Solid Earth Discuss., referee comment RC1
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Comment on se-2021-83

Anonymous Referee #1

Referee comment on "Biotite supports long-range diffusive transport in dissolution–precipitation creep in halite through small porosity fluctuations" by Berit Schwichtenberg et al., Solid Earth Discuss., https://doi.org/10.5194/se-2021-83-RC1, 2021

GENERAL COMMENTS - overall quality of the preprint

This paper re-addresses the long standing and still interesting question of the role of phyllosilicates in controlling pressure solution and multiscale transport in rock materials. It does so by means of micro-CT imaging of uniaxially compaction tests performed on brine-saturated NaCl aggregates containing biotite rich layers - in two different configurations and using one pure NaCl control sample. The results obtained for this rock analogue system demonstrate that the biotite-rich layers compact at a similar average (?) rate to the adjacent pure salt layers but that the porosity of the biotite-bearing layers decreases faster due to preferential precipitation of NaCl in the biotite layers. This is a nice, observational demonstration of transport on the length scale of the layer thickness as opposed to the grain scale, as put forward in previous work, such as that by Merino et al. (1983). The experimental approach is largely sound (some questions can be raised) and the results are mostly clearly and pleasingly presented. However, the discussion appears to contain several inconsistencies and non-sequiturs in reasoning, as well as some conflicts with previous literature and established understanding. These may be the result of mixed terminology and/or unfortunate expression or use of English, but the effect is confusing for the reader, undermining the strength and value of the conclusions drawn. In particular, given that there were no major differences in compaction strain in the different layers, it is not clear WHY there was diffusive transport from the NaCl layers to NaCl/biotite layers beyond a phenomenological similarity to the effect put forward by Merino et al. The proposed driving force for transport requires at least initially preferred compaction (grain contact area increase) throughout the biotite-bearing layers, which is not very clearly demonstrated or perhaps lost in the discussion of the uniform compaction observed in the samples. I am also left wondering what the imaging results add to the earlier work of Macente et al (2018) on the same system, beyond technical and methodological refinements. Nonetheless, the paper contains good observational work which deserves to be published if the improvements vs. Macente et al (2018) can be clarified, if aspects of the compaction experiments can be clarified, and if the discussion can be sharpened and the Merino hypothesis tested a bit more rigorously. On this basis, I am recommending major revisions, which ideally should contain some additional experiments. My specific comments are listed below.

SCIENTIFIC COMMENTS

Scientific points that require attention are as follows:

1) Title : I find the title misleading as it suggests that the observed effect is caused specifically by biotite. However, the authors seem to argue that it is not specifically the biotite that causes the observed effect but initially (?) reduced porosity in the biotite-bearing layers. If they are right, then a biotite-free but denser salt layer in the sample would show the same layer-scale mass transport phenomenon reported here and described by Merino et al. I would recommend a title more along the lines of "CT imaging demonstrates interlayer mass transport in layered halite-biotite aggregates undergoing dissolution-precipitation creep".

2) Abstract, lines 5-6 read: "We used time-resolved (4D) microtomographicdata to capture the dynamic evolution of the transport properties in layered NaCl-NaCl/biotite samples". This is not true. No attempt was made to calculate transport properties (or measure them). Only porosity evolution was studied. Best correct to porosity rather than "transport properties" – throughout the ms.

3) Abstract, lines 12-14 reads: "We propose that, in our experiments, the diffusive transport processes invoked in classical theoretical models of DPC are superseded by chemo-mechanical feedbacks that arise on longer length scales." This cannot be said if in the main text it is claimed that the sample scale compaction behaviour is consistent with compaction experiments on pure NaCl. The effect of interlayer transport in the present experiments is argued not to influence overall compaction strain, so it does not dominate over pressure solution as a deformation mechanism, it merely contributes and dominates porosity reduction in the bi0tite-bearing layers.

4) Introduction, lines 29-30 read: "Phyllosilicates have been recognised to have a reinforcing effect on the dissolution process ..". Yes, a but others have notes that pressure solution (compaction) can be inhibited or unaffected by phyllosilicates, e.g. Niemeijer & Spiers (2002). The enhancement effect comes mainly from observations on natural rocks where advective mass removal along phyllo-rich layers cannot be eliminated as playing a role.

