RESPONSE TO REVIEWER FRANK SPEAR

This is a well-presented manuscript about the applicability of Ti-in-quartz thermobarometry in low-grade quartzites. I thoroughly enjoyed reading the text and am pleased to say that I learned quite a bit in doing so.

I've made numerous comments keyed to lines in the text that the authors might wish to consider. My one major concern is the use in this manuscript of an "average geothermal gradient" to establish a context for interpretation of the TitaniQ results. As I understand the logic, independent temperature estimates are inferred largely from the deformation characteristics of the quartz (this is fine), and then the geothermal gradient is used to establish a pressure from this temperature so that this pressure can be used in the TitaniQ thermobarometry. I guess I find this a bit circular, and even more important, it might be missing some of the most important potential of this work. My thinking is this: the rocks have undergone a period of shortening and thickening (rates possibly as high as 9 cm/year), which will undoubtedly perturb the geotherm. I would suspect that this shortening was also accompanied by strain which might be responsible for the recrystallization of the quartz. So why not use the pressure dependence of TitaniQ to get an estimate of the pressure of this deformation and recrystallization and compare these with the thermal modeling? I think this might be far more interesting than a comparison of the two calibrations (also since the H&A calibration appears to be thermodynamically unreasonable.) However, this is not a requirement of revision of the manuscript, but rather a suggestion for the authors to consider. The manuscript (with some minor corrections listed in the pages below) is well-worthy of publication.

First I would like to thank Frank Spear for his review. Based on the comments of both reviewers I have prepared a revised manuscript and figures (incl. two new figures) that can be found attached to this comment. All references to page and line numbers I've made below refer to this updated version.

First, regarding pressure, I think it is important to note that we unfortunately have available no useful constraints on pressure from the (poorly developed) mineral assemblages in the area (page 5, line 22-23). This necessitates some assumption about pressure. I see two choices, either assume a geotherm of some type (as I've done), or use some model-derived geotherm, the most relevant of these being the output of the Simoes et al. model (I discuss our choice of using a linear geotherm in response to one of the detailed comments below). I've not taken the step, as suggested above, of using TitaniQ to calculate pressures because there are no independent constraints to compare the results to. Regardless of the potential flaws in the Huang et al. TitaniQ calibration, there is a significant debate surrounding the accuracy of TitaniQ in general (e.g. Thomas et al., 2012; Wilson et al., 2012) and I see a main goal of the paper to look into this issue.

Regarding the appearance of "circularity" mentioned above: I think this is simply an artifact of the presentation of the submitted paper and I've taken a number of steps to clarify what was done, mainly to modify figures 1r-18 to either mention or graphically indicate that the plotted temperature scales are dependent on TitaniQ calibration and the geotherm assumption. With this in mind, consider Fig. 14, focusing on the plotted data. The data in the histograms are Ti concentrations (nothing is assumed about P or T). The blue and orange lines show the Ti concentrations predicted by TitaniQ using independent T constraints and the geotherm assumption. There is nothing circular about this comparison of measured and predicted Ti concentrations. I believe the appearance of circularity comes from plotting the temperature scale (which also assumes a geotherm) at the top of the figure. The temperature scale could be

removed, but it is useful for thinking of the significance of the Ti concentrations in terms of temperature. I've adjusted Figs. 14 and 15 by adding a second scale for the Huang et al. calibration and coloring both the temperature scales. Hopefully this clarifies what is data (black) and what involves assumptions (colors).

Specific comments (keyed to lines in text)

Page 1, lines 23-24. This is an odd way of phrasing. The Thomas et al calib. doesn't make any predictions. It is a correlation between Ti concentration and T,P. Perhaps you could say something like: "Using lithostatic pressure and Ti concentrations measured by SIMS, the Thomas calibration yields temperatures consistent with other estimates (specify) of recrystallization temperature."

I've changed it to "Using lithostatic pressure and these temperatures, the Thomas et al. (2010) calibration yields Ti concentrations within error of concentrations measured by SIMS."

Page 2, Lines 12-13. There is evidence in Spear and Wark (2009) that detrital quartz does recrystallize at low temperatures. Specifically, the uniformity of Ti concentrations in schists of the garnet grade. Interestingly, these quartz grains yield TitaniQ temperatures less than the garnet isograd, suggesting that quartz recrystallizes more or less completely around 350-400 C then doesn't change unless affected by fabric evolution or metamorphic reaction.

I had understood a higher temperature for quartz formation in the garnet grade samples (425–475 °C, e.g. from the S&W abstract). I added the sentence "Spear and Wark (2009) found TitaniQ temperatures of 425–475 °C in samples with garnet-biotite temperatures of 475–530 °C, and suggested that the quartz recrystallized at the lower temperatures during prograde metamorphism." (Happy to correct this if I understood S&W incorrectly).

Page 3, line 6. Temperature-time (not Pressure-Temperature) in Fig. 4

Corrected

Page 3, lines 13-16. Why the switch in conditions? Any conclusions as to which are better?

The higher current in the later sessions allowed for faster analyses. I've added this to the text.

