RESPONSE TO REVIEWER WHITNEY BEHR

This is an interesting paper that takes a very detailed and thorough approach to understanding how titanium is distributed among detrital quartz grains, vein quartz, and dynamically recrystallized quartz grains in a low strain, greenschist facies metasediments in Taiwan's Hsuehshan range. This work provides a useful natural test of different calibrations of the Ti-in-quartz thermobarometer (known as TitaniQ), which is a newly developed technique with considerable potential for tracking the PT paths of low grade metamorphic rocks. The analytical techniques the authors employ, and their description and presentation of their data is mostly clear, and I unreservedly recommend this paper for publication in Solid Earth following minor/moderate revision. I do, however, outline some places below where I feel the manuscript could use more description and/or clarification.
I directly address the Solid Earth manuscript evaluation criteria as follows:
Scientific significance: (1) Excellent. The TitaniQ thermobarometer is a very popular new technique that needs detailed testing using natural rocks—and the authors have taken a very useful approach to doing this.
Scientific Quality: (1) Excellent. The methods are for the most part very good.
Presentation Quality: (2) Good. The text is mostly clearly written, but some sections require clarification. A few key points need to be discussed in more detail. Figures are for the most part excellent, but a few could be improved.

First I would like to thank Whitney Behr for a constructive review. Based on the comments of the reviewers I have prepared a revised manuscript and figures (inluding two new figures) that can be found in an archive attached to this comment. All references to page and line numbers I've made below refer to this updated version.

Specific points keyed to text

Pg. 665, lines 12-14: Note that Grujic's results were for prograde contact metamorphic rocks deformed under much shorter durations than long-lived shear zones. This is worth considering in your discussion as well, since the recrystallization in your rocks occurred during retrogression.

The time duration difference could be quite important and I've added a discussion of this possibility in section 6.6. Note however that deformation of these rocks was not in a shear zone and was also not "long-lived" (all the deformation occurred in <3.5 m.y.). I'm not sure why retrograde vs prograde would be important. If anything, prograde is often associated with water release, which might be expected to facilitate grain boundary diffusion. This wouldn't help explain our observations (we see grain boundary diffusion of Ti, they don't).

Pg 665, line 14: Huang and Auditat (2012) don't challenge the results of the studies you listed directly—better to say they question the Thomas et al. (2010) calibration used in previous studies.

I've changed this to, "the TitaniQ calibrations used in the most of the above studies was challenged by Huang and Audétat..."

Pg. 665, lines 10-11: the accuracy of the results in several of those studies were verified using qualitative methods similar to the ones you use later in the paper (e.g. basic observations of mineral assemblage, correlation with dynamic recrystallization regimes, cross-cutting relationships, consistency with flow laws etc. . .), so this statement is a little bit misleading (perhaps add 'quantitative' before 'PT' ?)

I've added "quantitative" as suggested.

Pg. 665, line 17: This is confusing and seems out of place here, and raises all sorts of questions that you don't address until pg. 679, so I would remove this sentence.

Removed

pg 666, line 7: change 'comprised' to 'composed' or use 'comprises' and remove 'is' and 'of'. (Comprises is synonymous with consists of)

Done

Pg. 666, line 15: Specify what kind of cleavage (presumably axial-planar?) Also, would be helpful to keep outcrop-scale observations (folds, cleavage) separate from microstructural ones (e.g. pressure shadows). Finally, none of the features you describe in this line uniquely require coaxial deformation, so rather than 'indicative', maybe use 'interpreted to represent'?

I've added "axial-planar" to modify cleavage. There are syn-kinematic fibers in the pressure shadows indicative of co-axial deformation. I've clarified that. I've also separated the microstructural information to a separate sentence (see pg. 3, paragraph 1).

Pg. 667, lines 25 28: ok, this makes sense, but it's a little bit worrying that the trend you observe in Figure 14 could be related to the lack of filtering. That is, the larger the grain size, the more analyses you will perform and the more likely you are to encounter a micro-inclusion that is not filtered out of the dataset. Hopefully this isn't the case, but it might be worth doing a filtering of analyses with anomalously high trace element concentrations and seeing how it affects your results?

This could only happen if larger grains had more impurities than small grains (in the scenario described, one would expect only a decrease in density to the right in the plot, not the progressive disappearance of high and low Ti measurements). If anything it's just the opposite, analyses of smaller grains are more likely to hit grain boundaries and non-quartz "stuff" along grain boundaries. I've tried removing spots that hit grain boundaries, and it doesn't change the trends in the figure. Another way is to look at this is with Fig. 15. The three subplots are clearly very different populations (B shows a substantial proportion of 1–10 ppm grains not present in A, C is nearly entirely below 10 ppm whereas A has around half the population >10 ppm). It is highly improbable that these trends could be generated in the manner suggested.

