Geochronology Discuss., author comment AC1
https://doi.org/10.5194/gchron-2021-24-AC1, 2021

Reply on RC1

Tibor János Dunai et al.

Author comment on "In situ-produced cosmogenic krypton in zircon and its potential for Earth surface applications" by Tibor János Dunai et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2021-24-AC1, 2021

In our reply to RC 1 we list our replies (normal font) below the individual comments (italic).

***RC1**: 'Comment on gchron-2021-24', Stephen Cox, 17 Sep 2021*

This is an interesting and useful manuscript that presents a straightforward case for making greater use of Kr isotope measurements in certain situations in geochemistry. I think a more in-depth discussion of the geological implications would be useful but is not required for this to rise to the level of a valuable contribution, so I suggest it be accepted subject to a few minor corrections. That said, if the authors are willing to provide a longer discusison of the likely scope of applications for these methods in the earth sciences (more in Section 5.3, in particular), I think that would add to the usefulness of the paper. The results section includes a lot of material that belongs in the discussion, and I think moving this text and then expanding the discussion to look more broadly toward other applications would be appropriate for a paper that seeks to inspire others to use these techniques.

I am including line-by-line comments that amount to minor suggestions and also a few notes about grammar and punctuation that will improve readability.

Remark: We are unsure which version of the manuscript the reviewer had at his disposal. Following the initial quality control by the editors the former appendix was removed incorporated into the text, however, reviewer 1 refers to an appendix; the online preprint (https://doi.org/10.5194/gchron-2021-24) has no appendix. It might be that the reviewer was sent the initial manuscript (i.e., pre quality control; the line numbers agree with this version). The changes made in response to the quality control pertain to the structure only, no content has been changed. Some of the reviewer's comments on the manuscript structure have been taken care of in the preprint that is online. As consequence of this mix-up the line numbers (and Fig. numbers) used by the reviewer mostly do not reflect the lines of the online preprint (starting from line 152 & Fig. 2; however later, starting from "Line 483" in the reviewer's comments, the line-numbering does again agree with numbering of the preprint. In our responses we provide the line/Figure numbers of the online preprint (https://doi.org/10.5194/gchron-2021-24) whenever they differ from the number used by the reviewer.

---Content---

-Lines 36-37: This is not strictly true. Stable and short-lived isotopes of argon are also produced by cosmic radiation.

We will add the sentence: ‘An exception is cosmogenic argon ($^{36,37,38,39}Ar$; Renne et al. 2001; Niedermann et al. 2007; Saldanha et al. 2019), which, due to inherent limitations (Renne et al. 2001; Dunai 2010), still awaits widespread application to Earth surface sciences (Ostingh et al. 2017).’

-Line 86: The 2002 Gilabert paper does not appear to address complex particle emission.

Gilabert et al 2002 do not explicitly address the nature of particle emissions that lead to their measured Kr isotope abundances. In line 86 we cited Gilabert et al 2002 for the Kr isotope abundances, i.e. we are independent of which reactions Gilabert et al 2002 implicitly use in codes for model calculations, which they also report in their paper. We are, however, certain that their code and underlying database includes alpha-emissions, otherwise it would be incomplete/wrong.

-Line 87: I find this wording confusing (energy bonus?). This is the alpha particle binding energy. I think more discussion (and sourcing) of the energy considerations is required to make this section understandable.

This discussion is provided in Dunai 2010, which we (now) cite (see the following two comments on Line 88)

-Line 88: Is the (1) here meant as a placeholder for a citation?

(1) was a placeholder for (Dunai et al., 2010), this will be amended in the revised version.

-Line 88: Separation energy is both particle-specific and fairly different for different isotopes. The number given here appears to be the binding energy per nucleon, which is not the same thing. I think this merits a bit more discussion and needs a citation that is not just a database.

We will rewrite and expand the sentence to : "….; binding energies of nucleons (neutrons and protons) are 8.7 MeV in this mass range (Soppera et al., 2014), protons additionally requiring >8 to overcome the Coulomb barrier. Consequently, individual separation of two neutrons and two protons from a nucleon in this mass rages would require an energy input from a cosmic ray particle of ≥50.8 MeV, whereas the separation of an α particle requires only ≥22.5 MeV."

