# Evaluation of zircon from the Pliocene Utaosa rhyolite Japan as reference material for (U-Th)/He thermochrnonometry

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- **Motivation:** Exploration of potential zircons for age standards of (U-Th)/He method
- **Samples:** BM4-iv (the Miocene Buluk Tuff, an age standard of zircon fission-track method), TRG04-21 and TRG07-21 (the Pliocene Utaosa rhyolite, Japan)
- **Method:** Conventional zircon (U-Th)/He (ZHe) analyses for ~30 zircon grains in each sample at the University of Melbourne

## ◆Highlights

- ✓ ZHe ages of 17.7 ± 1.74 Ma, 2.43 ± 0.14 Ma, and 2.95 ± 0.22 Ma (error ranges of 95% CI) were obtained for BM4-iv, TRG04-21, and TRG07-21, respectively.
- ✓ TRG04-21 shows a potentiality for ZHe standards, while TRG07-21 and BM4-iv are not suitable because of over-dispersion of single ZHe ages.

## ➢1. Introduction: Exploration for reference material zircons

### What is an ideal zircon for the (U-Th)/He age standard like?

- Collected from accessible and geologically well-documented horizon
- Supplied sufficient zircon grains, consisted of one generation (free from inherited ones)
- Easy to interpret its age and thermal history (e.g., rapid cooling, no possible reheating)
- Moderate size and euhedral shape with two terminations (no need to calibrate especially)
- Homogenous distribution of U-Th in single grain
- Less radiation damage as well as inclusions and/or dislocations etc.

to satisfy such conditions

The ZHe system has empirically employed the Fish Canyon Tuff (FCT) as natural zircon reference materials because FCT zircons are well-investigated as a fission-track age standard (e.g., Gleadow et al., 2015). ZHe grain ages of FCT sometimes over-dispersed owing to considerable parent isotope zonation in some crystals (Fig. 1: Dobson et al., 2008). Therefore, new candidates of ZHe reference material are required, inviting a recent search for alternative potential ZHe standards (e.g., Li et al., 2017; Yu et al., 2020; Kirkland et al., 2020). These works reported robust ZHe data with little age dispersion because of homogeneous U-Th distribution in zircon megacrysts. However, a practical issue still remains because ZHe analyses of unknowns are carried out grain-by-grain as opposed to analyzing large pieces of single grain. We have attempted to evaluate the capability of candidates expected as possible reference materials thermochronologically.

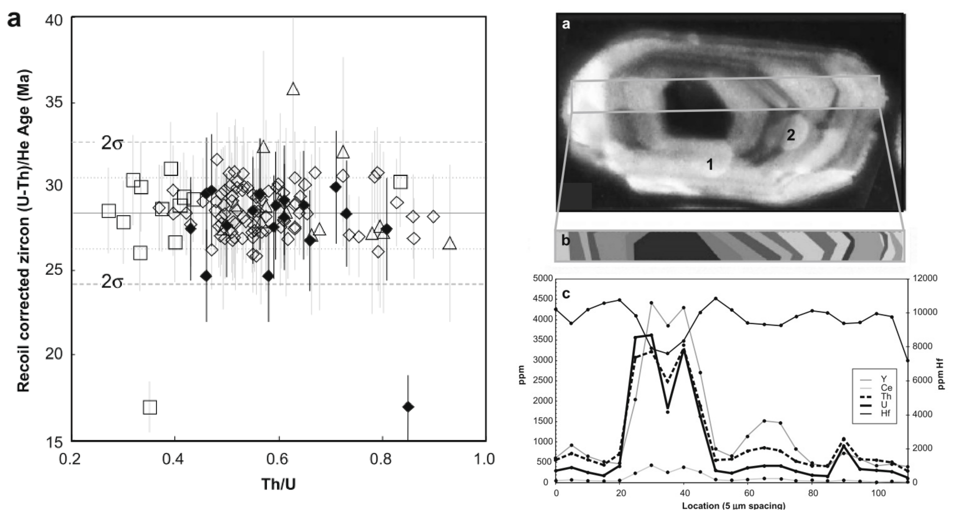



Fig. 1: Previous investigations of FCT based on ZHe analyses and chemical mapping (Dobson et al., 2008). All error bars of ages are 2 sigma in the left figure, and the average age of the FCT zircons is 28.3 ± 3.1 Ma (2 sigma, n=129). On the right, CL image of crystal was used for SIMS traverse, and chemical data indicated U-Th zonation of single zircon crystal.

