

We thank the reviewers and the associate editor for their feedback. Below, we address each comment individually.

**Reviewer #2 (authors' responses are shown in red after each numbered comment):**

It is good to see that authors have significantly improved the earlier version of manuscript. They have revised and clarified most of the scientific inconsistencies. The manuscript now reads well, measurement, results, and discussions are linked properly. There are several important aspects of manuscript, which will be useful for luminescence studies in future. The authors have done hard work in conducting measurements of individual grains and conducting measurements at sub-microscopic level for each grain. The finding related to correlation of elemental concentrations with anomalous IR-RF signal is interesting and needs further explorations. Thus, I feel manuscript should be published.

Although the major findings are interesting, yet I feel that manuscript still needs improvement in the English and clarity on scientific statements. I would like to encourage authors to read and write carefully to remove the inconsistencies. My comments are given below and points out some of the mentioned contradictions.

Comments

1. Line 43 (dose (Gy))
  - Changed to “(dose, with the unit Gy).”
2. Line 44 sampled sediments
  - Change incorporated.
3. Line 71, predicted instead of assumed
  - Change incorporated.
4. Line 76, It will be good to state some reasons which could be leading to the variabilities rather than just mention a term.
  - Added: “(e.g., differences in signal saturation or in proportions of RF emissions)”
5. Line 78, “what...” either put ? in end or rephrase
  - Rephrased to: “We [...] discuss the effect that the observed variability could have on multi-grain aliquots.”
6. Line 86, “identification.....” Is it right to presume and specify signal as contamination without justifying it. You may say that u-XRF and u-Xanes have capabilities to identify defects and isolate signals but presuming that it's a contaminating signal is not right without proving.
  - Indeed, at this point in the text we have not yet introduced the potential IR-RF contamination, so we have rephrased the sentence (changes in bold type): “... identification of the origin of **RF emissions** could help us to gain a better understanding about apparent saturation or quenching of the IR-RF signal.”

7. Line 97 “Though both .....geochemistry.” Authors pointed out important aspect in this statement that both crystallography as well as geochemistry is playing a role here but they are only focusing of geochemistry. So how it is justified to attribute the current study observations only to geochemistry without considering crystallography?
- Unfortunately, it was beyond the scope of this work to include crystallography, but we have rephrased the sentence to highlight that this should be done in the future and compared against our geochemical results: “Both the grain geochemistry and crystallography should be investigated to characterize the defect type and its environment. In the present study, we focussed only on geochemistry, though our results should be complemented with crystallographic studies in future work.”
8. Line 103 “Other reactions.....”. why do you say so??? May be it does not participate that's why not observed. I think it's better to rephrase as "involving higher oxidation states might be playing a role but not observed or suggested"
- We have incorporated the reviewer's suggestion: “Other reactions involving higher oxidation states would also be possible but have not yet been observed or formally proposed.”
9. Line 122 “Such a contribution.... $D_e$ .” In this case relative intensities play a vital role. If authors say it is only 5%, then it shouldn't significantly effect estimated dose. Please see numbers very carefully.
- Due to the flattening of the IR-RF curve as it nears saturation, small changes in signal can have a high impact on  $D_e$ . This statement is based on observations in Sontag-González and Fuchs (2022), cited in that sentence, where  $D_e$  changes of ~400 Gy were caused by signal changes of only a few percent. We have added in the main text that the effect is on  $D_e$  values “at doses near signal saturation” to clarify this issue.
10. Line 144 “between one and three grain.” Is ‘and’ right here?
- Yes, we mean 1–3 grains per sample.
11. Line 174-176 “We paid particular attention.....” Do you mean other regions are not responding to IRRF? what about other regions? How are you sure that these regions are responsible for anomalies.

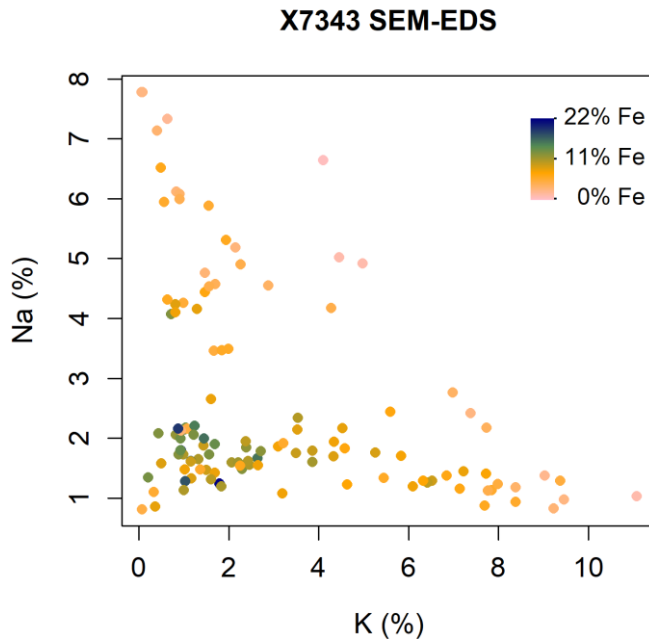
What about IR RF characteristics of Na? Is it not important?

