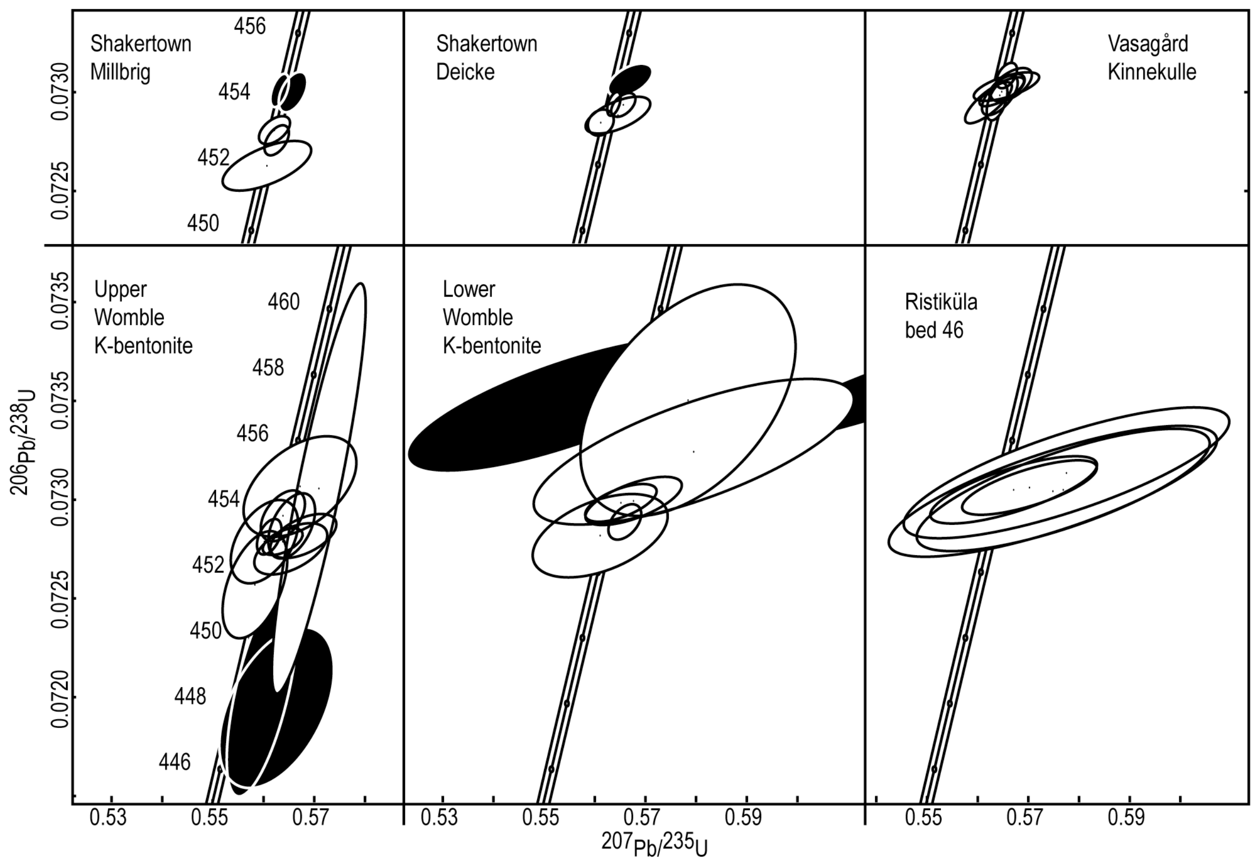
## Supplementary Material

**U-Pb Data Reduction.** Data (Supplementary Data Table 1) were reduced using Tripoli and U-Pb ages were calculated and plotted using UPb_Redux software (Bowring *et al.* 2011). Blanks were calculated on the basis careful measurement of $^{204}$Pb during each U-Pb analysis and in all reagents used in the process of preparing individual zircon crystals. Pb concentrations in all reagents were maintained consistently below 0.16 pg/g. A typical analytical session involved the measurement of various reagent blanks, NBS Pb standards, and approximately 15 unknown samples. Mass discrimination was continually monitored by regular measurements of in-house standard solutions. The decay constants for uranium used here are from Jaffey *et al.* (1971).




