Interactive comment on* "Surface paleothermometry using low temperature thermoluminescence of feldspar" *by Rabiul H. Biswas et al.

Anonymous Referee #1

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General comments:

The authors are investigating an interesting question–whether luminescence signals from K-feldspars in bedrock might archive changes in recent temperatures at Earth's surface. More specifically, they ask whether we can resolve recent changes in temperature periodicity. This question is important and worth pursuing.

I commend the authors for the layout of this study. Their approach involving sensitivity analyses, calibration to sample specific kinetics and attention to climatic complexity have resulted in an interesting manuscript with potential for significant scientific impact.

We appreciate the reviewer for discerning the potential of this work.

However, the present work needs significant clarification and expansion to yield a robust estimate of past temperatures. Specifically, the authors must determine how changes in amplitude, period, and mean temperature influence luminescence signal growth and depletion in a holistic way. Currently, the treatment is partial. Once this is done, the authors should give a more direct comparison of actual and predicted temperature histories in order for the reader to better examine the predictive success of the model.

Please see the replies below.

These points and others are detailed below.

1/22: "Earth's climate fluctuates in a cyclic way" While there are many internal cycles to climate systems, this characterisation might be too simplistic, especially at the timescales involved here (~10ˆ1 - 10ˆ2 kyr), where abrupt periods of change are common. Temperature changes during the Holocene, for example, can hardly be approximated as cyclic.

We have changed the sentence to… "*Earth's climate fluctuates, from seasonal to million-year time scales driven by Earth's orbital processes and rare shifts and extreme climate transitions over timescales of* 10^3 *to* 10^5 *years*".

1/35: "equivalent diffusion temperature that is always higher than the actual mean temperature" This statement, while true, gives the false impression that this is an intractable bias. For a system with well-characterised diffusion kinetics, the relationship between a given temperature history (e.g., a forward model) and the EDT is well known. In other words, paleothermometry using the He-3 paleothermometry technique must rely upon comparisons against prescribed temperature histories in the same way as paleothermometry with luminescence techniques. This is not a comparative disadvantage of the noble gas technique, but a similar limitation as faced in the current study.

This is true. We meant that a single thermometric system (OSL or ^{3}He) will always provide a single equivalent temperature (like EDT in ^{3}He) for a complex thermal history whereas a multi thermometric system (here TL) with different temperature and time sensitivities will have the potential to infer a more complex thermal history. The following text has been added: "*For a system with well-characterised diffusion kinetics, the relationship between a given temperature history and the EDT is well known, so the paleotemperature can be corrected and estimated.*"

2/6: The distinction between thermochronology and paleothermometry is not entirely clear in the language of this study. If what you aim to resolve is the temporal variation of temperature through time, you are describing thermochronology. If instead, you mean to resolve a past temperature which is representative of some time period (the measurement of which will be affected by seasonal variability and so on), then what you are describing is paleothermometry. I would encourage more precision when you describe these concepts.

Paleothermometry is a methodology for determining past temperature, and thermochronology is the study of the thermal evolution of rocks, and they both rely on the same principle. However, thermochronology is more commonly used for rock cooling related to exhumation. So to avoid confusion, we now use paleothermometry throughout the manuscript. We only refer to thermochronometry when we refer to previous work, which was developed for thermal evolution of rocks associated with exhumation.

2/12-21: Please add corresponding references for these observations.

Amended.

2/36ff: The physical meaning of this model is unclear. This is obviously of fundamental importance, as the kinetic model that is chosen will determine all predictions of past thermal history.

From Eq. 1, it would seem that the authors expect to model some number of individual traps, each with a singular values for D0, E, s, s-tilde, rho', a, and b. All of these traps are modelled as disconnected.

And yet, the transition in parameter values from one measurement temperature bin to another is smooth. This is true for D0, for rho', for E, for s, and for b within Fig. 1. This observation strongly suggests continuity in the underlying kinetics, not only for trap depth(s) but for the system as a whole. To fit each measurement bin as a separate and disconnected trap seems suspect. A unified treatment would be preferable.

