Referee's comments: Black (Arial)

Our replies: Blue (Arial)

Revisions made to the manuscript in response to the referees' comments: Red (Times New Roman). Descriptions from the original manuscript: Black (Times New Roman)

Replies to Referee #3's comments (Prof. A. Kronenberg)

This manuscript presents IR absorption spectra of OH stretching bands and maps of water content measured for deformed granite samples from the Wariyama uplift of NE Japan, including a Wariyama granite that is not deformed or only modestly deformed (designated as "almost deformed"), and weakly deformed and strongly deformed granites of the same unit. The deformation microstructures of quartz in these samples is described, including undulatory extinction, subgrains and recrystallized grains with characteristics of dynamic recrystallization during dislocation creep. I am pleased to see that the authors have found similar results for water in quartz during recrystallization as our group did for deformed and recrystallized quartz mylonites (Kronenberg et al., 2020). I will comment, in part, in response to remarks and discussion of other review that suggest that the results here are not new. I would counter that it is necessary to learn whether recrystallization routinely excludes water from quartz grain interiors or not. The fact that Finch et al (2016) found reductions in water content with strain in the El Pichao shear zone of NW Argentina, and we found reductions in water contents with recrystallization of the Moine Thrust, NW Scotland is no guarantee that water contents will be reduced in other deformed rocks undergoing dislocation creep and recrystallization. In other words, I'm pleased to learn that this result was obtained in the present study and with further confirmations, we may be able to generalize the conclusion that water contents always (or normally) decrease with recrystallization.

We thank positive comments and encouragement. Indeed, there is very limited information on behavior of water in quartz deformed by plastic deformation. We are pleased to hear that the referee agrees with the importance of our study.

On the other hand, I find that this manuscript includes new results for coexisting plagioclase grains of the same deformed granites, and I recommend that the authors revise the manuscript for publication, building on these results. Firstly, neither the title nor abstract prepare the reader for the interesting IR results for plagioclase of these deformed granites. The results section includes IR spectra for plagioclase but the discussion section could address these results further. Secondly, I cannot tell from the manuscript whether feldspars of these granites are internally deformed or not, and whether they are also recrystallized. The IR spectra show that coexisting plagioclase grains are very wet, compared with deformed quartz grains, and their spectra appear to include sharp high-wavenumber OH bands due to layer silicate (I assume sericite) inclusions. In an earlier IR study of Sierra Nevada granites deformed at greenschist grade conditions, Kronenberg et al. (1990) also found that feldspars had higher water

contents than quartz grains of the same granites. However, we found no evidence of plastic deformation of the feldspars so we could not say anything about water weakening of feldspars. Apparently the temperature of deformation was too low for any plastic deformation of feldspars.

I propose the following additions to this contribution: 1) describe the microstructures of plagioclase relevant to their brittle or plastic deformation, and any recrystallization that might have occurred (if no plastic deformation is evident, that's OK – simply report your observations), 2) if the plagioclase is recrystallized at grain margins, are they wet in these regions or are they dry? 3) please cite any papers or results that provide constraints on metamorphic temperatures during Wariyama granite deformation. Again, providing a link between temperature/metamorphic facies, deformation and water contents of feldspars and comparisons with the dislocation glide and creep of quartz would be very useful, and 4) please describe the fluid inclusions and white mica inclusions in plagioclase grains that relate to their large OH absorption bands. I would be curious if these rocks also reveal evidence of plastic deformation and recrystallization of plagioclase and potential water weakening of feldspars at conditions that favor dislocation creep, subgrain formation, and dynamic recrystallization of quartz. 5) With such results, the authors can also compare with results reported for other deformed granitic rocks. For example, Kilian et al. (2016) found that quartz deformed and recrystallized at higher temperature, amphibolite facies conditions are very dry. Feldspars in those same rocks were observed to be less deformed (appearing as augen) but they were recrystallized at their margins. The previous study did not characterize OH of feldspars but this study does, so adding the microstructural information is important.

As the referee states in comments 1), 2), and 3), we realized that we did not mention the deformation of plagioclase and deformation conditions in the original manuscript, even though we showed some IR spectra of plagioclase. With regard to the referee's comments 1) and 2), brittle deformation of plagioclase is dominant and no recrystallization is observed. We have added a new figure (Fig. 3 in the revised manuscript) that shows the general microstructures of the samples and have provided descriptions of the deformation of plagioclase. With regard to the referee's comment 3), we have also discussed deformation conditions based on this new figure in the revised manuscript.

