

Supplementary information on analytical methods

In situ zircon U–Pb isotope and trace-element analyses were carried out at ETH Zürich (three sessions) and at the University of Graz (two sessions) (Tables 1, 2). At Zürich, U–Pb isotopes were measured simultaneously with trace elements from the same ablated volume using a Thermo Element XR SF-ICP-MS instrument coupled to a Resonetics Resolution 155 ablation system. Analytical conditions included a 29 µm spot size, 4 Hz repetition rate, 2.5 J/cm² energy density (fluence), and an ablation duration of 30 seconds. For U–Pb dating, zircon GJ-1 (Jackson et al. 2004; Horstwood et al. 2016) was used as the primary reference, while validation was employed zircons 91500, Plešovice, AUSZ7-1, AUSZ7-5, AUSZ8-10, Rak-17, (Wiedenbeck et al. 1995; Sláma et al. 2008; Kennedy et al. 2014; von Quadt et al. 2016; Lukács et al. 2021; Webb et al. 2020). These reference materials span an age range from 1063.5 Ma to 1.431 Ma and were used to correct matrix-dependent age offsets (Sliwinski et al. 2017). Additional zircon dating was performed at the University of Graz using an ESI NWR 193nm laser ablation system coupled to a Nu Plasma II multi-collector ICP-MS. Analytical conditions included a 35 µm spot size, 5 Hz repetition rate, 2.7–2.8 J/cm² energy density (fluence), and an ablation duration of 15 s. Zircon GJ1 (Jackson et al. 2004) was used as primary reference, while zircons 91500 (Wiedenbeck et al. 1995) and Plesovice (Sláma et al. 2008) served as secondary reference materials to verify the reproducibility and accuracy. All zircon LA-ICP-MS U–Pb data were processed using IOLITE (Paton et al. 2011), with the VizualAge module (Petrus and Kamber 2012; Supplementary Table S1). Common Pb contents were not explicitly corrected; instead, integration intervals were selected to exclude signals contaminated by common Pb, and data were filtered based on discordance threshold of $[(^{207}\text{Pb}/^{235}\text{U Age}) - (^{206}\text{Pb}/^{238}\text{U Age})] / (^{207}\text{Pb}/^{235}\text{U Age}) < 10\text{--}15\%$. Correction for Th disequilibrium was applied for all data, in case of data from ETH Zürich after α -dose-correction (Sliwinski et al. 2017), assuming a stable Th/U partition coefficient of 0.33 ± 0.06 (1 σ ; Rubatto and Hermann 2007) and using Schärer's (1984) equations. For data from University of Graz, a magma Th/U value of 3.0 was used and the partition coefficients were calculated individually for each spot, yielding values between 0.1–0.4. The typical uncertainty of individual zircon dates ranges from 2.1–3.9 % (2 SE) for ETH Zürich data and 1.4–1.9% (2SE) for those from Graz.

For zircon trace-element analyses, NIST 610 and NIST 612 glasses served as the primary reference material, while zircon 91500 and an in-house Synthetic Zircon Blank were used for quality control. Elements analysed included Si (internal standard), Zr, REE, Y, Hf, Nb, Ta, U, Th, Ti, P, Al, and Ba (the latter three for monitoring inclusions of glass or apatite). Data are given in Supplementary Table S2. Cathodoluminescence images showing the analysed zircon grains and analytical spots are provided in Supplementary Data Sheet 2.

Table 1. LA-ICP-MS zircon U–Pb analysis performed at ETH Zürich.

Laboratory name	Department of Earth Sciences, ETH Zürich
Laser ablation system	
Make, Model & type	ASI Resolution 155
Ablation cell & volume	Laurin Technics 155, constant geometry, aerosol dispersion volume <1 cm ³
Laser wavelength	193 nm
Pulse width	25 ns
Fluence	~2.5 J cm ⁻²
Repetition rate	4 Hz
Spot size	29 µm
Ablation rate	~75 nm pulse ⁻¹
Sampling mode / pattern	Single hole drilling, 5 cleaning pulses
Carrier gas	100% He
Ablation duration	30 s
Cell carrier gas flow	0.5 l/min
ICP-MS Instrument	
Make, Model & type	Thermo Element XR SF-ICP-MS
Sample introduction	Ablation aerosol only, squid aerosol homogenization device
RF power	1500 W
Make-up gas flow	~0.95 l/min Ar, 2 ml/min N ₂ (gas mixed to He carrier inside ablation cell funnel)
Detection system	Single detector triple mode SEM, analogue, Faraday