-Lines 90-100: I think this section could also use some expansion and direct reference (maybe even a figure) to the structure of the chart of the nuclides around krypton to make it more useful for the typical reader.

We will include a new Figure showing an excerpt of the nuclide chart (corner points: ^{82}Zr, ^{96}Zr, ^{77}Br, ^{91}Br).

-Lines 109-110, 112-113, etc.: Again, the discussion here basically assumes the reader is either looking at a chart of the nuclides or has it memorized, which I doubt is true generally. I'd suggest simply providing the relevant portion of the chart as a figure and referring to it when making this type of statement.

See previous.

-Line 113: This phrase is not understandable, partially because of the misplaced hyphens. If anything, one is needed only between the two items in the relationship ("Coulomb barrier" and "reaction probability"), but I think the only way to write this clearly without requiring the reader to look up the original paper and see what is actually plotted is to say "Using the relationship between Coulomb barrier and reaction probability observed by . . ."

We will follow the suggestion of the reviewer.

-Lines 160-161 (lines 398-399 in preprint)*: This phrasing sounds negative when in fact this is a strength of the dataset. I would say something like "Most of the data fall on the air-cosmogenic mixing line with no apparent influence from mass fractionation [no hyphen] or nucleogenic Kr."*

We will follow the suggestion of the reviewer

-Lines 184-195 (lines 436-447 in preprint)*: It would probably be fair to acknowledge that the suite of samples controlling the upper end of this array includes a sample with clear evidence of nucleogenic contamination.*

We fail to see which sample the reviewer is referring to. All four samples that control the upper end of the array fit equally well/badly, when considering uncertainties shown.

-Lines 202-204 (line 425 in preprint)*: Please describe the regression model used and how the uncertainty was determined.*

We used the regression module of SigmaPlot 14.0. We state this in the figure caption of Fig. 6 (line 440-441). We will add in the revised version the regression is linear least square.

-Lines 220-234 (line 458-472 in preprint)*: Is there some geological context that could be discussed to address the question of which production ratio is more appropriate? It does not seem at all unreasonable that the samples would have experienced partial burial, especially given the range of 81/78 ratios in the rest of the sample suite.*

The fact that the $^{81}Kr/^{78}Kr$ ratios obtained from the samples from Grimsel Pass (which have a simple exposure) are inconsistent with the experimental value of 2.3 (proton irradiation) is discussed, within their geological/geomorphological context, in sect. 4.4.1 (lines 475-487) that directly follows lines 458-472.

-Line 228: Is "Table 2a of 5" a placeholder for something?

This has been amended during the initial quality control (see first page)

-Lines 236-249 (lines 474-487)*: Please include numbers when discussion sample concentrations and ages here rather than just referring to a figure and the appendix. What are the apparent production ratios of 81/78 for the Grimsel samples, for example? State the exposures ages suggested by these samples when comparing it to 13 ka.*

We will provide the numerical values of the $^{81}Kr/^{78}Kr$ ratios in the text. The appendix mentioned by the reviewer is Table 1 of the preprint, and precedes this text (see general remark first page). We will state in the revised manuscript by how much the calculated exposure ages (without snow cover correction) are lower than the expected ages (i.e. 40-50%).

-Lines 287-370 (Lines 526-578, sect. 4.4.2)*: It would be good to have briefly described the samples before describing the measurements of them rather than first introducing*

them here. Some of this information (and some of Appendix A) belongs in Section 1.2.4, perhaps. There should be enough geological description in the main text to assess these conclusions about the meaning of the data. Much of this is interpretation or speculation that belongs in the discussion section. There needs to be a discussion of uncertainty surrounding the inferred exposure histories, especially the complex ones.

