

Interactive comment on “Constraints on Alpine Fault (New Zealand) Mylonitization Temperatures and Geothermal Gradient from Ti-in-quartz Thermobarometry” by Steven Kidder et al.

Anonymous Referee #1

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Review of “Constraints on Alpine Fault (New Zealand) Mylonitization Temperatures and Geothermal Gradient from Ti-in-quartz Thermobarometry” by Kidder, Toy, Prior, Little, and MacRae.

General Comments: This manuscript integrates microstructural and geochemical data on quartzites to interpret temperature conditions during deformation and mylonitisation of the Alpine Fault zone. The field locality provides an ideal setting to test the Ti-in-quartz technique because there exist modern-day constraints on the rates, kinematics, and conditions of deformation from independent methods. The authors present an extensive dataset of Ti-in-quartz SIMS measurements reflecting a commendable

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undertaking of skill and analytical investment. The SIMS results indicate very low Ti concentrations in all samples, regardless of many of the variables tested. The authors are faced with a challenging task in interpreting a PT history from these data and ultimately invoke the activity dependence on Ti solubility (assuming $a_{\text{TiO}_2}=0.1$) and argue that their samples followed a PT path that paralleled the trajectory of Ti-in-quartz isopleths (i.e., the samples experienced a protracted PT history that is not reflected in changes in Ti concentration because they coincidentally traveled along an isopleth, or line of constant concentration). While it may seem ad hoc to assume $a_{\text{TiO}_2}=0.1$ (even in samples with rutile present), there is increasing evidence in the literature to support activity values substantially less than unity, and applying this assumption to Kidder's dataset provides the best agreement with independent lines of evidence. Regardless of the details of their interpretation, the remarkable consistency of Ti-in-quartz measurements from different rock types with different deformation histories, proximity to fault zone, deformation mechanisms, etc., speaks to an efficient kinetic and equilibrium process that is homogenizing quartz Ti contents across a large volume of deforming rock. My primary critique is a lack of supporting information for the SIMS measurements. Not only do these measurements provide the basis of the manuscript, but they are just above analytical detection limits and thus require additional analytical details to ensure confidence. Overall the manuscript is well written and richly documented, and aside from a few areas of concern, I can offer only minor suggested revisions and pose several questions, answering of which may be outside the scope of this paper. Below I provide a summary of general observations from my reading followed by a list of detailed comments linked to line numbers in the text.

Detailed Comments:

Page 2 line 15 “places new constraints on the temperatures and pressures at which mylonitization occur at deep levels of the fault”

Comment: Consider re-wording. I suggest “at which mylonitisation occurred at deep levels of the Alpine Fault.”

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Page 3 line 35 “changes in biotite chemistry indicating a change in temperature during mylonitic deformation of roughly $-340\text{ }^{\circ}\text{C}$ ”

Comment: Please add a reference for this statement

Page 4 line 5 “We used a regression line constrained through the origin to calculate Ti concentrations using National Institute of Standards (NIST) glasses 610 and 612 (434 ± 15 and 44 ± 5 ppm TiO₂ respectively; Jochum et al., 2005).”

Comment: Note misspelling of “through”. I recommend referencing the Jochum et al., 2011 GGR paper that publishes certified values for the NIST glasses instead of the 2005 paper that discusses the founding of the GeoReM database. Also, I would like to see more details regarding SIMS measurements added to this section. This is critically important given the very low values you measured from your samples. Please provide additional details on how you generated the SIMS calibration curve for your measurements – how many spots on the NIST glasses did you require in order to reduce precision on the calibration curve to acceptable levels? Did you make any measurements of the NIST glass as an unknown to evaluate the accuracy of your calibration curve? Why did you not also use the low concentration NIST glass SRM-614? Because your measurements are truly at the bottom of analytical detection limits, and your calibration curve is generated using two materials with considerably higher Ti concentration than your samples (434 ppm in NIST-610 and 44 ppm in NIST-612), the error on your calibration curve becomes magnified. It would be helpful if you plotted your calibration curve in the Supplementary Materials.