## ➢2. Sample selections: Rapid cooling and younger zircon

We considered to examine zircon samples of rapid cooling and relatively young (<100 Ma) ages. This is because such samples are expected to empirically exhibit simple thermal histories and little radiation damage, deducing that age dispersion caused by radiation damage can be relatively small. In this study, we adopted the Miocene Buluk Tuff from the a younger age standard of ZFT system, and the Pliocene Utaosa rhyolitic lava, Japan (see details of Figs. 2 and 3). Rapid cooling and younger ages have been verified based on other thermochronologic studies for the Buluk Tuff (e.g., ZFT: Hurford & Watkins, 1987; ZHe: Tagami et al., 2003, Tibari et al., 2016) and the Utaosa rhyolite (Bt K-Ar and Ar/Ar: Uto et al., 1994; 1997; ZFT: Uto et al., 1994; ZHe: Tagami et al., 2003).

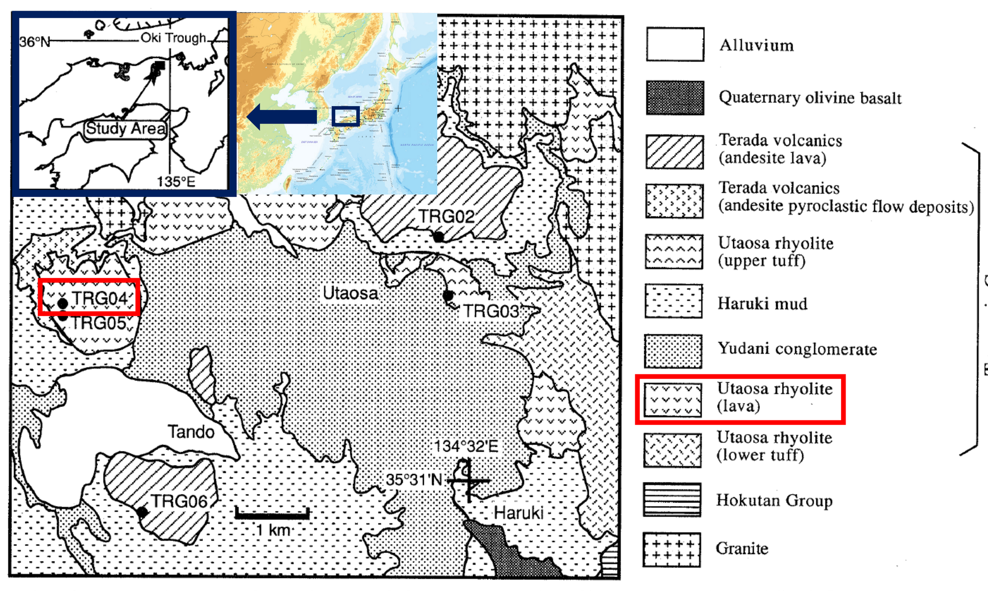



Fig. 2: Locations and geology of the Utaosa rhyolite, Japan (modified from Uto et al., 1994). TRG04-21 was collected from the same locality of TRG04 in this figure. TRG07-21 is located at the same rock body and ca. 50 m eastward from the TRG04(-21) site.

