

To: Douwe van Hinsbergen, Editor of *Solid Earth*
From: Whitney Behr

Dear Editor,

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 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.

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.

pg 665, line 14: Huang and Audinat (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.

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' ?)

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.

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

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'?

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?

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. Or something like that... 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 rock types?

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?

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.

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

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.

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.

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.

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.

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.

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.

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...)

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

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.

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.

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.

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.

Figure 9: nice figure!!

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

