

Interactive comment on “Transport processes at quartz-water interfaces: constraints from hydrothermal grooving experiments” by Klevakina et al.

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General Comments

The manuscript by Klevakina et al. presents results from a series of experiments on quartz-water interaction performed at ~400-600 °C and ~200 MPa in the system SiO₂-H₂O. The focus of the study was the physical aspects of quartz-water interface reactions with a detailed study on the surface and groove evolution on quartzite samples as a function of time and temperature. Additionally, the chemical aspects of quartz-water interaction were studied using kinetic rate law calculations and linked to the observed physical aspects to describe grooving. These results were then compared to the formation of healing fractures in the crust.

Although the system SiO₂-H₂O has been the subject to numerous studies in the past, the results of this study present a nice scientific contribution to our knowledge on quartz-water interface reactions linking physical and chemical aspects. The experimental results are generally well presented and the manuscript clearly written. The results were also fitted to theoretical predictions (e.g. Fig. 12) and analyzed grooving profiles are well characterized (e.g. Fig. 8). Additionally, I find the description of surface evolution during hydrothermal alteration as a function of crystallographic orientation (e.g. Fig. 4) very interesting. There are several points that need to be revised or clarified before final submission, but overall I recommend this manuscript for publication in *Solid Earth*.

The authors use the results of SiO₂-H₂O experiments to derive diffusion coefficients (Tables 1 and 3, Fig. 14) and then estimate the time-scale of fracture healing in the crust (subsection 5.3, lines 1-27, p.21). It is well known that crustal fluids contain NaCl, CO₂ and other components released during fluid-rock interaction such as Al, K and Ca. This will affect the chemistry of the fluids including the formation of aqueous complexes that may affect the solubility of quartz (e.g. Xie and Walther, 1993, *GCA*; Newton and Manning, 2010, *Geofluids*). The salinity (NaCl, CaCl₂ and KCl) has an influence on the solvent (i.e., ionic strength) and the activity of aqueous species that in turn will also be reflected in the dissolution/precipitation kinetics of quartz (e.g., Dove and Crear, 1990, *GCA*; Ganor et al., 2004, *GCA*) and in the retrieved diffusion coefficients. The kinetic mechanisms for quartz dissolution-precipitation may therefore be different compared to the more simple SiO₂-H₂O system. I am not suggesting that you have to do all these experiments, but it is essential that in your discussion you clearly present the limitation of the experimental system that you investigated for deriving kinetic parameters and for comparing your results with the healing of fractures in the crust. The authors state this in line 12 (p. 22), but this needs to be described/argued in more details with reference to other studies. A little more details on the controlling transport/diffusion mechanism expected in crustal veins and permeability distribution in the crust would strengthen your comparison with geophysical data (e.g., Ingebritsen and Manning, 2010, *Geofluids*; Wangen and Munz, 2004, *ChemGeol*).

Some parts of the manuscript (especially subsection 4.1, 5.1 and 5.2) are unfortunately less well structured and descriptions of experimental observations are missing or different sets of experimental observations are being described back and forth,

making it difficult for the reader to follow what are the major observations and conclusions being made. An example is subsection 4.1 (line 5-28, p. 11), where the morphological evolution of reacted grain surfaces and the development of grooves are being made. The authors describe the development of grooves (line 6-7, p. 11), then the development of surfaces during annealing (lines 7-14, p. 11), then the development of grooves (lines 14-17, p. 11), then the development of scratches from polishing (lines 18-24, p. 11) and then again surface alteration (lines 25-28, p. 11). In this example, I would have expected a systematic description of experimental observations as a function of temperature, time and pressure for the experiments in Table 2 rather than the more general observation given in this subsection. Each experimental temperature should at least be presented in the text, with surface evolution and groove development as a function of annealing time.

Then subsection 5.1 (p. 14-15) should be addressed. The authors discuss three possible processes in the experiments for the development of grooves. The authors need to strengthen here arguments for the different processes by giving more specific examples from the experimental result section and less general statements. For example, it could be: “the initial dissolution process of quartz (line 1-6, p. 16) can be observed at 392 °C by the development of steps on 0001 (Fig. 4) whereas with increasing annealing time (Fig. 9), 0001 is dominated by growth”. This example description is missing here and many others, and I suspect that a better organization of subsection 4.1 would help using the experimental observations as arguments for the different quartz-water interface processes mentioned in the discussion (subsection 5.1).

