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## **Comment on gchron-2021-42**

Pierre-Henri Blard (Referee)

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Referee comment on "Short communication: Mechanism and prevention of irreversible trapping of atmospheric He during mineral crushing" by Stephen E. Cox et al., Geochronology Discuss., <https://doi.org/10.5194/gchron-2021-42-RC2>, 2022

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### **Review by P.-H. Blard**

Cox et al. present in this manuscript a well-designed suite of experiments aiming to understand and quantify the trapping process of atmospheric helium at the surface of silicates during laboratory crushing. Crushing silicates (sometimes before melting them in vacuo) is a technique used in several labs for measuring helium isotopes and abundances (see for example Kurz et al., GCA, 1986; review in Blard, Chem. Geol., 2021). Since an unexpected atmospheric helium contamination may modify the geological signature of the samples, it is key to understand the physical process of this helium adsorption/trapping. This knowledge may improve the accuracy of future measurements.

Authors provide experimental observations confirming the previous conclusions of Protin et al. (GCA 2016), who initially reported this nearly-irreversible helium contamination. Cox et al. also identified mechanisms that favor (or limit) the adsorption of helium. They notably tested several procedures that may reduce this contamination, such as crushing in a liquid or a N<sub>2</sub> pure atmosphere. They also developed a - quite (too?) complex - model to quantify the impact of this contamination on (U-Th)/4He thermochronometry.

In summary, I think this follow-up study is useful, because it brings new data and because it improves our knowledge of this strange mechanism that had unfortunately been overlooked for a long time. In my view, it thus deserves to be published. However, I noticed several points that also need to be considered in a revised version of the manuscript, before it can be published in its final form. All of them are quite straightforward and easy to address.

## **Main concerns**

### **1 – Helium contamination when samples are crushed in vacuo before being exposed to atmosphere**

Author make a strong case about the fact that crushing in vacuo leads to undetectable helium contamination. I suggest to nuance this statement in different places of the manuscript. Here is why: it is true that based on authors' data, crushing in vacuo led to almost undetectable contamination. However, their protocol is not very sensitive and do not permit to detect small amounts ( $< 10^{-13}$  mol/g) of helium contamination. Moreover, some data (Blard et al., EPSL, 2006) showed that crushing olivines/pyroxenes in vacuo followed by exposition to atmosphere may lead to detectable amounts (in the range of  $10^{-14}$  to  $10^{-13}$  mol/g) of adsorbed atmospheric  $^4\text{He}$ . These isotopic data have been reinterpreted later in (Protin et al., GCA, 2016) and (Blard, CG, 2021) using a mixing equation between atmospheric and magmatic helium. In the line of Cox et al's results, the amplitude of this "post vacuum crushing" contamination is indeed much lower than the one occurring when the crushing is performed in a He-rich environment. However, even such a low amount of adsorbed helium can be an issue that yields inaccuracies, particularly in the case of cosmogenic  $^3\text{He}$  measurements in samples having a low  $^3\text{He}_{\text{cosmogenic}}/^4\text{He}_{\text{magmatic}}$  ratio (see for example discussion in Blard, CG, 2021).

### **2 – Complexity of the model used to compute the amount and impact of this contamination**

I maybe missed the point, but the model described in section 4.1 is not trivial and I am wondering if such complexity is necessary. I can be wrong, it is just a feeling based on the often right "simpler is better" motto. Wouldn't you get similar results by simply deriving an empirical relationship between the amount of He-contamination and the specific surface area of the samples (as Protin et al., 2016 did)?

Why assuming an exponential vs depth decrease and what is the gain of this assumption regarding the accuracy of the model? Is this exponential attenuation more accurate than simply assuming that  $n$  atoms of He can be adsorbed per grain surface unit? Moreover, it is for me not clear how you compute the attenuation length of  $0.29 \text{ micron}^{-1}$ , especially because you provide this number before describing the "onion shell" discrete model.

Equations should be numbered and better explained and quoted in the text, the rational would be easier to follow.