Na/K Feldspar normally are dominant remnants in feldspar separation process.

- Ideally, we would have preferred to use an instrument that also measured Na, since it is an important element in the feldspar ternary series, as mentioned by the reviewer. However, the SRX beamline is not set up for XRF analyses of elements with low atomic numbers. In the literature, Na has not been linked to the infrared but red/green RF emissions. Therefore, we focussed on Fe and Pb. We have no spatially-resolved IR-RF information, so we do not know in which regions in the grain the RF emissions originate. We are also not sure from which element or mineral the contaminant emission observed in the IR-RF is originating. A motivation of the current manuscript was to test whether there was a trend between the IR-RF curve shape and either Fe or Pb content, among other elements. Indeed, our  $\mu$ -XRF results support a link between Fe content and the unwanted IR-RF curve shape (category #2 grains). For more conclusive or definitive results, more work is needed on a larger number of grains and a

combination of different techniques would be advisable to characterise all elements of interest.

- For one sample (X7343) we have SEM-EDS measurements (introduced in section 4.1; data is available open-access). This technique allows for the quantification of Na. As shown below, for this one sample we see that the Fe-rich grains (plotted in green and blue) are present in grains low in Na and in K (all grains were low in Ca, i.e., <1wt%). Though the Fe-rich grains characterised by  $\mu$ -XRF that showed a trend with the unwanted IR-RF were in a different set of grains, the combination of both datasets suggests the unwanted grains are not Na-rich.



12. Line 231-232 “We hypothesized.....”. How good is this hypothesis. Is it not creating biasing? Normally Fe coating on the grains can be dissolved by long HCl treatment as suggested by Jayangondaperumal et al., 2012. Does that not mean that it may not be the external Fe coating? Sometimes K-Feldspar also have a pinkish hue and Na-Feldspar is white. Hope this is not creating issue for authors as Na is not being measured in current methods.

- We tested this hypothesis using similar treatments to that suggested by the reviewer and observed no difference in IR-RF curve shape. This result could be due to insufficient treatment, so we cannot entirely rule out the possibility of the signal emanating from a coating. However, we have added a conclusion to our hypothesis based on our results (changes in bold type): “We attempted to remove this signal contamination using different chemical treatments such as HF, regal water, and heated regal water, however, without success. **This suggests the signal is not originating from a coating.**”

13. Line 240-241, “Note that...” I raised this concern in my earlier comments also and didn’t get a satisfactory answer for this. Please refer comment 29. If Fe is in coating, it can be dissolved by HCl/HF treatment. If it is in the volume and goes as high as 10% then it should be part of stoichiometry formula as is case with K. This can change the interpretations. Authors must see to this aspect.

- The minerals with up to 22wt% Fe (determined by SEM-EDS) probably have Fe in their stoichiometric formula, but these are probably not feldspar minerals because the Fe content is too high (see also plot in comment 11). These might be inclusions of other minerals in a mostly K-rich feldspar matrix or these might be Fe-rich mineral grains with small inclusions of feldspar and/or other minerals. The SEM-EDS measurements are only of spots (not maps) so we cannot conclusively distinguish these two scenarios. We note that mineralogically heterogeneous grains have been described for volcanic sediments (e.g., O’Gorman et al., 2021), which make density separation especially unreliable to isolate K-rich feldspar grains.
- From our  $\mu$ -XRF maps (Fig. 6), we can see that none of the three elements (K, Fe and Pb) are homogeneously distributed. In the category #1 grain (top row), Fe appears in higher concentrations in areas with low K concentrations (this is apparent from the lack of dark blue or black areas). In the category #2 grain (middle row), most of the grain contains only Fe and no K or Pb (magenta); in the one region containing K, only a small area contains both K and Fe (dark blue). These results support our conclusions that Fe is not a stoichiometric element in feldspar grains but appears in more or less discrete locations.
- In reference to comment 29 of the previous round, XRF measurements would theoretically be able to detect concentrations down to a ppm range. However, in order to obtain true concentrations, the sample would need to be thinner than 1  $\mu$ m to avoid depth-effects and self-absorption, so we cannot make a statement as to the concentration in our grains. Additionally, as we have shown in comment 11 (and the plot therein), a low-K grain does not necessarily mean high Na or Ca.