**Supplementary Figure 1.** Concordia diagram showing data plotted with UPb Redux at the 95% confidence interval. Black ellipses, which are interpreted to represent either inheritance (older) or Pb loss (younger), are not included in the preferred $^{206}$Pb/$^{238}$U weighted mean age.

**Preparation.** All zircon crystals, except for the Ristiküla bed 46 sample, were extracted from a clay matrix (presumably K-bentonite), by physical disaggregation and washing with water. Ristiküla bed 46 could be considered a cryptotephra (*sensu* Turney *et al.* 2004) because the bed is defined by a relatively high concentration of microscopic volcanogenic crystals dispersed in a limestone matrix. The Ristiküla bed 46 zircon crystals were extracted by dissolution in concentrated HCl. The remaining heavy fractions of all samples were then placed in tetrabromoethane and then methylene idodide; both centrifuged at 300 RPM for 20 minutes to separate the heavy mineral fractions. Zircon crystals were then hand picked under a binocular, reflected light microscope. Crystals were selected that were slender and optically clear, while avoiding those large crystal with the greatest width to length ratio and those that appeared cloudy and metamict. The samples were then washed in clean 6N HCl prior to annealing in quartz crucibles at 900ºC for 48 hours. Annealed crystals were washed again in HCl prior to chemical abrasion in 3 mL Savillex beakers (placed inside a 125 mL Parr acid dissolution bombs) at 180ºC for 12-16 hours. Samples with relatively small zircon crystals (width approximately less than 10 microns) were removed for examination after 10 hours so as not to completely dissolve the material. The chemical abrasion used here is a modified version from Mattinson (2005). Concentrated HF with a few drops of 7N $HNO_3$ are the chemical abrading reagents. Zircon crystals were then selected from the chemically abraded lot based on clarity and size (many crystals did not preserve, or only partially so, during the chemical abrasion procedure). Each crystal was then placed in individual 3 mL Savillex and photographed under a binocular microscope. It was not possible to weigh each crystal; however, the mass of each fraction (Supplementary Data Table 2) is estimated from photographs. These crystals were then washed individually in 3 mL Savillex beakers in ultrapure $H_2O$, HCl, $HNO_3$, and HF several times each with each wash step in an ultrasonic bath.

**Tracer.** Cleaned zircons were placed in PTFE microcapsules with concentrated HF and a U-Pb tracer in $HNO_3$ prepared and distributed by the EARTHTIME organization (www.earthtime.org). A carousel containing 15 microcapsules was placed inside a 125 mL PTFE vessel with concentrated HF approximately 0.2 mL $HNO_3$.The tracer has a composition of:

| | | |
|---|---|---|
| $^{202}Pb/^{205}Pb$ | $9.992 \times 10^{-01}$ | $\pm 2.656 \times 10^{-04}$, 1σ |
| $^{204}Pb/^{205}Pb$ | $1.050 \times 10^{-04}$ | $\pm 9.158 \times 10^{-06}$, 1σ |
| $^{206}Pb/^{205}Pb$ | $4.825 \times 10^{-04}$ | $\pm 1.660 \times 10^{-04}$, 1σ |
| $^{207}Pb/^{205}Pb$ | $4.324 \times 10^{-04}$ | $\pm 1.377 \times 10^{-04}$, 1σ |
| $^{208}Pb/^{205}Pb$ | $1.042 \times 10^{-03}$ | $\pm 3.349 \times 10^{-04}$, 1σ |
| $^{233}U/^{235}U$ | $9.951 \times 10^{-01}$ | $\pm 5.384 \times 10^{-05}$, 1σ |
| $^{238}U/^{235}U$ | $3.080 \times 10^{-03}$ | $\pm 3.955 \times 10^{-07}$, 1σ |
| $^{205}Pb$ (mol/g) | $1.031 \times 10^{-11}$ | $\pm 2.578 \times 10^{-14}$, 1σ |
| $^{235}U$ (mol/g) | $1.034 \times 10^{-09}$ | $\pm 2.595 \times 10^{-12}$, 1σ |

