Replies to Reviewer-#1’s comments (Dr. Andreas Kronenberg)

The reviewer pointed out 1. Characterization of added water in Pt jackets, 2. Water loss through Pt jackets, 3. Possible changes in the water environments by talc dehydration reaction, 4. Water trapped in the quartz samples and its relation to water fugacity, 5. Validity of the water fugacity exponents associated with comments 1-4. Regarding these points, he gave the following five comments (The numbers raised here do not correspond to those in the reviewer’s comments, where some of the numbers here are overlapped). He also gave other comments after that. We will show all of his comments below and describe revised points of the manuscript.

1) I do not know enough about the pyrex/MgO/talc cells used in this study but I expect that members of the Orleans lab have lots of experience with this cell and might have papers/methods descriptions available to cite to confirm that this assembly is capable of establishing/controlling water fugacity within some given range. This would be an important addition to this manuscript so it does not leave readers wondering if there’s anything wrong (or variable) about fH2O for the range of experiments conducted.

As the reviewer commented, the Orléans lab has been using the cells and knows the validity of the assembly as well as the experimental techniques, characteristic of the piston cylinder apparatus, etc. In the revised manuscript therefore, we showed representative references from the group (Prouteau et al., 2001; Prouteau and Scaillet, 2013), which showed systematic changes in rock compositions (mid-oceanic basalt) depending on the amounts of added water. We also showed references from the group (Gaillard, 2004; Pommier et al., 2008; Laumonier et al., 2015), which measured electrical conductivity of various rock types with different amounts of water in glass. Some of these references performed measurements using the gas-pressure-medium vessel (namely, without talc which can be a water source). In any cases of the apparatus types, they succeeded in measuring systematic changes in electrical conductivity values as a function of water contents. We described these results in the revised manuscript (page 5, line 1).
In our study, we did not see any difference in grain growth due to different amounts of added water in the range of 0.2–10.0 wt%. This would mean that water is already saturated in the Pt jacket and water fugacity values calculated from given pressure and temperature conditions do not change in this range of added water.

The sample assembly is after e.g., Prouteau et al. (2001) and Prouteau and Scaillet (2013), which showed systematic changes in rock compositions (mid-ocean ridge basalt) in Pt capsules depending on amounts of added water. In addition, previous studies measured electrical conductivity for various rock types with different amounts of water (e.g., Gaillard, 2004; Pommier et al., 2008; Laumonier et al., 2015). They used the piston cylinder with the talc-pressure-medium assembly for pressure of up to ~3 GPa and a gas-pressure-medium vessel without talc for pressure of down to ~50 MPa under temperature conditions of 400–1300 °C. The results on pressure, temperature, and sample water contents using these two different apparatuses are systematically correlated.

2) The authors could describe if the talc dewatered during the experiments. This depends critically on the temperature of the outer talc sleeve. This dehydration reaction is usually very visible and talc assemblies have certainly established very wet, high fH2O environments.

The dehydration reaction of talc can occur in our experimental conditions. We added a new reference about it in the revised manuscript (Bose and Ganguly, 1995; page 5, line 7). As we also replied to comment (1), the previous researches by the Orléans lab proved that the talc assembly does not significantly change the water environment in Pt capsules including samples and water.

3) IR spectroscopy of the quartz samples could be done to confirm the presence of liquid water (fluid inclusions?) which would support the application of the Pitzer-Sterner calculation of fH2O when water is present as a distinct phase.

The samples become fragile after the experiments and easily fall apart during thin sectioning without epoxy resin. IR spectroscopy requires only samples without epoxy resin. We tried to make thin sections for IR spectroscopy at first but we could not because of this reason. However, we also have different samples from another grain growth experimental series that the first author (JF) performed at Texas A&M University using the same powder sample and solid salt assembly. The results of IR spectroscopy for some samples are shown in Fukuda et al. (2018).
In this experimental series, we confirmed a broad water absorption band in an IR spectrum at 3800–3000 cm\(^{-1}\) due to liquid water and several OH sharp bands due to crystalline water. Liquid water could exist as fluid inclusions and/or in grain boundaries. Gerretsen et al. (1989) experimentally succeeded in introducing water into the intracrystalline part of quartz and they observed fluid inclusions by transmission electron microscopy and corresponding broad IR bands. This experimental technique was expanded and good correlations between, water contents, pressure, and temperature, have been reported in recent studies (e.g., Stalder & Konzett, 2012; Baron et al., 2015; Frigo et al., 2016). Again, our samples fall apart during thin sectioning without epoxy resin. However, as a future study, for some samples with large grains enough for IR spectroscopy (usually >20 µm for a Globar light source), IR spectra could be measured for a single grain and compared with these studies.

4) Alternatively, if IR of the samples is not possible, the authors could measure the IR spectra of the pyrex, before and after an experiment. Pyrex glass we have in our lab is very wet and silicate melts are known to retain high water concentrations. And IR measurements of pyrex glass before the experiment is easy. Still it would be good to measure IR of the pyrex after experiments. This could then support the contention that the assembly maintains a high fH\(_2\)O outside the Pt jacket, thus maintaining a high fH\(_2\) and limiting loss of hydrogen from the jacket. This is an interesting idea. Since the kinetics of intracrystalline water loss and gain in quartz is not well known, Pyrex glass, whose kinetics seems faster than quartz, may rather be helpful to know the environment of water. Unfortunately, we disposed of the Pyrex glass and other assembly parts when we finished each experiment. This measurement will also be a future work, but cation would be needed as to where water is supplied from; talc dehydration and/or hydrogen escape from the Pt jacket.

Finally, it is interesting to note that the grain growth measured didn’t seem different for samples with added water versus experiments in which no water was added to the powder and novaculite). This would be consistent with the assembly controlling the fH\(_2\)O, if just a trace of H\(_2\)O is in the jacket and is retained as a distinct phase by a pressure medium outside the Pt that controlled fH\(_2\)O and fH\(_2\). Given the above, and the very brief, incomplete information about grain growth in a gas apparatus, I suggest the reference to "no significant grain growth" in the gas apparatus experiment can be deleted. This doesn’t add much to this study and is understandable in terms of very low fH\(_2\)O values during this experiment. When only the novaculite was used without added water in a Pt jacket, no grain growth was observed (PC17-2). In contrast, when the powder and novaculite were used without added water, grain growths of the two were observed (PC17-1) as the same with other experiments with added water. From these two experiments, we
concluded that only adsorbed water on the powder can give a wet condition to cause grain growth. Therefore, we do not think this evidence gives the idea about water fugacity controlled by the assembly. In other words, even when a certain assembly, which does not give water, is used, the same results could be obtained. In order to confirm whether or not an assembly giving water and resultanty controlling water fugacity of the inside of the Pt jacket, one would need to compare results using a water-giving assembly with those using a no-water-giving assembly. As we also replied to comment (1), following the results from the Orléans group, these two different assemblies do not seem to change the water environment in the Pt jacket.

Regarding the result of the gas apparatus, we understand the reviewer's point. This result may have been obvious. However, we would like to keep this fact for readers who in the future consider trying similar but successful quartz grain growth experiments using a gas apparatus under different pressure and temperature conditions. Therefore, we thought this statement would be helpful.

I have a minor issue with referring to the natural novaculite as a quartzite. Novaculites have different modes of origin than do quartzites and are distinct in a number of ways. For example, the starting grain sizes are only found for novaculites. I know of no quartzite with such a small grain size. Quartzites typically have iron oxide impurities (1-2%), while novaculated can be very pure and contain little Fe or other impurities. Please refer to the natural polycrystalline samples as novaculite. Also, please give the locality of the novaculite? Is is an Arkansas novaculite or from another locality?

We understand. We changed quartzite to novaculite throughout the manuscript. The novaculite we used is an Arkansas novaculite, which we also specified in the Samples section, but the exact locality in Arkansas is unknown.

The characterization of grain size and shape by SEM and EBSD is very nice, and I don’t know what the optical microscopy does that isn’t accomplished by the electron microscopy. Are any of the optical micrographs of starting materials or final experimental products needed? It is very difficult to see the grains; thus there’s not much microstructural content in these images. This could cut back on the manuscript without loss of much content.

We understand the reviewer’s point but we think visual images that give analytical data (i.e., grain size) are important. These images also give grain plucking during thin sectioning, open grain boundaries, pore closures with increasing grain sizes. Rather than only describing the results of these observations in text, we think showing the light photomicrographs would be helpful.
I like the section on application of the grain growth kinetics to metamorphic rocks, but think this could be strengthened by referring to reported grain microstructures of naturally heated rocks. For example, if you take observed grain sizes of metamorphic rocks subjected to known temperatures (by phase equilibria or other methods) and the grain growth laws of this study, what does this imply about time of metamorphism? If any geochronology of the metamorphic is known, do you have a match of time of metamorphism? If there is a mismatch, can it be explained by pinning of quartz grain boundaries by micas or other secondary phases? If so, could you infer the history of grain growth before the observed pinning occurred?