5) Intro, lines 30-35: What does the present study actually add to the paper by Macente et al (2018)? Would be wise to make this clear somewhere, e.g. in lines 46-48. Just seems like a technical refinement at present.

6) Intro lines 48-49 read: "Our aim was to determine length scales of diffusive transport in a dynamically evolving porosity during DPC". What about trying to explain them??

7) Section 2, line 53. Peach and Spiers 1996 is a study of the percolation threshold in dilating salt, not a study of deformation mechanisms. A far more relevant reference here and in line 57, would be the study of pressure solution in compaction by Spiers et al 1990, which specifically addresses the creep law for pressure solution in NaCl in 1D compaction and deviatoric creep – and emphasizes the analogue aspect.

8) Section 2, lines 58-59 read: "It is further a material used in geological nuclear waste repositories (Powers et al.,1978), and its deformation behaviour is well-characterised". Salt is not a material used in radioactive waste reporitories – it has been and still is widely considered as a HOST ROCK for repositories. A more recent ref than Powers should be added and refs should be added to underpin "well characterised". Urai , Schleder, Spiers and Kukla 2008 would be suitable here.

9) Section 2.3 Experimental setup, lines 95-96 reads: "The experiments were run inside a thermally insulated box where the temperature was logged and found to be stable within ± 1.7 °C over the course of the experiments." This is quite a large range in T for such a soluble material as NaCl (which would certainly cause sample-wide dissolution-precipitation effects) and raises questions regarding temperature GRADIENTS in the sample and their possible effect on convection and advective transport. Was temperature measured at different points along the length of the sample and if so what was the T profile or gradient? Could this have driven advective transport in the samples? Some calculation is needed to answer this. Of further interest here is the possible effect of differential heating of the sample during CT-imaging, as a result of x-ray attenuation – e.g. differential heating of biotite-bearing versus pure NaCl layers. Can effects such as this be eliminated?

10) A further point related to the above is the issue of radiation damage and its effect on NaCl solubility. Recent measurements that I have witnessed in a similar scanner show heating of NaCl by a few degrees accompanied by significant radiation damage of the salt – it turns yellow or purple at high doses. So my question to the present authors is: did the samples change colour after CT scanning? Did they check? And, if the colour did change, can they eliminate the possibility of damage gradients influencing dissol-precip transfer between layers of different composition hence different damage in the NaCl? Note that from a theoretical point of view, if the deposited energy due to radiation damage of NaCl is E, the increase in solubility for small E is 100.E/RT %. Could this effect, or the heating due to attenuation, be significant?

11) Also under Section 2.3, it is mentioned in line 98 that the applied effective stress on the compaction experiments was 6.64 to 10.5 MPa. That means that local stresses at NaCl and NaCl-biotite grain contacts would have been much higher – in the range 12 to 50 MPa. These stresses are well inside the regime where salt deforms plastically at room T, leading to a coupling between work-hardening plasticity on the grain scale and dissolution-precipitation transfer, as opposed to classical pressure solution seen in compacting NaCl at stresses below 3 -4 MPa (see Urai et al 2008 above; also Spiers & Brzesowsky. Densification behaviour of wet granular salt: Theory versus experiment. Seventh Symposium on salt 1, 83-92, 1993). The likleyhood that this plasticity-coupled mechanism played a role in the present experiments, rather than classical pressure solution, should be pointed out, especially as it is a mechanism where pore volume diffusion plays a role as

opposed to the grain boundary diffusion process that controls "normal" pressure solution.

12) Section 3 Results, Figure 3. The apparently straight portion of the compaction curves shown in this plot is referred to by the authors as steady state creep, whereas the inset in the Fig clearly shows that the strain rate is continuously decreasing within the resolution of the data. Moreover, the authors actually say that the compaction curves show asymptotic behaviour (e.g. line 271), which in itself means that steady state is not achieved. In addition, it is quite impossible to reach a steady state compaction rate in a compaction experiment of any kind, as porosity is continuously decreasing and therefore so must the strain rate – regardless of deformation mechanism. In this study, apparent steady state seen in the compaction curves is an artifact of the few, rather scattered strain-time data (clearly understood from the inset in Fig 3). Perhaps use of the term "apparent steady state" would be acceptable, but the term steady state creep should be removed throughout and all related points corrected accordingly.

