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Supplement of

U–Pb dating on calcite paleosol nodules: first absolute age constraints on the Miocene continental succession of the Paris Basin

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Contents in external database:

Supplementary Tables are available on the Zenodo repository system (Monchal et al., 2024).

EDS

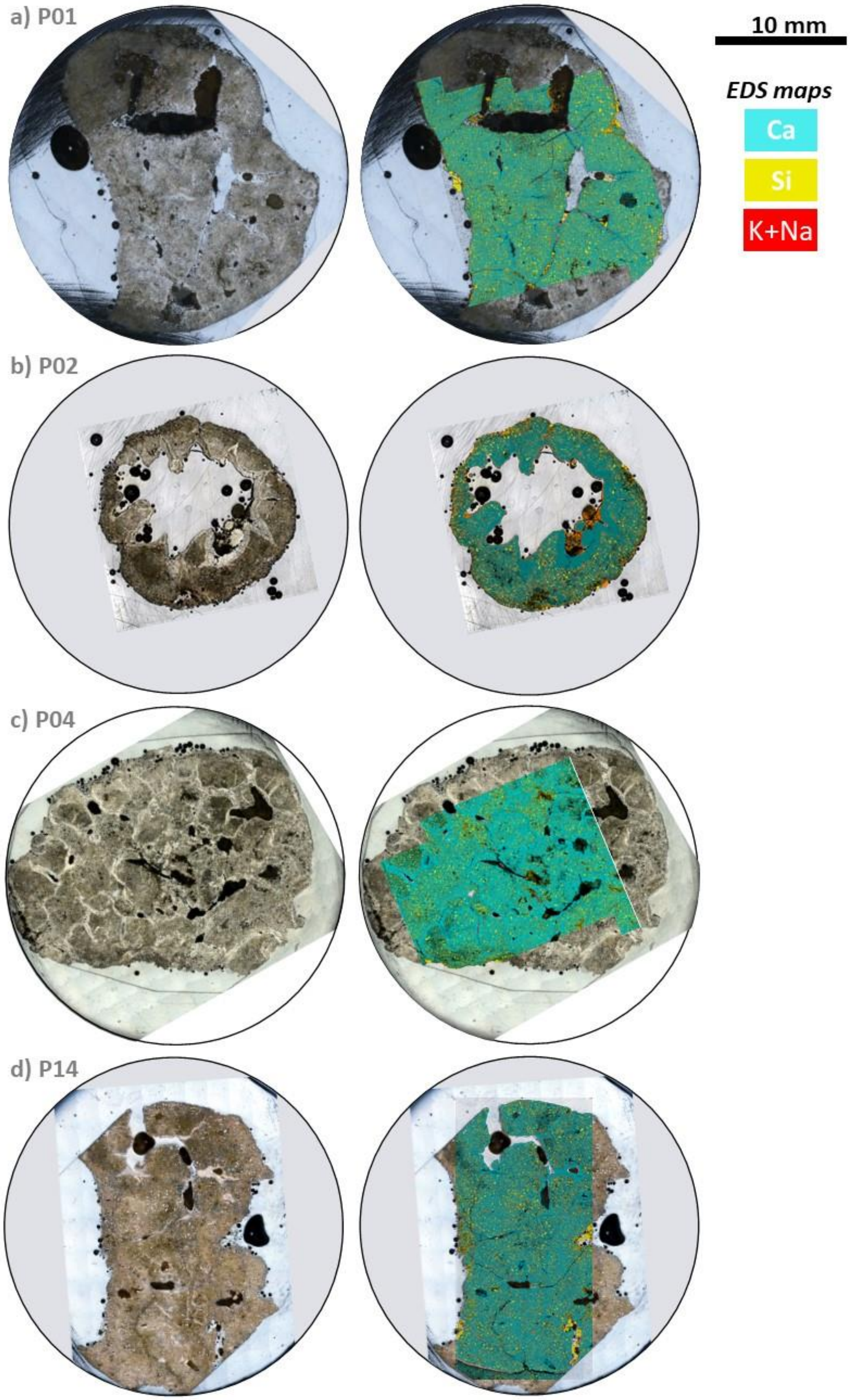

Figure S1: Photographic montage of nodule P01-P14 (labelled a to d) in a polished resin puck. The left hand side feature an optical microscopy image while on the right the same image overlain by a partial EDS map of the nodule showing Ca (a proxy for calcite, blue), Si (a proxy for quartz, yellow), and K,Na (a proxy for feldspar, red). Pure calcite veins were targeted, avoiding the zones of calcite-cemented quartz-rich sand.