Subsection 5.2 (p.17-18) was very difficult to follow and would need some clarification. This is partly due to the argumentation that needs the reader to switch between Figs. 13-14, calculated groove evolution (Eqs. 3-4), calculated diffusion parameters (Table 1), quartz solubility (Eq. 5) and resulting diffusion coefficients (Table 3). It may be useful to have a paragraph describing the calculations steps and the connection between Figures 13 and 14 at the beginning of the subsection. The authors give some details in line 9 (p. 18), whereas calculated diffusion coefficients were already given further up in the discussion. It was also difficult to estimate what parameters have been assumed to take certain values (e.g. Table 1), why and what are their limitations on the derived diffusion coefficients? It seems that the derived kinetic parameters fitting Mullin’s theory are taken from two different sets of experimental data; i) data from Table 2 with star (lines 11-14, p. 18), ii) another subset of experiments (lines 21-25, p.17) excluding sequential annealing experiments (line 5 p.18). This is not given in Figures 13 and 14, which results are from which subset? Finally, some general calculated numbers are given for the solubility of quartz (Table 1, Lines 6-7, p. 7) and for diffusion coefficients (lines 19-20, p. 17; Table 3). However, I would recommend adding these numbers in a separate Table for each experiment. The reader can then also for example identify more easily the numbers connecting Figures 13 and 14.

Statistical observation need more details and vague sentences should be omitted (e.g. “...exemplary statistics suggest the following typical inventory.” Lines 7-8, p. 13). In Figures 6c and 11 the frequency of observed grooves is given in percent, therefore I suspect that the authors must have analyzed a certain amount of grooves with a specific depth that has been measured, else it should not been shown in a figure. The number and measured grooves and types should also be given in a Table for each experiment.

Overall, there are some limitations in the experimental technique for the interpretation of groove development. For example, experiments with consecutive annealing yield an increase in groove depth (Fig. 6), whereas single annealing experiments don't (line 8-12, p. 14). This is an important observation and need to be added in the discussion. Is this due to precipitation of quartz during cooling, or the consecutive dissolution during each heating experiment? How do you expect the quartz surface to evolve? I would even add a new specific subsection (5.1), were you describe how experimental limitations (experiment type, development of scratches due to polishing, precipitation of qtz during cooling of the experiments etc...) are being separated from "useable" observations of groove development for retrieving kinetic parameters.

Detailed Comments

Text

Line 23, p. 3: should read "... and the potentially dominant"

Line 27-29, p. 3: this description should go in the method section 3.

Lines 9-11, p. 5: add t =time in (s)?

Line 2, p. 6: aqueous fluid

Line 24, p.6: Eq. 5 is from Fournier and Potter (1982) that should be cited.

Lines 6-12, p. 7: these calculations belong to the discussion

Lines 15-20, p. 7: I would add that this is the dissolution rate following transition state theory (TST, cite Tester but also Lasaga ref). And also add that this equation is limited, without any term for the actual mechanism of dissolution (breaking of Si-O bonds). It seems that the kinetic expression is wrong in Eqs. 6-7, there shouldn't be 2 exponentials (for k and in the $m(t)$ expression). Please check.

The forward qtz dissolution rate: $r_{+,geo} = A_{geo} * k * \exp(-E_a/RT) * (1 - m(t)/m_{sat})$ in [molSiO₂/s]

With k = rate constant

A_{geo} = geometric reactive surface area [m²]

$(1 - m(t)/m_{sat})$ = silica saturation state=departure from equilibrium

$m(t)$ = silica concentration at time t

m_{sat} = equilibrium silica concentration

E_a = activation energy

$m(t) = r_{+,geo} * t / M_w$

t = time [s]

M_w = mass of water [kg]

Line 19, p. 7: reactive surface area

Line 12-13, p. 8: From my experience, you cannot remove carbon coating with only a soft tissue, you need polishing.

Line 19, p. 8: "hydrothermal apparatus", what kind? cold seal, piston cylinder? Why do you have so much pressure variation in some experiments (Table 2), 60-400 MPa? Do you see a dependence on grooving and quartz solubility with pressure?

Lines 5-9, p. 9: I think the term in the kinetic expression (Eq. 6) indicating how close the system is to equilibrium (saturation state), may even have more influence and should be mentioned.

Line 28-29, p. 9: precise that precipitation during cooling is an experimental limitation. This should also be discussed in a subsection of the discussion (as explained in general comments above).

Lines 1-4, p. 11: please delete, this part is not necessary.

Line 5, p. 11: make subsection title more specific, for e.g. “Morphological evolution of grain surfaces and grooves”.

Line 28, p.11: there is no Figure 3f

Line 4, p. 12: structures should read microstructures

Line 4-5, p. 12: deformation lamellae and terraced growth? not described in the previous part...

In subsection 4.1, one paragraph should describe the evolution of grooves and the other one the evolution of crystal surface microstructures (e.g. surface roughness, edge pits etc...) using Figs. 2-3. Additionally, I find that more experimental descriptions are needed here. For example, line 6-7 (p.11) only describes in general way how time, temperature and pressure affect the grain surfaces and groove evolution. Is for example the annealing at 392 °C as a function of time the same than at 568°C? What is the effect of pressure for example at 392 °C and 63 MPa vs. 392 °C and 198 MPa after 24h. I would not describe in detail each experiment but add a typical example for each variable. The descriptions should be more systematic and describe: a) the effect of temperature, b) effect of time (as in Fig. 2 at 392 °C) and c) effect of pressure. If at 568 °C you do not see a significant change of morphologies with time, I would at least add this in the text, if the example is not shown in a figure like Fig. 2. Description of scratch evolution should be mentioned (line 18-24, p.11), but I am not convinced that Fig. 3a adds much except showing the scratch depth due to polishing issues. Additionally, powders in the scratch could have been removed before the experiment using an ultrasonic wash step after polishing.