L86,

In the almost undeformed and weakly deformed samples, mafic igneous minerals are partly replaced by epidote and chlorite (Fig. 3a–d). Although some or all chlorite may have replaced amphibole during late-stage hydrothermal alteration in the three types of sample (Fig. 3a, c, and e), chlorite is found in shear bands in the strongly deformed sample (Fig. 3e), suggesting that chlorite may have been stable during mylonitization. Grain interiors of plagioclase are commonly altered to epidote, muscovite, and clay minerals in the three types of sample. In the weakly and strongly deformed samples (Fig. 3c–f), brittle deformation of plagioclase dominates and plagioclase and amphibole form porphyroclasts, but there is no development of microstructures

indicative of dynamic recrystallization or pressure shadows at their margins. In the strongly deformed samples, amphibole (mainly hornblende) and epidote grains may have been stable during mylonitization because shear bands developed in the samples are composed of amphibole and epidote grains (Fig. 3e and f). According to Fujita et al. (1988), some metasedimentary rocks affected by the thermal effects of granitoid intrusions in the Wariyama area contain metamorphic andalusite, implying that these granitoids were emplaced into upper-crustal levels. On the basis of these observations, mylonitization at least of the strongly deformed sample is inferred to have occurred under epidote–amphibolite-facies conditions and within or near the andalusite stability field (i.e., \sim 500 °C; Spear, 1993).

L120,

Differences in the recrystallization mechanisms of quartz in the three types of sample may be due to differences in temperature, strain rate, and/or stress.



Figure 3. Optical photomicrographs showing microstructures of the Wariyama granite under plane-polarized (a, c, and e) and crosspolarized (b, d, and f) light. (a and b) Almost undeformed sample. (c and d) Weakly deformed sample. (e and f) Strongly deformed sample. Microstructures of quartz in the three samples are shown in Fig. 4.

With regard to the referee's comments 3) and 4), and as suggested by the referee, we have generated two example figures below from Figs 6 (Fig. 7 in the revised manuscript) and 7 (Fig. 8 in the revised manuscript) showing variations in integral absorbance at 2800–3750 cm⁻¹ for the broad band of water and at 3550–3700 cm⁻¹ for the OH peak seen in IR spectra. Plagioclase grains are largely altered to epidote, muscovite, and clay minerals, as we described above together with new Fig. 3 in the revised manuscript. It is likely that heterogeneities in the IR maps

below may be due to amounts of clay minerals altered from plagioclase as well as the amounts of quartz measured together. Thus, IR spectra of plagioclase may not give useful information that is comparable to behavior for the plastic deformation of quartz or the brittle deformation of plagioclase. We consider that an explanation of this fact should be sufficient, rather than showing these IR maps in the revised manuscript. In addition to the explanation about brittle deformation and alteration of plagioclase for the new Fig. 3, we have also given the following explanation about IR spectra of plagioclase.

L211,

In all of the studied samples, grain interiors of plagioclase are altered to epidote, muscovite, and clay minerals (Fig. 3). When ductile shear zones developed in the study area, plagioclase was not deformed plastically but was replaced by various minerals during late-stage alteration. Therefore, the IR spectra of plagioclase that includes altered minerals may not provide useful information about water in rocks during mylonitization.



100 µm

Figure caption: IR mapping results for the mapped area in Fig. 7 in the revised manuscript for integral absorbance at $2800-3750 \text{ cm}^{-1}$ (a, total water region) and $3550-3700 \text{ cm}^{-1}$ (b, sharp OH band region). Numbers in (b) represent raw IR spectra shown in (c). Linear baselines in these wavenumber regions are depicted by dashed red lines. Minerals included in the measurements were judged from the optical photomicrograph and structural vibrations at <2000 cm⁻¹ and are shown with values of integral absorbance in the two wavenumber regions.



100 µm

IR mapping results for the mapped area in Fig. 8 in the revised manuscript for integral absorbance at 2800–3750 cm⁻¹ (a, total water region) and 3550–3700 cm⁻¹ (b, sharp OH band region). Numbers in (b) represent raw IR spectra shown in (c). Linear baselines in these wavenumber regions are depicted by dashed red lines. Minerals included in the measurements were judged from the optical photomicrograph and structural vibrations at <2000 cm⁻¹ and are shown with values of integral absorbance in the two wavenumber regions.