**Isotope Separation.** Dissolved and spiked zircon crystals were then dried down and re-dissolved in 6 N HCl in the high pressure acid dissolution bomb. After this the dissolved fractions were then prepared for separation of lead and uranium by liquid chromatography following (Krogh 1973). Uranium and lead was collected together in the same 7 mL Savillex beaker and dried down with one drop of ultrapure $H_3PO_4$, which were later taken up in less than a microliter of silica gel emitter solution (Gerstenberger & Haase 1997) and loaded onto an outgassed rhenium filament.

**Analytical.** All samples were measured on a Thermo-Finnegan Triton thermal ionization mass spectrometer at the University of Geneva, Switzerland. The Pb was measured with a secondary electron multiplier (SEM) by peak hopping across all Pb masses for at least 100 ratios. SEM yield and dark noise was measured every day. Background was measured and peak centering with re-focusing performed for every 20 ratios and interferences were continuously monitored. Uranium was measured on the faraday cups in static mode for at least 200 ratios with baselines measured and peak centering with re-focusing performed for every 20 ratios. The gain was measured at least once everyday.

**Blanks.** The applied blank composition was determined by repeated analyses of the reagents and materials used in the preparation of the samples. The Pb blank composition is:

| | | |
|---|---|---|
| $^{206}Pb/^{204}Pb$ | 18.30 | ± 0.71%, 1σ |
| $^{207}Pb/^{204}Pb$ | 15.47 | ± 1.03%, 1σ |
| $^{208}Pb/^{204}Pb$ | 37.60 | ± 0.98%, 1σ |

**Supplementary References**


BOWRING, J.F., MCLEAN, N.M. & BOWRING, S.A. 2011. Engineering cyber infrastructure for U-Pb geochronology: Tripoli and U-Pb_Redux. *Geochemistry Geophysics Geosystems,* **12**, Q0AA19, doi: 10.1029/2010gc003479.

GERSTENBERGER, H. & HAASE, G. 1997. A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations. *Chemical Geology,* **136**, 309–312, doi: 10.1016/s0009-2541(96)00033-2.

JAFFEY, A.H., FLYNN, K.F., GLENDENI.LE, BENTLEY, W.C. & ESSLING, A.M. 1971. Precision measurement of half-live and specific activities of U-235 and U-238. *Physical Review C* **4**, 1889–1906, doi: 10.1103/PhysRevC.4.1889.

KROGH, T.E. 1973. Low-contamination method for hydrothermal decomposition of zircon extraction of U and Pb for isotopic age determinations. *Geochimica Et Cosmochimica Acta,* **37**, 485–494, doi: 10.1016/0016-7037(73)90213-5.

TURNEY, C.S.M., LOWE, J.J., DAVIES, S.M., HALL, V., LOWE, D.J., WASTEGÅRD, S., HOEK, W.Z. & ALLOWAY, B. 2004. Tephrochronology of last termination sequences in Europe: a protocol for improved analytical precision and robust correlation procedures (a joint SCOTAV–INTIMATE proposal). *Journal of Quaternary Science,* **19**, 111–120, doi: 10.1002/jqs.822.

