

Geochronology Discuss., author comment AC2
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Reply on RC2

Natacha Gribenski et al.

Author comment on "Cosmogenic ^3He paleothermometry on post-LGM glacial bedrock within the central European Alps" by Natacha Gribenski et al., Geochronology Discuss., <https://doi.org/10.5194/gchron-2022-1-AC2>, 2022

Comment on gchron-2022-1

Gribenski et al. (2022)

Geochronology Review

Referee #2 (Samuel Niedermann)

General comment

The authors have measured cosmogenic ^3He in quartz from two Alpine altitude profiles, with the aim to study paleo-temperature conditions in these areas that were gradually deglaciated after the LGM. They did the diffusion experiments that are required for a correct interpretation of the data and applied a lot of care in devising their experiments and model calculations, but obtained results that are difficult to interpret because temperatures recorded by cosmogenic ^3He are generally lower than expected based on the models. They discuss possible explanations for the discrepancy, but cannot give a final answer. Nevertheless, I think this is an important paper as it shows the difficulties (but also the potentials) involved in the rather new cosmogenic ^3He paleothermometry method and may thus prevent other scientists from misinterpreting their own data. With regard to the methods used, there is one thing that was not optimal in my opinion: Obviously, the helium analyses were confined to ^3He (at least nothing else is reported). Measuring ^4He also would have revealed any possible contributions of nucleogenic ^3He , which may lead to an overestimation of cosmogenic ^3He as argued in more detail below.

For the most part, the paper is written clearly and concisely. The English is generally fine, but suffers from quite a lot of small minor defects such as missing articles etc., which is a bit annoying given the fact that at least three co-authors are native English speakers. I have tried to point these out in the manuscript. Anyway, I recommend this manuscript for publication in Geochronology after minor revision has taken account of the specific and technical comments given hereafter.

We thank Dr. Niedermann for his positive appreciation of this study, his thorough reviewing of the manuscript and his very constructive comments.

We did measure ^4He in addition to ^3He ; we address this point further below in the corresponding specific comment ("lines 172-182" and "lines 523-537").

All the edits directly indicated as comments in the pdf manuscript attached with the submitted review will be implemented. Likewise, all the suggested or requested text/figure modifications listed in the specific comments below were carefully considered, and we will implement most of them (cf. detail below).

Specific comments:

lines 172-182, the authors briefly describe the methods used for ^3He determination. Surprisingly for me, they don't mention anything about ^4He , and because there are no ^4He or $^3\text{He}/^4\text{He}$ data in the tables either, I assume they have not even checked for ^4He concentrations (otherwise those data should be given). This is a pity in the context of the discussion that many samples seem to contain more cosmogenic ^3He than expected (see below).

We did measure the amount of ^4He released by our natural samples during the two heating steps at 800 and 1100°C. The amount of ^4He (in atoms; together with the amount of ^3He for comparison) released during the 800°C heating step will now be reported in an additional table in the Data Supplementary (new Table S3).

While there was often some ^4He released during the 1100°C step, no ^3He above the blank level was ever measured during this heating step. Based on experiments quantifying helium diffusion kinetics presented both here and in previous works (e.g., Tremblay et al., 2014b), we argue that the ^4He released during the 1100°C step is unlikely to come from the quartz itself but from mineral inclusions. Therefore, we will only report ^4He and ^3He amounts for the 800 °C heating step. Furthermore, because it is evident that we did not fully degas the ^4He present in each aliquot despite fully degassing the ^3He , we will report ^4He measurements as amounts (atoms), rather than concentrations (atoms/g).

Please refer to our answer below (specific comment "line 525-537") for further discussion about a possible contribution of nucleogenic ^3He , using the information from the measured amount of ^4He released during the 800°C heating step.

Line 177: Why were blanks (only) measured at room temperature? Did you ever check whether they remain the same at higher temperatures up to the level used in the experiments? Otherwise that assumption seems a bit optimistic.

During a diffusion experiment, it is not possible to measure high-temperature blanks on the PtIr packet because this would also heat the sample and therefore ruin the step-heating nature of the experiment. However, at the end of the experiment when the sample has been fully degassed, we in essence do measure high-temperature blanks on the PtIr packet. We find that the ^3He signals in these high-temperature 'blanks' are equal to those measured in the low-temperature blanks. Furthermore, in previous step-heating experiments we have heated empty PtIr packets from the same manufacturer and batch and found that they degas no helium above blank level. Aside from the PtIr packet and the sample inside of it, no other part of the diffusion cell apparatus is heated by the diode laser in our experimental setup.