In the following, I comment and ask the authors to correct or clarify technical issues.

First, the ability to measure IR spectra using very small apertures (25 x 25 microns) using a conventional FTIR and IR source (not IR of a synchrotron) is impressive and this leads to nice OH maps of the samples.

It would be useful to the reader to describe the use and characteristics of the glycol phthalate resin used in preparation of thin sections. I assume this resin was used to inject samples in order to polish the IR samples. However, I do not know anything about the IR spectra of this substance or whether it can be completely removed from samples after polishing is complete. Please describe the use of this resin and whether it represents an issue for the spectra of quartz and plagioclase.

According to the comment, we have carefully described the use and characteristics of the resin. Because the resin as well as acetone is an organic compound, CH peaks around 2950 cm⁻¹ can be an indicative of their contamination. We did not observe them so these substances are completely removed or at least below the detection limit in IR spectra.

L140,

The process for making thin sections followed that for regular thin sections with a thickness of ~30 μ m for observation using a polarizing microscope but there are a few exceptions: One side of the sample was polished down to #6000 aluminum oxide powder and glycol phthalate resin was used to attach the polished sample surface on a glass slide on a hot plate heated to 100– 120 °C. Then, the other side of the sample section was polished down to #6000 to give an approximate thickness of 100 μ m to minimize scattered IR light on the sample surface and interference fringes within the sample. Finally, the sample was removed from the glass slide by dissolving the resin in acetone. IR spectra obtained in this study did not show any CH peaks around 2950 cm⁻¹, which can be indicative of organic contamination from residuals of the resin and/or acetone; even if these peaks are detected in IR spectra, they do not affect water bands, as the wavenumbers are different (e.g., Kebukawa et al., 2009).

We have added Kebukawa et al. (2009) in the reference list.

Also, we measured IR spectra of the resin pasted on a glass slide. The results are shown below. We assumed undissolved amount of 1% as an example, which corresponds to the resin thicknesses of 1 μ m for the actual sample thickness of ~100 μ m (left) and 100 μ m for the sample thickness normalized to 1 cm in the manuscript (right). In the left figure, an intense peak around 1950 cm⁻¹ due to CH vibrations is observed. However, as in the right figure, the whole absorbance is far lower that of water in quartz. The actual raw IR spectra shown in the manuscript (Figs 6-9) do not show CH peaks. Thus, the resin is completely removed or at least below the detection limit in IR spectra.



The authors state very clearly their choice of the Paterson relationship between IR absorbance and OH contents for quartz grains, and comparisons between this relationship and other calibrations for quartz. However, the authors should state clearly that this calibration depends on integrated absorbance, and shape of the OH absorptions. Was the Paterson relationship and its method of integrating also used for the plagioclase grains?

According to the comment, we have stated that "this calibration depends on integrated absorbance, and shape of the OH absorptions.". To express water contents as wt. ppm in quartz, we used the molar mass of H_2O (18 g mol⁻¹) and density of quartz (2650 g ℓ^{-1}), which were applied to all of the mapped data. Therefore, water contents in plagioclase as well as phyllosilicate included are rough values but these minerals were used as markers for the locations mapped by IR spectroscopy.

L177,

This calibration is based on a linear trend of absorption coefficients for any type of water (H₂O and OH) in different materials but assumes isotopically distributed molecular H₂O for the orientation factor of 1/3, which is already included in the above equation. The mapped areas also include plagioclase and/or phyllosilicate, whose IR spectra exhibit a dominant band owing to molecular H₂O and accessory band(s) caused by structural OH. It is noted, therefore, that the calibration of Paterson (1982) used for these minerals gives approximate water contents. Other calibrations for contents of molecular H₂O and/or OH species in quartz have been given by Kats (1962), Aines et al. (1984), Nakashima et al. (1995), Libowitzky and Rossman (1997), Stipp et al. (2006), and Thomas et al. (2009). Fukuda and Shimizu (2019) compared these calibrations, and the ratios of calculated water contents between them based on Paterson (1982) as unity are 0.68:0.88:1.15:1.31:1.58:0.43. Previously reported absorption coefficients of water in quartz have been discussed by Fukuda and Shimizu (2019) and Stalder (2021). In this study, water contents are expressed as wt. ppm H₂O, which is converted from mol H₂O ℓ^{-1} using the molar mass of H₂O (18 g mol⁻¹) and the density of quartz (2650 g ℓ^{-1}). This conversion using these values was applied to other minerals, namely, plagioclase and/or phyllosilicate, which are commonly measured together with quartz in IR maps and used as markers for the locations measured. As the densities (averaged densities when mixed) of these minerals differ from that of quartz, albeit slightly, the water contents of the minerals reported in this study are approximate values.