Several studies suggest that broad TL glow curve from feldspar arises from a continuous distribution of trapping energies, which is suggested by several methods, like T_m-T_{stop}, the initial rise method, and analysis of fractional glow curves (Biswas et al., 2018; Grün and Packman, 1994; Pagonis et al., 2014; Strickertsson, 1985). Regardless, it is difficult to isolate a single trap with distinct kinetic parameters. Instead we assign the most probable kinetic parameters for each thermometer (glow curve temperature) along the TL glow curve and in this manner we determine kinetic values in a continuous, rather than in a disconnected manner. This is the method that we have adopted here and in Biswas et al. (2018). We then arbitrarily choose 10 °C TL temperature windows as distinct thermometers. A continuous distribution of trapping energies can be assumed as the sum of a large number of discrete traps (Pagonis et al. 2014). Thus a continuous distribution of trapping energies is discretized as shown in the figure below.

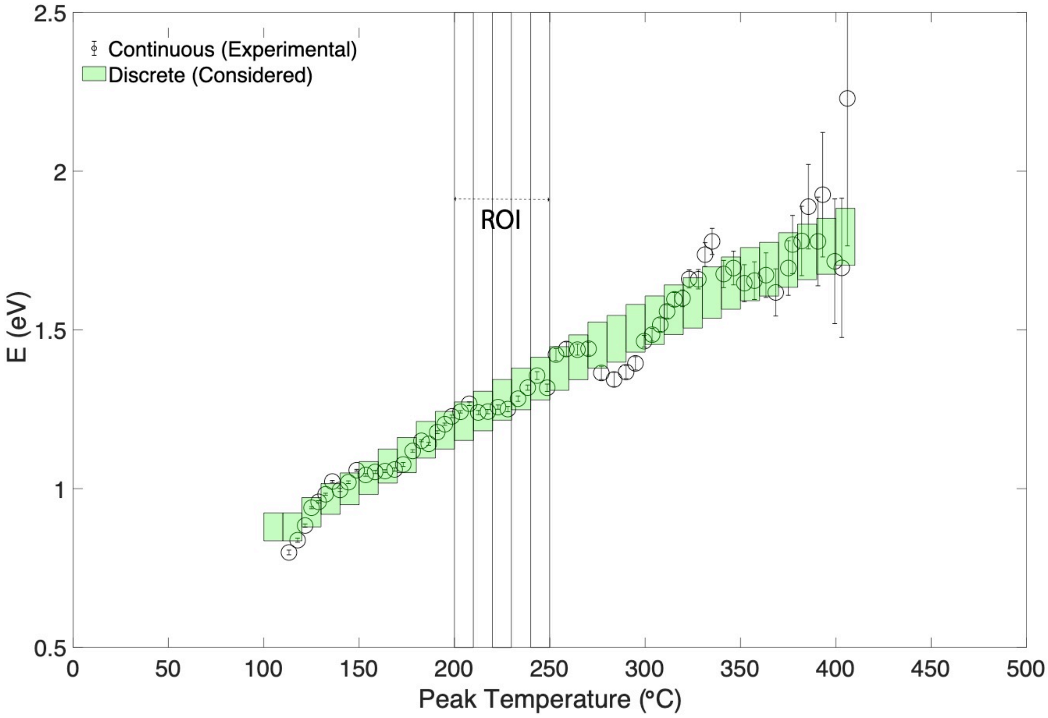

Fig. X: The evaluated continuous distribution of trap depth (E) of sample MBTP1 (circles with error bar) and its discretization in 10 °C windows (green box; width is 10 °C and height 5 % of the median value).

Another issue to address is whether the same recombination centers are accessed by this distribution of traps during athermal fading. If so, as would seem unavoidable to some degree, rho should be kept constant (the density of centers being a property of the material). rho' can then be related to the underlying activation energy via the alpha term. This should be attempted for internal consistency.

Here we only use ρ', which includes alpha as $\rho' = \frac{4\pi\rho}{3\alpha^3}$. Alpha controls the rate of fading through the lifetime $\tau = s^{-1}\exp(\alpha r)$. It is expected that with increasing activation energy fading rate (ρ') should decreases as the tunnelling depth increases. Indeed we get similar relationship between fading rate (ρ') and activation energy (Table 1) as shown in figure below.