14. Line 240-241 “Between 10 to 30.....” I know it’s difficult, but it is really important to establish the mineralogy of these grains. As authors used transparent shiny and pinkish white grains, which could be Na Feldspar and K-Feldspar respectively. This could really effect the interpretations.

- As highlighted in the conclusions (section 5), we do not recommend manually picking grains based on visual characteristics. We agree that establishing the mineralogy is important, which is why we introduced the  $\mu$ -XRF analyses in section 4.3. Future work should indeed use complementary techniques (e.g., SEM-EDS) to also characterise the Na-content of grains, even though the spatial resolution would not be comparable to that from the  $\mu$ -XRF.

15. Line 246-250: How does the manual picking and optical microscope observations related with respect to i) , ii) and iii).

- We have rephrased to clarify that, after manual picking, we measured the two subsets of grains, i.e., a smaller subset that yielded the expected decreasing IR-RF curve and a larger subset, which yielded an increasing IR-RF signal (changes in bold type): “By manually selecting the grains based on their shape and colour **and the subsequent multi-grain IR-RF measurements**, we made three important observations:...”

16. Line 273-276 “Further.....” It is difficult to accept that it is pure K-Feldspar. how does correlation stands for K%? Please verify on some standard sample.

This is a hypothesis, and it is difficult to justify unless it is quantified. At present, we can only relate it to the color, which authors are expecting due to Fe content. The authors must understand even K-Feldspar has pinkish appearance and Na-Feldspar has whitish appearance. Although other colours does exist. Therefore, it may not be right to attribute the colour to Fe content without quantification.

- The attribution to K-feldspar is based on the IR-RF curve shape of these grains and not on the grain colour. All IR-RF literature reports IR-RF and *decreasing* IR-RF signals for K-feldspar and this curve shape was only observed for one of the two groups of grains, which happened to be transparent shiny angular grains. The other group displayed a different IR-RF curve shape (i.e., increasing), which has yet to be reported for K-feldspar grains. Since many previous IR-RF studies of K-feldspar samples with known compositions are available (e.g., Trautmann et al., 1998; Kumar et al., 2018; Murari et al., 2021), we do not find it necessary to measure standards to confirm that K-feldspar displays a decreasing curve shape as it is the fundamental assumption of IR-RF measurements.

17. Line 284-285 "grains displaying..." This statement indicate that elemental concentration K, Pb, Fe and Ba are not representative IR RF signal and should not be correlated to signal shape. On the other hand Ca, Ti, Mn may be related.

- In this sentence, we are only considering the presence/absence of elements. It is true that the presence of K, Pb, and Fe cannot be correlated to signal shape, since most grains contain them. We have changed the text to highlight this: "Most grains across all categories contain K, Pb, and Fe, and other elements. Among the grains displaying a decreasing IR-RF signal (category #1), all contain Ba (Fig. 4, middle), which is less present in grains from categories #2 and #3." However, we note that later in the text we show that the relative proportions of the common elements appears to be correlated to signal shape. For example, in Fig. 5a, grains from categories #1 and #2 cluster separately (with a few exceptions) even though only K, Pb, and Fe are considered.

## References

Kumar, R., Kook, M., Murray, A. S., and Jain, M.: Towards direct measurement of electrons in metastable states in K-feldspar: Do infrared-photoluminescence and radioluminescence probe the same trap?, *Radiation Measurements*, 120, 7–13, <https://doi.org/10.1016/j.radmeas.2018.06.018>, 2018.

Murari, M. K., Kreuzer, S., Frouin, M., Friedrich, J., Lauer, T., Klasen, N., Schmidt, C., Tsukamoto, S., Richter, D., Mercier, N., and Fuchs, M.: Infrared Radiofluorescence (IR-RF) of K-Feldspar: An Interlaboratory Comparison, *Geochronometria*, 48, 105–120, <https://doi.org/10.2478/geochr-2021-0007>, 2021.

