

Response to review by J. Amalberti

The fundamental observation made in our manuscript is that Volcano Mountain olivines have a mantle He component that is not effectively removed by the crushing technique used most commonly to isolate mantle from cosmogenic ^3He . The inability to remove the mantle component of ^3He by crushing made it difficult or impossible to obtain a reliable estimate of cosmogenic ^3He in our samples using the standard crush/fusion approach. Nor does an isochron approach yield reliable results for these samples. As a consequence, we investigated a step heating technique as an alternative, and found it satisfactory for estimating the age of the most recent VM flow. So, in addition to the most recent eruption age estimate, the key point of the paper is that in these unusual samples with high concentrations of mantle helium that survive crushing to powder, step heating provides an alternative approach for cosmogenic ^3He dating.

Step Heating Component Resolution

Amalberti provides an extremely lengthy review of the manuscript. Specific comments are addressed in detail below, but Amalberti has one central issue that he claims challenges the basic premise of the step heating approach we are demonstrating in this paper. He is concerned that step heating is not separating matrix-hosted cosmogenic He from fluid-inclusion-hosted mantle He, but is instead separating two different mantle components, an OIB-like mantle component released "from small inclusions" at low temperature, and a MORB-like component released from larger inclusions at higher temperatures. We reject this alternative for the following reasons:

- 1) To our knowledge such a heterogeneously distributed mantle component has never previously been observed in a population of olivines from a single lava flow. Why is VM special in this regard? Moreover, it is difficult to accept that He isotopic heterogeneity could be maintained within olivine crystals at magmatic temperatures. While one could arbitrarily construct a story of a magma in which the $^3\text{He}/^4\text{He}$ ratio is changing and these changes are passively recorded as the olivines trap fluid inclusions, the diffusivity of He at magmatic temperatures is sufficiently high that He would be expected to equilibrate isotopically over the mm scale of individual olivines, and even among a population of such olivines (see discussion in Horton et al, 2019 and the aside in the next paragraph).

2) Amalberti justifies his proposed resolution of two mantle components via step heating by appealing to the novel idea that small fluid inclusions will have He diffuse out faster than large inclusions and will thus be sampled preferentially in the low temperature steps. This statement does not follow from the relevant physical phenomena. The process of diffusion is the same regardless of inclusion size: He partitions into the olivine matrix from the inclusion, then diffuses through the matrix and out of the grain. Diffusivity is not faster because the He was delivered to the matrix from a smaller inclusion. (As an aside, if He in these hypothetical small inclusions diffuses out of the olivines on an hour time scale in our experiments at 800 C as Amalberti suggests, then surely these bubbles would equilibrate He internally to the olivine at magmatic temperatures, as noted in item 1, above. The "two mantle component hypothesis" is not even self-consistent).

3) In contrast to multiple mantle components, isolation of a cosmogenic component at low temperature and a fluid inclusion component at high temperature has already been compellingly observed, e.g., by Swindle et al (2023), who found that $^3\text{He}/^4\text{He}$ ratios in excess of 150 Ra can be extracted at low temperatures, but mantle-like $^3\text{He}/^4\text{He}$ ratios around 5 Ra at high temperature, in cosmic--ray exposed olivines from the Twin Sisters massif. The revised manuscript will provide additional references to this effect. This is readily understood based on known siting of these gases. Cosmogenic He is confined to the olivine matrix which has relatively high He diffusivity. In contrast, He in fluid inclusions must partition out of fluid inclusions before diffusing - impeding its thermal extraction. See discussions by Blard et al 2008, Trull and Kurz, 1993, and Horton et al, 2019.

We thus stand behind our preferred interpretation that step heating is isolating a cosmogenic component from a mantle component, and the validity of our reported VM eruption age. In a revised manuscript we will include new olivine crush measurements on the samples we step heated that directly support this conclusion.

Isochron Plot

Amalberti takes issue with our presentation of the isochron plot objecting (again) to our assumption of a single mantle component. Obviously an isochron requires both homogeneity of the mantle component and the cosmogenic concentration. This is why our manuscript states:

"This same fusion data can be cast as an isochron provided we assume the flows have the same exposure age and mantle component."

Regardless, in the end we agree that the isochron plot does not usefully constrain the eruption age (see response to review by Blard). In a revised submission we will modify the discussion of the isochron approach instead focusing on how even if the fundamental

assumptions of the isochron approach are absolutely true, the high mantle He concentration and its limited range in our powder fusion analyses coupled with reasonable analytical uncertainties inevitably yields substantial uncertainties on cosmogenic He concentration. In other words, we test its use under ideal conditions, and assess the best-case precision that could be obtained.