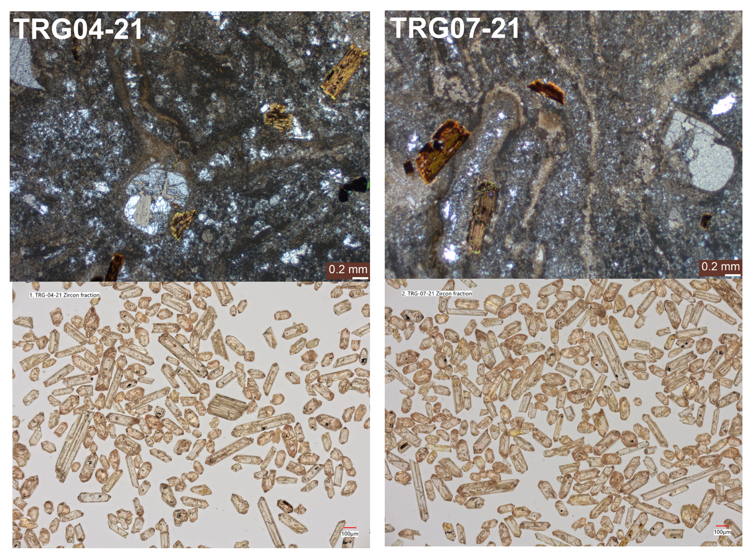


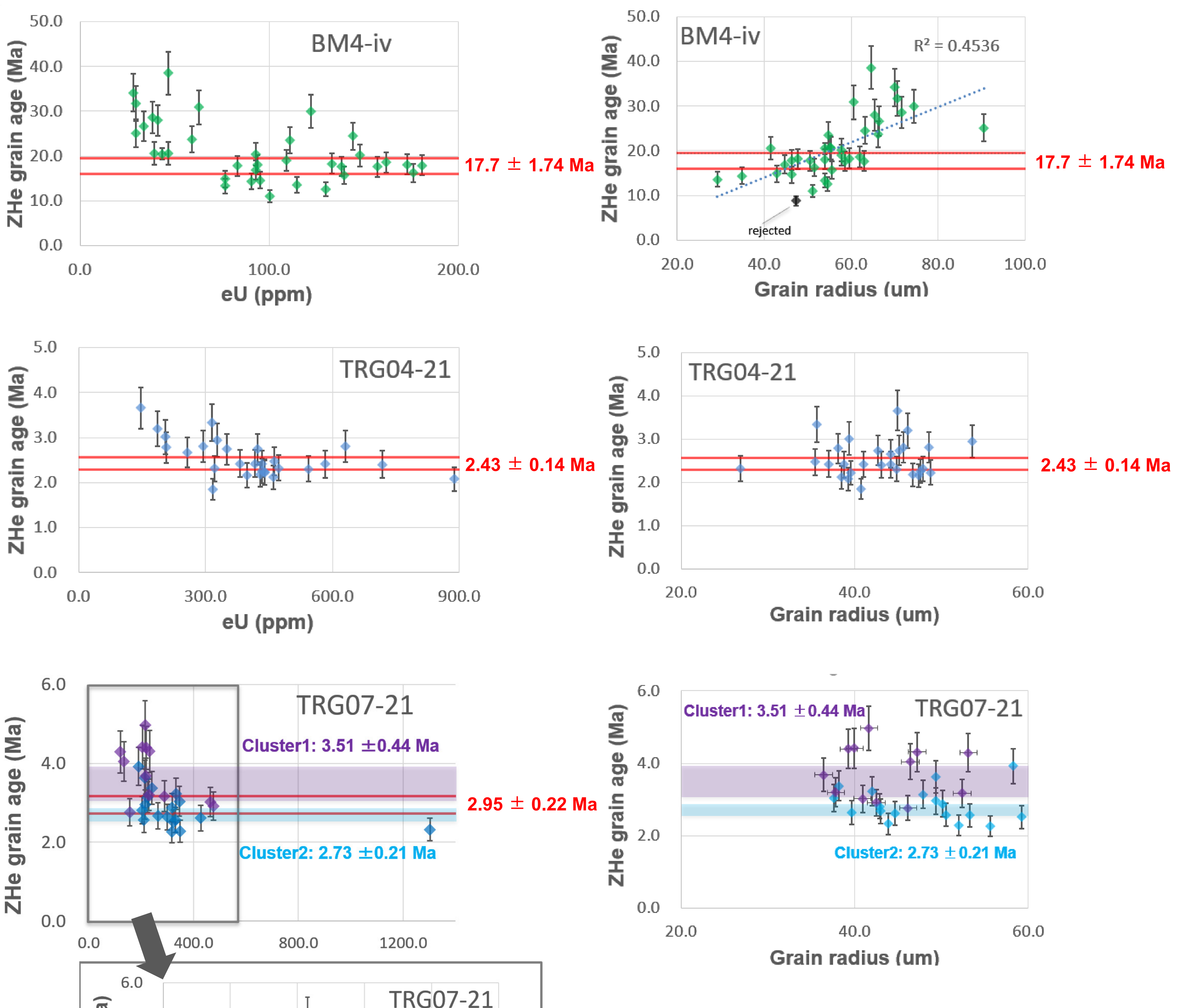

Fig. 3: Thin-section observations with a polarized microscope, and extracted zircon fractions of TRG04-21(left) and TRG07-21(right). These rocks appeared biotite-bearing rhyolites, and both samples yielded plenty of euhedral zircon crystals.

## ➢3. Zircon (U-Th)/He dating results and thermochronologic interpretations of BM4-iv,TRG04-21, and,TRG07-21

Table 1: Summary of ZHe data in this study.

| Sample code | No. of grains for age calculation | $^4He$ (ncc) | [U] (ppm) | [Th] (ppm) | Th/U ratio | $F_T$ | Weighted mean age ± 95%CI (Ma) | MSDW | Reference ZHe age ± 2 sigma |
|---|---|---|---|---|---|---|---|---|---|
| BM4-iv | 36/37 | 0.153–5.408 *(Ave.:1.558)* | 24.2–150.5 *(Ave.:87.3)* | 16.7–142.7 *(Ave.:66.5)* | 0.61–1.11 *(Ave.:0.75)* | 0.60–0.89 *(Ave.:0.79)* | 17.7 ± 1.74 | 20.2 | 16.1 ± 1.6 Ma: Tagami et al. (2003) |
