. 4-5: you did not run any fluid expulsion experiment, so what is the point? If you had, you very likely would have observed a smooth expulsion curve at decelerating rate (cf. your Fig. 5b).

<We modified this section of the discussion (see below).

>876, L. 18-27: Ko et al.'s (1997) experiments were performed under particular drainage conditions and under significant effective pressure on wet gypsum! That very likely is the reason. Wang and Wong (2003) refer to these conditions.

<In this part we aim to highlight that Ko et al.'s interpretation and consequently some of the input into Wang and Wong's model are possibly wrong. We modified it to emphasize that our observation and interpretation contrast Ko et al.'s (1997) and consequently Wang and Wong's (2003). Stretton (1996) performed very similar experiments, with similarly sized, jacketed samples, also drained to one side of the cylinder only, and found a very narrow reaction front, similar to ours. We therefore believe that despite the difference in the experimental setup, our model should be applicable to Ko et al.'s experiments. Consequently, Wang and Wong's theoretical/numerical postulation of a

very subtle increase of porosity conflicts our observations.

>878, L. 20: what about a heterogeneity in the temperature distribution?

<As indicated earlier, theoretically some heat loss may have happened through the thermocouple and the cement used to hold it in place. However, we believe this insignificant, due to the small sample dimension and the very effective heater. We now mention this explicitly in the text.

>880, L. 10: again, what do you mean by "run-away".

<See above.

>880, L. 13: again, this is very speculative.

<We do not consider this a speculation but provide a model based on our observations. The formation of porosity is a clear indication of dehydration initiation.

>Fig. 4: from the caption this figure is hard to understand.

<We modified the figure caption to "Distribution of porosity along a radius at 10, 70 and 130 minutes. Note the slightly increasing background porosity in the inner domain. Values exceeding 30 % porosity result from the comparatively small sampling volume used to determine the porosity values shown."

>Figs. 5, 6, 7, 8, 10, 11, 12, 14: try at least in some words to explain what one sees!

<Done.

>Technical corrections:

<All implemented.

>863, L. 9: analyze

<Text is in British English.

>Fig. 10: is "310-140 voxel" correct? Why green and orange circles for the same voxel

interval?

<We corrected the numbers. The stereo plots show data collected at three different times during the experiment, the colors correspond to the colors used for different time steps in all other diagrams.

References Freyer, D. and Voigt, W.: Can mixtures of α- and β-hemihydrates be quantified by means of thermoanalysis? ZKG Int. 62, 3, 47-53, 2009.

Please also note the supplement to this comment:
http://www.solid-earth-discuss.net/3/C622/2012/sed-3-C622-2012-supplement.zip

Interactive comment on Solid Earth Discuss., 3, 857, 2011.