

Reply to the comments by J. Durcan on the manuscript gchron-2024-10

We wish to thank the referee for the careful review of our manuscript and respond below to the points raised.

- Add a sentence to explain why there is a negative relationship between U concentration and TL sensitivity

The negative relationship between TL sensitivity and U content is thought to arise from damaging the crystal structure as a result from alpha-recoil, a process that can be reversed by high-temperature (950 °C) annealing (Vaz and Senftle, 1971; Amin et al., 1983). This information is added in the introduction of the revised manuscript. The same mechanism applies to radiation damage caused by internal Th, although the overall effect will be smaller than that induced by U, due to commonly lower Th abundances in zircon (compared to U) and the relatively smaller number of alpha-decays in the Th decay chain (about 25 % of the U alpha-activity if normalised to unit content).

In more general terms, the TL produced in a zircon following a storage period t_s may be written as

$$TL \sim c_U \cdot N_{TL} \cdot t_s$$

where c_U is the U content and N_{TL} the number of defects responsible for TL generation that are currently present in the crystal.

For simplicity, let us fix $t_s = \text{const}$ and study how do TL and TL_{sens} depend on c_U , provided all our experiments are conducted for the same storage time:

$$TL \sim c_U \cdot N_{TL}$$

For a given zircon crystallisation age, we can relate c_U to the number of U-induced alpha-decays N_{dec} accumulated in the crystal since the time of its crystallisation:

$$TL \sim k \cdot N_{\text{dec}} \cdot N_{TL}$$

where k is a coefficient of linear proportionality. However, the number of currently available TL-relevant defects N_{TL} is also a function of the number of decays (as the latter cause a destruction of TL-relevant defects):

$$TL \sim k \cdot N_{\text{dec}} (N_{TL \text{ initially present at the time of crystallisation}} - \varphi N_{\text{dec}})$$

where φ is a parameter signifying the mean number of destroyed TL-relevant defects per alpha-decay. As a first approximation, φ could be considered constant through geological time, though this only holds true provided the alpha-tracks do not interact with each other. For high U contents and old crystallisation ages, the tracks can intersect or otherwise interact with each other, thus reducing the mean number of destroyed TL-relevant defects per alpha-decay while the zircon is aging. The relevant modelling includes recurrent relationships that are easy to program as a computer code (numerical integration), but less easy to present as an analytical solution (i.e., as a single and compact formula integrating the number of the destroyed TL-relevant defects over the geological age). In this reply, for the sake of simplicity, we will consider φ as a constant, but we understand that the exact representation of it is worth a deeper study.

The above equation is of the form $y = ax - bx^2$, i.e., TL should first increase with N_{dec} before reaching a maximum at $a/2b$ and then decrease.

Let us now consider the TL sensitivity $TL_{\text{sens}} = TL/\text{dose}$. We have:

$$TL_{\text{sens}} \sim \frac{k \cdot N_{\text{dec}}(N_{\text{TL initially present at the time of crystallisation}} - \varphi N_{\text{dec}})}{\text{dose}}$$

For a given storage time, the dose is linearly proportional to c_U , as is the number of decays N_{dec} that were accumulated in the crystal since the time of crystallisation:

$$TL_{\text{sens}} \sim \frac{c_U(N_{\text{TL initially present at the time of crystallisation}} - \varphi N_{\text{dec}})}{d \cdot c_U}$$

where d is, again, a coefficient characterising the linear proportionality between the U content and the dose during the storage period.

The final relationship can be given as follows:

$$TL_{\text{sens}} \sim \frac{N_{\text{TL initially present at the time of crystallisation}} - \varphi N_{\text{dec}}}{d}$$

or simply

$$TL_{\text{sens}} \sim N_{\text{TL initially present at the time of crystallisation}} - \varphi N_{\text{dec}}$$

The above relationships provide a framework for further discussion, but do contain simplifications that are not limited to the exact conduct of the parameter φ that we assumed to be constant. Another level of detail comes into play once we consider the statistical performance of φ and possibly other parameters involved in the above calculus, which are in fact controlled by ordinary Poisson processes over space or over time.

- HF etching of zircon grains

The procedure of HF etching of heavy mineral samples to isolate zircons has been described in the literature, though not in great detail (e.g., Sutton and Zimmerman, 1976; Smith, 1988; Templer and Smith, 1988). While previous studies have typically used HF etching for 1 h, we found that, particularly for sample Can1, longer etching times were required to dissolve most of the non-zircon components. Since HF attacks all heavy minerals except zircon (Sutton and Zimmerman, 1976), extended etching times should not negatively affect sample quality. Aliquots of the etched samples were examined under a binocular microscope to assess zircon purity. Neither this inspection nor cathodoluminescence imaging or LA-ICP-MS analyses showed any evidence of etching pits or changes in zircon morphology resulting from HF etching.

Furthermore, we did not add H_2SO_4 , hence there is the possibility of accumulation of SiF_6^{2-} anions in the solution, buffering the silicates and slowing their dissolution. Adding H_2SO_4 will break the hexafluoride anion and liberate SiF_4 as a gas that escapes from the reaction mixture. Finally, it is expected that the dissolution rate of volcanic glass (and, actually, any silicate glass), is faster compared to crystalline phases. Therefore, the required etching time also depends on the type of sample hosting the zircons.

- Comparison of zircon photoionisation cross-sections with quartz OSL components

Thank you for this critical comment. We recognize that the components fitted in zircon and quartz OSL decay curves may not be physically related. However, the aim of this paragraph was also to provide the reader with a benchmark regarding the optical resetting rates of zircon in relation to minerals more

commonly used in luminescence geochronology, such as quartz. Following the recommendation, we adapt the paragraph and focus on the comparison of photoionisation cross-sections, without relating to quartz OSL components.

- Shortening the discussion by removing the section on the dating range

As both reviewers ask for adapting the discussion to better link it to the experimental data presented in our study, we decide to remove section 4.2.4.

- Figure 7

Following the recommendation, we remove the lines indicating the quartz s1 and s3 components from Fig. 7 in the revised version of the manuscript. In addition, we create a plot of photoionisation cross-section versus component number for the two samples, as suggested, and show this plot in the supplement.

References

- Amin, Y., Bull, R., Green, P., Durrani, S., 1983. Effect of radiation damage on the TL properties of zircon crystals. Third specialist seminar on TL and ESR dating.
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- Sutton, S., Zimmerman, D., 1976. Thermoluminescent dating using zircon grains from archaeological ceramics. *Archaeometry* 18, 125-134.
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- Vaz, J.E., Senftle, F.E., 1971. Thermoluminescence study of the natural radiation damage in zircon. *Journal of Geophysical Research* 76, 2038-2050.