This has been amended during the initial quality control (see also remarks first page). The samples are described in sect. 2 (Lines 151-241)

-Lines 292-294, 304-307 (lines 531-533; 540-542)*: Need to discuss the measurements and describe how the sample results indicate these things, what the expectations would be for each (and why), and therefore how the results are consistent with them. Use numbers and discuss the nature of the patterns in figure 3 (Fig.7).*

We will refer to Fig. 7 in the first case (lines 531-533) in the revised manuscript. In the second case we already refer to Fig. 7 (line 541). Using numbers in the text does not help the reader, they have to be able to read Figure 7. How to read Figure 7 is introduced in the figure caption of that figure. Figure 7 is analogous to a commonly used diagram for ^{10}Be and ^{26}Al data (so called two-isotope plot, or 'banana plot'), which is stated in the figure caption (with references that explain in detail how to read this kind of diagram). Admittedly this is not the easiest type of diagram, however, we think that practitioners in cosmogenic nuclide methodology will already be familiar with it.

-Lines 379-424 (lines 617-662, section 5.1.)*: This belongs in the introduction. A lot of it is already there and does not need to be repeated.*

We beg to disagree; we think summarizing the 'utility of Kr isotopes for cosmogenic applications' should be part of the discussion Many of the features discussed here will be only be clear to the reader after reading the previous sections, and as elucidated by the data shown. Also, we first have to establish the feasibility of the new methodology first, before exploring the utility of the various isotopes. Some repetition helps the reader to understand the case made.

-Line 427 (line 665 in preprint*): Zircon is common, but not ubiquitous, in igneous rocks. It is pretty hard to find zircon in most basalt. I suppose you'd probably find one with a big enough chunk of any rock, but I would dial back the expectations a little here, especially since the following discussion is all about granitic rocks.*

We expect that the majority of future applications of Kr_{it} in will not try to extract zircons from hardrock (e.g. granite or basalt), but rather use sedimentary zircon (see sect. 5.3), which may be naturally enriched in placer deposits. It is therefore not important that it is unlikely to find a zircon in a given piece of basalt, it is important that basaltic zircon can be found in placers while most primary minerals, but zircon, may be removed by chemically weathering. All continental basalt contain zircon (i.e. zircon is ubiquitous), albeit in trace amounts (not common). We see this as one of the main benefits of this method and the target mineral zircon (line 709-711).

-Line 449 (line 687 in preprint)*: It might be common knowledge to most readers of this journal, but for others finding this on Google Scholar, why not state approximate closure temperatures for each noble gas and give the citations separately?*

We will provide these values and citations in the revised version of the manuscript: "The closure temperatures for noble gases in zircon increase with increasing atomic mass: ^{4}He (160-200 ºC; Rainers et al. 2005), ^{21}Ne (400±50 ºC; Gautheron et al.; 2006), ^{86}Kr (560-580 ºC; Honda et al., 2004), ^{136}Xe (660-750 ºC, Honda et al. 2004)."

Rainers, 2005, Zircon (U-Th)/He Thermochronometry, Rev. Min. Geochem. 58, 151-179

Gautheron et al. 2006 (U–Th) /Ne chronometry, EPSL 243, 520-535

-Lines 457-463 (lines 693-699 in preprint)*: Why not include a mention of the age-U parameters required for metamictization to become a problem?*

We will include following in the revised manuscript: "Retention of helium in zircon decreases at cumulative alpha doses above 10^{18} α/g (Guenther et al., 2013; Rainers, 2005), zircon remains retentive for helium at environmental temperatures up to doses of $2\text{-}4{\cdot}10^{18}$ α/g (Rainers, 2005). Since retentivity of noble gases increases with atomic mass (see above), krypton will be retained quantitatively in zircon at environmental temperatures at least up to the dose of $2\text{-}4{\cdot}10^{18}$ α/g. A zircon with 1000 ppm U (with Th/U=0.5) requires $\sim 10^9$ years to receive a dose of $4{\cdot}10^{18}$ α/g (for a depiction of alpha dose as a function of age and U concentration we refer to Reiners, 2005). Thus, for most zircons, complete retentivity of krypton at environmental temperatures can be assumed.."