In the revised manuscript, we refer to a natural case by Wightman et al. (2006) and give a discussion about a possibility that their natural case can be well explained by our grain growth laws (new paragraph, page 11 and line 22). As we described in the original manuscript, they constructed a grain growth law using experimental data by Tullis and Yund (1982) although the methods for the determination were not shown. The data in Tullis and Yund (1982) would not be enough to discuss the effects of pressure and temperature individually (Table 1 in our manuscript). Wightman et al. (2006) managed to explain the grain growth time of their samples (~4 million years) that could have caused an increase in grain size from ≤1 to ~100 µm. They mainly varied temperature conditions of 400–500 °C to explain their grain growth estimation because their grain growth law is sensitive to temperature, meaning the activation energy is large (215 kJ/mol). Their grain growth law and parameter settings may be possible. However, Fig. 11 in our manuscript shows that their natural data may be easily explained. This is mainly because our grain growth law is less temperature sensitive because of the lower activation energy (e.g., 60 kJ/mol for the novaculite). The grain growth time estimated from our grain growth laws match well with their natural condition.

Grain growth of a natural quartz sample was discussed in Wightman et al. (2006). As we described in Section 5.1, they constructed a grain growth law using experimental data by Tullis and Yund (1982) to explain grain growth of their quartz sample. The grain size of their sample was considered to have increased from ≤1 to 100 µm during a post-deformation time of ~4 million years. They mainly varied temperature conditions of 400–500 °C, giving a significant difference in grain growth time (one order of magnitude) because of the high activation energy of 215 kJ/mol. The experimental data by Tullis and Yund (1982) do not seem enough to argue for the effects of temperature and pressure individually (Table 1). The parameter settings in Wightman et al. (2006) may be possible but in contrast, the lower temperature sensitivity of our grain growth laws (e.g., 60 kJ/mol for the novaculite) may easily explain their data, giving a consistent grain growth time (Fig. 11) (specifically, grain sizes up to a few hundred µm in a few million years for the range of their temperature and pressure conditions with corresponding water fugacities).
Figure 7 and the text refer to epitaxial growth locally in some samples. Is this important? I don’t see any conclusions that are drawn from this. If this process is widespread in the experiments, it needs to be described more fully, and the implications for results discussed. If it is merely a local process and grain sizes were measured in regions without this process occurring, then you need not describe this, unless you explicitly state how you avoided grain sizes of these regions to be included in your results. Again, this is a judgement call, depending on how widespread this was. Finally, I do not know whether I am looking at all quartz in Figure 7i or partly quartz and Pt (I would guess it’s all quartz) but if there is any Pt in this image, please label.

Quartz grains due to epitaxial growth from the Pt jacket as a substrate and normal grain growth inside of the jacket are distinguishable. Grain growth is a local process and grain sizes were measured excluding epitaxially grown grains. We do not focus on epitaxial growth very much in this study. However, epitaxial growth was enhanced when 10 wt% water was added. The texture showing no core-mantle contrast in the Cathodoluminescence image can be compared with that by grain growth showing a core-mantle contrast. Therefore, we consider that we should keep this fact in the text. In the revised manuscript, we gave a more detailed explanation about its growth texture from the Pt jacket and possible crystallographic orientations following previous studies (Cox and Etheridge, 1983 from natural samples; Okamoto et al. 2011 from experimental samples and simulation) (page 7, line 3). We feel that these observations may help to understand the process of grain growth better.

The Pt jacket is seen as a white contrast in the BSE image and labeled. In the revised manuscript, we also described this in the caption.

Page 7, Line 3,

The long axes of these grains are aligned perpendicular to the Pt jacket and inner sample. The crystallographic orientations of epitaxially grown grains would correspond to those of the seed crystals in the sample (namely, neighboring power and/or novaculite), on which quartz grains epitaxially grow, similar to studies for the quartz vein formations (e.g., Cox and Etheridge, 1983 from natural samples; Okamoto et al. 2011 from experimental samples and simulation). The epitaxial growth of quartz probably occurs because of the separation of the Pt jacket from the sample as a consequence of the injection of pore fluid.

Figure 7 caption,

(i) CL image (left) and BSE image (right) including a Pt jacket part (labeled in the BSE image) where epitaxial growth was observed (the powder part is on the inside).
Replies to Reviewer-#2’s comments (Anonymous reviewer)

The reviewer gave three major comments regarding (1) the use of the term “grain growth” associated with the process, (2) characteristics of epitaxially growth quartz, and (3) combination of static grain growth driven by grain boundary energy and strain-induced grain boundary migration under plastic deformation occurring in nature. He/she also gave other comments for specific places in the manuscript, some of which are associated with the major comments. We thank for these helpful comments. We will show all of the reviewer’s comments and revised points.

(1) It would be necessary that the authors early in the manuscript state, how they use the term “grain growth” with respect to grain boundary migration and driving forces. At some point a contrasting juxtaposition/discussion of the processes of grain boundary migration driven by the reduction in interfacial free energy and grain boundary migration driven by the reduction in stored elastic strain energy (i.e., reduction in dislocation density) would be helpful. In this context the wording “contribution of grain growth to deformation” used several times in the manuscript and the title “Experimental grain growth. . .and its application to deformation. . .” might get clearer.

This is a helpful comment. In this study, we used the term, “grain growth” as grain boundary migration driven by grain boundary energy under static pressure and temperature conditions. As the reviewer commented here, clarifying this process would be helpful. Also, as the reviewer commented in (2), we also observed epitaxial growth of quartz grains especially when 10 wt% of water is added. The shapes and growth features formed by epitaxial growth are obviously distinguished with those formed by grain growth. Thus, according to the reviewer’s comment here, we explained “grain growth” we focus in terms of the above process (page 1, line 26). In addition, as the reviewer commented in (3), we also described the contribution of strain-induced grain boundary migration under plastic deformation. To sum up, we distinguished the following wordings; grain growth, epitaxial growth, strain-induced grain boundary migration.

An increase in grain size, termed grain growth, is typically driven by the reduction in surface energy of grains, resulting in microstructures of larger grains with less curved boundaries. When grain growth takes place in a dense solid medium with grains touching one another, the process facilitating growth is the migration of grain boundaries. In a dry system, grain boundary migration constitutes the diffusion of atoms across a grain boundary. If fluid wets the boundary, grain boundary migration may involve solution, transport, and precipitation of the material. Grain boundary migration is a generic process that can be driven by surface energy (e.g., in grain growth) or by internal energy (e.g., strain energy in the form of dislocations = strain-induced grain boundary migration; Poirier and Guillopé, 1979). During viscous deformation, the competition between grain size reduction and grain growth (i.e., surface- or internal-energy-driven migration) controls the grain size and is the basis for piezometry (e.g., Derby, 1990, Shimizu, 2008, Austin and Evans, 2007). Furthermore, grain
size reduction and grain growth may control the processes of weakening through the transition from grain-size-insensitive to grain-size-sensitive creep (e.g., Schmid, 1982; Rutter and Brodie, 1988). Therefore, grain growth is an important process to understand microstructural development as a function of time (Olgaard and Evans, 1988).

(2) The authors also discuss non-hydrostatic conditions in their experiments, especially in the context of dissolution-precipitation and epitaxial growth: is there any systematic relation of the shape of the growing crystals and/or crystallographic orientation with respect to sample shape and/or position in the experimental apparatus or to platinum jacket, or similar? As the authors also analysed the microfabric, a few words on this topic might be useful. In this context also formation of “growth rims” in the sense of epitaxial crystallization by precipitation from the pore fluid should be compared and contrasted to grain growth.

We described the detailed textures of epitaxially grown grains in the revised manuscript (page 7, line 3): We observed an alignment of epitaxially grown quartz grains from the platinum jacket as a substrate, meaning that the quartz grains are elongated perpendicular to the jacket caused by a separation of the jacket wall from the inner sample part (namely, the powder and novaculite). As for the crystallographic orientations, we did not measure them, but according to previous studies for vein quartz grains (e.g., Cox and Etheridge, 1983 for natural samples; Okamoto et al., 2011 for experimental samples), they showed that the elongated axes are c-axes.

Page 7, Line 3,
The long axes of these grains are aligned perpendicular to the Pt jacket and inner sample. The crystallographic orientations of epitaxially grown grains would correspond to those of the seed crystals in the sample (namely, neighboring power and/or novaculite), on which quartz grains epitaxially grow, similar to studies for the quartz vein formations (e.g., Cox and Etheridge, 1983 from natural samples; Okamoto et al. 2011 from experimental samples and simulation). The epitaxial growth of quartz probably occurs because of the separation of the Pt jacket from the sample as a consequence of the injection of pore fluid.

(3) When discussing the relevance for natural conditions and application of paleopiezometers some information on how to evaluate the contribution of grain growth in nature, for example as opposed to strain-induced grain boundary migration during recrystallization, would be valuable. I feel, this should be discussed by citing previous studies published on this topic.

We agree. In the revised manuscript, we cited references for strain-induced grain boundary migration (White, 1977; Poirier and Guillopé, 1979; Jessell, 1987). Then, we discussed textures formed by static grain growth and by dynamic recrystallization, i.e., strain-induced grain boundary migration. The former gives straight grain boundaries and the latter does irregular grain boundaries. We also added theoretical assumptions by previous
studies for dynamic recrystallization (Austin and Evans, 2007; Shimizu, 2008), where grain boundary migration is balanced with static grain growth. When static grain growth overcomes strain-induced grain boundary migration, the texture by the former would be enhanced. We carefully discussed this possibility in the Discussion section (page 11, line 9).

