Rapid hydration and weakening of anhydrite under stress: Implications for natural hydration in the Earth's crust and mantle

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Reply to Reviewer Comments (RC1)

Comment from Author to Reviewer 1

We thank Reviewer 1 for their very thoughtful and knowledgeable comments. Based on the changes due to raised issues we believe that the manuscript has improved significantly.

Kind regards,

Johanna Heeb

General comments:

Comment about the importance of the increase in volume of solids as main characteristic of hydration

It probably explains the behavior of the reaction, particularly in the case of deforming reactant rock. The access of water to hydrate the rock requires the existence of a network of fluid pathways, which become sealed as the reaction progresses, given the large increase in volume of the solid during the reaction.

In a static environment, this may be a contributing factor to halt the progression of the reaction. In the case of a dynamic environment, the continuous introduction of micro fracturing, damage and pore space keeps the reaction going as it provides pathways for fluid to access unreacted material.

The experiments done by Heeb et al. gain more relevance when addressed from this point of view. Perhaps it is no surprise that the reaction progresses faster or earlier in the case of a dynamic or stressed environment (thus strained) in comparison with a static set up. The experiments presented illustrate this very well.

Thank you. Indeed. The key role of volume change on the reaction has indeed been discussed in section 4.3 under the aspect of observed mechanical-chemical coupling.

Comments about the experimental procedure

The main issue is regarding the description of the tests, particularly the differences between the different sets of experiments, in some cases because there are several things mixed or because of the terminology used.

For instance, the difference between "wet" and SSDC tests (steady-state differential compaction). Both require pore fluid pressure, the main difference resides in the magnitude of the effective pressure. But I'm not sure that this difference justifies their classification as different set, as there are other factors, mainly time. These also undergo large differences in time at pressure, the SSDC having almost a magnitude longer at stress that the "wet" ones.

The classification as different tests ("wet" and former SSDC, now renamed as CSDC) is necessary. Yes, time (i.e., duration) plays an important role, as mentioned in the text and listed in table 2. CSDC also means that fluid pressure is introduced only after reaching ~100 MPa of differential stress.

Therefore, the effective pressure changes significantly – i.e., abruptly. Additionally, the load is removed, and confining pressure held constant, which also justifies the difference in classification. We prefer to keep these categories for clarity.

The graph in fig 3 shows the mechanical data in all tests, but it does not show the differences in confining pressure, and also in effective pressure, where there is a large difference between Ò1 and Ò7 or Ò8.

It would be better for the reader to show separately the curves at different effective pressure, for instance, or color-coding tests under similar conditions.

Thank you. Figure 3 has been revised to better reflect the different test conditions. The names of the experiments have been changed to and a new colour code has been used to highlight similar conditions. To further highlight the differences in effective pressure, two stress strain diagrams have been made out of one. Differences of confining pressure and effective pressure are listed in table 2 as well.

The usage of "initiating the strain rate" is somehow confusing. I take it to mean initiating the loading, which is what it is normally used.

Thank you. The term was replaced by "initiating axial load" in the text when applicable.

But one needs to bear in mind that one thing is the moving rate of the piston, which is easily kept constant, another is keeping the strain rate constant, which requires to recalculate the speed at which the piston moves to keep strain rate constant. I'm aware the differences may be minimal at low strain, but they will increase as the shortening of the samples builds up. And by the look of some of the samples, we are probably closer to the latter than the former.

Thank you for pointing this out. Yes, the moving rate of the piston was used. After the 'CSDC' mode (former SSDC) and with reapplication of the axial load via moving the piston at the same rate as at the beginning of the test, the strain rate should be different from before, because the length of the sample has decreased. Throughout the manuscript, when it applies, the term "strain rate" was replaced with "axial load" and "displacement rate". It was important to have dynamic displacement.

With regards to the procedure of the testing, in some of the experiments, there are instances where the piston is stopped, but the differential stress is kept constant, which is odd, because as soon as you stop the loading, the sample will start to relax reducing the differential stress. In relaxation tests, the strain rate will vary with time, in that case orders of magnitude depending on the times at which the sample is left to relax.

How exactly is conducted this part of the experiments is not clear in the description, but in Fig 7 there is a segment in the loading curve where effective stress is kept constant while strain keeps accumulating, for several hours.

The time is perhaps not too relevant for the amount of strain, but it certainly is for the progress of the reaction, since at this stage the sample remains stressed, thus, in conditions potentially favoring the progress of the reaction.

We maintained an external differential stress – i.e., the axial stress and confining pressure were kept constant in the phase under discussion. The strain (and strain rate) evolution can only be judged from the axial displacement transducers. With the load (axial and radial) staying constant, stress relaxation was not observed. It can be speculated that with time a relaxation effect would set in.

The name given to the tests Ò1 and Ò2 is confusing: "steady-state differential compaction under fluid pressure" (line 219). As written it can be understood as the fluid pressure what produces the compaction, when in fact it is the effective pressure which does

Agreed, the term “SSDC under fluid pressure” was used twice in the manuscript before. ‘Under fluid pressure’ has been deleted for both cases and SSCD has been changed to constant stress differential compaction (CSDC).

If the “strain rate” is put on hold, probably meaning that the piston is stopped, then the reaction is progressing during relaxation at high effective stress, in this case provided by the initial 100+ MPa differential stress, which will reduce very likely over time. The time at which the samples are left loaded is important (I assumed is tssdc in table 2) as despite some relaxation of stresses, they presumably will still be high enough to favour compaction.