**Supplementary Table 1. CA-TIMS U-Pb zircon data.**

| | Composition | | | | Isotopic Ratios | | | | | | | | | Dates (Ma) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mass (mg) | Th/U [a] | Pb*/Pbc [b] | Pb* (pg) [d] | $^{206}Pb/^{204}Pb$ [e] | $^{208}Pb/^{206}Pb$ [f] | $^{207}Pb/^{206}Pb$ [f] | ±2σ % | $^{207}Pb/^{235}U$ [f] | ±2σ % | $^{206}Pb/^{238}U$ [f] | ±2σ % | Corr. coef. | $^{207}Pb/^{206}Pb$ [g] | ±2σ abs | $^{207}Pb/^{235}U$ [g] | ±2σ abs | $^{206}Pb/^{238}U_{<Th>}$ [h] | ±2σ abs |
| **Upper Womble K-bentonite** | | | | | | | | | | | | | | | | | | | |
| z4 | 0.0036 | 0.64 | 4.9 | 21.3 | 303.832 | 0.199662 | 0.056719 | 1.81 | 0.562661 | 2.01 | 0.071947 | 0.57 | 0.47 | 480.6 | 40.1 | 453.3 | 7.4 | 447.96 | 2.45 |
| z5 | 0.0021 | 0.54 | 14.4 | 17.5 | 874.232 | 0.168484 | 0.056684 | 0.74 | 0.570978 | 1.62 | 0.073057 | 1.42 | 0.89 | 479.3 | 16.4 | 458.6 | 6.0 | 454.63 | 6.23 |
| z6 | 0.0030 | 0.62 | 24.8 | 46.2 | 1464.13 | 0.192537 | 0.055899 | 0.39 | 0.561186 | 0.43 | 0.072812 | 0.12 | 0.46 | 448.3 | 8.6 | 452.3 | 1.6 | 453.16 | 0.54 |
| z7 | 0.0031 | 0.63 | 12.3 | 19.1 | 729.128 | 0.197561 | 0.056299 | 0.74 | 0.565628 | 0.82 | 0.072867 | 0.23 | 0.47 | 464.2 | 16.4 | 455.2 | 3.0 | 453.49 | 0.99 |
| z8 | 0.0024 | 0.72 | 10.4 | 12.6 | 607.264 | 0.224772 | 0.056366 | 0.95 | 0.559815 | 1.25 | 0.072032 | 0.74 | 0.65 | 466.8 | 21.1 | 451.4 | 4.6 | 448.47 | 3.21 |
| z11 | 0.0036 | 0.86 | 5.6 | 19.6 | 322.959 | 0.269748 | 0.056308 | 1.82 | 0.567266 | 1.96 | 0.073066 | 0.35 | 0.48 | 464.5 | 40.4 | 456.2 | 7.2 | 454.68 | 1.53 |
| z12 | 0.0015 | 0.48 | 13.7 | 18.1 | 842.829 | 0.151498 | 0.056183 | 0.65 | 0.563851 | 0.70 | 0.072787 | 0.09 | 0.54 | 459.6 | 14.4 | 454.0 | 2.5 | 453.02 | 0.40 |
| z14 | 0.0018 | 0.58 | 9.0 | 10.0 | 549.145 | 0.179877 | 0.055825 | 1.09 | 0.560254 | 1.19 | 0.072787 | 0.29 | 0.45 | 445.4 | 24.2 | 451.7 | 4.3 | 453.01 | 1.27 |
| z15 | 0.0020 | 0.70 | 14.1 | 16.6 | 819.857 | 0.219638 | 0.056087 | 0.71 | 0.563893 | 0.77 | 0.072918 | 0.18 | 0.47 | 455.8 | 15.7 | 454.1 | 2.8 | 453.80 | 0.77 |
| z16 | 0.0016 | 0.86 | 8.2 | 9.1 | 467.084 | 0.267484 | 0.056371 | 1.19 | 0.565450 | 1.27 | 0.072751 | 0.18 | 0.53 | 467.0 | 26.3 | 455.1 | 4.7 | 452.79 | 0.78 |
| z17 | 0.0024 | 0.67 | 8.5 | 21.1 | 507.057 | 0.209509 | 0.056568 | 1.07 | 0.567932 | 1.15 | 0.072816 | 0.15 | 0.54 | 474.7 | 23.7 | 456.7 | 4.2 | 453.18 | 0.67 |