Pg. 671, section 4.1: Somewhere you need a description of the field-scale characteristics of these rocks. The small amount of information in the geologic background leaves many open questions. Consider including: 1. what defines the foliation in the host rocks at the macro-scale? 2. Is strain in the different rock types uniformly distributed, or are there localized zones? 3. Spacing and abundance of the veins in different lithologies? 4. This would also be a good place to describe the different generations of veins. On pg. 671, line 8, you mention you used the 'orientation criteria of Tillman' as defining which veins were formed pre-collision vs. post-collision. This needs to be spelled out in more detail, especially since the Tillman paper is in a specialized journal that is difficult to access. Perhaps just categorize the veins sequentially. For example: Category A: pre-collisional veins distinguished by ———.

Category B: veins that are parallel to axial plane cleavage/foliation. Category C: veins located within the hinge zones of folds and which form conjugate symmetry about the fold axis. Category D: veins which clearly cross-cut the axial planar cleavage. This way when you get the section 4.2.2, it'll be much easier to explain the constraints on temperature simply by referring to the different categories of veins. 5. Do the successive generations of veins show differences in internal strain? E.g. shouldn't the precollisional veins show the greatest degrees of dynamic recrystallization, assuming strain was uniformly distributed in the bulk rock? 6. Also, what are the relative roles of pressure solution vs. dislocation creep in the different rocks types?

I have expanded the geologic background to address most of the above questions and provide additional references. In general my goal was to keep structural elements to the minimum needed to understand the geochemical aspects (the main theme of the paper).

1. This has been added "slatey cleavage, pressure solution seams, and flattened detrital grains"

2. I've addressed this in the second paragraph of the geologic background. Unfortunately this is not something that is well known since only minimum strain estimates are available in slates.

3. I've now added this information regarding the overall distribution of veins: "Veins are common in the core of the Hsüehshan range (within and between the two exposures of Tachien sandstone), and are concentrated within the axial zones of folds. Veins are virtually absent in the Chiayang formation east of the Tachien anticline."

4. I've recategorized the veins as suggested. This is given in section 4.1. I've also explained the criteria of Tillman et al. (1992) in section 4.1.

5. Yes, at least in places. This is evident in Fig. 9. I don't have any systematic data on this though, it's just a qualitative observation made from place to place.

6. I don't know. Both occurred, but I'm not aware of a way of quantifying this.

Pg. 672, lines 5-18: From what you describe and document in the figures, it's difficult to see why these 'midsized' grains are considered dynamically recrystallized grains as opposed to flattened and elongated detrital grains, especially since they are within the same size fraction (100-400 um for 'midsized grains' vs. 100 um to 3 mm detrital grains). I think it would help to show the circled areas in Figure 7 at higher resolution. Maybe also show an example of the 'mid-sized' subgrains?

I've added a new figure (11) showing evidence of a tectonic origin of the midsized grains (including images of subgrains) and changed the text to indicate that the most of these grains are closer to 100 μm (I estimate 130 μm in the companion JGR paper) rather than "100-400 μm" as I had previously. Certainly some of the midsized grains are sedimentary, but a lot of them are tectonic.

Pg. 673, Section 4.2.2: Describe the different generations of veins first in the macro-scale structure section, then leave this section for just the temperature constraints.

I've described the macro-scale structure as suggested and significantly revised this section

(now 5.1.2)

Pg. 674, Section 4.2.4: specify your assumptions regarding water fugacity

I've added that we assume the same water fugacity in the two regions (the numerical value doesn't affect the results of the calculation).

Pg. 675, Section 4.31. The veins should be classified according to generation in Figure 12 and according to the presence or absence of a Ti-bearing phase. Apparently, despite that there are different generations of quartz veins formed under different temperatures, the Ti concentrations in veins are basically all the same. This needs to be discussed somewhere—it seems to imply the veins are simply not in equilibrium with a Ti-bearing phase during emplacement nor during subsequent dynamic recrystallization.

I've added whether or not they have rutile in figure 12. There is a misunderstanding reflected in the comment. The blue and orange bars indicate the expected Ti contents (based on TitaniQ and independent PT information). Most of the veins were emplaced within a fairly narrow temperature window (note similar position of, for example, the blue bars), which is why they have very similar Ti concentrations. There is no reason to suspect disequilibrium.

Section 5.2 This section needs some rewording. Pg. 677, line 3-6: As far as I can tell you're describing solution-precipitation creep, rather than strain-induced grain boundary migration (SIGBM) here. SIGBM doesn't involve dissolution or precipitation, instead it involves bulging of pre-existing grain material and 'dragging' of the dislocation structure behind the bulging boundary leaving a region of lower dislocation density (see Humphreys and Hatherly, 1995, Figure 7.27). Relatedly, your statement that gradients in trace element concentration along grain boundaries can increase, thereby increasing their mobility needs a reference. Gradients in solute concentration would increase the chemical driving force for migration, but this is likely negligible compared to the driving force due to gradients in strain energy. In that case solutes have little effect on mobility at low concentrations, but at high concentrations the boundary velocity would be controlled by diffusion of the impurity atoms, so would actually decrease the migration rate, rather than increase it. It's much more likely that the high defect concentration at grain boundaries, coupled to smaller grain sizes (which both decreases the distance for volume diffusion, and enhance the activity of grain boundary diffusion) would lead to significantly higher Ti diffusivities in the vicinity of the migrating grain boundary than predicted by Cherniak et al. for static diffusion. This is essentially what Grujic et al. (2011) describe, but is different from what you have proposed.

