response to comments by A. Gysi:
This rebuttal uses the reviewer's written statements as backbone. Our response is directly given "in italic font" after a specific point. We took the liberty to mark key aspects of a comment in cases.

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.

We thank the reviewer for his benevolent assessment.

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).
We will happily add references and extend discussion as advised.

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.

In fact, we "struggled" with the presentation for some time, given that we have a number of experimental parameters (temperature, time, pressure, details of charge) and an illustrious inventory of microstructural features observed after the runs. At the end we felt that using the inventory as the "thread" seemed ok but obviously our attempt wasn't exactly a success. We will turn things around and use the experimental parameters as the guideline for the presentation of results as suggested by the reviewer.

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).==

Thanks for the constructive advice. We will revise subsection 5.1 accordingly with the intention to better present the support for the suggested processes.

==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.== *(We will provide such a paragraph.)* 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 <mark>recommend adding these numbers in a separate Table for each experiment</mark>. The reader can then also for example identify more easily the numbers connecting Figures 13 and 14.

We will add the requested paragraph and extend the information in the corresponding tables as requested. We will also discuss the consequences of uncertainties in used parameters for the derived kinetics parameters.

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 groves 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. <mark>The number and measured grooves and types should also be given in a Table for each experiment.</mark>

We will add quantitative statistical information in Table 2. We will revise the mentioned sentence to make clear that "exemplary" was meant such that not all samples but only samples taken at random were tested for the statistics of the various elements.

(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 <mark>add a new specific subsection</mark> (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 <mark>being separated from "useable"</mark> observations of groove development for retrieving kinetic parameters.

We will provide the requested "preamble" for the discussion section that comprehensively describes our approach with respect to selection of observations for further quantitative analysis.

Detailed Comments

Text

Please note that we shuffled the order of the comments to structure our response. Here also we took the liberty to mark key aspects of a comment in cases.

* suggestions regarding wording and other straightforward suggestions

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

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

Line 2, p. 6: aqueous fluid

done

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

Line 19, p. 7: reactive surface area
done

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

We polished with a soft tissue by hand until the coating was removed.

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

We employed externally heated hydrothermal "bombs". The range of 60 to 400 MPa corresponds to pressures explored by our study to investigate whether pressure actually has an effect (the intention of pressure variation was to see whether solubility with its known significant pressure dependence actually figures into overall kinetics). The pressures quoted in Table 2 are the pressures of the individual experiments.

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

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

Line 28, p.11: there is no Figure 3f
cross-references will be corrected

Line 4, p. 12: structures should read microstructures
done

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

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

Line 19, p. 14: Firstly, not First
Line 21, p. 14: Secondly, not Second
resived

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

done

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

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

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

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

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

* suggestion regarding placement/structure
Line 27-29, p. 3: this ==description should go in the method section 3.==
done

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

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).
We will collectively discuss experimental shortcomings in the "preamble" to the discussion.

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.

We will follow the various constructive suggestions and restructure the presentation of results (see above).

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

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

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).
done

Lines 14-17, p. 14: please delete, this part is not necessary. *done*
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).
Will be addressed in the "preamble" mentioned above.

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).
We will reorganize according to the suggestions.

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?
Will be done.

Lines 4-5, p. 20: the effect of pressure was not shown in the experimental section 4…
As described above we will revise the presentation of experimental results using experimental conditions as the "red thread".

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.
Statement will be transferred to the discussion section.

* comments on contents
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) {Lasaga, 1984 #91}. 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: $r_{+,geo} = A_{geo} \cdot k \cdot \exp(-E_a/RT) \cdot (1 - m(t)/m_{sat})$ in [molSiO2/s]
With k = rate constant
A_{geo} = geometric reactive surface area [m2]

(1-m(t)/msat) = silica saturation state=departure from equilibrium
m(t)= silica concentration at time t
msat= equilibrium silica concentration
Ea= activation energy
m(t)= r+,geo*t/Mw
t= time [s]
Mw= mass of water [kg]

We are not quite sure whether we understand the comment correctly. Anyway, we show how to derive the equation in question to facilitate judging its appropriateness. Dissolution is treated as an example for first order rate kinetics, i.e., the rate with which a quantity changes is linearly proportional to the current amount of the quantity. Here, the rate constant reads

$$r_{+,geo} = \frac{\mathrm{d}m}{\mathrm{d}t} = A_{geo}k(T)\left(1 - \frac{m(t)}{m_{sat}}\right)$$