| z18 | 0.0018 | 0.64 | 9.5 | 14.0 | 568.530 | 0.200700 | 0.055805 | 1.02 | 0.558379 | 1.14 | 0.072569 | 0.37 | 0.48 | 444.6 | 22.7 | 450.5 | 4.2 | 451.70 | 1.63 |
| **Lower Womble K-bentonite** | | | | | | | | | | | | | | | | | | | |
| z1 | 0.0017 | 0.84 | 9.1 | 6.3 | 519.444 | 0.263253 | 0.055892 | 2.25 | 0.561161 | 2.37 | 0.072817 | 0.29 | 0.47 | 448.1 | 50.0 | 452.3 | 8.7 | 453.19 | 1.27 |
| z2 | 0.0008 | 0.72 | 1.9 | 2.1 | 127.428 | 0.225442 | 0.057397 | 5.10 | 0.579631 | 5.45 | 0.073243 | 0.50 | 0.72 | 506.8 | 112 | 464.2 | 20.3 | 455.74 | 2.21 |
| z3 | 0.0007 | 0.96 | 8.6 | 8.1 | 478.716 | 0.301148 | 0.056171 | 1.17 | 0.565244 | 1.25 | 0.072984 | 0.13 | 0.62 | 459.1 | 25.9 | 454.9 | 4.6 | 454.18 | 0.57 |
| z4 | 0.0005 | 1.12 | 4.6 | 4.5 | 254.025 | 0.348710 | 0.057080 | 3.38 | 0.578486 | 3.67 | 0.073504 | 0.80 | 0.46 | 494.6 | 74.4 | 463.5 | 13.7 | 457.30 | 3.52 |
| z5 | 0.0011 | 0.96 | 6.8 | 5.2 | 379.422 | 0.300760 | 0.061917 | 5.84 | 0.628735 | 6.31 | 0.073648 | 0.50 | 0.94 | 671.2 | 125 | 495.3 | 24.7 | 458.17 | 2.21 |
| z6 | 0.0022 | 0.69 | 17.3 | 21.3 | 1008.01 | 0.214318 | 0.056322 | 0.53 | 0.566020 | 0.57 | 0.072887 | 0.12 | 0.45 | 465.1 | 11.7 | 455.4 | 2.1 | 453.61 | 0.54 |
| z7 | 0.0007 | 0.76 | 6.4 | 6.6 | 379.117 | 0.239225 | 0.056412 | 1.57 | 0.567755 | 1.67 | 0.072994 | 0.17 | 0.65 | 468.6 | 34.8 | 456.6 | 6.2 | 454.25 | 0.73 |
| z9 | 0.0023 | 0.57 | 1.8 | 2.1 | 124.186 | 0.179026 | 0.054730 | 5.26 | 0.554518 | 5.60 | 0.073484 | 0.46 | 0.76 | 401.2 | 118 | 448.0 | 20.3 | 457.20 | 2.02 |
| **Shakertown Millbrig K-bentonite** | | | | | | | | | | | | | | | | | | | |
| z1 | 0.0017 | 0.55 | 6.1 | 14.4 | 379.590 | 0.172084 | 0.055996 | 1.46 | 0.560737 | 1.56 | 0.072628 | 0.17 | 0.62 | 452.2 | 32.3 | 452.0 | 5.7 | 452.05 | 0.76 |
| z2 | 0.0016 | 0.72 | 19.0 | 13.1 | 1096.79 | 0.226585 | 0.056006 | 0.50 | 0.562234 | 0.55 | 0.072808 | 0.10 | 0.52 | 452.6 | 11.2 | 453.0 | 2.0 | 453.14 | 0.42 |
| z3 | 0.0023 | 0.73 | 35.9 | 46.3 | 2045.90 | 0.229282 | 0.055953 | 0.28 | 0.563247 | 0.32 | 0.073009 | 0.12 | 0.52 | 450.5 | 6.3 | 453.6 | 1.2 | 454.34 | 0.51 |
| z4 | 0.0019 | 0.79 | 23.1 | 17.9 | 1305.15 | 0.245687 | 0.056222 | 0.45 | 0.565891 | 0.50 | 0.073001 | 0.14 | 0.49 | 461.1 | 9.9 | 455.4 | 1.8 | 454.29 | 0.61 |
| z5 | 0.0020 | 0.81 | 27.5 | 23.3 | 1543.06 | 0.253674 | 0.056089 | 0.39 | 0.562669 | 0.43 | 0.072757 | 0.10 | 0.50 | 455.9 | 8.6 | 453.3 | 1.6 | 452.82 | 0.46 |