### **Other comments**

Line 14: "Low temperature" is a rather imprecise and subjective statement. Provide actual temperature number.

Line 16: "...that this is easily avoided by crushing under liquid or in an inert atmosphere." I suggest to revise and nuance this sentence. Indeed, as I wrote above, some data (Blard et al., EPSL, 2006) suggest that crushing in vacuo followed by an exposition to atmosphere may also be subject to atmospheric helium adsorption/contamination (see data re-interpretation in Protin et al., GCA, 2016 and Blard, CG, 2021).

Line 17: "samples to sizes smaller than typically used for geochronology". Provide grain sizes ranges in microns or mm.

Line 23: Quote few examples of relevant literature.

Line 23: Is "common" a synonym of "most abundant" in English? If not, you should prefer "most abundant".

Line 26: be more specific than "long-lived".

Line 27: "always" is a bit strong. I suggest "often".

Line 45: As written, this sentence may lead to think that "atmosphere" and "radiogenic" endmembers could have similar  $^3\text{He}/^4\text{He}$  isotopic ratios (which is not the case at all). I would rephrase. The main limitation is that He doesn't have a third isotope. If this was the case, it could permit to resolve a 3 components mixing.

Line 46: I suggest "mixture" instead of "contamination" here. In my opinion, contamination should be reserved to unexpected addition of helium during experimental procedures.

Line 48: It would be informative to quote here the most recent - high precision - survey published by (Boucher et al., GCA, 2018). Analytical precision of the  $^3\text{He}/^4\text{He}$  ratio is close to 1 per mil with this apparatus.

Lines 52-55: I think this statement should be nuanced, and you could recall here that the nucleogenic  $^3\text{He}$  contribution may be significant for the accuracy of cosmogenic  $^3\text{He}$  determinations, in minerals having pluri-million years He-closure ages (see for example figure 7 in Blard, CG, 2021).

Line 63: About the choice of the "best" granulometric window, you could also mention here the case of cosmogenic  $^3\text{He}$  analysis. (Blard, CG, 2021) proposes that the optimal granulometric window is probably 100-500 microns. Grains larger than 500 microns should be avoided since they bear large amount of magmatic helium, while fractions finer than 100 microns can be contaminated by too much atmospheric helium.

Lines 73 to 79: You should mention here two other important reasons that have often motivated the measurement of crushed fractions in previous studies devoted to cosmogenic  $^3\text{He}$  determinations: 1) crushing (followed by fusion of the obtained powdered phenocrysts) is the standard procedure proposed by Kurz et al., GCA 1986 to analyze the magmatic  $^3\text{He}/^4\text{He}$  endmember. 2) Several studies (Puchol et al. CG 2017; Blard CG 2021) also showed that small grains (< 500 microns) bear less fluid inclusions and hence much less amount of magmatic helium, leading to lower magmatic corrections, and lower uncertainty associated with the final cosmogenic  $^3\text{He}$  concentration (see Figure 5 in Blard, CG, 2021).

Line 95: Can you provide the range of this magmatic He estimates?

Line 95 (and everywhere else where this reference appears): Remove the "." after "Murty."

Line 96: "highest", "small". These subjective words are not very informative, especially for non-expert readers. Provide real numbers.

Line 133: What is the blank/signal ratio (in %) and what is the uncertainty associated with this blank?

Figure 1: I suggest to find a way to indicate on the figure that the dark green box represents the 1500°C extraction (and light green 800°C). Why the N<sub>2</sub> experiment yields 4He concentrations that are lower than the background? Do you suspect magmatic helium loss during the crushing? In that case, the "background" you use is a clear overestimate. Could you compute the 2 endmembers budget (magmatic He + atmospheric adsorbed He) by using the isotopic ratios measured with the MAP?

Lines 164-165: I suggest to nuance this statement here and elsewhere. Indeed, some data (Blard et al., EPSL, 2006) showed that crushing olivines/pyroxenes in vacuo followed by exposition to the atmosphere may lead to detectable adsorption of atmospheric helium. These data have been reinterpreted in Protin et al., 2016 and Blard, 2021. Yes, the amplitude of this contamination is much lower than the one occurring when crushing is performed in a He-rich environment.