In lines 523-537 the authors discuss a possible contribution of nucleogenic ^3He in the samples that has not been accounted for. They conclude that it "does not contribute significantly", but their arguments are not very convincing because they have (obviously) not measured ^4He . It is known that purely radiogenic/nucleogenic He is characterized by

typical $^3\text{He}/^4\text{He}$ ratios of $\sim(2\pm 2)\times 10^{-8}$. Thus, if the measured $^3\text{He}/^4\text{He}$ ratios in their samples were on the order of 10^{-6} for example, the nucleogenic ^3He would be in the percent range at most and could safely be neglected. In my lab, I have measured several samples from similar settings (Mont Blanc area as well; work in progress) using two extraction steps of 600°C and 1000°C . While the 1000°C steps showed ratios in the 10^{-8} range as expected for radiogenic/nucleogenic He, the ratios in the 600°C steps varied from $\sim 6\times 10^{-8}$ to several times 10^{-6} , implying that the nucleogenic ^3He contribution is not always negligible even in the low temperature step. Since the authors used 800°C as the first heating step, this is even more relevant for their samples. Their arguments for negligible nucleogenic ^3He are not very powerful. Assuming the same diffusion characteristics for nucleogenic and cosmogenic ^3He is probably not valid, since nucleogenic He is produced at different places in the minerals (namely, where Li is found, which is probably concentrated in mineral or fluid inclusions rather than in the quartz crystal itself). The fact that nucleogenic He is still degassed above 600°C while cosmogenic He is not shows on its own that the diffusion characteristics are different. Also, comparing the production rates of cosmogenic and nucleogenic He is not meaningful at all, since nucleogenic He has been produced over many millions of years, compared to the ~ 10 ka production of cosmogenic He. I don't say that the overabundance of cosmogenic ^3He in the authors' samples is indeed due to nucleogenic ^3He , but because of the lack of ^4He data it is difficult to rule it out.

As mentioned in our response to the specific comment lines 172-182, we did measure the amount of ^4He released by our natural samples and will report this information for the 800°C heating step in the newly added Table S3 in the revised Data Supplementary).

Dr. Niedermann is correct that nucleogenic ^3He derived from thermal neutron capture on Li is, presumably, present in our samples in some amount greater than zero. For background, the source of thermal neutrons for this reaction is decay of U and Th distributed throughout the whole rock, so the production rate of ^3He from Li per unit Li is the same in quartz and in any hypothetical inclusions that are more retentive than quartz. Thus, the distribution of nucleogenic ^3He from this process reflects the distribution of Li.

Dr. Niedermann hypothesizes that Li may be concentrated in retentive inclusions. In this case a significant amount of nucleogenic ^3He would be concentrated in these inclusions, and some of it would be released in the first heating step. If this is true, just as we see a large fraction of total ^4He in the higher-temperature heating steps, we would expect to detect ^3He above background in the higher-temperature heating steps. We did not see this in any sample. Instead, ^3He signals in all 1100°C steps measured were indistinguishable from blank. Therefore, retentive inclusions may contribute a nonzero amount of nucleogenic ^3He , but this amount is not detectable.

The alternative hypothesis that would allow for a significant contribution of nucleogenic ^3He in the low-temperature heating step would be that Li is present in the quartz or in inclusions with retentivity that is similar to or lower than quartz. If this were the case, the maximum concentration of nucleogenic ^3He that could be observed in our low-temperature heating steps would be limited by its production rate and the diffusion kinetics of quartz. The nucleogenic ^3He production rate in quartz for a granite with average composition (3.5 ppm, U, 16 ppm Th) and quartz with 70 ppm Li (maximum concentration measured for the Aare granite; Schaltegger and Krähenbühl, 1990) is approximately 1 atom/g/yr. For the diffusion kinetics measured in our quartz samples, and assuming a 0.850-mm radius quartz grain (in between the two median grain sizes for our samples) at 0°C , the steady state nucleogenic ^3He concentration would be at

most 2.8×10^4 atoms/g, which is two orders of magnitude less than our measured concentrations of cosmogenic ^3He and therefore undetectable.