CL

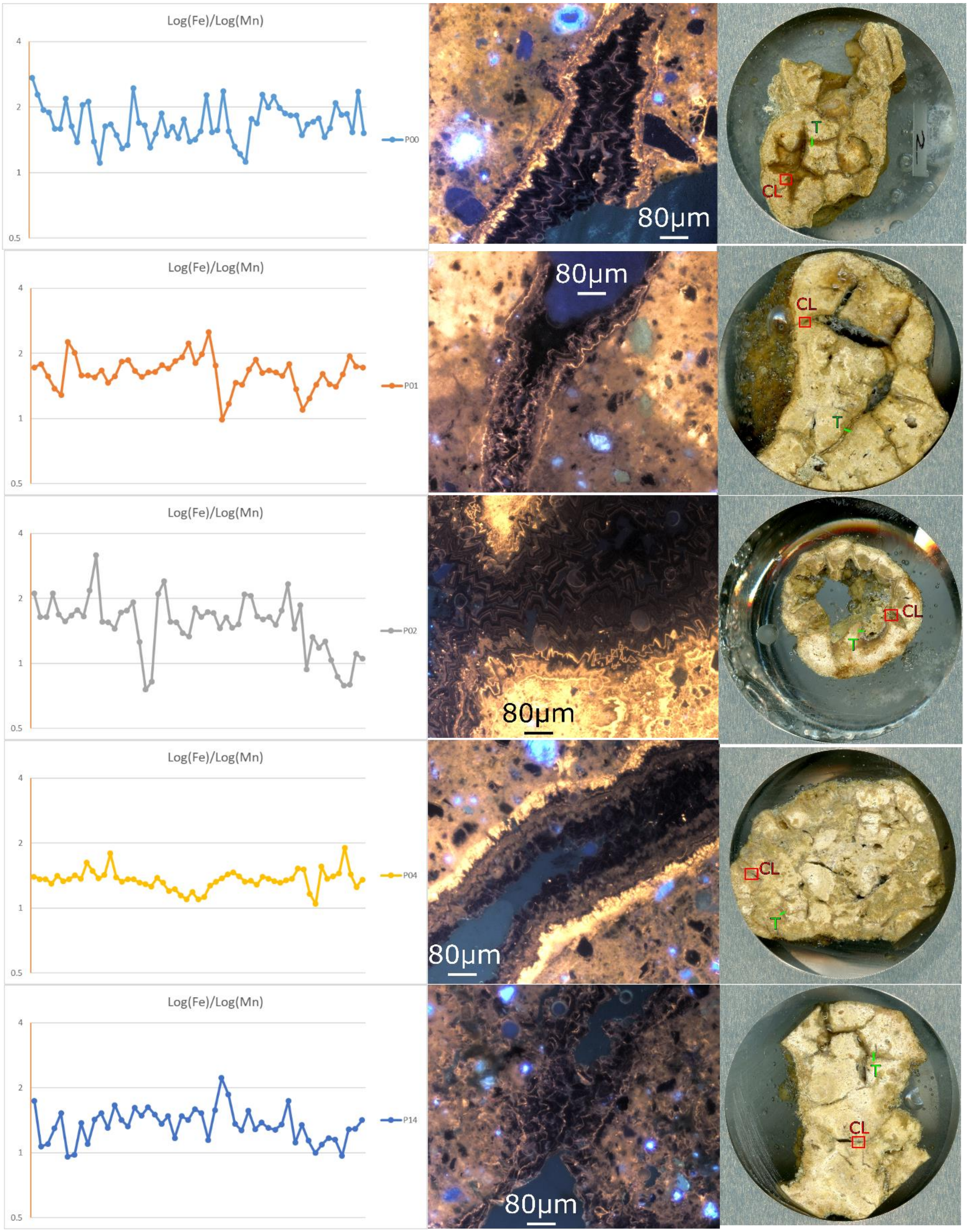

Figure S2: Plot of log [Fe]/log [Mn] with cathodoluminescence images from the samples at 10x magnification illustrating the relation between log [Fe]/log [Mn] and the oscillation of luminescence in the calcite crystals. P04 has the most discreet oscillations, while P00/P02/P14 display more contrasted oscillations. The positions of the CL image (CL) and the transect used for the plot (T) are, respectively, indicated by a red box and a green line on each sample photo.