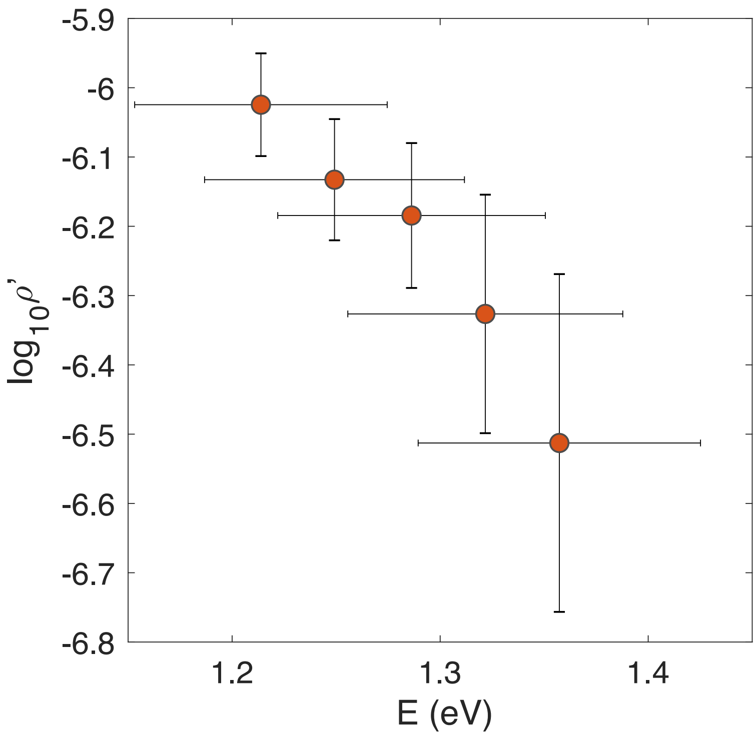

Fig. XX: Plot of distance dependent fading rate (ρ') and activation energy (E) of five thermometers (200-250 °C, 10 °C interval) of sample MBTP9.

According to the second term on the RHS of Eq. 1, it seems that the authors model thermally-activated recombination locally (since the term is dependent upon the nearest neighbor distribution). If so, then observations of signal loss at room temperature could also be caused by this pathway. This deserves comment.

Thermal loss of the TL signals which is a more diffusive process (athermal) can occur through the conduction band. However, the power term *b*, accounts for the nonlinearity (delayed) arise due to presence of band-tail states. However, athermal fading is known as a tunnelling process. Separate treatments of thermal and athermal loss has adopted successfully in several previous studies (Guralnik et al. 2015 for IRSL of feldspar; Biswas et al. 2018 for TL of feldspar).

3/29-30: Can we be confident that the kinetic parameters pertain to geologic timescales? Specifically, is there good evidence or reason to think that mixed order kinetics are predicted at low temperatures and long timescales (natural) as well as high temperatures and short timescales (lab)? Competition effects, for example, could easily produce observations of $b > 1$ for lab measurements whereas the concentration of charge activated on natural timescales would be orders of magnitude smaller.

This is a difficult question and can never be answered in true sense but the premises of the approach used here was validated in Biswas et al. (2018), by successful recovering temperatures experienced by rocks in the KTB borehole, which have been in thermal steady state for several millions of years. We have included that statement in the manuscript.

4/19 and Fig. 3: I find this figure a little difficult to interpret. In particular, the way that you have defined 'memory time' should be a bit clearer. If I've understood the meaning of this metric correctly, one suggestion would be to compare everything against 'tchange = 100ka' or to extend the x-axis to include 't-change=150ka.' By doing this, you could then visually show the meaning of the 't-memory' by comparing two horizontal lines, one at t-change=150ka (or 100ka, depending), and the other at the asterisk height. You could then annotate this difference as 20%.

Amended as recommended. In the figure the 20% changes have been demonstrated clearly and text has been added in the figure title (Fig. 3).

It would be good to consider also the influence of measurement uncertainty. Accurately resolving the difference between [n-bar] = 2.0e-3 and 2.4e-3 would likely involve a lot more relative uncertainty than discerning between, say, [n-bar] = 0.5 and 0.6.

Typical photon counts of the present sample for near saturation ($\bar{n} = 1$) is >10^5 counts per second (cps), our instrumentation can resolve a few hundreds of cps with 20% uncertainty ($\bar{n}$ of the order of 10^{-3}). This is discussed in Section 4.3 as "*Typically, the minimum detectable limit for the present instrument is ~ 300 photon counts per second (cps) considering the signal should be three times of background level which is ~ 100 cps. The present highly luminescent feldspar has maximum photon count of ~10^6 cps. This restrict to use the TL signals up to ~10^{-3} % of maximum TL signals*"

4/30-31: '10 - 100 kyr timescales' This should be a bit more specific. During the Quaternary, the 100kyr and 41kyr periods were most dominant (e.g., Raymo et al., 2006; Hinnov, 2013).