It has become common practice to report water contents of minerals as weight ppm H2O rather than molar (or atomic) ppm (H/Si) but some OH absorption bands of quartz are due to hydrogen interstitials (OH) and do not represent H2O defects. In addition, the original measurements by which OH absorption bands of standards have been determined (such as calibrations of Kats 1962) are not necessarily measurements of H2O weight per oxide (SiO2) weight. As I result, I don't favor this choice of concentration units of measure, even though the authors have every right to use the units of choice that are now in wide usage. More importantly, the authors should clarify how they map water contents in their maps when some of the map area consists of quartz and some consists of plagioclase. Have separate calibrations been used for quartz and plagioclase to map water contents? The contouring is in wt ppm, but I find it difficult to compare these for two minerals with different formula weights. This becomes even more complicated for plagioclase grains that include a sharp band at 3630 cm-1 due to sericite inclusions, which represent OH of layer silicates and are probably strongly polarized relative to the crystallographic axes of the sericite inclusions. The methods of determining and plotting H2O over areas of multiple phases should be described. I wonder if it isn't safer to map and contour integrated absorbances over OH bands of the mapped area, and infer water contents from these maps, rather than attempt to plot water contents using multiple conversions of OH absorption to water content.

We know that some people prefer the ppm H/Si unit because of the reasons that the referee commented. When only "hydrogen interstitials (OH)" is discussed as in Kats (1962), the use of ppm H/Si can be valid. On the other hand, this study and some studies after Kats (1962) deal with molecular H₂O as fluid inclusions and in grain boundaries. In this case, the ppm H/Si unit, which may infer "hydrogen interstitials (OH)", seems odd for us although there may be some association between molecular H₂O and hydrogen interstitials as in their mutual transformations (Stünitz et al., 2017) but may not always. Therefore, we used the wt. ppm unit in our study.

Regarding "Have separate calibrations been used for quartz and plagioclase to map water contents?", we did not separate calibrations for quartz and plagioclase; in the aperture size of 25 x 25 µm, plagioclase as well as phyllosilicate is often measured together with quartz. We could have performed IR mapping measurements or just

shown the IR results only for quartz but we were worried that readers might not be able to visually see where the mapped areas were by comparing the IR mapped data with the photomicrographs. Then, minerals other than quartz were mainly used markers for the mapped locations. Another (minor) reason was that readers might be interested in IR spectra of other minerals so we showed their spectra as well. To determine water contents in wt. ppm, densities of minerals are needed and we have also clarified the method to determine wt. ppm in the revised manuscript. Again, quartz, plagioclase, and phyllosilicates are often measured together so their accurate densities are unknown. However, the density of quartz is 2650 g l^{-1} and those of plagioclase and phyllosilicates are around 2700 g l^{-1} and 3000 g l^{-1} , respectively. Since these values are not significantly different, water contents for the latter two minerals and mixtures of them with quartz using the quartz density can give rough values. We have also clarified it in the revised manuscript.

As the referee says, we could only show "integrated absorbances over OH bands of the mapped area, and infer water contents from these maps" as we showed above. However, because readers can directly see water contents in quartz in the IR mapped data, we prefer to keep the original IR maps in wt.ppm.

To sum up, in the revised manuscript, we have given careful descriptions of how we determined water contents (in wt. ppm) and why these estimations can give approximate values for water contents in plagioclase and phyllosilicates, which are often measured with quartz. The revised parts are shown above regarding the referee's comment on the use of Paterson's (1982) calibration (L177 in the revised manuscript).

There are a few places that the author might reword the manuscript text.

For example, in the Samples section, I recommend replacing "by the naked eye" by "as observed in hand specimen" According to the comment, we have revised the expression in the manuscript.

L84,

on the basis of the development of foliations of mylonitic rocks as observed in hand specimen

L684,

three types based on the degree of deformation, as observed in hand specimen

In the same section, I recommend replacing "as an equivalent circle diameter" by "as the diameter of a circle of equivalent area to the diameter of the grain"

Revised.