XRD

The powders were analysed using a Siemens/Bruker D5000 power X-ray diffractometer (Cu Kα radiation, 0.01° step−1 from 5 to 60° 2θ at 1° min-1, 4.5 hours per sample). Mineral identification was undertaken with DIFFRAC.EVA (Bruker) using the Powder Data File (PDF-4, The International Centre for Diffraction Data) (Gates-Rector and Blanton, 2019).

Powder XRD results

The PXRD patterns of the three analysed nodules consistently show two dominant families of peaks identified as calcite (*e.g.*, ICDD PDF no. 00-047-1743) and quartz (e.g., ICDD PDF no. 00-046-1045). Minor feldspar (e.g., ICDD PDF no. 00-09-0466[Albite] and 00-19-0932[Microcline]) (Figure S3) and several unidentified minor peaks corresponding to one or more accessory phase(s) in the nodules are also present. The confirmation that the carbonate phase is calcite allows accurate matrix-matching with the WC-1 calcite age reference material in the LA-ICP-MS U-Pb dating procedure (Roberts et al., 2017).

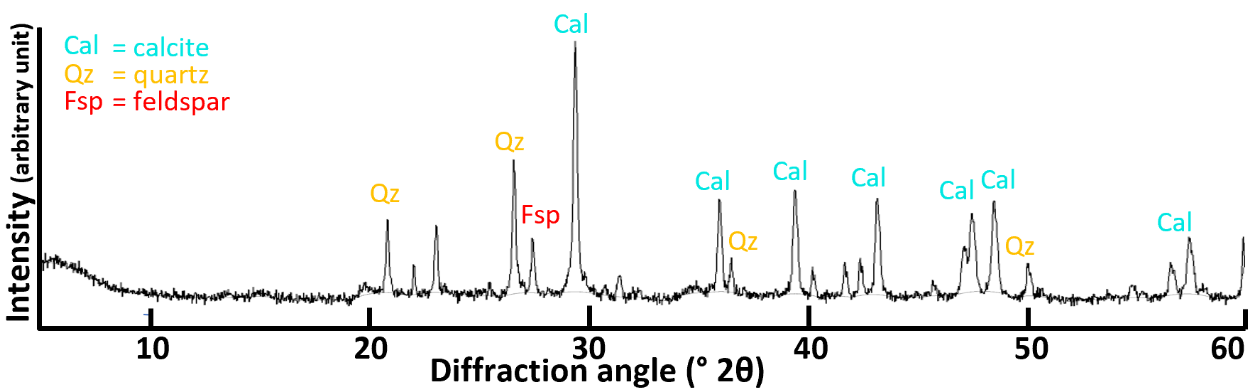

Figure S3: Representative PXRD patterns from a calcite nodule showing the dominance of calcite and quartz.

References

Gates-Rector, S. and Blanton, T.: The Powder Diffraction File: a quality materials characterization database, Powder Diffraction, 34, 352-360, 10.1017/S0885715619000812, 2019.

Monchal, V., Rateau, R., Drost, K., Gagnaison, C., Mennecart, B., Toullec, R., Torremans, K., & Chew, D.: Supplementary Tables : U-Pb direct dating on calcite paleosol nodules: first absolute age constraints on the Miocene continental succession of the Paris Basin [Data set], Zenodo, https://doi.org/10.5281/zenodo.14500416.

Roberts, N. M. W., Rasbury, E. T., Parrish, R. R., Smith, C. J., Horstwood, M. S. A., and Condon, D. J.: A calcite reference material for LA-ICP-MS U-Pb geochronology, Geochemistry, Geophysics, Geosystems, 18, 2807-2814, 10.1002/2016gc006784, 2017.

Analytical setup, operating conditions and data processing for LA-ICP-MS U- Pb analyses