Below we list Amalberti's specific comments highlighted in gray, with our response unhighlighted.

The article seems to point out that they developed a new methodology to analyze ^3He cosmogenic signal by step heating the samples (see lines 68-69, and 292). This method, however, is not recent and has been used and developed by other authors before (Kurz 1986a). It would be more appropriate to refer at the step heating method as an already known approach (such as the crush/fusion or the isochron) but mentioning that you have adapted it with three temperature steps (800, 1000 and 1400°C).

This comment is ungenerous. Kurz 1986a did not use a step heat to quantify the cosmogenic component in an olivine sample with extremely retentive mantle component.

Line 20: “precise estimates of cosmogenic” is not really supported by the original manuscript as the step heating experiment (where the ^3He is the best measured) shows only one low temperature step, which already limit the precision of the ^3He determination. Indeed, very low $^4\text{He}^*$ contribution (Kurz 1986a) or a variable mantle component cannot be investigating with such low-resolution step heating, and could likely affect the $^3\text{He}/^4\text{He}$ ratio.

This statement is exaggerated. As described in the text VM olivines are very likely disaggregated mantle xenoliths. Such xenoliths have extremely low U and Th concentrations, likely much less than 0.1 ppm (e.g., see measurements of Twin Sisters peridotites in Swindle et al 2023). This amount of U would generate less than 0.5% of the ^4He we measure in our low temperature steps. This would make a tiny difference to the correction for mantle helium. We also reject the idea of multiple mantle components in the step heated olivines for reasons already mentioned. Of course we could do more experiments with more temperature steps, but the results would not meaningfully change our conclusions.

Line 66: I disagree here. The isochron method was not used in the paper, otherwise aliquot from same olivine population would have been used. In addition, the equation for the isochron given by Blard and Pik (2008) is not used here. The authors simply plot ^4He vs. ^3He following equation 5 in the text which correspond to the classic crush/fusion method and called that an isochron. I would either remove isochron method statement, or if you

want to assume that the 6 lava flows have same age, and can be used as one population, it should be clearly stated and the proper isochron equation should be used to verify the validity of the method. Please see my major comment above for more detailed discussion on the crush/fusion and isochron dataset.

This is a very frustrating comment. We stated *exactly* what the reviewer states about assumptions on line 172: " This same fusion data can be cast as an isochron provided we assume the flows have the same exposure age and mantle component."

The statement that we did not use an isochron is wrong. The form of the isochron we used was shown in Blard (2008) and follows from exactly the same set of assumptions and equations as the form preferred by this reviewer. On what grounds is this reviewer claiming we did not use an isochron method? Our approach is NOT just the traditional crush and fuse method, utterly evident from the fact that the crush data never enters into the plotted data!

Line 68: "we developed" should be replaced by "we used" or similar phrase.

Yes, this ungenerous point was made earlier.

Line 91-92: The authors specified that they have additional notes on the samples, such as vegetation cover or average sample depth, but failed to provide those data (or I didn't see them). I would have like to get them in a supplementary material, specially that some detailed sample information could have be beneficial.

The sample depths are shown in Table 1, apparently missed by the reviewer. We do not believe the effects of vegetation cover are significant especially at the level of (im)precision we can obtain, so have not included these data in the Table.

Line 102-103: The authors specify in this section that 4 samples are disregarded and 8 samples are selected due to the mm-sized olivine. Could you please specify if no mm-size olivine were found in those 4 lava samples or if the olivine quality was insufficient for proper $^{3}\text{He}/\text{C}$ investigation? It is unclear from the description why those samples are disregarded. In addition, where is sample VM-07? It is supposed to be used in the study (see line 96 and line 103) but I cannot find this data in the text, the tables or the plots.

This question was clearly addressed in the text: "VM-01-3, 06, and 08 through 11 (Table 1) were chosen for this study due to their higher modal abundance of mm-sized olivine grains (~5%) compared to samples VM 04, 05, 12, and 13". We concentrated on samples where

we could pick sufficient olivine for this study. VM 07 was inadvertently left off the list of low modal ol abundances.

Table 1: This table could be more interesting if more information regarding the sample notes were included such as the vegetation cover or the topography shielding.

The shielding correction is shown in Table 5, which includes the other data used to calculate exposure ages.