Lines 8-21, p. 12: I would add a new subsection here, for e.g. “4.3 Annealing as a function of crystal orientation”.

Line 8, p. 12: you have first Fig. 5 in the text but you should cite first Fig. 4 then 5.

Lines 7-8, p. 13: Vague statement, if not quantified omit.

Line 10, p. 13: what about the remaining 80% of the grooves?

Lines 8-11, p. 14: this description of Fig. 6 belongs to the beginning of the subsection.

Lines 11-12, p. 14: Fig. 13 should belong to the discussion section, where also the single annealing vs. sequential annealing results should be (Fig. 6) mentioned further (as explained in general comments above).

Lines 14-17, p. 14: please delete, this part is not necessary.

I recommend to add a subsection 5.1 to describe the experimental limitation for studying groove evolution and the selection criteria for later calculating kinetic parameters (as explained in general comments above).

Line 19, p. 14: should read "... distinguish three processes responsible for the observed groove and surface geometries.

Line 19, p. 14: Firstly, not First

Line 21, p. 14: Secondly, not Second

Line 22, p. 14: should read "involves diffusion to some extent"

Line 19, p. 16: (Holness 1992, 1993)

Lines 15-17, p. 17: cite here Fig. 12 that nicely illustrates this

Line 20, p. 17: Please add a paragraph describing the calculation steps that will follow and a Table with calculated results (as explained in general comments above).

Lines 3-5, p. 18: not clear what is meant here

Lines 7-8, p. 18: yes, this should be described in a separate section 5.1 to describe the experimental limitations (as explained in general comments above).

Line 13, p. 18: "n accordingly" misses a space

Line 9, p. 18: should read "...apparent activation enthalpy and apparent activation volume)

Line 16, p. 18: "and we use the standard deviation", delete found

Lines 19-21, p. 18: please discuss the limitation of using these values for these parameters! For example the quartz surface in the experiment does it behave isotropic?

Lines 4-5, p. 20: the effect of pressure was not shown in the experimental section 4...

Lines 8-10, p. 20: unclear statement, please indicate from the experimental evidence the most likely rate-controlling processes.

Before section 5.3 add a paragraph or subsection describing the limitation of the experimental system $\text{SiO}_2\text{-H}_2\text{O}$, what fluid composition do you expect in the crust, what effect has NaCl on the reaction rate and quartz solubility (see paper by Manning et al.)

Line 22, p. 22: "It is not clear..." this belongs to the discussion. In the conclusion you need to add the main points you conclude from your experimental observations. The uncertainty belongs to the discussion part.

Tables

Table 1: please add somewhere the meaning of E_i (supposedly activation energy) shown in the diffusion coefficient footnote. What is the meaning of B and lambda parameters in the table? Equilibrium concentration m_{sat} were calc. by Eq. 5 not Eq. 4 right?

Table 2: I would add here calculated equilibrium SiO_2 concentration of the fluid

Table 3: caption should read growth law (Eq. 3). I would add here that you used the equation in Table 1.

Figures

Fig. 1: nice schematic, eventually you could add a schematic 0001 and 1010 crystal surface as example for later (Fig. 4) referring back to this figure.

Fig. 2: please remove/crop on the bottom row the non-visible text

Fig. 3: Do you have a picture after 0 hours at room temperature? I would add this instead of the scratches in (a). in (c) at 568 °C it seems 0 hours are wrong. In the caption I would precise that the growth structures correspond probably to dissolution+growth (d)

Fig. 4: I would add the temperature on the top row of the Fig. In the caption should read "... of neighboring grains. Relation between groove depth of ... orientation (c-f)". Last sentence: $a=\{1120\}$; $b=\{\dots\}$; $c=\{\dots\}$.

Fig. 5: maybe add estimated crystallographic orientation from Fig. 4, 0001 and 1010 showing the step growth.

Fig. 6: Elaborate statistics of groove frequency either in text or Fig. caption. Why is it that (b) the groove depth decreases exactly around 15 grooves for all 3 experiments? Isn't that the number of analyzed grooves?

Fig. 9: I would add b/c in the graph, and maybe an arrow indicating that with increasing temperature we are more on the left side if I understood correctly. Orientation between b/c seems important to indicate dissolution from growth processes, please add this in the discussion!

Fig. 11: The duration time is missing on the graph.

Fig. 12: I would add directly on the left graph the 3 different process next to the calculated lines: dissolution, surface diffusion and diffusion through liquid.

Fig. 13: in caption you describe volume diffusion, was never mentioned in the text... what do the colors mean?

Figs. 13-14: unclear which data subset were used for these calculations, describe better in the figure caption or in subsection 5.2

Fig.14: 3 different processes were calculated for these diffusion coefficients, please add this somewhere in the figure. There are two types of bold line next to "this study", what is the dashed one?