Laboratory & Sample Preparation	**Maps**
Laboratory name	Dept of Earth Science, Trinity College Dublin
Sample type/mineral	Calcite crystals from pedogenic nodules
Sample preparation	polished rock slab in 1 inch resin mount, 1μm polish to finish
Imaging	high-resolution scan of mount
Laser ablation system	
Make, Model & type	Teledyne/PhotonMachines Analyte Excite, 193nm, Excimer
Ablation cell & volume	HelEx II Active 2-volume cell; 100mm × 100mm sample area
Laser wavelength (nm)	193nm
Pulse width (ns)	<4ns
Fluence ($J.cm^{-2}$)	2.5 J/cm^2
Repetition rate (Hz)	50 Hz
Spot size (um)	80 μm square
Sampling mode / pattern	line raster, 1 pass, 30 μm/sec scan speed
Carrier gas	optimized daily: 100% He in the cell (0.33 l/min), Ar carrier gas (0.62 l/min) and N_2 (10 ml/min^1) added at ARIS adaptor
Ablation duration (secs)	18x70s NIST614, 18x70s WC-1, 6x180s Duff Brown Tank, P00: 59x35s
Cell carrier gas flow (l/min)	optimized daily: 0.33 l/min in the cell and 0.10-0.11 l/min in the cup
ICP-MS Instrument	
Make, Model & type	Agilent 7900 quadrupole ICP-MS
Sample introduction	Ablation aerosol via ARIS
RF power (W)	1550W
Carrier gas flow (l/min)	0.62 l/min Ar
Detection system	Dual-mode discrete dynode electron multiplier
Masses measured and [Integration time per peak (ms)]	25 [2], 43 [4], 51 [2], 55 [2], 57 [2], 63 [2], 66 [2], 71 [2], 85 [4], 88 [2], 137 [2], 140 [2], 175[10], 202 [1], 204 [1], 206 [40], 207 [80], 208 [40], 232 [20], 238 [40]
Total integration time per reading (secs)	301 ms / 1505 ms after averaging
Sensitvity / Efficiency (%, element)	0.02% U
IC Dead time (ns)	38ns
Data Processing	
Gas blank	20s on-peak zero subtracted
Calibration strategy	NIST614 as primary reference material, WC-1 carbonate standard for matrix matching of $^{206}Pb/^{238}U$, DBT carbonate for QC

Reference Material info	NIST614 (concentration data Jochum et al., 2011; Pb isotopes Woodhead and Hergt, 2001) WC-1 (Roberts et al., 2017) DBT (Hill et al., 2016)
Data processing package used / Correction for LIEF	Iolite V3.6 (Paton et al., 2011) & Monocle (Petrus et al., 2017) & in-house spreadsheet; no LIEF correction for linear rasters
Normalisation and age calculation	standard bracketing; Iolite Data Reduction Scheme VizualAge_UcomPbine (Chew et al. 2014; based on U-Pb Geochronology DRS of Paton et al., 2010 and VizualAge DRS of Petrus and Kamber, 2012) is used to correct for down hole fractionation and drift and to normalize to primary reference material. Downhole fractionation for linear rasters is modelled using a linear correction (y=a+bx) with zero slope (b=0). U/Pb ages and initial Pb compositions are calculated using Isoplot v4.15 (Ludwig, 2012).
Common-Pb correction, composition and uncertainty	Unanchored regression in Tera-Wasserburg, isochron and 86TW plots, respectively. All model 1. Except WC-1: Anchored regression in TW using an initial $^{207}Pb/^{206}Pb$ of 0.85±0.04 (Roberts et al., 2017) to receive a non-matrix-matched lower intercept age, the corresponding ratio of which is used to calculate the matrix-dependent factor for correction of $^{206}Pb/^{238}U$ ratios of QC and unknowns (WC1 error : ± 3.1; WC1 MSWD : 1.07).
Uncertainty level & propagation	Ratios and ages are quoted at 2s or 95% confidence level. Uncertainty propagation was carried out according to the recommendations of Horstwood et al. (2016) and Roberts et al. (2020). The first uncertainty quoted is a session wide estimate including the data point uncertainty, uncertainty on weighted means of primary reference material ratios and their excess scatter. The second uncertainty quoted additionally includes systematic uncertainties such as the uncertainty on the reference age of WC-1, uncertainty on the ^{238}U decay constant and a laboratory-specific long-term reproducibility based on the results of the QC material.
Quality control / Validation	*DBT (Hill et al., 2016: 64.04 ± 0.67 Ma / 0.738 ± 0.010)* Lower Intercept Age = 63.01 ± 0.75 / 2.18 Ma, $^{207}Pb/^{206}Pb_{initial}$ = 0.7176 ± 0.013 (2s, MSWD = 1.13)
Other information	All samples were cleaned with ethanol followed by sonication in DIW. Potentially remaining surface contamination was removed during a preablation of all ablated sites. Detailed information on the general analytical protocol and data processing is given in Drost et al. (2018).