The only way this reasoning could truly be tested would be to obtain samples of the same lithology from the deep subsurface that have not been exposed to the cosmic-ray flux. Nonetheless, the above reasoning strongly indicates that significant nucleogenic ^3He is not present in our quartz samples. Thus, we conclude that the contribution of nucleogenic ^3He to our measured ^3He concentrations in the first heating steps is at or below the level of measurement error and therefore undetectable.

Even if we ignore all of the above reasoning and estimate a non-cosmogenic ^3He amount using a $^3\text{He}/^4\text{He}$ ratio for a radiogenic/nucleogenic component of $\sim(2\pm 2)\times 10^{-8}$, as quoted by Dr. Niedermann, we find that this amount of non-cosmogenic ^3He is not significant. Specifically, the calculated amount of non-cosmogenic ^3He released during the 800°C step is in all cases smaller than the uncertainty of the total ^3He amount measured. Finally, we observe no correlation between amounts of ^3He and ^4He released in the 800°C heating steps in samples from either transects (see plots in Fig.RN1 in attachment), and we would expect to observe a correlation if there were a nontrivial amount of nucleogenic ^3He present in our samples.

We will now modify the main text in order to consolidate our argument for negligible nucleogenic ^3He as follows:

"[...] However, we think it is unlikely that there is significant nucleogenic ^3He in our samples for several reasons. First, the $^3\text{He}/^4\text{He}$ ratios we measured during the 800°C heating step are on the order of 10^{-6} to 10^{-7} (Table S3). This is more than an order of magnitude above the $^3\text{He}/^4\text{He}$ ratio of $\sim 10^{-8}$ expected from U/Th decay and ^6Li neutron capture (Niedermann, 2002). Second, no ^3He above the detection limit was measured in the 1100 °C heating step despite nontrivial amounts of ^4He being released in this step. This indicates that retentive mineral and fluid inclusions, if present in the samples, are not contributing a significant amount of non-cosmogenic ^3He to the measured ^3He amounts. Third, based on the diffusion kinetics of ^3He in quartz, we anticipate that any nucleogenic ^3He produced in the quartz itself over geologic timescales will be diffusively lost before the sampled rock surface is exhumed at near-surface temperatures. Furthermore, the production rate of nucleogenic ^3He is low compared to the cosmogenic production rate of ^3He . We do not have direct data of major and trace element for the MBTP and GELM samples in order to calculate the nucleogenic ^3He production rate directly. However, we can say that a rough maximum estimate for the production rate of nucleogenic ^3He in the GELM samples is ~ 1 at/g/yr, which is based on a maximum Li concentration of 70 ppm for the Aare granite (Schaltegger and Krähenbühl, 1990) and the production rate estimate of Farley et al. (2006) for an 'average' granite. This is 0.3% of the local, scaled production rate of cosmogenic ^3He for sample GELM18-9, which has the lowest cosmogenic ^3He production rate of all of our samples. Given this maximum production rate estimate for nucleogenic ^3He , and using the Holocene-calibrated diffusion kinetics for our samples, we estimate that the maximum steady-state concentration of nucleogenic ^3He is 2.8×10^4 atoms/g, which is two orders of magnitude smaller than the measured ^3He concentrations in our samples and well within the uncertainties of those measurements. It is therefore unlikely that not correcting for nucleogenic ^3He affected our modeled ΔEDTs in any significant way." (line 579-595)

Technical comments: (numbers refer to line numbers in the manuscript)

5-10 Please give zip codes of European cities before the city name (without comma), as

customary here.

We will modify the text as suggested.

19 Should be "... in quartz from the Mont Blanc site and complex Arrhenius behavior in quartz from the Aar site...", as "behavior observed from the Aar site" is an odd wording.

We will modify the text as suggested.

31 Tremblay et al. 2014a or 2014b?

We will specify "Tremblay et al., 2014a".

57 It is odd to say "glaciers retreated quickly behind the Little Ice Age moraines" when considering a time long before these moraines were there! Change to something like "behind the position where today the Little Ice Age moraines are located".

The sentence will be modified as follows: "[...] glaciers retreated quickly behind the position where the Little Ice Age moraines are located today, [...]". (line 57-59)

64 I assume this should rather read "High-resolution $\delta^{18}O$ in Alpine speleothems ..."

We will modify the text as suggested.