Please see the answer to comment 2.3. We have constant applied stress (an external boundary condition) and are not speculating on the internal deformation (relaxation) of the sample.

However, in line 260 it is said that the piston is stopped before fluid pressure was applied, is that correct??

This is correct.

If that is the case, then it is possible that a lot of fracturing is induced by reducing effective pressure. This part requires more detail. If it is how it is said, then certainly “steady-state” is not the right word to describe this type of experiment.

Thank you. We have no diagnostic criteria as to exactly determine when the fracturing happened (e.g., from acoustic emissions). All mentions of “steady state differential compaction” have been changed to “constant stress differential compaction” and “SSDC” has been changed to “CSDC” throughout.

<u>Rebranding of names of the tests</u>

The microstructural work is outstanding and complements very well the lab work, once the procedures are presented more clearly. I would also suggest to rebrand the names of the tests to reflect more objectively the type of test.

Thank you. New names have been assigned to better reflect the test modes of individual samples. (H1, H2 for the CSDC tests, W1-4 for the ‘wet’ tests, and D1 and D2 for the dry tests).

<u>Comment on emphasizing time as the key factor to enhance further hydration</u>

Time has been emphasized more as a key factor for hydration rate in the discussion. It is also important to that the degree of hydration depends on other key factors as well, as it is important what happens in that ‘time’, for example with the space available, nucleation rate, which can both control and stop hydration.

Specific comments and replies:

Graphical Abstract:
Thank you, that is absolutely right. The arrows marking the shear sense in the right sketch have been changed to realistic direction, following the sketches in the middle.

Line 88:
Agreed, this is a very good adjustment that will be adopted.

Line 90
Done, with the addition of ‘mineralogy’ to include mineral content, as this is not included in the Earth Science definition of ‘microstructure’

Section 1.2 Mechanisms of anhydrite hydration

Thank you. Volume change is referred to as ‘swelling’ and mentioned in the introduction with reference to 3 papers. This then links to section 4.3 Mechanical-chemical coupling. I have added to the sentence in the introduction (lines 83, 84), which reads now: “… and the complex expansion or swelling of theoretically up to 60 % volume increase associated with hydration …”

3.1.2 Mechanical data

Thank you for pointing this out. To address this issue, the following three sentences have been deleted: “All samples show an initial phase of rapid hardening up until approximately 10 to 20 MPa differential stress. After this, total strain either stabilises or shows a minimal increase, with increasing stress. The next stage is a phase of linear elastic deformation until yield stress is reached, after which the differential stress decreases.”

Line 280

Thank you. An assessment has been done by analysing SEM images with ImageJ. Results can be found in the Supplement material in Fig. A16, A17, A18 and A19. Table A1 lists the % of black and white pixels. Estimation of porosity is biased by black pixels due to grain boundaries. Reviewer 2 made a comment addressing threshold analysis as method.

Fig. 5 & lines 309-321:

Yes, it is roughly the same. The pole figures of gypsum grains using 1 point per grain are included in the supplement material to this publication (Fig. A10), where X and Y axis are not aligned to the core orientation. The 1 point per grain dataset of gypsum contains 2385 data points, m.u.d. spans from 0.01 to 4.94 and displays clustering of data points at similar positions.

4.2.1. Rapid hydration of anhydrite under stress

Thank you. The missing clarification of application of fluid pressure during the CSDC tests has been addressed by adjustments of Figure 7.

Line 385

The last sentence in the paragraph has been modified to address this comment and reads now as follows: “This suggests that there is an intrinsic link (or links) between the application of a non-hydrostatic (effective) stress field and the rate of the hydration reaction.”

Line 390

Thank you, “re-application of strain rate” has been replaced by “reloading of the sample from SSDC differential stress”

Fig. 7

Agreed. The time has been added in a revised version of the figure.

Fig. 8.

Yes, very true. The figure has been adjusted accordingly.

Line 468-470

This sentence has been adjusted: “due to the appearance of mechanically weaker gypsum and dynamic opening and filling of cracks”.

Line 474

Thank you. This has been adjusted.

Line 476

Thank you, yes there is something wrong. The strain rates do differ in speed, from fastest W1 (former Ò3) to slowest W2 and D1 (former Ò4, and 7). The sentence was changed as follows: Faster strain rate (W1, $4.4 \cdot 10^{-5} s^{-1}$) and higher stress conditions (W2, P_c = 100 MPa, P_f = 90 MPa) generate weaker peak strengths.

Lines 482-486

Thank you. There is no stress relaxation, but indeed constant stress is maintained during this phase. The term has been changed to “constant axial and radial stress conditions” to address this.

Line 498

Thank you. The quote was checked and adjusted accordingly. The words ‘relatively minor’ have been deleted.

Line 546-549

The connection is that fluid migration can produce embrittlement and at the same time facilitates the reaction. Therefore, we find that the system can serve as an analogue for gypsification. Two sentences have been added according to the missing information provided by the reviewer: “However, weakening in the case of granulite is the consequence of fracturing, not necessarily of hydration, unless the eclogites were deformed.” and “Although the difference in strength between granulite and eclogite is not as significant as that of anhydrite and gypsum.”