O’Gorman, K., Tanner, D., Sontag-González, M., Li, B., Brink, F., Jones, B. G., Dosseto, A., Jatmiko, Roberts, R. G., and Jacobs, Z.: Composite grains from volcanic terranes: Internal dose rates of supposed ‘potassium-rich’ feldspar grains used for optical dating at Liang Bua, Indonesia, *Quaternary Geochronology*, 64, 101182, <https://doi.org/10.1016/j.quageo.2021.101182>, 2021.

Sontag-González, M. and Fuchs, M.: Spectroscopic investigations of infrared-radiofluorescence (IR-RF) for equivalent dose estimation, *Radiation Measurements*, 153, 106733, <https://doi.org/10.1016/j.radmeas.2022.106733>, 2022.

Trautmann, T., Krbetschek, M. R., Dietrich, A., and Stolz, W.: Investigations of feldspar radioluminescence: potential for a new dating technique, *Radiation Measurements*, 29, 421–425, [https://doi.org/10.1016/S1350-4487\(98\)00012-2](https://doi.org/10.1016/S1350-4487(98)00012-2), 1998.

**Additional comments from the associate editor (authors' responses are shown in red after each comment):**

When “luminescence” is used but what you actually meant was IR-RF, it is better to replace it with IR-RF (e.g. line 27, 70) to avoid potential confusion.

- We have replaced 5 instances of ‘luminescence’ with ‘IR-RF’. In the remaining ones, we are referring to luminescence in general (i.e., not specifically IR-RF).

Line 43-58: Please make the comparison of dating limit between IRSL and IR-RF using the same (range of) dose rate. Also, 600 Gy limit of IRSL seems to be the lowest among the reported values, and I think that both signals have the natural limit of ~1500 Gy, because the lower D<sub>0</sub> values of pIRIR were compromised by the test dose.

- Apologies for this inconsistency. We have changed it to (changes in bold type): “allows for the **routine** dating of older deposits of up to **~300 000 years or ~900 000 years** (considering a dose rate of **3 Gy ka<sup>-1</sup> or 1 Gy ka<sup>-1</sup>, respectively**)”
- We agree that 600 Gy is a very conservative estimate for the pIRIR dating limit. We have revised it to 900 Gy, which is the saturation limit in Liu et al. (2016) (based on 2D<sub>0</sub>) and is also given as the upper range for the reliable limit in the Murari et al. (2021) literature review (we had previously used the lower range). Test doses of >30% of D<sub>e</sub> were used by Liu et al. (2016), but we acknowledge that this is an aspect under current investigation by the luminescence dating community. Since we are aware that several researchers have obtained significantly higher doses under specific circumstances, we have added the word “routine” to the sentence in question.

Liu, J., Murray, A. S., Buylaert, J.-P., Jain, M., Chen, J., and Lu, Y.: Stability of fine-grained TT-OSL and post-IR IRSL signals from a c. 1 Ma sequence of aeolian and lacustrine deposits from the Nihewan Basin (northern China), *Boreas*, 45, 703–714, <https://doi.org/10.1111/bor.12180>, 2016.

Line 140: Feldspar mineralogy (mostly anorthoclase) and chemistry were reported in detail by Phillips et al (2023) for Gele Tuff. Please add more information sample feldspars here, rather than saying at later stage that the IR-RF characteristic of these samples could be different due to volcanic nature. Also, I think you could have selected K-richer grains by using a lower density heavy liquid, as the end member density of sanidine is 2.52.

- We have added details on the Gele tuff from the suggested paper: “Previous compositional analyses of Gele Tuff pumice feldspars (crushed clasts without density separation) indicate they are mostly composed of anorthoclase with smaller proportions of sanidine and plagioclase; K, Na and Ca contents ranged ~1–6 wt %, ~5–6 wt % and ~0–3 wt %, respectively, without appreciable differences between the grains’ cores and rims (Phillips et al., 2023). Relatively high Ba contents of up to 0.8wt% were also reported in that study, with a positive correlation between Ba and Na contents.” However, we stress that those results cannot be directly compared to ours because our sample underwent density separation to increase the proportion of K-rich feldspar and their feldspar grains were obtained by crushing pumice clasts and then visually selecting grains.
- In future work, we will consider testing a lower density, thank you for the suggestion.

### **Other changes by the authors**

- 1) Correction of Ar/Ar age of the Gele tuff: “ $1.315 \pm 0.002$  Ma (Phillips et al., 2023).”
- 2) Correction of ‘normalised’ to ‘normalized’ in Fig. 8 legend.