| TRG04-21 | 29/30 | 0.146–1.017 *(Ave.:0.473)* | 124.1–740.1 *(Ave.:340.2)* | 93.0–630.2 *(Ave.:297.3)* | 0.70–1.48 *(Ave.:0.87)* | 0.61–0.80 *(Ave.:0.75)* | 2.43 ± 0.14 | 5.89 | 2.61 ± 0.36 Ma: Tagami et al. (2003) |
| TRG07-21 | 30/30 | 0.326–1.597 *(Ave.:0.701)* | 99.2–1107.2 *(Ave.:251.5)* | 90.9–831.7 *(Ave.:217.0)* | 0.63–1.18 *(Ave.:0.89)* | 0.71–0.83 *(Ave.:0.78)* | 2.95 ± 0.22 | 10.8 | No ZHe data available |
| *cluster1* | 18/18 | 0.407–1.597 *(Ave.:0.795)* | 159.5–1107.2 *(Ave.:283.3)* | 131.9–831.7 *(Ave.:240.0)* | 0.75–1.18 *(Ave.:0.87)* | 0.71–0.83 *(Ave.:0.79)* | 2.73 ± 0.21 | 5.98 | *Bt K-Ar of 2.42 ± 0.42 Ma, *ZFT of 3.07 ± 0.36 Ma |
| *cluster2* | 12/12 | 0.326–0.794 *(Ave.:0.560)* | 99.2–414.9 *(Ave.:203.9)* | 90.9–393.9 *(Ave.:182.6)* | 0.63–1.15 *(Ave.:0.91)* | 0.73–0.82 *(Ave.:0.77)* | 3.51 ± 0.44 | 9.87 | (Uto et al., 1994) |
| FCT | 2/2 | 4.482, 5.925 | 238.5, 446.7 | 146.4, 230.1 | 0.61, 0.52 | 0.77, 0.76 | 28.3 ± 2.4 | 3.43 | 28.5 ± 0.4 Ma: Gleadow et al. (2015) |