We have changed the sentence to "*In nature, climate varies on a daily and seasonal basis and follows periodic variations in the Earth's orbit, known as Milankovitch cycles, at 25.77, 41 and 100 kyr*"

Fig. 4: This is a nice figure. Please adjust so that the 'thermometer' labels correspond to each panel. For example, in panels j-l, if the reader uses the labels on the far righthand side, they might conclude that the bottom-most series in panel k refers to the 220-230C chronometer.

Amended as recommended (Fig. 4).

5/7: 'implies a gradient' I would say this behavior more accurately 'results' from a gradient in thermal stability, given that the kinetic parameters are imposed and known.

Amended.

5/9: 'the thermal stability decreases with increasing temperature.' I disagree with this statement. The thermal stability for a given TL thermometer is known and fixed in your setup. So it is not the stability that is changing, but rather the probability of detrapping.

Thanks for pointing this out. The sentence has been reworded to "*This is because the probability of detrapping increases with increasing temperature*".

5/10: 'the higher temperature TL thermometers remain relatively insensitive to such periodic temperature forcing.' This is misleading. The insensitivity of the higher-T thermometers reflects the mean temperature values that you have chosen. If the temperature oscillated about a higher mean value, the same periodic filling/emptying behavior would be seen with the high-T thermometers. This is evident in Fig. 4 panels j-l, where different thermometers oscillate with comparable magnitude when a range of mean temperatures are tested.

The sentence has been changed to "*Finally, the higher temperature TL thermometers (near to 300 °C) remain relatively insensitive to such periodic temperature forcing (T_{mean} up to 30 °C); with increasing T_{mean} the higher temperature TL thermometers become more responsive.*"

5/13: '10 ka to 1 Ba' If Ba represents 'billion years,' please change to 'Ga.'

Amended.

5/15: 'For P « tau' This comparison must be qualified. The lifetime (tau) will depend on a chosen, singular temperature value. Choosing a singular temperature value for oscillating temperature requires some simplification that is not described (e.g., mean temperature? EDT?). Please clarify this issue.

The sentence has been clarified to "*For $P<<\tau$ (e.g. Fig. 4d where P=1 ka and τ spans ~10 ka to 1 Ga for the 200 to 300 °C TL thermometers for T_{mean}= 0 °C), the value of $\bar{n}_{osc}$ exhibits small fluctuations but always remains lower than $\bar{n}_{iso}$*"

5/16: 'This result implies that smaller periods (<1 ka) do not influence trapped charge equilibrium levels in an oscillating fashion and cannot be differentiated from the trapped charge population resulting from an isothermal condition.'

This statement is incomplete and only conditionally true. For argument's sake, assume that the 200C TL thermometer has a lifetime of 10 ka at 0C. If the ambient temperature oscillated with an arbitrarily large amplitude (say 100C to make the point obvious) but with a period of only 1 ka or 100 yr, you would find that the fractional saturation would oscillate in response to the temperature forcing, depleting completely and then partially regenerating.

This won't happen if the temperature period is much smaller than the growth timescale (D0/Ddot). If that is the case, then the thermal imprint upon the sample approaches a steady value determined by the maximum temperature experienced.

Temperature amplitude and the relationship between the forcing period and sample growth timescale both matter. To make this comparison between lifetime and period, these factors must be incorporated.

The sentence has been modified to "*This result implies that smaller periods (<1 ka) and T_{mean} (<30 °C) do not influence trapped charge equilibrium levels of 200 to 300 °C TL thermometers in an oscillating fashion and cannot be differentiated from the trapped charge population resulting from an isothermal condition. We must mention here, if the amplitude of oscillation increases the oscillating response to trapped charge equilibrium levels will be relatively prominent.*"

5/19: ’remains correlated’ and ’deviates from...temperature forcing’ The meanings of these statements are unclear. n-bar behavior is distinct between isothermal and oscillating temperature histories for all periods; it is not an issue of matching and not matching, except for the highest-temperature systems, which are insensitive to the temperatures prescribed here. Please be more specific with these observations and, following from the previous comment, please do incorporate growth timescales, as these are of obvious relevance here.