-Line 483: Please give some quantitative hint for what is "notable"

Sufficient to reduce the time-integrated cosmic ray flux by 40 to 50 %. We will state in the revised manuscript by how much the calculated exposure ages (without snow cover correction) are lower than the expected ages (i.e. 40-50%).

-Line 492 etc: This figure caption is too long. It is hindering the ability of the caption to guide the reader in deciphering what is a pretty complex figure. I would simplify it to describing what is in the figure as succinctly as possible and move some of this detail to the discussion text.

The caption of Figure 7 is long and somewhat complicated due to the intricate nature of the plot. Understanding will not be helped by having to refer to text that might be on the next page and so we prefer to keep the current encapsulated format. See also discussion of Figure 7 above.

Section 4 generally: A lot of this material should be moved from results to discussion, and I would suggest generalizing more from these specific cases as well to discuss the broader implications of the method for the earth sciences.

The goal of this manuscript is to test the feasibility applying Kr_{it} to Earth surface processes. The ability to interpret the first results obtained with this new method is therefore a 'result' and not necessarily a discussion. The generalized, broader implications are provided in section 5.3 in the discussion.

-Line 667-668 (lines 288-289 in preprint): Please state the temperature or heating power used for the getters, and state the alloy used.

This information is provided in Ritter et al 2021. At the beginning of the methods section (lines 244-246), we state that 'The general layout of the noble gas set-up at Cologne is described in Ritter et al. (2021), who focus on the analysis of cosmogenic neon. Here we reproduce some aspects of this description (Ritter et al., 2021), adding details that are pertinent for Kr-extraction from zircon and cosmogenic Kr-analysis.'

-Lines 693-694: Maybe the original plan was to use "m" more than once? I think this way of explaining how you arrive at the detection limit is unnecessarily confusing here. Just state that the detection limit is defined as three times the background.

Since this is a matter of personal preference, we prefer to keep it as is.

Data reporting: Perhaps there is going to be a repository item attached that I cannot see yet. At minimum, report in the appendix the actual measured intensities for each species with the fit uncertainties for samples and accompanying blanks and standards.

This has been amended during the initial quality control (see also remarks first page).

---Grammar and Punctuation---

-Perhaps there's another convention of which I'm unaware, but I've always seen the symbol for half-life expressed with a lowercase t.

-Lines 29 and 38: typo in "half-life" ("half-live")

-Lines, e.g., title, 27, 32, 43: The manuscript is inconsistent on hyphenation in "in situ produced." Generally "in situ" should not be hyphenated. Some style guides might allow for compound adjectives like "in-situ-produced," but definitely not "in-situ produced." I would go with the version in the title, but whatever choice made should be consistent.

-Lines 49, 50, etc.: Not to harp on about hyphens, but "Kr-isotopes" (and "Zr-isotope," "Kr-data," etc.) and "Kr-concentrations" should definitely not be hyphenated, and ranges like 50–100 MeV should be written with an en dash and no space. I would also urge consistency on use of elemental abbreviations or not. Both "krypton" and "Kr" are used throughout.

-Line 128 and following: amu (or "AMU") isn't an accepted unit (https://goldbook.iupac.org/terms/view/U06554). Regardless, it seems odd to suddenly introduce units at this point after previously just stating mass numbers (e.g., lines 51, 93), and I would suggest sticking to the latter since amu/u/Da is defined as an exact rather than nominal mass and this usage appears in only this one paragraph.

-Line 131: Bromine should not be capitalized.

-Line 132: The Geochronology style guide says to use abbreviations for SI-accepted units.

-Lines 153-155: Remove all hyphens in this paragraph except in "U-Pb".

-Line 164: comma after 81Kr

-Line 181: remove hyphen

-Lines 221, 222: remove hyphens

-Line 315: do not capitalize "zircon"

-Line 329: remove hyphen

-Lines 423, 438, 440, 442, etc: remove hyphens

-Line 450: There should be a space in "600 oC"

All suggestions/corrections concerning Grammar and Punctuationr will be incorporated in the revised manuscript