$F_T$: the alpha-ejection correction after Farley et al. (1996), MSWD: mean square weighted deviation. Corrected grain ages by $F_T$ were used to calculate weighted mean ages by IsoplotR (Vermeersch, 2018). All analyzed crystals have euhedral geometries with two terminations (2T).



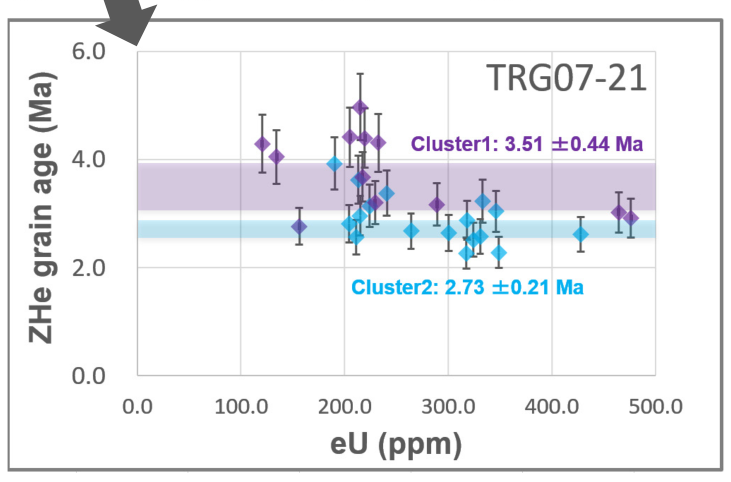




Fig. 4: Single ZHe ages versus effective Uranium concentrations (eU), and grain radius of BM4-iv , TRG04-21, and TRG07-21. The values of eU were calculated as the following equation: [eU]= [U]+0.235[Th] (ppm). All error bars of single ZHe ages are 2 sigma. Horizontal red lines indicate weighted mean ages within 95%CI in Table 1. As to BM4-iv, one grain was statistically rejected and removed in the ZHe vs. eU plot (eU of that is 369.4 ppm). Regarding TRG07-21, the U-Th analyses were conducted in two separate batches. Two distinct clusters were identified as cluster1 (n=18) and cluster2 (n=12), and each weighted mean age does not overlap regarded with the error range.