In this case, strain-induced grain boundary migration during dynamic recrystallization (i.e., reduction of dislocation densities) will dominate and form irregular grain boundary shapes as has been studied by experiments and natural samples (e.g., White, 1977; Jessell, 1987; Hirth and Tullis, 1992; Stipp et al. 2002; Tullis, 2002, and references therein). In this case, theoretical calculations for dynamically recrystallized grain size assume that strain-induced grain boundary migration and static grain boundary migration are balanced, resulting in an equilibrium grain size (e.g., Austin and Evans, 2007; Shimizu, 2008). However, when the strain rate is slower, grain growth may become competitive and may dominate the microstructure. When this is the case, it is important to compare such microstructures (with more straight boundaries and larger sizes) to those of nearby quartz containing some impurities, which may have pinned grain growth. Thus, careful microstructural inspections are required before evaluating grain sizes for piezometry. In addition, as evaluated experimentally by Heilbronner and Tullis (2002), grain growth after dynamic recrystallization preserves pre-existing crystallographic preferred orientations formed by plastic deformation although grains show straight grain boundaries. Therefore, a crystallographic preferred orientation test is not sufficient to infer a potential dominance of grain growth.

A few specific comments/suggestions are listed as follows:

Abstract
Page 1, line 10: Delete the first word of the abstract “The”
Done.
Page 1, Line 11,

Grain growth

Page 1, line 11: please specify “large porosity” or rephrase
We changed “large” to “substantial”. In our samples, porosities can not be evaluated quantitatively because of fracturing during unloading and plucking of grains during thin sectioning.
Page 1, Line 12,

a substantial porosity
We deleted "dense".

in the novaculite

Page 1, line 19: What is the contribution of grain growth to plastic deformation? See point (1)

According to the reviewer’s major comment (1), in the early Introduction section, we clarified the process of grain growth in terms of grain boundary migration and the driving force producing larger grains with straight grain boundaries (i). Then, in the Discussion section, as we replied to the major comment (3), we described strain-induced grain boundary migration due to plastic deformation producing irregular grain boundaries (ii). Then, we gave a discussion with the competition between the processes (i) and (ii) following our reply here.

Page 2, Line 3 (Introduction section),

During viscous deformation, the competition between grain size reduction and grain growth (i.e., surface- or internal-energy-driven migration) controls the grain size and is the basis for piezometry (e.g., Derby, 1990, Shimizu, 2008, Austin and Evans, 2007). Furthermore, grain size reduction and grain growth may control the processes of weakening through the transition from grain-size-insensitive to grain-size-sensitive creep (e.g., Schmid, 1982; Rutter and Brodie, 1988). Therefore, grain growth is an important process to understand microstructural development as a function of time (Olgaard and Evans, 1988).

Page 11, Line 9 (Discussion section),

In this case, strain-induced grain boundary migration during dynamic recrystallization (i.e., reduction of dislocation densities) will dominate and form irregular grain boundary shapes as has been studied by experiments and natural samples (e.g., White, 1977; Jessell, 1987; Hirth and Tullis, 1992; Stipp et al. 2002; Tullis, 2002, and references therein). In this case, theoretical calculations for dynamically recrystallized grain size assume that strain-induced grain boundary migration and static grain boundary migration are balanced, resulting in an equilibrium grain size (e.g., Austin and Evans, 2007; Shimizu, 2008). However, when the strain rate is slower, grain growth may become competitive and may dominate the microstructure. When this is the case, it is important to compare such microstructures (with more straight boundaries and larger sizes) to those of nearby quartz containing some impurities, which may have pinned grain growth. Thus, careful microstructural inspections are required before evaluating grain sizes for piezometry.

Introduction
Here, I feel that some aspects on grain boundary migration driven by the reduction in strain- and surface energies, i.e. a contrasting juxtaposition of strain-induced grain boundary migration (or recrystallization) and grain growth, would be helpful, see point (1).

According to the comment, we explained the process of grain growth we focus, which is driven by grain boundary energy and movements of smaller grains with higher grain boundary mobility. As for strain-induced grain boundary migration (dynamic recrystallization), we discussed it in the Discussion section.

The revised points are shown in our reply to the reviewer’s comment on page 1, line 19.

Page 2 line 16: Again: What is the contribution of grain growth to deformation? See point (1)

As we mentioned in the original manuscript, grain growth changes grain size, which can control deformation behavior (grain-size-insensitive creep and/or grain-size-sensitive creep). To recall this, we mentioned it again here in the revised manuscript.

Page 2, Line 25,

As mentioned above, the contribution of grain growth to deformation can be important by a change in grain size which leads a change in deformation mechanism (grain-size-insensitive creep and/or grain-size-sensitive creep).

Samples

Page 3, line 21: A few more information of the sample of novaculite would be helpful. Why is the term “quartzite” used, is it a metamorphically overprinted novaculite?

The novaculite sample is not metamorphically overprinted. We realized that calling the sample novaculite is suitable not to give confusion. We changed “quartzite” to “novaculite” throughout the manuscript.

Discussion

Page 8, lines 20/21: Please reorganize, the influence of porosity is discussed later in detail.

The reviewer is right. We deleted this paragraph and moved some of the sentences from here to the later paragraph that discusses pores and grain growth (page 9, line 32).

Page 9, Line 20,

The powder sample included many more pores than the novaculite sample (Fig. 4b, e, and h). Grain growth of the powder sample with pores was slower than that of the dense novaculite sample because of the limited areas of contact between grains in the powder sample, as water in pores might act as a secondary phase that impedes grain growth, as discussed by Karato (1989) for the grain growth of olivine aggregates. Pore closure was achieved by precipitation, after
which the rate of precipitation would be slower than grain boundary migration, which explains the slower grain growth in the powder sample. As grain sizes increased in both types of quartz sample, differences in their grain sizes were smaller (Fig. 6). This is interpreted to have resulted from the closing of pores in the powder samples (Fig. 4b, e, h and Fig. 7a–d). Grain growth of both types of quartz sample became similar when grain sizes were ~70 µm, obtained at 2.5 GPa and 1000 °C for 24 hours (Fig. 6), indicating that the pores in the powder had almost closed.

Page 8 line 26-31: Please discuss, why/where dissolution and why/where precipitation should take place. Why is at specific sites epitaxial growth occurring? See points (1, 2)

Dissolution can occur anywhere since water can dissolve quartz in our experimental conditions (experimental study by Hunt and Manning, 2012). We confirmed epitaxial growth on the quartz grains next to the Pt jacket because the Pt jacket is removed from the quartz grains (probably due to excess pore pressure effects). We discussed this in page 9, line 20 in the revised manuscript. Please also see our reply to the major comment (2) and revision there.

Dissolution–precipitation was confirmed in the form of epitaxial growth when 10 wt% water was added (Fig. 4m and 7i). Hunt and Manning (2012) determined that quartz solubility in water is 0.05–0.50 in mole fractions with increasing pressure and temperature of 1.0–2.0 GPa and 800–1100 °C. Dissolved quartz can precipitate in pores that are filled with water. Large amounts of water can also assist dissolution–precipitation as remarkable as the epitaxial growth in the Pt capsule, although we did not see a significant difference in the central capsule part. Quartz grains epitaxially grow with the long axes perpendicular to the Pt jacket and the inner sample (Fig. 4m).

Page 9, line 2: Please discuss why the dihedral angle effects grain growth. If the dihedral angle changes at the different conditions, what is the effect on the process of grain growth? For example any discussion on the interfacial free energy would be good here (see point 1).

We realized that we did not discuss the effect of wet grain boundaries on grain growth, which is summarized as follows. Wet grain boundaries assist diffusion of Si (Farver and Yund, 2000), resulting in faster grain growth than in dry grain boundaries. We added this sentence with the reference in the revised manuscript (page 9, line 27). Furthermore, wet grain boundaries may be formed or not under fluctuation in the experimental condition that we discuss here (900 °C and 1.5 GPa). This may explain the large data scatting. We also added sentences about this in the same place.

Page 9, Line 27,
Wet grain boundaries would assist diffusion of Si (Farver and Yund, 2000), resulting in faster grain growth than in dry grain boundaries. Formations of wet grain boundaries or not under fluctuation might explain some of the large scattering of data for our experiments at 900 °C at 1.5 GPa (Fig. 10), and a similar effect is also seen at the same condition for different durations in the data of Tullis and Yund (1982) (fig. 5 in their study).

Page 9, line 8: That grain growth of quartz takes place by grain boundary migration assisted by H2O is not new, please state references. Here, the term grain boundary migration occurs for the first time in the manuscript – too late for a paper on grain growth. . . (see point 1)

We deleted this sentence because we added a new sentence according to the reviewer's comment on page 9, line 2 in the original manuscript. This new sentence includes a new reference (Farver and Yund, 2000), which showed faster Si diffusion in wet grain boundaries, resultantly causing faster grain growth than in dry grain boundaries. As for the term “grain boundary migration” of grain growth, we explained the process in the Introduction section according to the major comment (1).

The deleted sentence is as follows.

Thus, the grain growth of quartz with water takes place by grain boundary migration assisted by H2O.

Page 9, lines 11/12: When considering non-hydrostatic conditions: is there any control of principal stress directions on crystallographic orientation and/or shape of the growing crystals? See point (2)

We have omitted the sentence, because the discussion of the island and channel structures and its consequences would take too much room in this manuscript, and the point is not that important as to include this discussion here.

The deleted sentence is as follows.

In addition, in the solid quartzite the stress state will deviate from a perfect hydrostatic case, so that an additional driving potential for solution–precipitation might arise,

Page 9, line 13: Please provide some more information on the island-channel structure transport and its role on grain growth.