Page 4, lines 33-34. I question whether the assumption of a constant, linear, steady- state geothermal gradient is warranted in a terrane undergoing convergence at 9 cm/year. This magnitude of tectonic velocity will perturb the geotherm, and quartz may be recrystallizing during this perturbation or during subsequent thermal relaxation.

I agree that this assumption is questionable, however we have no independent pressure data and only one available numerical model (Simoes et al.) that makes PT predictions for the Hsüehshan range rocks. We could force TitaniQ results to fall on the model PT curve, however the model results themselves could be questioned (e.g. as pointed out by you, the model assumes an initial condition involving a 20-km thick undeformed sedimentary basin. Internal deformation of the rocks is also not accounted for in the model. In any case, the linear assumption we make incorporates some uncertainty (±5 °C/km) that is carried through, for example, into the TitaniQ estimate ranges in Figs. 14 and 15. The simplicity of the approach we take also has benefits like transparency, and the ability for a reader to estimate

for themselves the effect of a different PT curve/history on the temperature calculations (e.g. using Fig. 6).

Page 5, line 8. I would think the largest uncertainty is (a) the local Ti activity (i.e. is it consistently 1.0 along every grain boundary?) and (b) uncertainty in the instantaneous geotherm.

This comment relates to the methods section where we listed what was included in the reported errors. We do include a ±5 °C/km geotherm error in the "systematic error" column of table 1), and as just mentioned, the ±5 °C/km geotherm error is included in the blue and orange bars in figures 14 and 15, so this isn't just hidden in the table. ±5 °C/km is a reasonable estimate, it's about the same magnitude of variation predicted by the Simoes et al. model (Figure 6) although our 25 °/km is a bit warmer than the time-averaged model geotherm.

I don't see any way to involve uncertainty in the local Ti activity in the statistics, but this certainly could be significant and may partly explains the scatter in our measurements (e.g. Figs. 12 and 13).

Page 5, lines 20-21. What is the wavelength sensitivity of this detector? It is well established that only CL in the blue (ca 415 nm) correlates with Ti concentration.

The wavelength of the EPSE photomultiplier is 300–650 nm. As seen in figures 10, 12, and 13, this CL signal shows a moderate correlation with Ti concentration. I also mounted a broad scale blue filter in front of the CL detector that cuts out wavelengths of ~500–700 nm. Surprisingly the resulting CL signal switched to being anticorrelated with Ti content (see Fig. 13). I also tried a 415 nm bandpass filter and got the same result (this image is in a new supplement I've added). I've also added a short section (5.3) discussing this puzzling result.

Page 5, line 29. Could you add a sentence describing these criteria used by Tillman? Also "before or after collision" requires substantial interpretation. Is there a more observation-based criteria you could cite?

I've added the following information (now in section 4.1): "Type A veins are bedding-perpendicular veins with NNW to NE strikes (i.e. roughly perpendicular to modern plate convergence) when bedding is restored to horizontal. Tillman et al. (1992) noted that these veins are overprinted by compression-related faults, folds, and cleavage and assigned them a "pre-collisional" extensional origin." They also state that the pre-collisional nature of these structures is "easily established" based on these overprinting relationships and relatively simple history these rocks have experienced (deposition, extension, collision). I've also substituted "compression" for "collision" in a number of places to minimize interpretation where unnecessary.

Page 6, line 33 and Fig 2c. Shouldn't you put error bars on the grey diamonds? ±50C is substantial and would reveal overlap with much of the TitaniQ data.

Now added to the figure.

Pages 6-8 (Section 4.2 about temperature constraints). Are there any independent estimates of pressure for any of these rocks? It's too bad if not, because the discussion gets a bit circular otherwise (i.e. choose a temperature and a geothermal gradient to get the

There are no independent pressure constraints. The potential circular reasoning issue is
addressed above (It's not circular. I think the figures in the submitted draft just gave that
impression).

Page 8 lines 5-7. Regarding strain rates and shear heating. Using bulk strain assumes
uniformity of strain distribution. More likely the strain is partitioned and not uniform, so it's
difficult to interpret what you say here.

This isn't a shear heating calculation. It's a calculation assuming that the quartzites obey a
dislocation creep flow law and noting that higher temperatures are needed in the Tachien
anticline in order for deformation to occur at the lower stresses recorded there. I've reworded
the section (5.1.4) to clarify this. Regarding the strain rates, there is actually a better-than-
usual case to be made that strains were relatively uniformly distributed in the Hsüehshan
range (Kidder et al., 2012). Distribution of strain isn't really at issue though for this
calculation, since the anticline core rocks (e.g. 148d) clearly experienced a penetrative strain
at a lower differential stress than the rocks to the west (e.g. Fig 11 shows the elongation of
detrital grains in the foliation plane of sample 148d but not in western rocks shown in panels
A & B).

Page 8 lines 15-17. The uniformity of Ti concentrations is a very important and significant
observation.

Page 9 Lines 13-15. Yes - I agree that your data strongly indicate an approach to equilibrium!

Good

Page 10, lines 4-5. I agree that bulk diffusion is not evident, but isn't the important process
grain boundary diffusion? We have no quantification of this at all, but your data strongly
suggest that grain boundary diffusion was sufficiently fast to allow equilibration with rutile at
some distance from the recrystallizing quartz.