13) Figure 7. Lines 223-224: "Figure 7 shows the vertical displacement rate of the biotite-bearing layer and the bulk sample for different increments of progressing deformation". And in Lines 225-226 "At the beginning of the experiment the rate of both bulk samples was elevated compared to the biotite-bearing layers." OK for the displacement rates, but any meaningful comparison requires normalization with respect to the thickness of the NaCl and NaCl-biotite layers considered , i.e the average strain rates in each zone should be plotted versus compaction stage (time proxy). This is crucial because of later discussion around the issue of enhanced compaction (lower contact stresses) causing interlayer mass transfer.

14) Section 3.2 Strain analysis. The usage of the terms volumetric strain (isotropic) , deviatoric strain and compaction strain becomes a bit confused from here on, I feel. In 1-D, compaction strain is equal to volumetric strain, but not equal to the isotropic strain component of the strain tensor of course. However, the isotropic vol strain does seem to be referred to as compaction at some points in the ms. Somewhere early in the ms, these terms need to be strictly defined and differentiated from each other, and then used consistently. It is also important to note that deviatoric strain cannot occur during 1D compaction independently of the isotropic component of volume reduction, because the pressure solution process (even when accompanied by plasticity) is serially coupled to intergranular sliding – you cannot have one without the other (in pure NaCl or in NaCl-biotite mixtures). In isotropic compaction under 3D loading with S1=S2=S3 you can get compaction with little or no intergranular sliding.

15) The above point comes into play in Figs 8-11, where isotropic volumetric strain (called volumetric strain) is used as an indicator of compaction, whereas macroscopically measured compaction is 1-D compaction. I would strongly advise the authors to present a complete picture in Figs 8-11 by adding contour plots of vertical compaction strain, in addition to the isotropic vol and deviatoric strains. This would make what is going on clearer with a complete set of all information.

16) Section 3.4 NaCl redistribution, Fig 13 and text referring to it (e.g. lines 254-255).

Here, changes in NaCl content within the samples are specified per horizontal slice through the sample. That should be made clearer in the text as it reads as though the mass of the samples is not constant. That also raises the question as to whether the mass of NaCl in the samples is indeed constant. Do the changes in NaCl mass/vol fraction seen in individual samples add up to the original NaCl solid mass? This needs to be clarified.

17) Section 4 Discussion, lines 269-270 read: "The general compaction behaviour we observed was consistent with previous studies on NaCl compaction". Well, yes, the data do show increasing compaction with time. But that is no basis to claim consistency with previous work. First, no other compaction data on salt show the apparent steady state portion claimed by the authors, so they are not qualitatively consistent. Second, a comparison with the isostatic compaction tests of Schutjens & Spiers is not expected to be consistent because of the different boundary conditions imposed. Third, no evidence is presented that the present amounts and rates of compaction are consistent with previous 1D compaction tests on samples of controlled grain size, such as those reported by Spiers et al (1990 – low applied stresses) or Brzesowsky and Spiers (1993 – stresses similar to the present). To claim any consistency or detect any interesting differences, a quantitative comparison should be made by adding a few curves from previous 1D compaction studies on salt of the same grain size – or calculating compaction curves for the present conditions from the compaction data or laws given by previous authors.

18) Lines 272-276. The authors claim a change in deformation mode beyond 200 hours here. But they also argue that their data are continuous and show a continuous asymptotic decrease in strain rate. The continuous nature of their strain rate data is also apparent from Fig 3 (see point 12 above). It does not seem justified then to claim a change in deformation mode here, so the point should be removed or weakened.

19) Lines 305-306 read: "the upper NaCl layer did develop a pronounced gradient towards the interface with the biotite-bearing layer though, which could be evidence for a diffusive salt redistribution". Yes agreed. But it could also be evidence of advective redistribution if there were even small internal T-gradients. Can this possibility be eliminated? If not that should be stated.