Masses measured	27, 29, 31, 49, 89, 91, 93, 137, 139, 140, 141, 146, 147, 153, 157, 159, 163, 165, 166, 169, 172, 175, 178, 181, 202, 204, 206, 207, 208, 232, 235, 238 amu
Integration time per peak	11 ms except for masses 49 (25ms) and 206, 207 (50ms)
Total integration time per reading	0.648 s
Dead time	8 ns
Typical oxide rate (ThO/Th)	0.18%
Typical doubly charged rate (Ba ⁺⁺ /Ba ⁺)	3.5%
Data Processing	
Gas blank	30 s prior to each ablation spot
Calibration strategy	GJ-1 (Jackson et al. 2004) used as primary calibration material in all sessions for data reduction of U-Pb dates, while NIST610 (sessions in 2019) or NIST612 (session in 2022) of trace elements. Validation reference materials used in sessions: session 20191204: Plešovice, 91500, AUSZ7-1, AUSZ7-5, AUSZ8-10 session 20191203: Plešovice, 91500, AUSZ7-1, AUSZ7-5, Rak-17 session 20220211R3: Plešovice, 91500, AUSZ7-1, AUSZ7-5 References: Plešovice [Sláma et al., 2008; Horstwood et al., 2016], 91500 [Wiedenbeck et al., 1995; Horstwood et al., 2016], AUSZ7-1 [Kennedy et al. 2014], AUSZ7-5 [von Quadt et al., 2016] and AUSZ8-10 [Lukács et al., 2021], Rak-17 [Webb et al., 2020]
Reference Material info	GJ-1 ²⁰⁶ Pb/ ²³⁸ U 0.09761 ± 0.0002 (weighted mean of ID-TIMS analysis ± 2σ, [3])
Data processing package used	IOLITE v3.4 [Paton et al., 2010, 2011] with VizualAge [Petrus and Kamber, 2012]
Mass discrimination	Mass bias correction for all ratios normalized to calibration reference material
Common Pb correction	No common-Pb correction applied
Uncertainty level & propagation	Ages are quoted at 2 SE absolute, propagation is by quadratic addition. Reproducibility of reference material uncertainty (i.e. external uncertainty:1.5%) is propagated.

Table 2. LA-ICP-MS zircon U-Pb analysis performed at University of Graz & Graz University of Technology.

Laboratory name	NAWI Graz Central Lab for Water, Minerals and Rocks (University of Graz & Graz University of Technology)
Sample type/mineral	zircon
Sample preparation	Conventional mineral separation. Single grains embedded in 1 inch resin mount. Final polishing with 1 µm diamond paste
Imaging	VEGA/TESCAN scanning electron microscope, equipped with an Oxford detector
Analytical session(s)	
Date	06/11/2019; 20/11/2019
Laser ablation system	
Instrument	NWR193 ArF Excimer laser (ESI, Portland. U.S.A.)
Cell type	Two volume ablation cell
Laser wavelength	193 nm
Pulse duration	4-6 ns
Fluence	~ 2.7-2.8 J/cm ²

Sampling mode	Single hole drilling, circular shape
Pre-ablation cleaning	None
Spot diameter (nominal)	35 µm
Repetition rate	5 Hz
Ablation duration	15 s
Carrier gas	He gas (combined with Ar outside the ablation cell)
He gas flow rate	0.75 L/min
Ar mix gas flow rate	0.75 L/min
Signal smoothing device	None
ICP Mass Spectrometer	
Instrument	Nu PlasmaII HR-MC-ICP-MS (Nu Instruments, Wrexham, U.K.)
Sample introduction	Ablation aerosol only
RF power	1300 W
Monitored masses	^{202}Hg , $^{204}(\text{Hg} + \text{Pb})$, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U
Detectors	5 electron-multiplier, ion-counting detectors (IC) and 2 Faraday collectors (H) : IC4 for ^{202}Hg , IC3 for $^{204}(\text{Hg} + \text{Pb})$, IC2 for ^{206}Pb , IC1 for ^{207}Pb , IC0 for ^{208}Pb , H7 for ^{232}Th , H9 for ^{238}U
Tuning	Line scan on NIST SRM 612 glass to optimize sensitivity and peak shapes for all monitored masses
Analysis mode	Time Resolved Analysis
Integration time for single data point	0.2 s
Data processing	
Mass discrimination	Instrumental mass bias corrected by bracketing of unknown samples with primary reference material for isotope ratios and element concentrations
Data reduction	U-Pb zircon geochronology Data Reduction Scheme (U_PbGeochron4) for Iolite 3.71 (Paton et al., 2010; 2011) Blank and signal integrations imported using laser log file Blank windows selected between 25 and 5 s before signal, Signal windows trimmed for ~1 s (start) and ~2-3 s (end)
Gas blank	Gas blank (20 seconds) acquired before each analysis and subtracted with step-forward method
Primary reference material	GJ-1 zircon (Jackson et al., 2004)
Normalization values	$^{206}\text{Pb}/^{238}\text{U} = 0.097860$, $^{207}\text{Pb}/^{235}\text{U} = 0.81117$, $^{208}\text{Pb}/^{232}\text{Th} = 0.03074$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.060139$, U content = 230 ppm, Th content = 15 ppm, Pb content = 28 ppm (Horstwood et al., 2016)
Common-Pb correction	None
Uncertainties	Single spot : Internal error and excess scatter from primary standard analyses propagated by quadratic addition (2SE) Weighted mean results : single spot error and long-term variance of validation material (1.3%) propagated by quadratic addition (2SD)