Clarifications have been made. The sentence has been changed to “*Similarly, the present day* $\bar{n}_{osc}$ *remains indistinguishable from* $\bar{n}_{iso}$ *when* $P>>\tau$ *(e.g. see the behaviour of the low temperature TL thermometer shown in Fig. 4l)*”

5/24: ’Therefore, temperature variations can be reconstructed...’ Just to reiterate, you must demonstrate the complex relationship among mean temperature, temperature amplitude, trap stability and regenerative timescales before attempting to reconstruct temperature variability. Additionally, what has been shown in Fig. 4 is that, for a given amplitude, different periods leave different imprints upon the shown thermometers. You have not yet demonstrated that you can accurately reconstruct differences in variability. Moreover, the results from Fig. 5 (panels b, c) seem to indicate that you cannot easily differentiate between various amplitudes or periods.

This is discussed in section 2.2.2 and Fig. 4 where we show that the present day trapped charge population ($\bar{n}_{present}$) is highly sensitive to the mean temperature (T_{mean}) and less sensitive to the amplitude of oscillation (T_{amp}) and period (P). Moreover, we also mention that “*Although the* $\bar{n}_{present}$ *is less sensitive to the amplitude and the period, the pattern of* $\bar{n}_{present}$ *for different thermometers is distinguishable*”. Additionally, now we have added a new synthetic test to emphasis the sensitivity of the three periodic parameter (T_{mean}, T_{amp} and P) on the present day trapped charge population ($\bar{n}_{present}$) in section 3 as follows:

“We choose three arbitrary periodic thermal histories, Path1 (T_{mean}= 10 °C, T_{amp}= 10 °C and P= 25.77 ka), Path2 (T_{mean}= 20 °C, T_{amp}= 10 °C and P= 25.77 ka) and Path3 (T_{mean}= 10 °C, T_{amp}= 20 °C and P= 25.77 ka). For each thermal history, the present day trapped charge concentrations ($\bar{n}_{obs}$) are calculated for four TL thermometers (210-250 °C, 10 °C interval) as described in section 3.1. We then invert the TL data ($\bar{n}_{obs}$) into a thermal history as described in section 3.2. For the inverse modelling, we first generate a large number of random periodic histories (300,000) with T_{mean} and T_{amp} randomly varying from 0 to 50 °C, P randomly varies between three cycles, 25.77, 41 and 100 ka. The reason we do not vary P in a completely random fashion is that $\bar{n}_{obs}$ is less sensitive to P; it is difficult to resolve close periods (as discussed in section 2.2.2 and Fig. 5). The results are shown in the figure below (Fig. XXXa,b,c). Although this approach predicts the very recent temperature well (up to max 5 ka) it loses the periodic information (25.77 ka) because of the significant number of accepted thermal histories with different periods (41 and 100 ka). The same exercise was repeated but fixing the period to 25.77 ka for the inversion. The results are shown in Fig. XXXg,h,i. Interestingly, this approach enables to recover the actual solution within 1σ uncertainty. This shows that a periodic thermal history can be predicted well if the period is known a priori; it enables to constrains T_{mean} and T_{amp} satisfactorily. To circumvent the limitation (period) of this method we use the $\delta^{18}O$ data to impose the shape of the thermal histories as a priori information. This is typically done for inversion problem when appropriate. We then constrain T_{mean} and T_{amp} of the spectrum (as discussed in section 3).