L125,

as the diameter of a circle of equivalent area to the diameter of the grain

In the section on Analytical Procedure for IR spectroscopy, I assume that the sample translation stage translates the sample in X-Y while the IR beam was fixed in place (not as described by a "beam-moving function"). The IR beam is actually moved by adjusting mirror positions in the apparatus and "the sample translation stage" is fixed. We have clarified as follows.

L165,

Mapping measurements were performed using a beam-moving function in the sample area of up to $400 \times 400 \ \mu\text{m}$; the sample stage was fixed, and IR light irradiated to the sample was moved.

In section 5.1 of the Discussion, I am not sure what is meant by "OH dislocations". Do you mean OH at dislocation cores? Or do you mean a fully hydrated dislocation (OH completely saturate dangling bonds of dislocations)? We meant Si-OH in the quartz crystal structure and it is not necessarily fully hydrated. We have clarified it based on the discussion in Stünitz et al., (2017).

L264,

The redistribution of fluid inclusions has similarly also been reported from IR spectroscopic measurements of an experimentally deformed single quartz crystal (Stünitz et al., 2017). Those authors demonstrated that original fluid inclusions with sizes of up to 100 µm transformed into Si–OH as Si–O–Si + H₂O $\leftarrow \rightarrow$ Si–OH \cdots OH–Si, where Si–OH showed a sharp band at 3585 cm⁻¹ in IR spectra. ... Stünitz et al. (2017) also demonstrated that the above Si–OH, which could have originally been visible fluid inclusions with sizes of a few micrometers under an optical microscope, are again transformed into much smaller fluid inclusions measuring less than 100 nm in size by subsequent annealing.

Referring to the last line of the Section 5.3 of the Discussion, I agree with the authors and doubt that many water contents measured in deformed quartz actually represent equilibrium concentrations. They are generally too large for equilibrium defects and highly variable spatially.

Thank you for supporting our idea. Water especially in undeformed quartz, where water diffusion can be slow, may be trapped during the crystallization stage from magma and may not reflect the equilibrium concentrations during the deformation stage.

Caption to Figure 9 – minor typo- "addiction" should be respelled as "addition" Revised.

L747,

In addition,

Commenting on Data Availability, are the Jasco data files formatted in a way that readers can download Jascoformatted IR files and plot the results as open-source files without purchasing special, analysis software? If so, great. If not, it would be good to make files available as csv or other open-source file formats.

The Jasco original data files with extensions of ".jwa" require special software to open. Therefore, in the data sets, we also uploaded text files for those who do not have the software. In the revised manuscript, we have clarified this point.

L410,

The text files can be used for those who do not have JASCO's IR software.

In summary, this is an interesting contribution that will help us understand deformation of quartz and feldspars at natural strain rates. The results for quartz appear to support and corroborate previous reports of water losses from shear zones undergoing dislocation creep and recrystallization, and the results for plagioclase are new. The plagioclase results will have increased impact on the field by including the same detail of microstructural descriptions for plagioclase as for quartz.

The scientific quality of the results presented is very good, but the methods, as discussed above, need to be more clearly stated, and water contents and microstructures of plagioclase need further evaluation and representation, to the same extent as presented for quartz. The changes I propose are not truly major but they involve more than a simple rewrite, so I characterize them as "major".

We have added a new figure as Fig. 3 to discuss microstructures of plagioclase and other minerals that can show the deformation behavior and conditions of the samples studied in this study. As we described above, brittle deformation of plagioclase is dominant and grain interiors of plagioclase are altered to clay minerals. In this response file, we showed IR maps and IR spectra focusing grain interiors of plagioclase in terms of integral absorbance at 2800-3750 cm⁻¹ for the broad band of water and at 3550-3700 cm⁻¹ for the OH peak around 3630 cm⁻¹. As a result, as we described above, these IR data for plagioclase do not give useful information that can be compared with or applied to plastic deformation of quartz which is focused on in this study. Therefore, we would like to keep them in this response file. The referee was interested in water in plagioclase and we realized that we had not carefully described deformation of plagioclase as well as other minerals in the studied samples in the original manuscript. Therefore, we have carefully described information about plagioclase, other minerals, and deformation conditions in the revised manuscript.

I look forward to seeing this paper in print,

Andreas Kronenberg