

Interactive comment on “Experimental grain growth of quartz aggregates under wet conditions and its application to deformation in nature” by Junichi Fukuda et al.

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This contribution is clearly organized and easy to read. The results are significant for silicate rocks (especially quartz-bearing rocks) subjected to elevated metamorphic temperatures in the presence of water or hydrous minerals that govern the fugacity of water. I find the results interesting and significant and confirm that this will constitute an important contribution to studies of metamorphosed and deformed rocks.

The principal contribution made by this manuscript is the explicit relationship determined between the grain growth rate of polycrystalline quartz and the fugacity of water. The current results are in good agreement with previous measurements of grain growth

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made by Tullis and Yund (1982) and Fukuda et al (2018), including the extent of grain growth at known temperatures and annealing times, and the activation energy of grain growth kinetics. However, in the previous studies, grain growth was only reported to depend on the presence of water without an actual determination of the functional dependence. Thus the most significant contribution to this study is the explicit relationship between grain growth and water fugacity.

While I cannot know what the functional dependence of grain growth on water fugacity should be, the exponent that the water fugacity is raised to (the value of r determined by these experiments) seems rather large (1.9-2.3), well over a value of 1.0, which might be expected if a process depends on the activity of the component H_2O . For this reason, and the stated importance of this determination to this study, I strongly suggest that the authors be more explicit in their characterization of fH_2O during the experiments. As demonstrated by the authors' attempt to measure grain growth in a gas apparatus (which normally is considered to be a more precise apparatus when it comes to P , T , stress, etc), controlling fH_2O can be a real challenge. Thus, just because water is added to a metal jacket with the sample does not guarantee that the fugacity of water is known. For example, water is commonly lost from metal jackets in gas apparatus with a dry argon medium outside of the metal jacket, which can well explain the result reported by the authors for the lack of grain growth in the gas apparatus.

It is a common observation using some cell designs (for example salt cells) in Griggs and DDIA apparatus that water can be retained (at least partially) within metal jackets that are permeable to hydrogen, which is commonly attributed to the high water contents of salt (which becomes wet prior to the experiment by adsorption). However, other cell designs (MgO , $AlSiMag$, $hi\ T$ glass, $CaCO_3$) do not appear to allow retention of water within jackets (see recent results of Durham) and all results appear to reflect behavior under anhydrous conditions.

Petrologists have faced the issue of hydrogen diffusion through metal jackets for years, which has led to the design of sophisticated double-jacket designs with outer jackets

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that are only partially permeable to hydrogen and an inner jacket made of Pt, which is chosen for its high diffusivity to hydrogen. Of metals used in experiments, the least permeable (by diffusion) to hydrogen is gold. However, the melting temperature of this metal precludes its use above $\sim 1060\text{C}$ (depending on pressure). Pt is nice as it doesn't melt at any of the temperatures of the present experiments, but it is highly permeable to hydrogen. As water is dissociated to equilibrium concentrations of hydrogen and oxygen, the hydrogen can diffuse out of the jacket, leaving oxygen. If the pressure medium outside the jacket is very dry, then all of the hydrogen can be removed and the experiment may be conducted under high oxygen fugacity but low water fugacity within the jacket.

The unusual values of r determined in these experiments, the importance of this evaluation to this contribution, and the use of Pt as the jacket material, makes characterization of water fugacity of the cells used in these experiments extremely important. There are a number of ways the authors can choose to confirm the fugacities of water in these experiments:

- 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 $f\text{H}_2\text{O}$ for the range of experiments conducted.
- 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 $f\text{H}_2\text{O}$ environments.
- 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-Stern model.

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calculation of $f\text{H}_2\text{O}$ when water is present as a distinct phase.

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 $f\text{H}_2\text{O}$ outside the Pt jacket, thus maintaining a high $f\text{H}_2$ and limiting loss of hydrogen from the 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 $f\text{H}_2\text{O}$, if just a trace of H_2O is in the jacket and is retained as a distinct phase by a pressure medium outside the Pt that controlled $f\text{H}_2\text{O}$ and $f\text{H}_2$.

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 $f\text{H}_2\text{O}$ values during this experiment

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 it an Arkansas novaculite or from another locality?

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 experi-

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mental 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.

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?

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.

Regards, Andreas Kronenberg

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