We have omitted the sentence, because the discussion of the island and channel structures and its consequences would take too much room in this manuscript, and the point is not that important as to include this discussion here.

The deleted sentence is as follows.
and this could be the case especially with island-channel structure transport where growth can be orders of magnitude faster than on a normal grain boundary (den Brok, 1998). Additional driving potentials and enhanced transport could therefore be the reasons for enhanced growth rates in the solid quartzite.

Page 10: Any discussion on how to evaluate that grain growth took place in natural rocks would be helpful. This relates to the comparison on grain boundary migration driven by the reduction in stored elastic strain energy (i.e. reduction in dislocation density) versus grain boundary migration driven by the reduction in interfacial free energy, as well as formation of growth rims, see point (3).

We distinguished these two mechanisms of grain boundary migration (i.e., reduction in dislocation density here vs. reduction in interfacial free energy in the Introduction section; see our reply to comment (1). We have expanded the discussion of how to distinguish grain growth from dynamic microstructures in this section.

Page 11, Line 9,
In this case, strain-induced grain boundary migration during dynamic recrystallization (i.e., reduction of dislocation densities) will dominate and form irregular grain boundary shapes as has been studied by experiments and natural samples (e.g., White, 1977; Jessell, 1987; Hirth and Tullis, 1992; Stipp et al. 2002; Tullis, 2002, and references therein). In this case, theoretical calculations for dynamically recrystallized grain size assume that strain-induced grain boundary migration and static grain boundary migration are balanced, resulting in an equilibrium grain size (e.g., Austin and Evans, 2007; Shimizu, 2008). However, when the strain rate is slower, grain growth may become competitive and may dominate the microstructure.

When this is the case, it is important to compare such microstructures (with more straight boundaries and larger sizes) to those of nearby quartz containing some impurities, which may have pinned grain growth. Thus, careful microstructural inspections are required before evaluating grain sizes for piezometry. In addition, as evaluated experimentally by Heilbronner and Tullis (2002), grain growth after dynamic recrystallization preserves pre-existing crystallographic preferred orientations formed by plastic deformation although grains show straight grain boundaries. Therefore, a crystallographic preferred orientation test is not sufficient to infer a potential dominance of grain growth.

As another revision, we deleted some hyphens for compound modifiers (e.g., grain growth law, grain size reduction, etc.) because their uses were inconsistent in the original manuscript and expressions without hyphens are more common.
Experimental grain growth of quartz aggregates under wet conditions and its application to deformation in nature

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Abstract. The grain growth of quartz was investigated using two samples of quartz (powder and novaculite) with water under pressure and temperature conditions of 1.0–2.5 GPa and 800–1100 °C. The compacted powder preserved a large substantial porosity, which caused a slower grain growth than in the dense novaculite quartzite. We assumed a grain growth law of \(d^n - d_0^n = k_0 f_{H_2O}^r \exp\left(-Q/RT\right)t\) with grain size \(d\) (µm) at time \(t\) (second), initial grain size \(d_0\) (µm), growth exponent \(n\), a constant \(k_0\) (µm\(^n\) MPa\(^r\) s\(^{-1}\)), water fugacity \(f_{H_2O}\) (MPa) with the exponent \(r\), activation energy \(Q\) (kJ/mol), gas constant \(R\), and temperature \(T\) in Kelvin. The parameters we obtained were \(n = 2.5 \pm 0.4\), \(k_0 = 10^{-8.8 \pm 1.4}\), \(r = 2.3 \pm 0.3\), and \(Q = 48 \pm 34\) for the powder, and \(n = 2.9 \pm 0.4\), \(k_0 = 10^{-5.8 \pm 2.0}\), \(r = 1.9 \pm 0.3\), and \(Q = 60 \pm 49\) for the quartzite novaculite. The grain growth parameters obtained for the powder may be of limited use because of the high porosity of the powder with respect to crystalline rocks (novaculite), even if the differences between powder and quartzite novaculite vanish when grain sizes reach ~70 µm. Extrapolation of the grain growth laws to natural conditions indicates that the contribution of grain growth to plastic deformation in the middle crust may be small. However, grain growth might become important for deformation in the lower crust when the strain rate is <10\(^{-12}\)/s.

1 Introduction

Grain size is one of the key factors contributing to the rheological behavior of materials. A reduction of grain size during deformation operates in all rheological levels of the crust, as it can be caused by fracturing, dynamic recrystallization, dissolution–precipitation, and reaction [summarized in Handy (1990) with natural examples]. An increase in grain size, termed grain growth, is typically driven by the reduction in surface energy of grains, resulting in microstructures of larger grains with less curved boundaries. When grain growth takes place in a dense solid medium with grains touching one another, the process facilitating growth is the migration of grain boundaries. In a dry system, grain boundary migration constitutes the
diffusion of atoms across a grain boundary. If fluid wets the boundary, grain boundary migration may involve solution, transport, and precipitation of the material. Grain boundary migration is a generic process that can be driven by surface energy (e.g., in grain growth) or by internal energy (e.g., strain energy in the form of dislocations = strain-induced grain boundary migration; Poirier and Guillopé, 1979). During viscous deformation, the competition between grain-size reduction and grain growth (i.e., surface- or internal-energy-driven migration) controls the grain size and is the basis for piezometry (e.g., Derby, 1990, Shimizu, 2008, Austin and Evans, 2007). Furthermore, grain size reduction and grain growth may control the processes of weakening through the transition from grain-size-insensitive to grain-size-sensitive creep (e.g., Bercovici and Ricard, 2009, Ricard and Bercovici, 2012; Schmid, 1982; Rutter and Brodie, 1988). Therefore, grain growth is an important process to understand microstructural development as a function of time (Olgaard and Evans, 1988).

Grain-growth laws for constituents of the Earth have been determined experimentally for calcite (Tullis and Yund, 1982; Olgaard and Evans, 1988; Davis et al., 2011), quartz (Tullis and Yund, 1982; Fukuda et al., 2018), feldspar (Dresen et al., 1996), olivine (Karato, 1989), and other materials (Evans et al., 2001; Karato, 2008). A grain-growth law is written as follows:

\[ d^n - d_0^n = k t, \]  

(1)

where \( d \) is the grain size at time \( t \), \( n \) is the growth exponent, \( d_0 \) is the initial grain size, and \( k \) is a rate constant. A simple rate constant can be written as follows:

\[ k = k_0 \exp \left( -\frac{Q}{RT} \right) t, \]  

(2)

where \( k_0 \) is a constant, \( Q \) is the activation energy, \( R \) is the gas constant, and \( T \) is the temperature in Kelvin. Nishihara et al. (2006) determined a grain-growth law for wadsleyite, and they proposed additional terms such as oxygen fugacity and water content, the latter being a function of water fugacity and water activity. However, there have been few studies in which other parameters, in addition to those in Eq. 2, have been investigated. The \( n \) value is generally assumed to be 2 or 3 when it is not determined. This is based on a theoretical assumption, which includes simplified grain-boundary-free energy, grain shape, grain-boundary mobility, grain curvature, effects of impurity, etc. (Brook, 1976; Atkinson, 1988). However, even the difference between \( n = 2 \) and \( n = 3 \) gives a drastic change in the rate of grain growth (Karato, 2008). The experimental studies mentioned above reported \( n \) values of up to ~10.

For our study we focused on the grain growth of quartz, which is a major constituent of the crust. As mentioned above, the contribution of grain growth to deformation can be important by a change in grain size which leads a change in deformation mechanism (grain-size-insensitive creep and/or grain-size-sensitive creep). There have been many deformation experiments on quartz to derive flow laws for grain-size-insensitive creep (e.g., Jaoul et al., 1984; Luan and Paterson, 1992; Gleason and Tullis, 1995; Rutter and Brodie, 2004a; Holyoke and Kronenberg, 2013, and references therein) as well as a theoretical approach (Fukuda and Shimizu, 2017), grain-size-sensitive creep (Rutter and Brodie, 2004b), and mixtures of these two creep types (Fukuda et al., 2018; Richter et al., 2018). When grain-size-insensitive creep operates, a reduction in grain size due to dynamic recrystallization has commonly been observed. Grain growth can operate in parallel with grain-
size reduction, thus stabilizing the grain size towards an equilibrium value, which can be expressed, for example, as a paleopiezometer (Twiss, 1977; Stipp and Tullis, 2003; Stipp et al., 2006; Shimizu, 2008; Cross et al., 2017) or a paleowattmeter (Austin and Evans, 2007). Grain-size paleopiezometers and flow laws have been applied to natural samples under targeted pressure and temperature conditions. The strain rate can often be estimated, because the flow law involves strain rate ($\dot{\varepsilon}$) as a function of stress ($\sigma$) with a stress exponent ($p$) (namely, $\dot{\varepsilon} \propto \sigma^p$) (e.g., Stipp et al., 2002; Menegon et al., 2011; Okudaira and Shigematsu, 2012). However, when the relationship between grain size and deformation is considered, the contribution of grain growth needs to be considered.