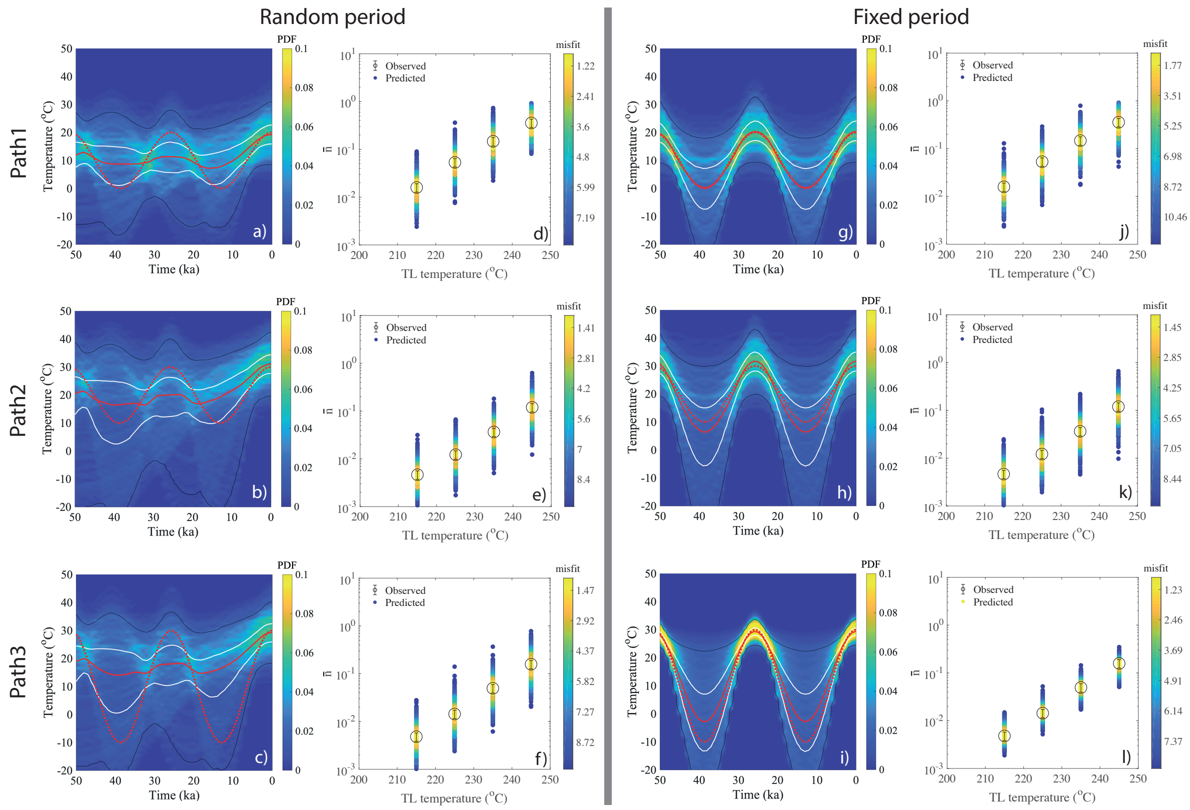

Fig. XXX: Result of synthetic experiments for the three periodic thermal histories as described above. a), b) and c) are the inferred probability density functions when T_{mean}, T_{amp} and P are randomly varied. d), e), and f) depict the fit between the observed TL (obtained through forward modeling). The solid red lines show the predicted median, white lines and black lines show the 1σ and 2 σ confidence intervals in the probability density distribution g), h) and i) are the inferred probability density functions when T_{mean}, and T_{amp} are randomly varied but P is fixed. j), k), and l) depict the fit between the observed TL (obtained through forward modeling)

5/31-33: 'This ensures that complex thermal histories...can be reconstructed.' Following from the previous comment, this is not yet demonstrated.

See the answer above.

6/11: 'considering that the other parameters are identical.' Unclear what this means. From Fig. 1, it would seem that the kinetic parameters other than the thermal parameters (E, s) vary between the thermometers. Or do you mean something else?

We agree this was confusing. We have now removed these unnecessary words.

Fig. 7: This is not the most informative way to show your predictive ability. Unlike with thermochronology studies, where the T-t path is really the predicted feature, what you are more accurately doing is predicting the temperature minimum and amplitude (e.g., ll. 5/24-29). So, it would be much more informative to see these values, actual and predicted.

It is true that the only difference with the inversion of thermochronometric data is that we impose the shape of δ^{18}O. To address the reviewer's comment we have added histograms of the two main scaling parameters: the minimum temperature T_{base} (temperature at 20 ka) and the present temperature, $T_{present}$ (which is $T_{base}+T_{amp}$ as shown in supplement Eq. S9).

Additionally, the current figure makes it appear as if you are able to resolve the fine structure of the T-t series, which of course you are not.

Indeed, we cannot. Rather this figure shows the scaling of the δ^{18}O curve. The reply to the previous comment should have addressed this comment.