Laboratory & Sample Preparation	Spots
Laboratory name	Dept of Earth Science, Trinity College Dublin
Sample type/mineral	Calcite crystals from pedogenic nodules
Sample preparation	polished rock slab in 1 inch resin mount, 1µm polish to finish
Imaging	high-resolution scan of mount and SEM-EDS map
Laser ablation system	
Make, Model & type	Teledyne/PhotonMachines Analyte Excite, 193nm, Excimer
Ablation cell & volume	HelEx II Active 2-volume cell; 100mm × 100mm sample area
Laser wavelength (nm)	193nm
Pulse width (ns)	<4ns
Fluence ($J.cm^{-2}$)	2.2 J/cm^2(Carbonates) 2.5 J/cm^2(Glass)
Repetition rate (Hz)	12 Hz
Spot size (um)	85 µm round
Sampling mode / pattern	spots, 480 shots/spot
Carrier gas	100% He in the cell (0.40 l/min), Ar carrier gas (0.70 l/min) and N_2 (5 ml/min^1) added at ARIS adaptor
Ablation duration (spots)	23-May-24: NIST614 (24), WC-1 (24), Duff Brown Tank (24), P01(50), P02(54), P14(50) 13-June-24: NIST614 (21), WC-1 (21), Duff Brown Tank (21), P00(60) 20-June-24: NIST614 (21), WC-1 (21), Duff Brown Tank (21), P04(57)
Cell carrier gas flow (l/min)	0.300-0.350 l/min in the cell and 0.050-0.100 l/min in the cup
ICP-MS Instrument	
Make, Model & type	Agilent 7900 quadrupole ICP-MS
Sample introduction	Ablation aerosol via ARIS
RF power (W)	1550W
Carrier gas flow (l/min)	0.68 l/min Ar
Detection system	Dual-mode discrete dynode electron multiplier
Masses measured and [Integration time per peak (ms)]	all : 25 [4], 43 [5], 55 [1], 57 [2], 85 [5], 88 [2], 140 [3], 202 [1], 204 [1], 206 [70], 207 [150], 208 [70], 232 [35], 238 [70]
Total integration time per reading (secs)	450 ms
Sensitvity / Efficiency (%, element)	0.02% U
IC Dead time (ns)	38ns
Data Processing	
Gas blank	20s on-peak zero subtracted
Calibration strategy	NIST614 as primary reference material, DBT carbonate standard for matrix matching of $^{206}Pb/^{238}U$, WC-1 carbonate for QC

Reference Material info	NIST614 (concentration data Jochum et al., 2011; Pb isotopes Woodhead and Hergt, 2001) WC-1 (Roberts et al., 2017) DBT (Hill et al., 2016)
Data processing package used / Correction for LIEF	Iolite V3.6 (Paton et al., 2011) & in-house spreadsheet; Intercept method
Normalisation and age calculation	standard bracketing; Iolite Data Reduction Scheme VizualAge_UcomPbine (Chew et al. 2014; based on U-Pb Geochronology DRS of Paton et al., 2010 and VizualAge DRS of Petrus and Kamber, 2012) is used to correct for down hole fractionation and drift and to normalize to primary reference material. Downhole fractionation was modelled using a linear correction (y=a+bx). U/Pb dates and initial Pb compositions are calculated using Isoplot v4.15 (Ludwig, 2012).
Common-Pb correction, composition and uncertainty	Unanchored regression in Tera-Wasserburg, isochron and 86TW plots, respectively. All model 1. DBT is used to determine a non-matrix-matched lower intercept age, the corresponding ratio of which is used to calculate the matrix-dependent factor for correction of $^{206}Pb/^{238}U$ ratios of QC and unknowns Except WC-1: Anchored regression in TW using an initial $^{207}Pb/^{206}Pb$ of 0.85±0.04 (Roberts et al., 2017) to use it as QC material. The data point spread for WC-1 is not sufficient to determine a lower intercept age value without an $Pb_{initial}$ anchor. 23-May-24: DBT error : ± 1.8; DBT MSWD : 1.8 13-June-24: DBT error : ± 2.2; DBT MSWD : 1.12 20-June-24: DBT error : ± 2.6; DBT MSWD : 1.3
Uncertainty level & propagation	Ratios and ages are quoted at 2s. Uncertainty propagation was carried out according to the recommendations of Horstwood et al. (2016) and Roberts et al. (2020). The first uncertainty quoted is a session wide estimate including the data point uncertainty, uncertainty on weighted means of primary reference material ratios and their excess scatter. The second uncertainty quoted additionally includes systematic uncertainties such as the uncertainty on the reference age of DBT, uncertainty on the ^{238}U decay constant and a laboratory-specific long-term reproducibility based on the results of the QC material.
Quality control / Validation	*WC-1 (Roberts et al., 2017: 254.4 ± 6.4 Ma / 0.85 ± 0.04)* 23-May-24: Lower Intercept Age = 250.0 ± 4.4 / 7.1 Ma, Anchored (2s, MSWD = 2.5) 13-June-24: Lower Intercept Age = 253.4 ± 7.3 / 9.2 Ma, Anchored (2s, MSWD = 2.7) 20-June-24: Lower Intercept Age = 250.6 ± 6.4 / 8.5 Ma, Anchored (2s, MSWD = 4.0)
Other information	All samples were cleaned with ethanol followed by sonication in DIW. Potentially remaining surface contamination was removed during a preablation of all ablated sites. Detailed information on the general analytical protocol and data processing is given in Drost et al. (2018).