20) Lines 309-319: Here it is proposed, quite reasonably, that Merino's model of diffusion from more porous to denser layers may occur because of a higher solute concentration (supersaturation) in the more porous material than the denser material. This is consistent with pressure solution theory and fine. However, appealing to the high supersaturations discussed by Desarnaud et al (2014) or Zimmerman et al (2015) is misplaced here as these are concerned with pre-nucleation supersaturations. There is no evidence for a nucleation stage in the present experiments as it is quite clear from the grain scale images, and from previous compaction work on NaCl, that precipitation occurs mainly by OVERGROWTH on the pre-existing grain (pore) walls. If fine grains are nucleated in the pores in the present experiments, that would be new and should be described. Only then should the above nucleation argument can be kept.

21) Lines 320-322. Here the authors argue that the Merino model may apply because the

biotite-bearing layers compacted more than the pure NaCl layers in the early stages of the experiments, so had lower porosity, lower contact stresses and hence a lower supersaturation on NaCl in the pores – giving a driving force for diffusion of dissolved NaCl from the pure to the mixed layers. For the reader, however, this seems to be a strange statement after so much emphasis has been placed on the lack of evidence for any strain enhancement in the biotite-bearing layers (at many points, but also again in lines 336-337). The argument seems inconsistent. Can the authors please clarify this picture – it is most confusing in the present form???? Was strain only uniform in the late stages but not initially? If so, please make this clearer.

22) In relation to the above point, I also wonder if the authors should mention the possibility that the preferential "cementation" of the biotite rich layers that they see could reflect an INSTABILITY caused by the Merino effect progressively reducing grain contact stresses and supersaturation in the biotite layers faster than in the NaCl layers.

23) Line 331. The authors suggest here that electrochemical effects at the NaCl-biotite interface may enhance dissolution at those sites, following the references cited. However, as far as I recall those refs deal with the effects of micas at mica-quartz interfaces. I do not think one can then assume that the same enhancement effects will occur at a mica-salt (ionic solid) interface. Line 331 should read "…..which MAY accelerate dissolution of NaCl.".

24) Lines 336-334: This explanation of what goes on inside a biotite-bearing layer is reasonable. However, is it not a remarkable coincidence that "the additional NaCl contributes to a load-bearing framework whose compaction rate is in sync with the bulk sample's"??? Would it not be better (i.e. more accurate) to replace "is in sync with" by "roughly matches" ?? Otherwise there would have to be some strong coupling which is hard to argue.

25) Lines 374-386. The issue of volumetric strain versus compaction strain versus isotropic strain raises its confusing head here again, further underpinning the need for better definition of these terms at an early stage in the paper, followed by consistent use in a way that distinguishes between physical compaction and the math properties of the isotropic part of the strain tensor – see point 14 above. MORE INTERESTING though is the issue of what was observed in the glass bead layers in the biotite-bearing samples. Presumably there was no actual compaction of these layers, beyond some rearrangement effects or possible bead breakage or chipping. This should be clarified in the Results. There, it should also be made clear whether there was any precipitation of salt in the bead layers. If there was at both sample ends, this would support the Merino model, as there would be no stress-induced supersaturation in the brine in the pores between beads. If there was precipitation between beads at one end of the sample but not the other, this would suggest a role of convection and advective transport, or double diffusive convection. If there was no precipitation at all between the beads, this could be explained by the nucleation barrier at these sites – thus supporting neither the Merino model nor an advective transport model.

26) The issue of the glass beads does raise the question of why the authors did not do an additional control compaction experiment with a layer of denser NaCl instead of a layer containing biotite? This would more rigorously test whether the Merino model may apply, i.e. whether diffusive transport is caused by porosity hence supersaturation differences, as opposed to some special effect of biotite. This would be a worthwhile addition to the paper, if time and money allow - as would an experiment substituting calcium fluoride cleavage flakes for biotite flakes. That would be useful because the diffusive properties of NaCl-CaF2 interfaces have been directly measured during active pressure solution of the NaCl by De Meer et al (2002 EPSL 200).

TECHNICAL ISSUES (language, typographics etc)

Overall the paper is well written and in good English. Nonetheless a few small improvements can be made as follows:

- i) an asterisk * is not a mathematical symbol. Proper multiplication and scalar, vector or tensor product symbols should be used.
- ii) Figures 8-11 would benefit from an explicit indication of which sample is being displayed.

P.S. The references cited above but not listed in the ms can be easily found in an online search from the information I have given. I checked this.