Line 111: The authors specify that the crushing protocol is derivated from Blard et al., 2008. There is no Blard et al., 2008 in the reference list. I found however, Blard and Pik (Chemi. Geol. 2008) and Blard and Farley (EPSL 2008). Please be careful when referencing literature (see comment at line 182 as well). In any case, both Blard and Pik (Chemi. Geol. 2008) or Blard and Farley (EPSL 2008) papers do not contain any indication (or I couldn't find any) for a crushing step at 2min followed by a step at 5min for proper ^3He extraction. Could you please provide information where this protocol has been taken? In addition, early crushing steps can potentially release ^3He from the matrix (see Blard and Pik (Chemi. Geol. 2008) and Blard and Farley (EPSL 2008) papers for more details). Do you have investigated such ^3He loss/contamination on the $^3\text{He}/^4\text{He}$ crush signal? This could lead to important impact on ^3He measurements if not well estimated. It should be at least mentioned here.

We will correct the reference to the crusher we used (Blard, Puchol and Farley 2008). We did not do a study of how much cosmogenic ^3He might be released by this device, but it is the same device described in Blard et al (2008), where the release of matrix-sited He as a function of crush time is shown. There is no observed release for the crush durations we used.

Line 121-122: Please add the re-extraction data to the dataset (in the main text or in supplementary). I noticed also that fusion is performed at $\sim 1200^\circ\text{C}$ for 25min but step heating experiments show un-degassed samples at $T \sim 1400^\circ\text{C}$ for 30min step (last temperature step at table 3). I would recommend therefore to provide all the re-extract dataset to ensure that the fusion and step heating samples have been properly outgassed. At the moment, it seems difficult to fully outgas the samples with one temperature step at $\sim 1200^\circ\text{C}$ for 25min. If re-extraction shows significant He, did you then add them to the total? Please provide additional information.

We will add text stating that re-extracts were repeated until no He above blank levels was obtained, and the reported concentrations reflect the sum of all steps. The reviewer is mistaken about the 1400 C. This step integrates any helium that was released by the sample between 1000 and 1400 C. It says nothing about retention above 1200 C. We have certainly degassed the entire sample.

Line 124-125: The authors are using a blank correction for the He analysis with an empty furnace while using Sn foils to wrap their samples. I would have expected blanks to be run with empty Sn-foil packet instead, to better account the blank value. Same comment can be given for step heating experiment (see line 135). Given the blank level is given at 5% (without Sn-foil contribution), I suspect that blank could be underestimated if He outgassing for the Sn foil is not accounted for. In addition, 5% He blank contribution is not insignificant to my opinion.

Sn foil carries no substantial additional blank above that which came out of the hot furnace in this set of experiments. We will add text to this effect and eliminate use of the word "insignificant".

Line 134-135: Please provide the re-extract data.

Same comment as above.

Line 157: What means early measurement here?

Sentence removed - it was irrelevant.

Line 166: Using equation 5, for sample VM-08, I calculate a $^3\text{He}_c$ at 2.8 Matoms/g instead of 2.58 Matoms provided by the authors. I am using an average $^3\text{He}/^4\text{He}_{\text{crush}}$ at 1.12×10^{-5} (from VM-06 and VM-09). I suspect that you are either using VM-06 or VM-09 crush value but without any justification. Therefore, for the sake of consistency, I would recommend to use VM-06 and VM-09 average crush value for all VM samples at the exception of VM-06 and VM-09 where $^3\text{He}_c$ can be properly determined. Otherwise please justify which crush values you are using for all VM analyzed samples.

Strangely, this reviewer is proposing exactly what we did. Apparently the reviewer missed our text that reads: "Given that the crush ratio of $8.1 \pm 0.2 R_A$ is likely representative of all VM samples, there are six crush-fusion pairs that can be used to calculate $^3\text{He}_c$ concentrations using Eq. 5."

We will clarify the sentence to make it more noticeable.

Table 2: For clarity purpose, I would add a special label for the two samples that have coupled crush/fusion data. The other could be labelled as uncrushed olivine.

Good idea.

Fig. 2: Please give the linear regression value in the plot. This is important information and should be display clearly in the plot, not in the caption. Also, as mentioned in my major comments above, the data plotted here is not representing the data in table 2. Please check why this is not the same as this might lead to different $^3\text{He}/\text{g}$ given by this regression line based from equation 5.

There was a plotting error that will be fixed in the revised manuscript. We can add the numerical results of the regression to the plot since this reviewer was unsatisfied by its location in the caption.

Line 182: Thirumalai et al., (2011) and York et al., (2004) are not listed in the reference section. Please be sure all the references are included.

Good catch. Easily fixed.