For the grain growth of quartz, experimental data were reported by Tullis and Yund (1982) and Fukuda et al. (2018). However, their data for various pressure and temperature conditions are limited. Moreover, Tullis and Yund (1982) assumed a grain growth law of $d - d_0 = k t^p$ with $p = 0.5$, while Fukuda et al. (2018) assumed $n = 2$ in Eq. 1. The grain growth of natural quartz was also investigated by Joesten (1983) and Okudaira et al. (2013), and growth exponents of $n = 2$ were assumed in both studies, although Joesten (1983) also assumed $n = 3$ for Eq. 2. Thus, the growth exponent needs to be determined carefully. Michibayashi and Imoto (2012) performed grain-growth experiments on agate, and their original samples showed shape and crystallographic preferred orientations (SPO and CPO). After the experiments, their samples maintained the CPO and SPO, and showed a growth exponent of $n = 4.4$. Maintaining CPO and SPO during grain growth is unusual, so their samples and results might be special cases. Tullis and Yund (1982) discussed the effects of pore-H$_2$O pressure on quartz grain growth. However, their data at different pressures are limited, and the effect of water was not given in their grain-growth law. A confining pressure effect was discussed by Wightman et al. (2006) using the experimental data of Tullis and Yund (1982). For the grain growth of the mineral wadsleyite, instead of considering the effect of confining pressure, Nishihara et al. (2006) considered the effect of water fugacity. Water fugacity is also important for plastic deformation, and it has been discussed and/or introduced in flow laws since the mid-1990s (e.g., Gleason and Tullis, 1995; Kohlstedt et al., 1995; Rutter and Brodie, 2004a, b; Holyoke and Kronenberg, 2013; Fukuda and Shimizu, 2017; Fukuda et al., 2018). Water fugacity could be a simplified parameter that involves water content and water activity, etc. (e.g., Kohlstedt et al., 1996; Nishihara et al., 2006). Based on these studies, a water fugacity term $f_{{H_2}O}$ with an exponent $r$ can be added to Eq. 2 as follows:

$$k = k_{o} f_{{H_2}O}^r \exp \left(-\frac{q}{pT}\right) t.$$  (3)

For our study we followed the grain-growth law defined by Eqs. 1 and 3, and we determined the parameters experimentally. We used two different quartz samples, quartzite-novaculite and powder, and for both we added different amounts of water under different conditions of temperature and pressure. We will first discuss the differences in grain growth between the two types of starting material, and we will then discuss the contribution of grain growth to deformation under natural conditions.
2 Samples

The Arkansas quartzite (novaculite) is composed of fine grains of quartz 0.5–10 µm in size under a light microscope. Large clasts up to 100 µm in size are also visible, and these may be the relics of fossils (Fig. 1a). Some cracks and pores can be observed (Fig. 1b–f). Many apparent pores are surface effects due to the plucking of grains during polishing, as observed in the reflected light mode of the microscope (Fig. 1f) and in the secondary electron (SE) mode of the scanning electron microscope (SEM) (Fig. 1g). More than 99% of the material is quartz, and other phases include mica and magnesite, etc. The SEM–SE image for a broken surface of the quartzite-novaculite shows dense grains and tight grain boundaries (Fig. 1h). An electron backscattered diffraction (EBSD) band contrast image shows clear grain shapes (Fig. 1i).

The powder material (Min-U-Sil 5) is >99% quartz, and according to the product sheet, very small amounts of Fe, Al, Ti, Al, Ca, Mg, Na, and K are also present. The SEM–SE image of the powder sample shows grains from sub-micron size to ~8 µm (Fig. 1j). The amount of adsorbed water in the powder is ~0.25 wt%, as measured by weight loss after heating at 120 °C. The powder re-adsorbs the same amount of water after ca. 1 hour. In contrast, the amount of adsorbed water in the quartzite-novaculite is below the detection limit, using the same method.

The grain size of the starting quartzite-novaculite sample was determined from EBSD band contrast images (Fig. 1i). Outlines of each grain were traced and grain sizes determined using Image J software as diameters of equivalent circles (root mean square; Fig. 2a). The grain size of the powder sample was determined with a Beckman–Coulter particle counter in H₂O suspension (Fig. 2b). The grain-size ranges of the quartzite-novaculite and powder samples are 0.6–10 µm and 0.2–10 µm, respectively, which are consistent with those observed in Fig. 1. The average grain sizes of the initial samples of quartzite-novaculite and powder were determined with standard deviations as 3.1 ± 1.6 µm and 2.4 ± 1.7 µm, respectively. These two average grain sizes are used as $d_0$. The grain-size range of the powder and the average grain size are consistent with those reported by Kim et al. (2005), and the median value reported by the manufacturer is 1.7 µm. The techniques of grain-size determination for these two initial samples were different from the techniques used for the samples after the experiments (using light photomicrographs; shown later). However, the $d_0$ values are small compared with the grain sizes after our experimental series ($d$), so they would not significantly affect the determinations of the other parameters in the grain-growth law (Eqs. 1 and 3).

3 Methods

3.1 Experimental procedures

We performed grain-growth experiments using a piston cylinder apparatus. Pressure conditions were 1.0, 1.5, 2.0, and 2.5 GPa, and temperature conditions were 800, 900, 1000, and 1100 °C. Annealing durations were from 6 to 240 hours. We used sample assemblies with total diameters of 12.5 or 18.8 mm for experiments at high (2.0 and 2.5 GPa) or low pressure (1.0
and 1.5 GPa), respectively (Fig. 3). The sample assembly is after e.g., Prouteau et al. (2001) and Prouteau and Scaillet (2013), which showed systematic changes in rock compositions (mid-ocean ridge basalt) in Pt capsules depending on amounts of added water. In addition, previous studies measured electrical conductivity for various rock types with different amounts of water (e.g., Gaillard, 2004; Pommier et al., 2008; Laumonier et al., 2015). They used the piston cylinder with the talc-pressure-medium assembly for pressure of up to ~3 GPa and a gas-pressure-medium vessel without talc for pressure of down to ~50 MPa under temperature conditions of 400–1300 °C. The results on pressure, temperature, and sample water contents using these two different apparatuses are systematically correlated. The dehydration reaction of talc can occur in our experimental conditions (e.g., Bose and Ganguly, 1995) and may be an additional water (hydrogen) source. However, these studies proved that the dehydration reaction of talc does not affect on the water environment in Pt capsules including samples and water. Water fugacities at given conditions of pressure and temperature were calculated from the molar volume and the equation of state of pure water using the data of Pitzer and Sterner (1994) and Sterner and Pitzer (1994).

We used up to two 2.5-mm diameter Pt capsules for the 12.5-mm assembly, and up to three 2.5-mm diameter Pt capsules or one 5.0-mm diameter Pt capsule for the 18.8-mm assembly. The total lengths of the capsules were 10–14 mm. The differences in the lengths of the Pt capsules as well as their orientations distinguished the samples during sample preparation and after the experiments. The preparation of Pt capsules was as follows. First, one side of a Pt tube was welded. Second, a powder sample of ~0.02 g was put into a welded 2.5-mm Pt tube, or a powder sample of ~0.1 g was put into a 5.0-mm tube. Third, a similar amount of a quartzite novaculite core with a diameter of 2.0 mm was put into the 2.5-mm Pt tube, or a quartzite novaculite block into the 5.0-mm tube. The powders were compressed by pressing the quartzite novaculite samples into the capsules. For some experiments, the quartzite novaculite was wrapped in Pt foil, and the presence of this Pt foil was useful in distinguishing samples after experiments in a section of a Pt capsule. Then, water of 0.2, 2.0, or 10 wt% of the total weight of the two samples was added onto the quartzite novaculite using a microsyringe. The quartzite novaculite was never entirely wrapped in Pt foil, so that water could diffuse into the quartzite novaculite. Finally, the open side of the Pt tube was weld-sealed. We also prepared another quartzite novaculite core or small block that had previously been annealed and dried at 900 °C in a furnace, and then placed it in a Pt capsule with the powder and the original quartzite novaculite. The grain sizes of the dried quartzite novaculite after grain growth experiments were not different from those of the original quartzite novaculite, and all grain sizes we show in this study were obtained from the original quartzite novaculite. We also performed experiments without added H2O (i.e., with only quartzite novaculite or with quartzite novaculite + powder) to test the effects of adsorbed water on the powder.

Recovered Pt capsules were cut in half and/or ground along the long axes of the capsules to make thin sections for observation under a polarizing microscope. Epoxy resin was added continuously during thin sectioning to minimize grain plucking from the sample surfaces. Polished sample surfaces and broken surfaces were used for SEM observations after carbon coating. All the experimental conditions and the grain sizes determined are listed in Table 1. Results from Tullis and Yund (1982) for quartzite novaculite and Fukuda et al. (2018) for quartz powder (Min-U-Sil 5) are also shown, and they will be discussed later.
We also used a gas-pressure-medium vessel and performed experiments at 0.3 GPa and 900 °C for up to 240 hours. However, the powder samples were not sufficiently compressed, and no significant grain growth was observed in either of the samples. Therefore, we will not discuss any further the results from the gas-pressure-medium vessel.

3.2 Grain size analysis after experiments

We determined grain sizes from photomicrographs taken under cross-polarized light, in which each grain is most clearly seen. As the misorientation between grains is always large and grains are not deformed (i.e., no addition of low-angle boundaries), the grain-size analysis yielded similar results to the EBSD band contrast images (Fig. 1i). We outlined grains and determined grain sizes using Image J as diameters of equivalent circles (root mean square). Some of the recovered samples showed open grain boundaries that were visible in the photomicrographs, especially when grain sizes were relatively large (ca. >15 µm; shown below). In such cases, the grains were visible in reflected light, and the grain sizes determined using this mode of observation were not different from those determined using cross-polarized light images. When grains were very small, not every grain could be distinguished under reflected light or with the SEM.