I agree that this section needed some rewording, however I disagree that I am implying solution-precipitation creep. Perhaps the use of the word "dissolve" was confusing, as it implies fluid presence (likely here, but not required). I am describing what happens during the strain-induced migration of grain boundaries (SIGBM). "Grain boundary migration... is the essential process where recrystallization in the most literal sense occurs: material from the grain that is being consumed enters the grain boundary region and eventually recrystallizes on the lattice of a neighbouring grain that is growing." –Urai et al. (1986). To hopefully clarify things I've removed the word "dissolved" from the sentence.

I have removed the sentence about grain boundary mobility.

Pg. 677, lines 20-28: It's true that 'static diffusion' would probably produce systematic gradual shifts in Ti concentration, but there is no reason that diffusion along defects (e.g.

pipe diffusion, diffusion along fluid inclusions) should produce this effect. In other words, static diffusion was probably negligible, but enhanced Ti diffusion along migrating grain boundaries was likely very significant.

There are two things mentioned here: what might be called “defect-modified static diffusion” and grain boundary diffusion. I’ve added a short section (6.3) to address Ti diffusion along grain boundaries. Regarding the effect of defects on expected diffusion profiles, I agree that this might lead to a different signal than suggested however I’m not aware of any studies showing what sorts of features might be result.

Pg. 678, line 10: Again, I don’t think precipitation is an important process here unless you’re talking about dissolution-precipitation creep/ pressure solution. The microstructural features you focus on for TitaniQ do not look like pressure solution microstructures.

I think the misuse of the word “precipitation” threw you off. I didn’t mean to imply presence of a fluid (though it’s likely). I’ve clarified the sentence: “Ti concentrations in the fine grains were reset in essentially the same fashion as we propose above for the midsized grains, i.e. exchange of Ti between quartz and grain boundaries during grain boundary migration.”

Pg. 679, line 20-26: Looking at your data, it’s clear they do not exhibit wild spikes and the standard deviation per grain and per sample is rather large, so your non-filtering approach makes sense for your data. That said, filtering data based on ‘wild spikes’ or clear statistical outliers (e.g. a few analyses that are more than 2-sigma outside the mean) is still statistically significant, particularly in cases where the standard deviation in the analyses is low, so I don’t really agree with your generalization in the last sentence of this paragraph. Also, comparing datasets just requires the same filtering techniques to be used in each dataset.

I’ve softened the sentence significantly to simply “We are unaware of an established, rigorous procedure for distinguishing between inclusions and high impurity concentration minerals.

Pg. 681, lines 9-20: Again, it’s worth noting that Grujic’s results were for short-duration, prograde deformation, whereas your results, and those of Behr and Platt (2011) were for longer duration, retrograde deformation.

See comments above.

Pg. 682, lines 9-10: note that Behr and Platt (2011) were referring to fluid pressures in the brittle field as being less than lithostatic, whereas fluid pressure was assumed to be lithostatic in all rocks deforming by dislocation creep. (What happens at the transition is an open question, and a critical one. . .)

I’ve removed the reference to Behr and Platt (2011)

Pg. 682, lines 10-11: Did you take this into account when estimating temperatures using the Hirth et al. flow law?

No, but it only affects the result by a negligible amount (~5 degrees).

Figures and Tables

Table 1: Can you classify the veins in more detail according to generation? You describe cross-cutting relationships that provide more detail than just pre-collisional and collisional.

I've now reclassified the veins as suggested (types A–E) and indicated crosscutting relationships with an asterisk (e.g. A* would be a crosscutting type A vein).

Figure 4: Just for convenience, I'd recommend putting these two figures side by side, rather than one on top of the other. I know this is a digital journal, so you can always zoom in, but it's just easier when you can read both the figure and the caption on the screen, rather than having to zoom out to read the caption, then zoom in to see the figure.

Done

Figure 7: The circled areas in the crossed-polars photo in this figure are too small to resolve even when zoomed in completely. I would take a separate photo of these features. Also, your plane light photomicrographs are very yellow—this can be fixed in Photoshop easily, and it will be easier to see the microstructure.

I've added a new figure (Fig. NEW2) showing the midsized grains in more detail. I've also fixed the yellow color in the figures.

Figure 8: I'd recommend adding a photomicrograph to this Figure, of the same region, but zoomed out and in plane light so that we can see the vein morphologies at a larger scale. It's very difficult to make out the supposed horizontal foliation at this scale.

I think you are referring to figure 9a (since this is where I mentioned foliation). Note that the field of view given here is already quite large (1.2 cm). Unfortunately the vein is quite thick and I don't have any publication-worthy images of the foliation-vein relationship. It's an unambiguous slately cleavage, so it isn't something that needs to be "proven" photographically. I've clarified in the caption that foliation isn't something the reader is expected to see in the figure.

Figure 9: nice figure!!
I think you are referring to old figure 10. Thanks.

Figure 12: Can you specify on this figure a) which generation each vein belongs to, and b) whether the vein has rutile or ilmenite or neither?

I've noted on the figure when rutile is present in the veins and also added the vein classification to the figure.