Fig. 3: The red solid line for $^3\text{He}/\text{g}$ is likely to be wrong. The calculated $^3\text{He}/\text{g}$ from equation 5 using VM-1 data at $T \sim 800^\circ\text{C}$ lead to $^3\text{He}/\text{g}$ calculated at 3.1 Matoms/g (which represent 92% of the total $^3\text{He}/\text{g}$ for VM-01), but in the figure, the red solid line is showing a value >5 Matoms/g. The black solid line seems ok, but could you please check if the plot has the proper values calculated for $^3\text{He}/\text{g}$? In addition, the last temperature step ($T \sim 1400^\circ\text{C}$) is very likely not fully outgassed. The signal is still showing high He content. If you have the re-extraction, please provide them to ensure that total outgassing of the sample is performed.

This plot will be redrafted because it is indeed incorrect. We have already refuted this reviewer's belief that we have not completely extracted He from these olivines.

Lines 240-241: I think the argument for more detailed step heating is important here. Knowing that early temperature step can contain important information, especially for $^4\text{He}^*$ contribution that can lead to a lower Ra value at low T-step (see Kurz 186a), or if we suspect some $^3\text{He}/^4\text{He}$ lower mantle contribution from the tiny inclusions. I would have

therefore, expected a better resolution for the step heating experiments. The SFT is capable of analyzing significantly lower values of ^3He , much lower than ~ 0.4 pcc/g (^3He concentration given at $T \sim 800^\circ\text{C}$), especially knowing that blanks value is given at ~ 0.8 fcc, and therefore, in the worst-case scenario, acceptable values for ^3He could be potentially measured as low as 0.008 pcc (~ 10 times the blank). However, as a theoretical example, if a lower temperature step ($T \sim 500^\circ\text{C}$) is performed on sample VM-01, and if ^3He signal is measured 100 times lower than the one at $T \sim 800^\circ\text{C}$ (i.e. ~ 0.07 Matoms), therefore the blank contribution given at 0.002 Matoms should “only” represent $\sim 3\%$ of the signal, which is quite acceptable. ^4He signal, on the other hand is more complicated and could lead to some limitation under the current analytical blank of the double wall furnace. The ^4He blank is given at 0.2 ncc which limit the measured signal at ~ 2 ncc of ^4He (~ 10 times the blank to ensure sufficient precision). It is noteworthy that signal lower than 10 times the blank can be measure but then larger error is expected and could limit the interpretation. Nevertheless, ^4He signal 10 times lower than the measured ones at $T \sim 800^\circ\text{C}$ (i.e. 4.3×10^4 Matoms) could still be measured for a hypothetical step at $T \sim 500^\circ\text{C}$. Blank error could account for $\sim 12\%$ (5380 Matoms). I would like, however, to point out that the double-wall furnace (where step heating experiment is performed) is not baked but solely pumped out overnight (see lines 120-121), and ^4He blank given by the authors are quite high compared to some double wall furnace blanks given by other studies (Blard et al., 2015; Kurz, 1986; Williams et al., 2005, Yokochi et al., 2005, Zimmermann et al., 2012; 2018, Zimmermann and Marty, 2014), where blank values are given as low as ~ 300 -600 Matoms. If we assume that blank values can be reduced significantly in the range of 0.02 ncc (~ 600 Matoms), then previous blank contribution of $\sim 12\%$ (for a hypothetical $T \sim 500^\circ\text{C}$ step) will drop at $\sim 1.5\%$, and ^4He concentration 100 times lower could be even analyzed. In addition, peak jumping analyses can also be performed to measure ^4He on the CDD to keep good ^4He measurement precision for very low signals. Consequently, I think the authors could safely performed a more detailed step heating experiment with limited loss of the analy

This reviewer is proposing acquisition of additional step heat data. We decline as it would require substantial additional work and in our opinion would add nothing new. We have already offered our refutation to both of this reviewers motivations for this additional work.

Line 245-247: Why the authors are using the crush value here, while they have the mantle component determined with the highest temperature ($T \sim 1400^\circ\text{C}$, where no cosmogenic contribution is estimated, see line 249)? I would rather use the high temperature $^3\text{He}/^4\text{He}$ ratio for the mantle composition instead of using a crush value from another lava flow (VM-

06, VM-09 or average). My understanding is that no crush step is needed when step heating experiment is performed, as all the information are retrieved from the step heating (i.e., $^3\text{He}/^4\text{He}$ and $^3\text{He}/^4\text{He}_{\text{mantle}}$). Please justify the use of a crush value instead of the high-T value for mantle component.

The revised manuscript will include a crush analysis on the olivine from this flow, eliminating this concern.

Table 4 and Table 5: I found those two tables redundant. They show almost similar information, only isochron dataset is added to table 4. I would merge those two tables altogether in one clear table with the concentration and their associated calculated ages for all the methods used. It would be easier to have a table summarizing everything instead of two.

Agree. Tables will be streamlined in revised version.