Line 167: I propose that "virtually no additional" should rather be "non-detectable adsorption in excess to the magmatic helium background of the samples". Since the uncertainty associated with this background may be large, maybe your experiment does

not permit to detect the adsorbed helium (notably in the case of the N<sub>2</sub> crushing experiment).

Line 192: Quote here (Niederman and Eugster, GCA, 1992), who were the first to evidence the adsorption of xenon and krypton on silicate surfaces.

Lines 193-194: The words "shortly" and "minimal" should be revised. As written above, previous data (Blard et al., 2006; reinterpreted in Protin et al., 2016 and Blard 2021) show that exposing phenocrysts to the atmosphere (24 to 48 hours after they had been crushed in vacuo) may induce a [10<sup>-14</sup> – 10<sup>-13</sup>] mol/g contamination by atmospheric helium.

Lines 201-202: Nuance this statement. Atmospheric helium can also be adsorbed and detected after in vacuo crushing (Blard et al., EPSL, 2006; revised interpretation in Protin et al., 2016 and Blard, 2021). The amplitude of the contamination is lower in the case of in vacuo crushing, but it may remain an issue in some cases, for example for cosmogenic <sup>3</sup>He determinations that require very accurate and precise magmatic <sup>3</sup>He estimates (case of samples having a low  $^{3}\text{He}_{\text{cosmogenic}}/^{4}\text{He}_{\text{magmatic}}$  ratio).

Lines 204-206: Even if this statement is true for samples being very rich in radiogenic <sup>4</sup>He (> 10<sup>-11</sup> mol.g<sup>-1</sup>), it is much less true in the case of samples used for cosmogenic <sup>3</sup>He measurement. In the dataset presented by (Blard et al., 2016), the <140 microns of in vacuo crushed samples were affected by magmatic <sup>3</sup>He overcorrection representing from 10 to 100% of the cosmogenic <sup>3</sup>He concentration.

Line 209: I don't understand the justification of using the adverb "only" here. On the

contrary, 90% of He removal seems to be a significant proportion.

Line 217: It would be very useful if you could provide a number to characterize the detection limit of your methodology. I guess this is the average of the magmatic  $^4\text{He}$  concentrations of the San Carlos olivine, plus 3 times its associated uncertainty? How well do we know these two values?

Lines 220-225: Here again it would be useful to quote (Niederman and Eugster, GCA, 1992), since they explored these mechanisms for heavy noble gases.

Section 4.1 – Model description. If you wish (and have enough energy and time!) to add half a page and one figure, I suppose that the same modeling approach applied to cosmogenic  $^3\text{He}$  dating would be great (considering the impact of the atmospheric contamination on the magmatic  $^3\text{He}$  correction). If you stay with the evaluation of the impact of this contamination to (U-Th)/ $^4\text{He}$  thermochronology only, then replace the word "geochronology" (line 229) by "thermochronology".

Line 233: Are there any experimental or theoretical basis justifying the choice of an exponential law to describe the vertical attenuation of the trapping?

Lines 237 to 239: In the case of cosmogenic  $^3\text{He}$  measurements, atmospheric  $^4\text{He}$  adsorption is the biggest potential issue: if overlooked, this may induce an overestimate of the magmatic  $^3\text{He}$  correction, and an underestimate of the cosmogenic  $^3\text{He}$  (see discussions in Protin et al., 2016 and Blard 2021).

Line 249: Add "microns" after "22.5".

Line 256: So,  $a = R(n) - R(n-1)$ ?

Line 263: "total concentration" should be replaced by "total contamination", because the magmatic and matrix-sited Helium species are not considered here (I think).

Line 266: "...for He measurements **in thermochronology**". In the case of cosmogenic  $^3\text{He}$  determinations, the most commonly used minerals are olivines and pyroxenes.

Line 295: Suggestion: "... **the** geometric model."

Line 298: Suggestion: "need **to** be".