**Supplementary Table 1. CA-TIMS U-Pb zircon data contnued...**

| | Composition | | | | Isotopic Ratios | | | | | | | | | Dates (Ma) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mass (mg) | $Th/U_a$ | $Pb^*/Pb_{cb}$ | $Pb^*$ $(pg)_d$ | $^{206}Pb/^{204}Pb_e$ | $^{208}Pb/^{206}Pb_f$ | $^{207}Pb/^{206}Pb_f$ | ±2σ % | $^{207}Pb/^{235}U_f$ | ±2σ % | $^{206}Pb/^{238}U_f$ | ±2σ % | Corr. coef. | $^{207}Pb/^{206}Pb_g$ | ±2σ abs | $^{207}Pb/^{235}U_g$ | ±2σ abs | $^{206}Pb/^{238}U_{<Th>h}$ | ±2σ abs |
| **Shakertown Deicke K-bentonite** | | | | | | | | | | | | | | | | | | | |
| z1 | 0.0021 | 0.61 | 22.4 | 26.5 | 1325.52 | 0.189343 | 0.055882 | 0.45 | 0.561279 | 0.45 | 0.072846 | 0.09 | 0.19 | 447.7 | 9.9 | 452.4 | 1.7 | 453.37 | 0.40 |
| z2 | 0.0020 | 0.60 | 13.0 | 14.3 | 777.088 | 0.187564 | 0.056294 | 0.72 | 0.567085 | 0.78 | 0.073061 | 0.11 | 0.51 | 464.0 | 16.1 | 456.1 | 2.9 | 454.66 | 0.50 |
| z3 | 0.0022 | 0.59 | 8.6 | 14.6 | 520.621 | 0.184767 | 0.056189 | 1.06 | 0.564657 | 1.13 | 0.072884 | 0.13 | 0.61 | 459.8 | 23.4 | 454.6 | 4.1 | 453.60 | 0.56 |
| z4 | 0.0017 | 0.66 | 45.9 | 26.1 | 2662.90 | 0.206018 | 0.056066 | 0.20 | 0.563862 | 0.23 | 0.072941 | 0.08 | 0.49 | 455.0 | 4.5 | 454.0 | 0.8 | 453.94 | 0.36 |
| z5 | 0.0018 | 0.64 | 23.7 | 18.9 | 1391.06 | 0.200532 | 0.056255 | 0.39 | 0.565723 | 0.42 | 0.072936 | 0.08 | 0.49 | 462.5 | 8.6 | 455.2 | 1.5 | 453.90 | 0.36 |
| **Vasagård Kinnekulle K-bentonite** | | | | | | | | | | | | | | | | | | | |
| z1 | 0.0049 | 0.43 | 29.9 | 42.9 | 1844.21 | 0.135751 | 0.056086 | 0.31 | 0.563902 | 0.36 | 0.072952 | 0.13 | 0.52 | 454.8 | 7.0 | 454.1 | 1.3 | 454.01 | 0.57 |
| z6 | 0.0087 | 0.51 | 15.8 | 14.2 | 961.387 | 0.159210 | 0.056225 | 0.57 | 0.565866 | 0.62 | 0.073026 | 0.09 | 0.55 | 460.3 | 12.7 | 455.3 | 2.3 | 454.45 | 0.40 |
| z7 | 0.0035 | 0.64 | 14.3 | 11.0 | 842.469 | 0.200239 | 0.056300 | 0.65 | 0.566714 | 0.72 | 0.073038 | 0.12 | 0.58 | 463.2 | 14.5 | 455.9 | 2.6 | 454.52 | 0.51 |
| z8 | 0.0076 | 0.87 | 9.0 | 8.1 | 512.710 | 0.271785 | 0.056212 | 1.08 | 0.565760 | 1.14 | 0.073029 | 0.10 | 0.66 | 459.8 | 23.9 | 455.3 | 4.2 | 454.46 | 0.43 |
| z12 | 0.0020 | 0.23 | 26.1 | 31.9 | 1700.24 | 0.073300 | 0.056175 | 0.32 | 0.565817 | 0.36 | 0.073084 | 0.09 | 0.47 | 458.3 | 7.2 | 455.3 | 1.3 | 454.81 | 0.39 |