70 "which resulted in ... North Atlantic atmosphere patterns"??? Do you mean in variable atmosphere patterns? Then you should repeat that word (it's in singular in the first part, so it doesn't seem to belong to the plural term in the second one).

This sentence will be reworked for clarification as follows: "Indeed, major climate forcing components, such as ice sheet extent, atmospheric greenhouse gas concentrations, and changes in ocean circulation, also underwent large-scale changes between the LGM and the Holocene transition (Clark et al., 2012). This resulted in variable atmospheric circulation patterns (Eynaud et al., 2009) and variable latitudinal temperature gradients (Heiri et al., 2014b) in the North Hemisphere during this period." (line 68-72)

77 There is no Bartlein et al. 2014 in the reference list (only B. et al. 2010).

We thank Dr. Niedermann for pointing out this mistake. We will correct this reference in the main text and in the reference list, with Bartlein et al. (2011).

79 Please explain ELA for those readers who are not familiar with that term.

The explanation of ELA will be implemented in the text as follows: "[...] reconstructed ice limits and estimates of paleo-Equilibrium Line Altitude (ELA; i.e., the elevation at which annual net ice budget in a glacier equals zero [...]". (line 79-80)

132 "from the exact same locations previously collected" seems to imply you sampled surfaces from which some rock had already been knocked off before, i.e your surfaces would have been covered until a few years ago. I'm sure that's not what you did, but please clarify it!

Samples for ^3He analyses were collected at the same sample locations previously reported in Lehmann et al. (2020) and Wirsig et al. (2016b). We will clarify the

location of ^3He samples relative to the previous ^{10}Be sampling points as follow: "In this study, new samples were collected for ^3He experiments from the same rock surfaces and locations as the sampling sites previously collected for ^{10}Be dating by Lehmann et al. (2020; MBTP profile, samples MBTP18 -1, -2, -11 and -9, n=4) and Wirsig et al. (2016b; GELM profile, samples GELM18 -12, -1, -5, -11, -6 and -9, n=6; Fig. 1, Table 1)". (line 140-143)

Fig. 2: On the y axis labels, remove dot after m because the symbol m for meter is never written with a dot. In the caption, it is confusing to write (a-c), (b-d) which seems to mean a to c and b to d, while obviously a and c, b and d is meant. So change to (a, c), (b, d).

Changes requested for the y axis labels on the figure and in the caption will be implemented.

Table 1: Lehmann et al. 2019 and Borchers et al. 2016 are not found in the reference list (but L. et al. 2020, B. et al. 2015). Give details about the method to estimate Mean Annual Rock Surface Temperatures. Please explain EDT or, at least, refer to the text section where it is explained.

We thank Dr. Niedermann for pointing out the mistake regarding the references. We will correct the main text and reference list in order that references to Lehmann et al. (2020) and Borchers et al. (2016) will be consistent.

Effective Diffusion Temperature will now be written in full in the caption.

The method to estimate (modern) Mean Annual Rock Surface Temperatures and associated Effective Diffusion Temperature is described in section 3.1 ("Effective Diffusion Temperature estimates"; which will be moved to section 3.5 in the revised manuscript, cf. answer to general comment from reviewer 3 for Analytics approach). To avoid confusion and following Dr. Niedermann's suggestion, we will explicitly refer to section 3.5 in the caption of Table 1 for the detailed explanation regarding modern MARST and EDT estimates.

184 Tremblay et al. (2021): Only Tremblay (2021) in reference list.

We will correct the reference to Tremblay et al. (2021) throughout the text and in the reference list.

191 Is this the spallogenic or total ^{10}Be production rate?

This is the spallogenic ^{10}Be production rate. We will state this in the main text.

192 Borchers et al. 2016 see above (Table 2)

We will correctly report Borchers et al. (2016) in the reference list.

243 What is "0.5 increment"? Do you mean increments of 0.5 kJ/mol? If so, you must give the unit!

We will add the unit kJ/mol.

244 Baxter et al. 2010 is not in reference list (only Baxter 2010).

We thank Dr. Niedermann to point out this mistake. The correct reference is Baxter (2010) and will be implemented throughout the main text.