4 Results

4.1 Observations by light microscopy and grain sizes

Representative light photomicrographs are shown in Fig. 4. The figures include two parts in the case that both the powder and quartzite novaculite samples were used together. We refer to “powder sample” or “powder” for convenience, even though the starting material becomes compacted during the experiments. Figure 5 shows the results of representative grain-size analyses in our experimental series where the average grain sizes are small, medium, and large. The grain sizes of the quartzite novaculite are up to twice as large as those of the powder samples when the grain sizes are small (<10 µm). As observed under plane-polarized and reflected light, grain boundaries are usually open (compare Fig. 4a–i), and the openings probably developed during unloading. The open grain boundaries caused grain plucking during thin sectioning, as described previously by Tullis and Yund (1982). Therefore, porosities cannot be clearly determined, but the porosities of the powder samples appear to be higher than those of the quartzite novaculite samples (Fig. 4b, e, and h). All the determined grain sizes are listed in Table 1. Grain size heterogeneities were not observed in the Pt capsules, and the choice of capsule diameter (2.5 or 5.0 mm) did not result in any difference in grain size.

The grain sizes increased with increasing pressure (compare Fig. 4a and d; Fig. 4l, n, and o), temperature (Fig. 4g and l), and duration of the experiment (Fig. 4a and l). See also Table 1 for other experimental results. The grain sizes were similar regardless as to whether or not water was added to the powder and quartzite novaculite (e.g., Fig. 4g, where 2.0 wt% of water was added, and Fig. 4j, where no water was added). On the other hand, when quartzite novaculite only was used without water, and no water was added initially, no grain growth was observed (Fig. 4k). This was also described by Tullis and Yund (1982). Thus, the water adsorbed on the powder, representing a proportion of ~0.25 wt%, was sufficient to
enhance grain growth in the samples composed of powder + quartzite novaculite. The rate of grain growth did not increase with added water of 0.2, 2.0, or 10 wt% (Fig. 4l and m). However, when 10 wt% water was added, epitaxial growth of quartz grains in the Pt jacket was observed, and the aspect ratios of these grains were up to 4:1 with long axes up to 150 µm (Fig. 4m). The long axes of these grains are aligned perpendicular to the Pt jacket and inner sample. The crystallographic orientations of epitaxially grown grains would correspond to those of the seed crystals in the sample (namely, neighboring powder and/or novaculite), on which quartz grains epitaxially grow, similar to studies for the quartz vein formations (e.g., Cox and Etheridge, 1983 from natural samples; Okamoto et al. 2011 from experimental samples and simulation). The epitaxial growth of quartz probably occurs because of the separation of the Pt jacket from the sample as a consequence of the injection of pore fluid.

As the grain sizes of the powder and quartzite novaculite samples increased, the differences in their grain sizes were reduced (Fig. 6). When the grain sizes of the powder samples were <10 µm, the grain sizes of the quartzite novaculite samples were twice as large. The largest grain size of powder in our experiments was ~70 µm, obtained at 2.5 GPa and 1000 °C for 24 hours (PC18; Table 1). In this experiment, the grain sizes of the two samples were not different (Fig. 6). Since the initial grain sizes of the two samples were similar (d₀ of the powder was 2.4 µm and d₀ of the quartzite novaculite was 3.1 µm), the similar largest grain sizes of the two samples probably resulted from the closing of pores in the powder samples as grain sizes increased (compare Fig. 4b, e, and h, and the SEM observations shown later).

4.2 Observations by SEM

We used the SEM to observe microstructures on the polished and broken surfaces of the two types of quartz sample (Fig. 7). The SE images of the polished surfaces showed voids with sizes similar to the quartz grain size, especially when the average grain size was small (Fig. 7a and b). These voids were most likely caused by the plucking of grains during thin sectioning. Such voids were less commonly observed when the average grain sizes were larger than ca. 20 µm (Fig. 7c and d). Other smaller voids may represent either plucked grains or pores (Fig. 7a–d). Similar features were observed in the starting quartzite novaculite sample (Fig. 1g). Porosities might be reduced with increasing grain size.

The SE images of the broken surfaces show angular grains and straight grain boundaries regardless of grain size (Fig. 7e–h), and similar features were seen in the starting quartzite novaculite (Fig. 1h). Although our experiments confirmed the role of water in enhancing grain growth, the broken surfaces did not show the water pockets or rough/irregular grain surfaces that were considered by previous researchers to be associated with the dissolution–precipitation of quartz by water [Mancktelow and Pennacchioni (2004) for wet deformed natural samples and den Brok and Spiers (1991) and Vernooij et al. (2006) for wet deformed experimental samples]. The cathodoluminescence (CL) image of Fig. 7i shows dark-colored cores in single quartz grains inside a Pt jacket. The quartz grains that grew epitaxially from the Pt jacket, as seen in the 10 wt%–water-added sample (Fig. 4m), did not show such a contrast in core and mantle colors.
4.3 Grain growth parameters

We determined grain growth parameters from grain sizes of the powder and quartzitennovaculite samples obtained at different pressures, temperatures, and durations (Table 1). Figure 8a shows grain sizes of the two samples for different durations and a fixed pressure condition of 1.5 GPa. We also plotted grain size data from Tullis and Yund (1982) for quartzitennovaculite (novaculite) and from Fukuda et al. (2018) for the powder (Min-U-Sil 5). Tullis and Yund (1982) subjected their material to “pre-grain growth” treatment at 1.5 GPa and 1000 °C with 1–2 wt% added water for 1.5 hours before performing their targeted pressure and temperature condition experiments. The “pre-grain growth” produced a grain size of 8.4 µm, which was set as \( d_0 \). They then performed experiments at 0.2–1.5 GPa and 800–1100 °C for up to ~776 hours (Table 1). They obtained large data sets at 1.5 GPa and 1000 °C, which we have plotted in Fig. 8. However, their data for other PT conditions are limited, and any trends are unclear, so those data are only listed in Table 1. Since we assume a grain growth law of Eq. 1, the slopes of \( \Delta \log(d^n - d_0^n) \) should be unity for specific \( n \) values, which were determined from Fig. 8b.

The averaged \( n \) values for the powder and quartzitennovaculite in our experiments were \( n = 2.5 \pm 0.4 \) and \( 2.9 \pm 0.4 \), respectively. Our data set for the quartzitennovaculite at 1.5 GPa and 1000 °C in Fig. 8b is similar to the data set of Tullis and Yund (1982) for their quartzitennovaculite, since Fig. 8b excludes differences in \( d_0 \) values. The \( n \) value calculated from the data of Tullis and Yund (1982) for these conditions is \( 2.6 \pm 0.3 \), which is consistent with our value.

To evaluate the water fugacity dependency, we performed experiments at 1000 °C and 1.0–2.5 GPa, which correspond to water fugacities of 2.0–28.4 GPa (Table 1). The grain sizes of the powder and quartzitennovaculite varied widely from 7.3 to 68.7 µm and from 14.4 to 67.9 µm, respectively. The largest grain sizes of both samples were not different in this experimental series at 2.5 GPa. Following the grain growth law (Eqs. 1 and 3), the relationships between \( \log(d^n - d_0^n) \) and \( \log(f_{H2O}) \), where the slopes correspond to the water fugacity exponent \( r \), are fairly clear for the powder and quartzitennovaculite with their \( n \) values determined above (Fig. 9). The \( r \) values determined are \( 2.3 \pm 0.3 \) for the powder and \( 1.9 \pm 0.4 \) for the quartzitennovaculite. The activation energies were determined with these \( n \) and \( r \) values to be \( 48.2 \pm 34.2 \) kJ/mol for the powder and \( 59.9 \pm 48.8 \) kJ/mol for the quartzitennovaculite (Fig. 10). The errors are relatively large, and this may be due to dissolution–precipitation and changes in wetting angles under different conditions of pressure and temperature, which we will discuss below.

We determined the constant \( k_0 (\mu m^2 MPa^{-r} s^{-1}) \) for the two samples using all the experimental data in our study, and then obtained the following the grain growth law defined by Eqs. 1 and 3.

For the powder,

\[
d_{2.5 \pm 0.4}^{2.5 \pm 0.4} - d_0^{2.5 \pm 0.4} = 10^{-8.8 \pm 1.4} f_{H2O}^{2.3 \pm 0.3} \exp \left(- \frac{48 \pm 34 \text{ kJ/mol}}{RT}\right) t
\]

For the quartzitennovaculite,

\[
d_{2.9 \pm 0.4}^{2.9 \pm 0.4} - d_0^{2.9 \pm 0.4} = 10^{-5.8 \pm 2.0} f_{H2O}^{1.9 \pm 0.3} \exp \left(- \frac{60 \pm 49 \text{ kJ/mol}}{RT}\right) t
\]

with \( d \) and \( d_0 \) in µm, \( f_{H2O} \) in MPa, and \( t \) in seconds.
5 Discussion

5.1 Grain growth parameters and growth mechanisms

We obtained the growth exponents of $n = 2.5 \pm 0.4$ and $2.9 \pm 0.4$ for the powder and quartzite novaculite samples, respectively. The $n$ value of $2.6 \pm 0.3$, using the data of Tullis and Yund (1982) for their quartzite novaculite at 1.5 GPa and 1000 °C, is similar to ours (Fig. 8b). Wightman et al. (2006) estimated a value of $n \geq 3$ to account for grain growth in their natural quartzite case (Alpine Fault, New Zealand). They also reported $n = 3.2$ and other grain growth parameters (in terms of the effect of pressure) using the data of Tullis and Yund (1982), although the methods of determination were not shown. According to the theoretical estimation of Brook (1976) [summarized in Atkinson (1988)], growth exponents depend on the microprocesses involved: $n = 4$ (pore control + surface diffusion), $n = 3$ (pore control + lattice diffusion), $n = 2$ (boundary control + pure system), $n = 1–4$ (boundary control + different mechanisms of impurity). In our experiments, added water of 0.2–10 wt% as well as adsorbed water of 0.25 wt% in the powder could be an impurity in the form of pores, although it also enhances grain growth at grain boundaries. Adsorbed water on the powder will diffuse throughout the two types of sample in a short time and assist grain growth in both the powder and quartzite novaculite samples (Fig. 4g–k). The quartzite novaculite samples do not show heterogeneities or gradients in grain size within a Pt capsule. Therefore, it is expected that the H$_2$O is uniformly distributed in the “wet” condition. In addition, we note that the temperature and pressure gradients within a Pt capsule were also negligible.