Secondary reference material for quality check	Plesovice zircon ($^{206}\text{Pb}/^{238}\text{U}$ age = 337.13 ± 0.37 Ma, ID-TIMS; Slama et al., 2007; Horstwood et al., 2016); 91500 zircon ($^{206}\text{Pb}/^{238}\text{U}$ age = 1063.51 Ma, ID-TIMS; Wiedenbeck et al., 1995; Horstwood et al., 2016)
Secondary reference material results	Plesovice : Weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age = $338.2 \pm 1.5/4.7$ Ma (2 SD, MSWD = 0.34) 91500 : Weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age = $1063.3 \pm 4.6/14.3$ Ma (2 SD, MSWD = 1.7)

In-situ Lu-Hf isotopic analysis was performed using a Nu2 MC-ICP-MS at ETH Zürich. Ablation conditions were: 50 μm spot size, 5 Hz laser pulse repetition rate and 4 J/cm² energy density. Accuracy and precision were monitored using well characterized reference materials: Mud Tank (0.282507; Woodhead and Hergt 2005), 91500 (0.282307; Wu et al. 2006), Temora (0.282680; Wu et al. 2006), and GHR1 (0.283050; Eddy et al. 2018). Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and ϵ_{Hf} were calculated using the crystallization age of each sample, the decay constant of ^{176}Lu = 1.867×10^{-11} a⁻¹ (Söderlund et al. 2004) for CHUR parameters of Bouvier et al. (2008).

Glass trace-element analyses were conducted on fresh glass shards at the University of Perugia (Italy) using an Agilent 8900 ICP-MS coupled to a Coherent GeoLas ArF 193 nm Excimer laser. Operating conditions were 5 J/cm² fluence, 10 Hz repetition rate, and 24 μm crater diameter. Ten major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and 31 trace elements were measured. Data reduction was performed in IOLITE with manual signal-integration and preliminary calibration. Concentrations were normalised to 100 wt% oxide totals (Pettke et al. 2004) using Si as the internal standard. Instrumental drift was corrected using the ATHO-G reference glass (Jochum et al. 2006). Data are reported in Supplementary Table S4.

For whole-rock chemical analyses of tuff samples from the Aflenz Basin, representative aliquots of four samples, milled to homogeneous powder, were analysed at Activation Laboratories Ltd (Ontario, Canada). Major and trace elements were determined following procedure “Code 4LITHO.” Major elements and selected trace elements (Sc, Be, V, Ba, Sr, Y, Zr) were measured by fusion ICP-OES, and all other trace elements by fusion ICP-MS. Calibration was based on USGS and CANMET certified reference materials for each batch of ten samples, with three blanks and five control analyses included per batch.

Trace element calculations:

Ti (re-calc) ppm = Ti(measured in sample)/(Average of Ti(measured in 91500))*4.73 (see details in Szymanowski et al. 2017) in Zircons

Nb = Nb(measured in sample) - (Average Nb(measured in Synth Zirc Blank) in Zircons

Eu/Eu* = (Eu/0.058)/(SQRT(Sm/0.153*Gd/0.2055))

Ce/Ce*(Loader) = (Ce/0.613)/((Nd/0.457)²/(Sm/0.148)) (Loader et al. 2017)

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