Fig. 3: I can't see any gray lines, just gray areas between red and blue lines! This whole figure is very confusing and difficult to decipher, and the explanations in the caption do not help a lot. I ask the authors to think about how this figure could be improved, e.g. by showing several panels per location, and how it could be explained better.

We will modify the figure 3 by:

- thinning the lines to make them more visible in the main Arrhenius plots (a, b)
- adding 3 panels (c, d, e) showing forward ^3He simulation runs using the different diffusion kinetic parameter solutions fitting the laboratory heating step degassing experiments (grey lines), and testing which of those parameters allow to reproduce ^3He concentrations observed from samples exposed during the Holocene period only (blue lines). For the MBTP site (b), only one sample (MBTP18-9) was used for the Holocene calibration step, while for the GELM site, two Holocene samples were available (GLM18-6 and -9).

The figure caption will be modified accordingly, as well as references to the different panels throughout the text.

284 Related to the above, I don't understand how the parameters E_a and $\ln(D_0/a^2)$ can be obtained from Fig. 3.

Please refer to our detailed answer to the comment above regarding the modifications we will conduct on Figure 3.

We believe that by adding these three panels (c, d, e) in Figure 3 will permit to better illustrate the Holocene calibration step applied in addition to the MDD analyses of laboratory data from heating-step degassing experiments. In addition, we will explain in the caption of the figure how the parameters E_a and $\ln(D_0/a^2)$ are derived from the Arrhenius plots: "(E_a is proportional to the slope of each line, and $\ln(D_0/a^2)$ is given by the intercept)" (line 309-310). Lastly, we will rework the text in the subsection "Diffusion kinetics determination" to further clarify this multi-steps procedure that allowed us to determine the final (Holocene calibrated) diffusion kinetics parameters used in the numerical simulations thereafter.

Table 2: 4th column from left, MBTP d3: Range 8.67 to 10, is that 8.67 to 10.00? If so, don't omit the .00, because otherwise it looks like this value was much less precisely determined than the other ones.

10.00 will be added in Table 2.

Fig. 4: At such a limited range of values ($\sim 2000-20,000$), I don't see why a logarithmic scale is used for the y axis.

We will modify figure 4 by applying a linear scale to the y axis.

341-342 I assume what you mean is "... from the highest sample (...) partially overlaps that from MBTP18-9 within uncertainty."

We will modify the sentences as suggested: "...from the highest sample (...) partially overlaps that from MBTP18-9 within uncertainty". (line 385)

Fig. 5: What is the difference between the solid and dashed green lines in panels e and f?

There are two Holocene samples along the GELM deglaciation profile. The two green lines represent the two modern EDTs associated with those samples,

however because only one modern EDT could be used as reference for applying the lapse rate correction to temperature presented in panel f, we made a distinction: the modern EDT used as reference for applying the temperature correction is represented by the solid green line (and associated with the sample with a black asterisk on panel f). The other modern EDT represented by a dashed line was not used for the temperature correction.

This will now be specified in the caption as follows: "Green solid and dashed lines are modern EDTs for Holocene samples, with the solid line indicating the modern EDT taken as reference for the lapse rate correction". (line 391-392)

374 Instead of "experiments", which may imply something physical, better write "model runs" or similar.

We will replace "experiments" by "model runs". In addition, in other places of the main text where the term "experiments" was used alone for designating numerical model simulations, we will change the wording and use either "numerical simulation" or "model run".

487 Prud'Homme or Prud'homme as spelled in reference list?

We will spell it "Prud'homme et al., 2020" in the main text, as spelled in the reference list.

514 Feldspar is not a mineral that is retentive for ^3He ; actually it is even less retentive than quartz! I don't think Masarik and Reedy have based their numbers on feldspar.

The other retentive mineral referred to was indeed not feldspar but olivine. This will be corrected. In addition, we will modify the way the references are ordered in this sentence to improve clarity: "Alternative approaches using artificial targets (e.g., Vermeesch et al., 2009) or scaling $P_{^3\text{He}}$ measured in retentive minerals (i.e., olivine; e.g., Cerling and Craig, 1994; Goehring et al., 2010) have hence been used. [...] a ~10% higher ^3He production rate has also been proposed from olivine ^3He measurements scaled to quartz (e.g., Masarik and Reedy, 1995; Ackert et al., 2011)". (line 565-568)

The reference list will be updated accordingly.