The powder sample included many more pores than the quartzite sample (Fig. 4b, e, and h), and these pores would have resulted in a slower grain growth of the powder than the quartzite (Figs. 8–10). As grain sizes increased in both types of quartz sample, differences in their grain sizes lessened (Fig. 6). This is interpreted to have resulted from the closing of pores in the powder samples (Fig. 4b, e, h and Fig. 7a–d). Grain growth of both types of quartz sample became similar when grain sizes were ~70 μm, obtained at 2.5 GPa and 1000 °C for 24 hours (Fig. 6), indicating that the pores in the powder had almost closed.

Dissolution–precipitation was confirmed in the form of epitaxial growth when 10 wt% water was added (Fig. 4m and 7i). Hunt and Manning (2012) determined that quartz solubility in water is 0.05–0.50 in mole fractions with increasing pressure and temperature of 1.0–2.0 GPa and 800–1100 °C. Dissolved quartz can precipitate in pores that are filled with water. Large amounts of water can also assist dissolution–precipitation as remarkable as the epitaxial growth in the Pt capsule, although we did not see a significant difference in the central capsule part. Quartz grains epitaxially grow with the long axes perpendicular to the Pt jacket and the inner sample (Fig. 4m). In CL images, quartz grains in the powder and quartzite novaculite showed contrasts between original and grown grains (Fig. 7i), a phenomenon that has also been observed in natural samples sometimes accompanied by zoning (e.g., Götz et al., 2001; Holness and Watt, 2001; Piazolo et al., 2005).

For grain growth, differences in the dihedral angles can be considered. For example, experimental studies by Watson and Brenan (1987) and Holness (1992, 1993) showed that the transition from dihedral angles of less than 60° (wet grain boundaries) to those larger than 60° (dry grain boundaries) took place at around 900–1000 °C at 1.0 GPa, where the angle
decreases with decreasing temperature and increasing pressure. Wet grain boundaries would assist diffusion of Si (Farver and Yund, 2000), resultantly causing faster grain growth than in dry grain boundaries. This—formations of wet grain boundaries or not under fluctuation might explain some of the large scattering of data for our experiments at 900 °C at 1.5 GPa (Fig. 10), and a similar effect is also seen at the same condition for different durations in the data of Tullis and Yund (1982) (fig. 5 in their study).

The powder sample included many more pores than the novaculite sample (Fig. 4b, e, and h). Grain growth of both types of quartz sample became similar when grain sizes were ~70 µm, obtained at 2.5 GPa and 1000 °C for 24 hours (Fig. 6), indicating that the pores in the powder had almost closed. Thus, the grain growth of quartz with water takes place by grain boundary migration assisted by H₂O. Grain growth of the powder sample with pores was slower than that of the dense quartzite sample because of the limited areas of contact between grains in the powder sample, as water in pores might act as a secondary phase that impedes grain growth, as discussed by Karato (1989) for the grain growth of olivine aggregates. In addition, in the solid quartzite the stress state will deviate from a perfect hydrostatic case, so that an additional driving potential for solution–precipitation might arise, and this could be the case especially with island-channel structure transport where growth can be orders of magnitude faster than on a normal grain boundary (den Brok, 1998). Additional driving potentials and enhanced transport could therefore be the reasons for enhanced growth rates in the solid quartzite.

Pore closure was achieved by precipitation, after which the rate of precipitation would be slower than grain boundary migration, which explains the slower grain growth in the powder sample. As grain sizes increased in both types of quartz sample, differences in their grain sizes lessened were smaller (Fig. 6). This is interpreted to have resulted from the closing of pores in the powder samples (Fig. 4b, e, h and Fig. 7a–d). Grain growth of both types of quartz sample became similar when grain sizes were ~70 µm, obtained at 2.5 GPa and 1000 °C for 24 hours (Fig. 6), indicating that the pores in the powder had almost closed.

### 5.2 Application to nature and relation to deformation

We applied the grain growth laws determined from the powder (Eq. 4) and quartzite-novaculite (Eq. 5) to natural conditions. We note here that the powder included pores that slowed down grain growth, but the porosity could not be evaluated quantitatively because of fracturing during unloading and plucking of grains during thin sectioning. In addition, pores closed with increasing grain size (Fig. 6). Therefore, although the grain growth law obtained from the powder is used here for comparisons with the grain growth law obtained from the quartzite-novaculite, its use in nature might not be realistic.

We assumed a representative mid-crustal temperature of 400 °C and lower-crustal temperature of 600 °C. We set a temperature gradient of 25 °C/km and a pressure gradient of 27 MPa/km, which gave water fugacity values for the two temperatures using the molar volume and the equation of state of pure water from Pitzer and Sterner (1994) and Sterner and Pitzer (1994). The temperature of 400 °C gave a depth of 16 km, a pressure of 432 MPa, and a water fugacity of 96 MPa. The temperature of 600 °C gave a depth of 25 km, a pressure of 648 MPa, and a water fugacity of 464 MPa. We set initial
grain sizes of 5, 20, 100, 300 µm and calculated grain growth over time. These initial grain sizes could have been formed, for example, by dynamic recrystallization, and we will discuss the relationships between these initial grain sizes, grain growth, strain, and strain rates below. The results are shown in Fig. 11. To discuss the relationships between grain growth and plastic deformation, which causes dynamic recrystallization, we calculated the strain accumulated over time under different strain rates in Fig. 12. We note, however, that the volume of recrystallized grains as time passed was not well known. The grain growth period was calculated up to 10 Myr, which corresponds to possible exhumation rates of 1–10 km/Myr (e.g., Ring et al., 1999), where grain growth can be the dominant process.

At 400 °C, when the initial grain size was 5 µm, the grain growth became significant in 10^2 years for the two grain-growth laws (Fig. 11a and b). Initial grain sizes of 5 and 20 µm became the same in 10^4 years (30 and 40 µm using the grain-growth laws obtained from the powder and quartzite/novaculite, respectively). This is important when one considers the effects of plastic deformation. Researchers who have studied natural samples have estimated strain rates from the deformation histories and/or the relationship to stresses (\( \varepsilon \propto \sigma^p \)) as \( 10^{-10}–10^{-14}/s \) (e.g., Hirth et al., 2001; Stipp et al., 2002; Wightman et al., 2006; Menegon et al., 2011; Okudaira and Shigematsu, 2012; Shimizu, 2014). At this temperature of 400 °C, a strain rate of \( 10^{-13}/s \) for 10^4 years gives a strain of only ~3%, and almost no strain is accumulated at a strain rate of \( 10^{-14}/s \) (Fig. 12). The grain size formed by dynamic recrystallization can be correlated with a function of stress as \( d \propto \sigma^{-q} \) [Shimizu (2008) by theory, Stipp and Tullis et al. (2006) by experiment, with the stress corrected by Holyoke and Kronenberg (2010)]. Then, if these annealed grain sizes of 30 and 40 µm are wrongly incorrectly used as grain-size piezometers, the stress will be underestimated by up to ~280 MPa (i.e., if the grain size of 5 µm was initially formed by dynamic recrystallization, the corresponding stress was 351 MPa according to Shimizu (2008), whereas the grain size of 40 µm, which was caused by grain growth but wrongly incorrectly used as a grain-size piezometer, corresponds to an apparent stress of 67 MPa).

At 600 °C, the effect of grain growth becomes more significant. Grains with initial sizes of <100 µm grew to ~200 µm in 10^4 years (Fig. 11c and d). For a strain rate of >10^{-12}/s (Fig. 12), dynamic recrystallization can be the dominant process: A strain rate of \( 10^{-12}/s \), for example, results in 30% strain in 10^4 years. In this case, strain-induced grain boundary migration during dynamic recrystallization (i.e., reduction of dislocation densities) will dominate and form irregular grain boundary shapes as has been studied by experiments and natural samples (e.g., White, 1977; Jessell, 1987; Hirth and Tullis, 1992; Stipp et al. 2002; Tullis, 2002, and references therein). In this case, theoretical calculations for dynamically recrystallized grain size assume that strain-induced grain boundary migration and static grain boundary migration are balanced, resulting in an equilibrium grain size (e.g., Austin and Evans, 2007; Shimizu, 2008). However, when the strain rate is slower, grain growth might may overcome become competitive and deformation may dominate the microstructure. When this is the case, it is important to compare such microstructures (with more straight boundaries and larger sizes) to those of nearby quartz containing some impurities, which may have pinned grain growth. Thus, careful microstructural inspections are required before evaluating grain sizes for piezometry. In addition, as evaluated experimentally by Heilbronner and Tullis (2002), grain growth after dynamic recrystallization preserves pre-existing lattice-crystallographic preferred orientations...
formed by plastic deformation although grains show straight grain boundaries. Therefore, a crystallographic preferred orientation test is not sufficient to infer a potential dominance of grain growth.