(as also stated by the reviewer). Integration yields of this differential equation from time "0" to some time "t" gives

$$\int_{m_0}^{m(t)} \frac{\mathrm{d}m'}{1 - \frac{m'}{m_{sat}}} = Ak(p,T)\int_0^t \mathrm{d}t' \Leftrightarrow -m_{sat}\ln\left(1 - \frac{m'}{m_{sat}}\right)\Big|_{m_0}^{|m(t)|} = Ak(p,T)t\,\Big|_0^t$$

Upon algebraic manipulation we arrive at the equation quoted in the manuscript (that contains a "double-exponential" due to the inversion of the natural logarithm and the thermal activation considered for the kinetics parameter k. One may argue the choice of m_0. In the manuscript we used $m_0 \to m_{sat,0}$ reflecting the notion that quartz and water were at equilibrium at the start of the experiment. Setting $m_0 \to 0$ could equally be justified since the solid charge and the distilled water may not have had time to equilibrate. Either of these two choices is however much smaller than m_{sat} at the run conditions and therefore our calculations aren't affected by the choice. We note that the given equation is just an isothermal and isobaric approximation since heating and pressurization protocols are neglected. Actually, one had to solve $\int_0^t k(p_{(t')}, T_{(t')})\mathrm{d}t'$. For our estimates of times required until equilibration we apply the equation in a step wise manner, i.e., we numerically solve the integral.

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.
We will emphasize that the experimental charges are at disequilibrium for some time.

Lines 7-8, p. 13: Vague statement, if not quantified omit.
Line 10, p. 13: what about the remaining 80% of the grooves?
The paragraph will be revised.

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

Will be done.

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

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

Before section 5.3 <mark>add a paragraph or subsection</mark> describing the limitation of the experimental system SiO2-H2O, 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.)
We will critically discuss the limitations of our quantitative kinetics parameters stemming from the investigated "model system". The various references indicated by the reviewer will be incorporated.

Tables

Table 1: please add somewhere the meaning of Ei (supposedly activation energy) shown in the diffusion coefficient footnote. What is the meaning of B and lambda parameters in the table? Equilibrium concentration msat were calc. by Eq. 5 not Eq. 4 right?
The requested information is added in the following way:

Table 1: Parameters of analytical models for grooving following the generic equations **Error! Reference source not found.** and **Error! Reference source not found.** controlled by the listed diffusion processes {see \Mullins, 1957 #5; , 1960 #6}

diffusion process	exponent	B_i	λ_i
diffusion through the solid	$n = 3$	$B_v = \dfrac{D_v \gamma_s \Omega}{\kappa T}$	$\lambda_{v,d} = 1.01$, $\lambda_{v,w} = 5$
diffusion through the liquid	$n = 3$	$B_l = \dfrac{D_l C_0 \gamma_s \Omega^2}{\kappa T}$	$\lambda_{l,d} = 1.01$, $\lambda_{l,w} = 5$
diffusion along the interface of solid and liquid	$n = 4$	$B_s = \dfrac{D_s \gamma_s \Omega \delta}{\kappa T}$	$\lambda_{s,d} = 0.973$, $\lambda_{s,w} = 4.6$

Ω molecular (atomic) volume (1.13 10^{-28} m^3)

γ_s surface free energy per unit area (1 J/m^2)

δ thickness of the layer in which surface diffusion takes place (2 nm)

κ Boltzman constant

D_i diffusion coefficient with $D_i = D_{0,i} \exp(-E_i + pV_i / RT)$ and the counter

   $i = v,\ l,\ s$ serving as an indicator of the diffusion path

R universal gas constant

C_0 equilibrium concentration of solute in the solvent calculated from m_{sat} (see eq. **Error! Reference source not found.**, varies from 1.2·10^{25} to 4·10^{25} atoms/m^3 depending on run temperature and pressure, **Error! Reference source not found.**)

n growth exponent

Table 2: I would add here calculated equilibrium SiO2 concentration of the fluid
We added the requested column (as well as information on the number of investigated grooves, see above).

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

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.
This is the very only comment we do not quite understand.

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

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)
Will be done.

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={…}; c={…}.
Will be done.

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

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?
Will be clarified.

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!
The requested modification of the figure as well as the addition to the discussion text will be done as suggested.

Fig. 11: The duration time is missing on the graph.
We will deal with this sloppy omission.

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.
Will be done.

Fig. 13: in caption you describe volume diffusion, was never mentioned in the text… what do the colors mean?
Revised to "diffusion through solid". Meaning of colours will be explained

Figs. 13-14: unclear which data subset were used for these calculations, describe better in the figure caption or in subsection 5.2
We will revise running text and caption to better explain the statement already present: Only those grooves were used to determine average groove parameters at given conditions that exhibit a width-depth ratio that does not deviate from the value of the Mullins theory by more than 0.1 (see eqs. (3) and (4)).

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?
Requested information will be added to the caption.