533 Farley et al. 2006 is not in reference list.

The reference will be added in the reference list.

547 Liu et al. 2021 is not in reference list.

The reference will be added in the reference list.

557 Berger and York 1981 is not in reference list.

The reference will be added in the reference list.

596, 601 Baxter et al. 2010 is not in reference list (only Baxter 2010).

The reference to Baxter (2010) will be corrected throughout the main text.

Data supplementary:

Fig. S1 Please use consistent sample labels throughout the manuscript. Here, GELM18-1 and GELM18-6 is written in the legend but GELM18-01, -06 in the figure caption.

The sample labels in the figure are the right ones. Sample names in the figure caption will be corrected accordingly.

Tab. S1, S2: The uncertainties given for ^3He are unrealistically small, in some cases <1 permil! This is obviously nonsense, no mass spectrometer is able to measure as precisely as that. I assume the authors only considered the statistical error of the measurement, disregarding other error sources such as mass spectrometer sensitivity or linearity. Even if the systematic errors (such as the uncertainty of the He concentration in the standard that is used for sensitivity determination) are not taken into account, which makes sense in such a step-heating experiment (but should be noted), short-term variations of the sensitivity or deviations from the calibrated or assumed linearity of the mass spectrometer signal will be in the percent rather than the permil range.

Uncertainties associated with the ^3He amount (in atoms) released during our diffusion experiments and reported in the Tables S1 and S2 were indeed calculated without taking in account short-term mass spectrometer sensitivity variation/deviation from assumed linearity.

Following our initial approach, reported ^3He uncertainties for step-heating experiments varied between:

- for GELM18-1 (Table S2; which will become Table S5 in the revised version of the Data Supplementary): 0.3 to 5%. We do not assess these uncertainties to be unreasonably low considering the large amount of ^3He released (in the range of 10^7 to 10^8 atoms per heating step). It is worth noting that these ^3He amounts released from the proton-irradiated quartz grains are much larger than the natural amounts measured in unirradiated aliquots, so the uncertainties associated with the former measurements tend to be smaller.

- for MBTP18-9, there was an error in the reported uncertainties associated with the conversion of mols into atoms, leading to unreasonably low uncertainties ($<0.1\%$ for steps with ^3He amounts of 10^7 to 10^8 atoms). After correction of this mistake, uncertainties range between 0.4 to 5% for ^3He release amounts of $\sim 10^7$ - 10^8 atoms per step, and are hence assessed as reasonable. The supplementary table will be updated accordingly (Table S4, in the revised version of the Data Supplementary). The reported mistake didn't affect our diffusion kinetic analysis with the MDD model. We thank Dr. Niedermann for helping us to identify this error in our reported data.

Following the suggestions of Dr. Niedermann, we calculated the uncertainties including short term mass spectrometer sensitivity deviations from linearity. The calculated uncertainties range between:

- For GELM18-1: 5 and 8%

- For MBTP18-1: 4 and 7%

We will also report these uncertainties in Tables S4 and S5 in the updated Data Supplementary.

Tab. S3: Similar to the ^3He uncertainties in Tab. S1 and S2, here the ^{10}Be uncertainties in the permil range are unrealistic. Again, it looks like only the $^{10}\text{Be}/^9\text{Be}$ measurement error was taken into account, without considering the uncertainty of the standard or carrier for example.

Footnote 2 should refer to Table S4 rather than Table S2.

We acknowledge a mistake in the uncertainties for the ^{10}Be concentrations initially measured by Lehmann et al. (2020) and Wirsig et al. (2016b) and which were incorrectly reported in this table.

We will correct this in the updated Table (Table S1) of the Data Supplementary, such that the reported ^{10}Be concentration uncertainties will be in the percent range (between 3 and 8%).

Similarly, final uncertainties for the re-calculated ^{10}Be ages will also be corrected (age uncertainty increase by 0.1 to 0.3 ka) in the updated Table 1. This error however does not affect our numerical simulations of ^3He diffusion for varying time-EDT scenarios.

At last, ^{10}Be error bars in figures 2, 5, 7 and 10 will also be corrected accordingly.

The reference in the footnote will also be corrected and refer to the correct table (Table S2 in the updated version).