| z13 | 0.0020 | 0.28 | 18.1 | 14.5 | 1171.90 | 0.086766 | 0.055922 | 0.71 | 0.562212 | 0.82 | 0.072947 | 0.14 | 0.79 | 448.3 | 15.8 | 453.0 | 3.0 | 453.98 | 0.63 |
| z14 | 0.0007 | 1.13 | 19.3 | 24.3 | 1013.91 | 0.353052 | 0.056140 | 0.71 | 0.564833 | 0.78 | 0.073003 | 0.10 | 0.74 | 456.9 | 15.7 | 454.7 | 2.8 | 454.29 | 0.44 |
| z15 | 0.0036 | 0.31 | 18.4 | 17.6 | 1179.02 | 0.097794 | 0.056117 | 0.55 | 0.564456 | 0.63 | 0.072984 | 0.14 | 0.64 | 456.0 | 12.2 | 454.4 | 2.3 | 454.20 | 0.60 |
| **Ristiküla bed 46** | | | | | | | | | | | | | | | | | | | |
| z1 | 0.0007 | 1.18 | 1.9 | 4.2 | 115.932 | 0.369653 | 0.057087 | 5.29 | 0.574927 | 5.63 | 0.073042 | 0.45 | 0.78 | 494.9 | 117 | 461.2 | 20.9 | 454.53 | 1.99 |
| z2 | 0.0020 | 0.86 | 3.5 | 4.0 | 209.532 | 0.267932 | 0.056312 | 2.73 | 0.567178 | 2.90 | 0.073049 | 0.23 | 0.74 | 464.7 | 60.5 | 456.2 | 10.7 | 454.58 | 1.02 |
| z3 | 0.0005 | 0.79 | 2.1 | 3.2 | 136.947 | 0.245547 | 0.058024 | 4.41 | 0.604968 | 4.71 | 0.075617 | 0.40 | 0.75 | 530.7 | 96.7 | 480.4 | 18.0 | 469.99 | 1.82 |
| z4 | 0.0007 | 0.61 | 1.9 | 2.1 | 129.414 | 0.190089 | 0.057283 | 4.70 | 0.576956 | 5.01 | 0.073049 | 0.42 | 0.76 | 502.4 | 103 | 462.5 | 18.6 | 454.59 | 1.86 |
| z5 | 0.0008 | 1.09 | 4.8 | 4.1 | 266.947 | 0.341318 | 0.056613 | 2.20 | 0.570304 | 2.33 | 0.073061 | 0.19 | 0.72 | 476.5 | 48.6 | 458.2 | 8.6 | 454.65 | 0.83 |
| z10 | 0.0007 | 1.18 | 1.9 | 4.2 | 116.664 | 0.370482 | 0.057280 | 5.22 | 0.577607 | 5.56 | 0.073136 | 0.45 | 0.78 | 502.3 | 115 | 462.9 | 20.7 | 455.09 | 1.99 |

a Th contents calculated from radiogenic $^{208}Pb$ and the $^{207}Pb/^{206}Pb$ date of the sample, assuming concordance between U-Th and Pb systems.

b Ratio of radiogenic Pb (including $^{208}Pb$) to common Pb.

c Total mass of common Pb.

d Total mass of radiogenic Pb.

e Measured ratio corrected for fractionation and spike contribution only.

f Measured ratios corrected for fractionation, tracer and blank.

g Isotopic dates calculated using the decay constants $\lambda_{238}$ = 1.55125E-10 and $\lambda_{235}$ = 9.8485E-10 (Jaffey et al. 1971).

h Corrected for initial Th/U disequilibrium using radiogenic 208Pb and $Th/U_{[magma]}$ = 4.00000.