

The authors present an extensive dataset of Ti-in-quartz SIMS measurements reflecting a commendable undertaking of skill and analytical investment.

Thank you

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.

We now provide more information on the routine (see below). We also note that it was not made sufficiently clear that the SIMS measurement procedure followed that of Kidder et al., 2013 (Solid Earth), which provided significantly more documentation and verification of the analytical procedure than given here. In the revised version we explicitly state this, and provide additional information such as the calibration curve and analyses of the standards (in a supplement).

The detection limit of the SIMS instrument, incidently, is far below even the lowest values we measured. For example, in 2013, we determined a Ti-in-quartz concentration of 4.5 ± 2 ppb for the Herkimer quartz standard using nearly the same analytical setup as in the current study. The lowest Ti quartz analyzed as part of the current study contained about two orders of magnitude more Ti.

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.”

Ok, changed the wording as suggested

Page 3 line 35 “changes in biotite chemistry indicating a change in temperature during mylonitic deformation of roughly -340°C ”

Comment: Please add a reference for this statement

We moved the reference to Toy et al. (2008, 2010) to the end of the sentence to clarify where this number came from.

Page 4 line 5 “We used a regression line constrained though the origin to calculate Ti concentrations using National Institute of Standards (NIST) glasses 610 and 612 (434 ± 15 and 44 ± 5 ppm TiO_2 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.

We corrected the misspelling and changed the reference as suggested. Twelve analyses of NIST glass were acquired and used for the calibration. This information is now added to the methods section. We now provide the calibration diagram and data in supplementary materials. We did not use the lower Ti NIST standard mainly because it was not available in the Caltech SIMS lab. Because SIMS measurements of quartz show linear increases in Ti+/Si+ ion ratios with increasing Ti content (e.g. Behr et al., 2010) we would not expect a significant change in the calibration from using a standard with lower Ti content.

As mentioned above, the detection limit (and background) of Ti on the SIMS instrument used is much lower than the ppm levels, e.g. as demonstrated by Kidder et al., 2013 who measured the Ti concentration of Herkimer quartz to 4.5 +/-2 ppb. In the current study, we deliberately shortened acquisition time in order to collect more data at the expense of somewhat noisier results. Using the shortened acquisition time, most our measurements (~2-3 ppm) are still more than an order of magnitude above the levels measured in the Herkimer quartz “blank” (~0.08 ppm, as mentioned in the text).

Finally, the same instrument and protocol were used in the Kidder et al. (2013) study. In that study, we tested the calibration curve against quartz standards obtained from Jay Thomas and found results within error of the independently-obtained values. The difference between the current and 2013 calibration is insignificant in terms of the final temperatures that are calculated (about 1 degree difference).

We did not use any NIST measurements as an unknown, but inspection of the calibration curve in the supplement shows that the standards measurements were quite uniform.

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 ~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.

We changed it to simply say “No blank correction was made.” (removed “since this value is far below Ti concentrations measured in the study.”)

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?

52 data points, or ~7% of the measurements were removed (this has been added to the text). And, yes, all of the samples contain Fe-Ti oxide. We do not mean to suggest that there was interference (almost certainly there wasn't)—simply, if a trace amount of Fe-Ti oxide were analyzed along with quartz, the analysis would show both elevated Fe and Ti levels. We interpret that the elevated Fe counts associated with elevated Ti values indicate this scenario, not actual high Ti sourced from the crystal lattice of quartz. (Possibly one might correct for this by subtracting out equivalent contents of the Fe and Ti to isolate the quartz concentration, however we also observe in backscatter images that Fe-Ti oxides are sometimes intermingled with variable amounts of a pure Ti phase.)

We've added to the text that “small grains of Fe-Ti oxide are common in all of the samples”

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?)

We added this text (section 6.1) “In samples containing rutile, it's abundance relative to other oxides varied from about 2% to 97%, but these values are not correlated with average Ti concentrations of the samples.” We made the plot but it doesn't show a trend so don't think it should be added as a figure. We also now list (section 6.1) the most common “dark” minerals observed: “biotite, hornblende, ilmenite, magnetite or rutile”

Page 6 line 18 “A paucity of Ti values <1 ppm Ti at distances <5 μm 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.

We had the same understanding, however the wording wasn't clear. We infer that low Ti quartz was analyzed along grain boundaries, but that it was contaminated (brought to higher levels) such that we don't actually get any low-Ti measurements of grain boundaries. We have changed the wording to clarify our meaning here.

Page 7 line 32 "The characteristic diffusion timescale (e.g. Spear, 1995) for 250 μm grains using the experimental data of Cherniak et al. (2007) at a peak Alpine Fault 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).

Good point. And actually for a distance of 125 microns the time scale is 1.5 b.y. We have modified the text accordingly

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.

The formulation presented by Huang and Audetat does not contain an activity variable, however we believe they intended that a simple correction for activity be made and implemented in their formulation (using the product of Ti concentration and Ti activity in place of Ti concentration). This was previously done in several publications already, e.g. Cross et al., 2015; Audetat, 2013; and implicit in Huang and Audetat (2012) since they tested their calibration using quartz with non-unity Ti activity. It seems clear to us that Huang and Audetat did not intend that their calibration only be used in cases where Ti activity was 1.0, and assumed that users would make the correction we have made.

In any case, the point made in our paragraph is that not only do we often not know Ti activity, but even in cases of quartz crystallized at a well-constrained temperature, uncertainty is introduced by the existence of two TitaniQ calibrations. We have modified the wording slightly to clarify this.

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.

We were suggesting both (variation locally but only at low temperature). We've clarified this and heavily edited the paragraph to present the idea more clearly. It now reads "While it is convenient to assign a single value of a_{TiO_2} to a suite of rocks such as our sample set—and the overall consistency of Ti-in-quartz concentrations in different lithologies generally supports this (Figure 5)—sample- or micro-scale variations in a_{TiO_2} due to local differences in bulk or fluid composition may exist. Additionally, activity of TiO_2 could also vary with temperature (Ashley and Law, 2015). An absence of Ti values less than ~1 ppm at distances <50 μm from phases containing stoichiometric quantities of Ti (Figure 7B) hints at both types of a_{TiO_2} variation. The absence of Ti values <1 ppm could be explained if a_{TiO_2} was higher than 0.1 in the vicinity of high-Ti minerals during the latest phase of quartz recrystallization. A change in a_{TiO_2} to a value of 0.5 in the immediate vicinity (<50 μm) of Ti-bearing phases at temperatures of 300 °C would stabilize Ti concentrations at 1 ppm and explain the local absence of lower Ti measurements. The extent of recrystallization at these conditions was relatively minor, as suggested by the low frequency of such analyses (Figure 7) and their location only within 30 μm of grain boundaries (Figure 7a)."

Page 10 line 26 Comment: Include units for strain rate

Done

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

Changed to "whereas we hypothesize that larger grains were preserved from before and throughout Alpine Fault deformation and that these grains record a history of equilibrium Ti concentrations that happen to have varied little over time."

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

We agree and changed the order accordingly.