Tab. S3, S4: In sharp discrepancy from the former two tables, ^3He errors are very high (on the order of 10%) here. While this may be realistic, the reason for the much higher uncertainties should be explained even when those in Tables S1 and S2 have been adjusted to a more realistic level.

We explain the difference in relative ^3He uncertainties between the diffusion kinetics measurements (Tables S1, S2; Tables S4, S5 in the revised version) and the natural ^3He measurements (Table S4, S5; Tables S1, S2 in the revised version) by the significantly larger amount of ^3He contained in the proton-irradiated samples used for diffusion kinetic experiments, compared to the natural samples.

When both data sets are evaluated as total amounts of ^3He in atoms, the measured ^3He amounts are 10^7 – 10^8 atoms per heating step for the proton-irradiated samples and around $\sim 10^5$ atoms for the natural samples (except for GELM9, with $\sim 10^4$ atoms). On the other hand, the absolute uncertainty based on counting statistics in both cases is 10^4 – 10^5 atoms. Therefore, the relative uncertainty appears significantly higher for the natural ^3He measurements than for the diffusion kinetics measurements carried out on proton- irradiated samples.

The ^3He concentrations and their uncertainties are given with unreasonable precision, i.e 6 significant digits for the errors. It is inappropriate (and confusing) to give more than two significant digits for an uncertainty, because uncertainties are not precise numbers but just represent probabilities. Therefore, values such as 520,929 should be rounded to 520,000, and of course the corresponding values should always be given with the same precision as the uncertainties. The first entry in Table S3 would thus be $6,400,000 \pm 520,000$, or better readable (and easier to round in Excel, e.g.) 6.40 ± 0.52 in units of 106 at/g.

Tables S3 and S4 (Tables S1, S2 in the revised version) will be corrected with correct significant figures and with ^3He concentrations reported in 10^6 at.g^{-1} , as suggested.

I wonder how the average values from the three replicate measurements were calculated. For three measurements agreeing within error limits, as seems to be the case looking at Table S4, an error-weighted mean could be calculated. Obviously, the authors calculated an unweighted average instead and, very strangely, used the average of the errors as the error of the average. I don't think this is a statistically correct way.

The unweighted mean was indeed taken to estimate the final ^3He concentrations. The unweighted means and error weighted means (EWM) do not differ significantly (by 0.1 to 3.5%), due to the fairly constant relative error between the replicate measurements.

Regarding the final uncertainty, we indeed took the average of the 1σ errors recorded from the three replicate measurements per sample.

We recognize that a more conventional practice would have been to take the standard deviation, allowing us to estimate averaged ^3He concentrations to a 68% confidence level. This would have led to differences in the relative error of the mean ^3He concentrations of up to 10% for all the samples but one (GELM18-9, Holocene sample), with no systematic decrease or increase in the percent error.

Using the standard deviation instead of the average error would affect:

- the range of solutions of diffusion kinetic parameters that match the ^3He concentration from the Holocene samples during the Holocene calibration step (cf. section "Diffusion kinetics determination"). However, this will not affect the final set of diffusion kinetic parameters used for this study, which was selected based on the closest match with the average ^3He concentration.**
- the final results from our forward ^3He simulations for varying time-EDT scenarios (two last sets of experiments described in section 4.3, cf. figs. 7 and 8), as simulated ^3He concentrations were compared with observed ^3He concentrations with uncertainties. However, this does not change significantly our results, as shown in Fig.RN2 in attachment, where we compare the solutions of time-EDT scenario explaining our observed ^3He concentrations for the MBTP samples obtained using ^3He errors either derived from the average error (left panel, as done in our study) or from the standard deviation (right panel). Scenarios with significantly colder past temperatures than expected and maintained until very recent times are still necessary to explain our observed ^3He concentrations.**

To limit any confusion, we will 1) clearly specify in the footnote of Table S1 in the updated Data Supplementary how ^3He concentrations and uncertainties have been calculated; 2) modified the heading of the column where final ^3He concentration errors are reported with the term "Avg. Unc." for average uncertainty (instead of " $\pm 1\sigma$ " previously used); 3) added a column with the standard deviation.

Please also note the supplement to this comment:

<https://gchron.copernicus.org/preprints/gchron-2022-1/gchron-2022-1-AC2-supplement.pdf>