Grain growth of a natural quartz sample was discussed in Wightman et al. (2006). As we described in Section 5.1, they constructed a grain growth law using experimental data by Tullis and Yund (1982) to explain grain growth of their quartz sample. The grain size of their sample was considered to have increased from ≤1 to 100 µm during a post-deformation time of ~4 million years. They mainly varied temperature conditions of 400–500 °C, giving a significant difference in grain growth time (one order of magnitude) because of the high activation energy of 215 kJ/mol. The experimental data by Tullis and Yund (1982) do not seem enough to argue for the effects of temperature and pressure individually (Table 1). The parameter settings in Wightman et al. (2006) may be possible but in contrast, the lower temperature sensitivity of our grain growth laws (e.g., 60 kJ/mol for the novaculite) may easily explain their data, giving a consistent grain growth time (Fig. 11) (specifically, grain sizes up to a few hundred µm in a few million years for the range of their temperature and pressure conditions with corresponding water fugacities).

Our grain growth laws give a possible contribution of grain growth during and after plastic deformation. Therefore, the effect of grain growth needs to be considered carefully when grain-size piezometers are applied to dynamically recrystallized quartz samples. Thus, our study reveals shows that under mid-crustal wet conditions, the effect of grain growth might not be negligible, and that under lower-crustal conditions, grain growth might significantly overcome deformation to dominate the microstructure.

6 Conclusions

Grain growth laws for samples of quartz powder and quartzite novaculite were determined under wet conditions. The presence of water was necessary for grain growth to occur. Nevertheless, the addition of water above 0.25 wt% did not result in increased rates of growth in the quartzite novaculite samples. Furthermore, pores filled with water impeded grain growth, as can be inferred from comparisons between the powder and quartzite novaculite samples. The growth exponents, which significantly change growth rates, were determined as $n = 2.5 \pm 0.4$ for the powder and $n = 2.9 \pm 0.4$ for the quartzite novaculite. The two types of quartz sample also showed a dependence on water fugacity, and the fugacity exponents were $r = 2.3 \pm 0.3$ for the powder and $r = 1.9 \pm 0.4$ for the quartzite novaculite. We extrapolated our grain growth laws to natural conditions, and we discussed the effects on plastic deformation. Our grain growth laws indicate that after the deformation stage, dynamically recrystallized grains can grow, especially under lower-crustal conditions, when the system has enough time for grain growth. As a consequence, when grain-size piezometers are applied to natural quartz, we should bear in mind that these are minimum stresses because grain growth might have taken place. Even during the deformation stage, grain growth might compete with grain-size reduction in dynamic recrystallization when the strain rate is $<10^{-12}$/s.
Competing interests. The authors declare that they have no conflict of interest.

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References


**Figure Captions**

**Figure 1.** Textures of two different starting samples of quartz. (a)–(i) Quartzite, novaculite. (j) Quartz powder. (Min-U-Sil 5). (a)–(c) Light photomicrographs and (d)–(f) enlarged images. (a) and (d) in cross-polarized light. (b) and (e) in plane-polarized light. (c) and (f) in reflected light. (g) SEM image of a polished surface. (h) SEM image of a broken surface. (i) EBSD band contrast image. (j) SEM image of the powder.

**Figure 2.** Grain size analyses of the starting samples. (a) Quartzite, novaculite grain sizes obtained from grain outlines in EBSD band contrast images. The average grain size is 3.1 ± 1.6 µm (standard deviation). (b) Grain sizes of the quartz powder sample measured with a particle counter. The average grain size is 2.4 ± 1.7 µm. These two average grain sizes were used as d₀.

**Figure 3.** Sample assembly (left) and preparation of the quartzite, novaculite, quartz powder, and water in a Pt tube (right).

**Figure 4.** Light photomicrographs of the samples after experiments. Photos taken under plane-polarized or reflected light are labeled as such. The other photos were taken under cross-polarized light. Boundaries between the quartz powder and quartzite, novaculite samples are marked by Pt foils or dashed lines. The magnification for photos without scale bars is the same as that for (a).

**Figure 5.** Examples of grain size analyses for (a) small, (b) medium, and (c) large grain sizes in our experimental series.
Figure 6. Grain size ratios between the quartzite novaculite and quartz powder samples. The ratios decrease with increasing grain size for both types of quartz sample. This is related to the closing of pores in the quartz powder samples.

Figure 7. SEM images of samples after experiments. (a)–(d) SE images of polished surfaces. (e)–(h) SE images of broken surfaces. (i) CL image (left) and BSE image (right) including a Pt jacket part (labeled in the BSE image) where epitaxial growth was observed (the powder part is on the inside).

Figure 8. Grain sizes at a pressure of 1.5 GPa and for different durations. (a) log $d$. (b) log ($d^n - d_0^n$) with changing $n$ values to obtain slopes $= 1$. Grain sizes in $\mu$m. Also shown are data from Tullis and Yund (1982) (denoted as T&Y82) for quartzite novaculite and from Fukuda et al. (2018) (F18) for powder.

Figure 9. Dependence of water fugacity on grain size. Temperature of 1000 °C and pressures of 1.0, 1.5, 2.0, and 2.5 GPa. Grain sizes in $\mu$m.

Figure 10. Dependence of temperature on grain size. Pressure of 1.5 GPa. Grain sizes in $\mu$m and water fugacity in MPa.

Figure 11. Extrapolation to natural conditions using the grain growth laws obtained from the powder and quartzite novaculite samples. Initial grain sizes of 5, 20, 100, 300 $\mu$m. (a) and (b) 400 °C. (c) and (d) 600 °C. See text for the settings of other parameters.

Figure 12. Time evolution of strain under different strain rates. Compare with Fig. 11.

Table 1 Experimental conditions and grain sizes determined.
Figure 1.
Figure 2.
B-type TC: 30%Rh/Pt + 6%Rh/Pt in Al₂O₃ tube

Stainless
Pyrophyllite
Talc
Pyrex glass
Al₂O₃
MgO powder
Graphite
MgO

Syringe

2.5 or 5.0 mm φ

Water (0.2, 2.0, or 10.0 wt%)
Novaculite (2.0 mm φ core or block)
Pt foil (surrounding with open space)
Quartz powder
Pt tube (welded)

12.5 or 18.8 mm

Figure 3.
Figure 4.
Figure 5.

(a) PC13, 2.0 wt%, 1.0 GPa, 1000°C, 96 h

(b) PC10, 2.0 wt%, 1.5 GPa, 1100°C, 24 h

(c) PC22-1, 0.2 wt%, 2.0 GPa, 1000°C, 24 h

- Powder $d_{av} = 7.3 \pm 2.5 \mu m$
- Novaculite $d_{av} = 14.4 \pm 4.9 \mu m$

- Powder $d_{av} = 16.6 \pm 5.3 \mu m$
- Novaculite $d_{av} = 32.2 \pm 12.2 \mu m$

- Powder $d_{av} = 34.5 \pm 12.4 \mu m$
- Novaculite $d_{av} = 42.8 \pm 15.9 \mu m$
Figure 6.
Figure 7.
Figure 8.
Figure 9.

Log $f_{\text{H}_2\text{O}}$ (MPa)

Log $(d^n - d_0^n)$

Novaculite ($n = 2.9$)
$r = 1.9 \pm 0.4$

Powder ($n = 2.5$)
$r = 2.3 \pm 0.3$
Figure 10.
Figure 11.
Figure 12.
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<th>Duration (hours)</th>
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Fukuda et al. (2018)
Solid-pressure-medium deformation apparatus (Griggs-type), NaCl assembly, same powder sample (Mn-U-Si 5), no added water, adsorbed water of ~0.25 w%  

TMQ11 1.5 1000 5.145 24 9.5 4.2  
TMQ23 1.5 900 5.034 24 7.2 3.6  
TMQ26 1.5 900 5.034 72 12.0 5.7  
TMQ25 1.5 900 5.034 240 25.0 12.1  

Tullis & Yund (1982)
Solid-pressure-medium deformation apparatus (modified Griggs-type)  
Durations and grain sizes read from their figures 4 and 5 for novaculite (The original grain size of ~4 μm in their description)  
NaCl assembly for T ≤ 900°C, CaCO3 assembly for T at 1000-1150°C, added water of 1-2 w%  
Pre-treatment at 1.5 GPa and 1000°C for 1.5 hours giving 8.4 ± 0.5 μm; set as δ, in their study  

| 1.5 | 9.8 |  
| 2.0 | 11.5 |  
| 6.6 | 15.2 |  
| 6.6 | 17.6 |  
| 49.0 | 26.6 |  
| 49.0 | 36.6 |  
| 168.0 | 34.7 |  
| 169.8 | 49.1 |  
| 158.5 | 64.0 |  
| 158.5 | 82.5 |  
| 8.9 | 16.5 |  
| 8.9 | 16.5 |  
| 158.0 | 46.7 |  
| 0.2 | 1000 | 0.190 | 74.3 | 10.2 |  
| 0.4 | 800 | 0.339 | 501.2 | 10.2 |  

Table 1.