I've added an order of magnitude Ti diffusivity calculation for grain boundary diffusion. See
page 12, lines 3–17.

Page 10, lines 30-35 regarding H&A calibration. Of course, the H&A calibration also predicts
a very unlikely curvature to the isopleths, which makes little thermodynamic sense (it would
require a radical P-T dependence of the molar volume of the TiO2 component in quartz,
which seems highly improbably for a trace element in the Henry's Law limit.

I mention this now in section 6.4, page 13 lines 5–13.

Page 11, Line 8. . . "there is no reliable procedure for distinguishing between inclusions and
high impurity concentration. . .". You might be able to distinguish if you analyzed many more
elements be able to distinguish quartz from impurities.

Perhaps, but it probably wouldn't be practical for large datasets such as ours. I've softened the

statement a bit though to say, "We are unaware of an established, rigorous procedure for distinguishing between inclusions and high impurity concentration minerals."

Page 11, line 31-32. Why do you say "compressional deformation began". Biotite in pressure shadows only constrains deformation to be ongoing at peak T. How about "...indicating that compressional deformation was operative (or ongoing) while temperatures were at or near peak conditions."

I've made the proposed change.

Page 11, line 38. re "onset of collision". I guess I just don't like this term because it requires significant interpretation of observations that aren't really a part of this paper. How about using instead the term "onset of deformation".

Fair enough. I've changed things to simply say that temperatures were high during "early deformation."

Page 12, lines 9-10. Why do you say "lack of resetting?" The quartz veins have 0.2-1 ppm Ti. Can't this be the equilibrium Ti content at the conditions the veins formed - i.e. there would be no driving force for resetting.

I agree. I was referring to the Grujic study where Ti concentrations in recrystallized veins does not appear to have reequilibrated during deformation. I've clarified this now by specifically mentioning the Grujic study (section 6.6).

Page 12, line 16, line 20, line 30 and elsewhere. Some odd typos e.g. "te16" (possibly just a font issue with Adobe pdf.)

Corrected

Page 13, lines 5-11. I think we know the sensitivity of TitaniQ. The question is, what pressure do the quartz and rutile feel? For matrix quartz and rutile, I would suspect it must be lithostatic, since the phases are under a column of rock. For veins it is not clear since the quartz veins are likely precipitated from aqueous fluids. But this is a good and important question.

Page 13, lines 4-8. Your paper really isn't about the deformation per say - you only use it to establish a temperature framework. Although this statement is true, I wouldn't say it is a "conclusion" of your study.

The conclusion section has been removed

Page 13. Conclusion section. I don't think this conclusion section is really necessary, since the abstract says everything you mention here quite well.

The conclusion section has been removed

Figure 2 caption. At what pressure were Thomas et al temperatures calculated? Also, assuming what activity of TiO2? Also, Figure shows both blue and purple are TitaniQ temperatures, but last line of caption is ambiguous. Do you mean that the blue are TitaniQ temperatures for which there are also dynamic recrystallization temperatures?

The requested information and clarifications have been added. (Purple is for unrecrystallized vein quartz, blue is dynamically recrystallized quartz in veins and quartzites).

Figure 3. You mention conjugate veins. Conjugate veins should have intersection angles of less than 60 degrees. I don't see this - what I do see are angles more like 90 degrees. Do you really mean "contemporaneous (with folding) veins"?

Yes. "Conjugate" has been removed here and in the text.

Figure 9 caption. Do you mean "Photomicrographs" (rather than microphotographs)?

Yes, this is now corrected.

Figure 10 and 11. CL images. You need to add some text about the wavelength of light that the CL is detecting. Only in the blue region is CL sensitive to Ti concentration.

I've added in the figure captions that these are "full-spectrum (300–650 nm)" CL images. As discussed in (new) section 5.3 this full-spectrum signal correlates with Ti concentration.

Figure 12 caption. I understand this caption after reading the text, but it would be better to rewrite it so it can stand on its own. Specifically the last 3 lines don't make much sense. Here are the things I pondered when I first read the caption. . .. (1) How can temperatures based on Ti calibrations be based on independent T constraints? (2) How can you base a Ti temperature on a geothermal gradient? (3) How can you base a temperature scale on a Ti calibration and then show the blue bar not exactly coincident with the histogram bars?

I've rewritten the figure caption taking these comments into account.

Figure 6. The P-T path is worthy of additional consideration. (1) The path starts at 9 Ma. but doesn't show how the rocks got to the depth of 20 km. This can only be the result of thickening due to thrusting and shortening. If so, the prograde PT path would be much steeper than the 25 C/km used here (I suspect that the Simoes et al model has these data - it would be worth looking at). And isn't it likely that deformation started then - i.e. during shortening? You could be crossing the TitaniQ isopleths for 0.2 to 1 ppm in this part of the prograde path when the detrital quartz is recrystallizing.

The Hsüehshan range rocks in the Simoes et al. (2007) model at 9 Ma are assumed to be part of an undeformed continental margin sequence, with this rather thick sequence attributed to deposition in a graben (see their figures 13 and 18).