7/16-18: '[Fig. 7a,b,c shows] it is possible to recover all three thermal histories within the 1-sigma confidence level.' My previous comment will apply here as well. What matters for this experiment is the degree to which you are able to predict amplitude and minimum.

To demonstrate that you could recover an arbitrary thermal history well, you would need a different test.

Please see the reply of previous comment. We clearly mention we need prior information for the pattern of the thermal history (δ^{18}O), as typically done for inversions, but that we can constrain the temperature minimum and amplitude.

8/7: 'This restrict...' Grammar

Amended.

8/15: This dose range, with upper doses at 0.9 and 1.9 kGy may not be sufficient to observe saturation in K-feldspar TL. Please demonstrate that these signals are saturating or add greater doses to better constrain lab saturation intensity.

1.9 kGy is sufficiently high as it is greater than $2D_0$; maximum D_0 is less than 800 Gy (see Table 1).

8/33: 'no effect for doses below 100 Gy' Wouldn't the far more important question be whether there is sensitivity change above 100 Gy? After all, the majority of given doses are above 100 Gy and these responses allow you to determine the saturation values.

The sensitivity change in the NCF method permits determination of the equivalent dose correctly by correcting for possible sensitivity changes during a sample read out and is generally tested on low doses (see Singhvi et al. 2011).

9/13-15: 'The rationale here is that all temperatures follow the delta O-18 data, but the amplitude...and mean temperature are unknown.' Please make clear that this is a stated assumption and not an inference from studies (unless it is, in which case state that). I think is not obvious that the climate signal on Mont Blanc would mirror a Greenland ice core signal, so this assumption probably warrants justification.

To clarify, the text has been modified as follows "*It is assumed that the atmospheric temperatures of the Mont Blanc massif followed the trend observed for the Greenland ice core data over the last 60 kyr. Note that temperature increase during the last glacial cycle was synchronous with the temperature anomalies observed in Greenland (e.g., Schwander et al., 2000; van Raden et al. 2013).The rationale here is that all temperatures in the Mont Blanc massif follow the Greenland ice core $\delta^{18}O$ data but the amplitude of temperature oscillation (minimum temperature at ~20 ka to maximum temperature at the present day) and mean temperature are unknown.*"

Fig. 9: Is Fig. 9 referenced in the main text?

Now it is mentioned.

Fig. 9 and 10: As with Fig. 7, please recast to compare the predicted and actual values for the amplitude and base temperatures as these are the variables being investigated.

We have now added subplots (histograms) of the two parameters, temperature minimum which we define as T_{base} (temperature at 20 ka) and present temperature, $T_{present}$ (which is $T_{base}+T_{amp}$ as shown in supplement Eq. S9).

9/28: 'can constrain thermal history of ~50kyr.' I do not think this has been demonstrated yet, as an extension of my comments regarding pg. 5.

In Fig. 3 we show that t_{memory} can be up to 50 kyr for typical temperature of 10-20 °C. If the amplitude of temperature change is higher, the method will be sensitive, thereby improving our ability to constrain the thermal history constraining of thermal history will be more precise.

Also, unclear what 'A higher temperature fluctuation' means and whether you've actually shown this.

This is shown in Fig. 3.

10/14: 'At those depths [of 7 and 62 cm], mean temperature should be constant.' Certainly, there will be seasonal temperature variability at a depth of 7 cm. Is this what you meant to say?

We mean that at depths of 7 and 62 cm the rock temperature will be equilibrium with the atmospheric temperature. The sentence has been modified to "*At those depths, mean temperature should be in equilibrium with atmospheric temperature (e.g. Hasler et al. 2011)*"

10/17: For inverse modeling of a natural sample, the time-temperature histories were completely random' If I have understood the previous text correctly, the histories are very much not random, but are tied to the Greenland delta O-18 temperature proxy with variability only in amplitude and initial temperature. Please reword.

The sentence has been reworded to "*$\delta^{18}O$ data is used as a prior on the shape of the thermal histories, but we leave two scaling parameters free – minimum temperature at 20 ka, and amplitude (temperature difference between at 20 ka and present)– and we did not include the role of ice on setting the rock temperature while it was ice covred.*"

Discussions generally: I won't comment much on these inferences about past climate systems at this stage, because I think it will be very important to first demonstrate model success in capturing simple variations within a periodic forcing model, which, at this stage, has not been done.