Page 4 line 10 “No blank correction was made since this value is far below Ti concentrations measured in the study.”

Comment: Not entirely true. The upper confidence bounds of the Herkimer measurement (~ 105 ppb) are $\sim 40\%$ of your lowest measurement results (240 ppb). Even if you don't apply the blank correction because it makes concentrations even lower than they already are, I would consider omitting the above sentence.

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Page 4 line 16 “We interpret that all, or nearly all, of the analyses with Ti >5 ppm were contaminated, possibly by trace amounts of Fe-Ti oxides”

Comment: This data filtering step needs to be better documented. What percentage of your measurements were omitted based on this 5 ppm cutoff? Do you have evidence from your EDS particle analysis that supports Fe-Ti oxides in samples with elevated Fe/Si ratios? With such high mass resolving power why do you think there would be interferences of Fe mass 56 on the Ti mass 47 and 49 measurements? Do you see this same contamination effect on both Ti masses?

Page 4 line 35 Comment: I would like to see more details of the results of the automated EDS particle analysis “Feature”. As far as I can tell the only mention of these results is y/n for rutile or chlorite in Table 1. How much did rutile content vary between samples? Was there any relationship between rutile abundance and sample Ti concentration? It would be helpful to plot this in similar fashion to grain size vs. Ti conc. plots. This would provide evidence for your activity assumption, and could also shed light on discussion involving local activity buffering (absence of low-Ti measurements in proximity to rutile grains). (I later saw Figure 7: Which minerals are included as “dark minerals”? Biotite, ilmenite, rutile?)

Page 6 line 18 “A paucity of Ti values <1 ppm Ti at distances $<5\text{ }\mu\text{m}$ may be a function of minor contamination of analyses that include grain boundaries (figure 7a)”

Comment: This is counter to my intuition. I would expect partial analysis of grain boundaries to, if anything, result in higher Ti measurements (instead of lower) because of the possibility of intersecting a Ti-bearing phase along the grain boundary. It makes less sense to assume that a low measurement reflects a partial grain boundary measurement because if Ti counts were low because you were in the boundary then the Si counts would be correspondingly low as well.

Page 7 line 32 “The characteristic diffusion timescale (e.g. Spear, 1995) for $250\text{ }\mu\text{m}$ grains using the experimental data of Cherniak et al. (2007) at a peak Alpine Fault

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mylonitization temperature of $\sim 550^{\circ}\text{C}$ (Cross et al., 2015; Toy et al., 2010) is 6 b.y.,”

Comment: Technically you should use the grain radius (since diffusion would progress from the grain centre to the margin) as the effective diffusion distance instead of the diameter, yielding 3 b.y. (your point remains).

Page 9 line 36 “The question of Ti activity is further hindered by competing calibrations of TitaniQ (Huang and Audétat, 2012; Thomas et al., 2010; Thomas et al., 2015).”

Comment: Consider re-wording. Important to note here for the readers that the Huang and Audetat calibration has no activity dependence.

Page 10 line 19 “An absence of Ti values less than ~ 1 ppm at distances $< 50 \mu\text{m}$ from phases containing stoichiometric quantities of Ti (Figure 7B) may indicate such variation”

Comment: Confusing as written. Not sure if you are referring to the previous sentence (that temperature might affect Ti activity) or the sentence before that (that activity might vary spatially within a sample). You don't have any evidence to suggest that activity varies with temperature, and indeed this would complicate your interpretation that exhumation followed the ~ 3 ppm isopleth with activity=0.1.

Page 10 line 26 Comment: Include units for strain rate

Page 11 line 10 “whereas we hypothesize the partial preservation of Ti concentrations and individual larger grains from the entire time period including and predating Alpine Fault deformation.”

Comment: Consider re-wording

Comment: I recommend ordering references chronologically instead of alphabetically, this allows the reader to see the progression of work on a particular topic.

Interactive comment on Solid Earth Discuss., <https://doi.org/10.5194/se-2018-12>, 2018.