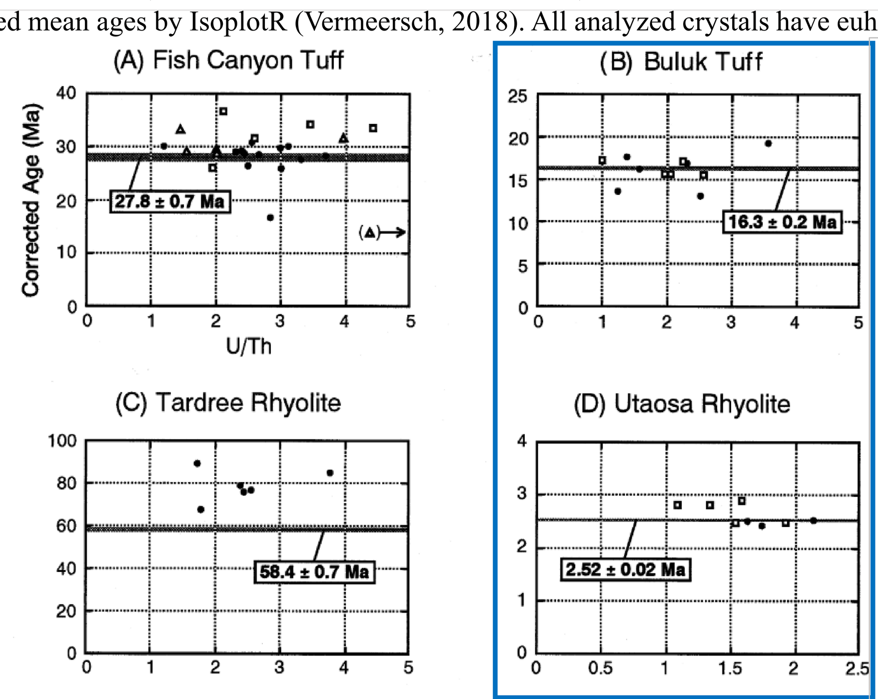



Fig. 5: ZHe age vs. Th/U ratio plots of four samples (Tagami et al., 2003) . Horizontal shaded zones indicate reference ages of other thermochronometric data such as Ar/Ar or zircon U-Pb methods, not their weighted mean ZHe ages.

ZHe dating results are shown in Table 1. As a ZHe age standard in this study, FCT zircons was simultaneously analyzed, indicating reasonable ages with the reference one (e.g., Gleadow et al., 2015). The FCT data thus verified the accuracy of analyses in this study.

Regarding TRG04-21, most of the single ZHe ages overlap with its range of weighted mean age, while those of TRG07-21 and BM4-iv over-disperse and have relatively high MSWDs (Fig. 4 and Table 1). In particular, two clusters were identified in TRG07-21, yielding significantly different ages. A global weighted mean age of 2.95 ± 0.22 Ma was also obtained for TRG07-21, indicating inconsistent with the age of TRG04-21. Different thermal histories possibly caused such discrepancy, although TRG07-21 was collected from the same rock body of TRG04-21 and they seemed to be similar lithologies (Fig. 3). Further analyses will contribute to interpret this observation. Note that single ZHe ages of BM4-iv correlated with grain radii weakly ($R^2 = 0.45$) , but those of TRG04-21 and TRG07-21 show no correlations. In addition, grain ages of all samples have little correlations with eU ($R^2 < 0.4$).

Consequently, weighted mean ZHe ages of BM4-iv and TRG04-21 show consistent with reference ages within error ranges of 2 sigma (Table 1 and Fig. 5). TRG07-21 has no available reference data, the age is also consistent with previous age of TRG04. Note that the older weighted mean age of cluster1 indicates inconsistent with previous ZHe data of TRG04, while the younger one of cluster2 is consistent.

## ➢4. Discussion: Evaluation as reference materials

- ◆ **Buluk Tuff**: Weighted mean age was acceptable but the wide spread in single ages (ca. 10–40 Ma). Lower U-Th concentrations (<200 ppm) in single crystal and the grain geometry (e.g., too long length, rough surfaces, large different between width 1 and 2) are far from ideal for ZHe dating.
- ◆ **TRG04-21**: Reasonable weighted mean age and the relatively focusing in single ages (ca. 1.9–3.7 Ma). All previous ages lie around ca. 2.5 Ma based on other thermochronometers (e.g., Bt K-Ar; Bt Ar/Ar; ZFT; ZHe). These results possibly deduced the capability of a reference material.
- ◆ **TRG07-21**: Consistent with previous ZHe data of TRG04, but scattering in single ages (ca. 2.3–5.0 Ma) and two clusters were identified. No evidence are available to explain such age discrepancies between the clusters, as well as TRG04-21.

### Future prospects

- ✓ Other possible candidates of ZHe age standards will be analyzed (e.g., Mt. Dromedary, etc.).
- ✓ Further investigations are required such as U-Pb dating and U-Th mapping based on EPMS and/or LA-ICP-MS.
- ✓ The round-robin test among other laboratories is desirable.

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