References

Chew, D. M., Petrus, J. A., and Kamber, B. S.: U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb, Chemical Geology, 363, 185-199, https://doi.org/10.1016/j.chemgeo.2013.11.006, 2014.

Drost, K., Chew, D., Petrus, J. A., Scholze, F., Woodhead, J. D., Schneider, J. W., and Harper, D. A. T.: An Image Mapping Approach to U-Pb LA-ICP-MS Carbonate Dating and Applications to Direct Dating of Carbonate Sedimentation, Geochemistry, Geophysics, Geosystems, 19, 4631-4648, 10.1029/2018GC007850, 2018.

Hill, C. A., Polyak, V. J., Asmerom, Y., and P. Provencio, P.: Constraints on a Late Cretaceous uplift, denudation, and incision of the Grand Canyon region, southwestern Colorado Plateau, USA, from U-Pb dating of lacustrine limestone, Tectonics, 35, 896-906, 10.1002/2016tc004166, 2016.

Horstwood, M. S. A., Košler, J., Gehrels, G., Jackson, S. E., McLean, N. M., Paton, C., Pearson, N. J., Sircombe, K., Sylvester, P., Vermeesch, P., Bowring, J. F., Condon, D. J., and Schoene, B.: Community-Derived Standards for LA-ICP-MS U-(Th-)Pb Geochronology – Uncertainty Propagation, Age Interpretation and Data Reporting, Geostandards and Geoanalytical Research, 40, 311-332, https://doi.org/10.1111/j.1751-908X.2016.00379.x, 2016.

Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D. E., Stracke, A., Birbaum, K., Frick, D. A., Günther, D., and Enzweiler, J.: Determination of Reference Values for NIST SRM 610–617 Glasses Following ISO Guidelines, Geostandards and Geoanalytical Research, 35, 397-429, https://doi.org/10.1111/j.1751-908X.2011.00120.x, 2011.

Ludwig, K. R.: User's Manual for Isoplot 3.75: A geochronological toolkit for Microsoft Excel, 2012.

Paton, C., Hellstrom, J., Paul, B., Woodhead, J., and Hergt, J.: Iolite: Freeware for the visualisation and processing of mass spectrometric data., Journal of Analytical Atomic Spectrometry, 26, 2508–2518, 2011.

Paton, C., Woodhead, J. D., Hellstrom, J. C., Hergt, J. M., Greig, A., and Maas, R.: Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction, Geochemistry, Geophysics, Geosystems, 11, 10.1029/2009GC002618, 2010.

Petrus, J. A., Chew, D. M., Leybourne, M. I., & Kamber, B. S.: A new approach to laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using the flexible map interrogation tool 'Monocle', Chemical Geology, 463, 76 –93, 2017.

Petrus, J. A. and Kamber, B. S.: VizualAge: A Novel Approach to Laser Ablation ICP-MS U-Pb Geochronology Data Reduction, Geostandards and Geoanalytical Research, 36, 247-270, https://doi.org/10.1111/j.1751-908X.2012.00158.x, 2012.

Roberts, N. M. W., Drost, K., Horstwood, M. S. A., Condon, D. J., Chew, D., Drake, H., Milodowski, A. E., McLean, N. M., Smye, A. J., Walker, R. J., Haslam, R., Hodson, K., Imber, J., Beaudoin, N., and Lee, J. K.: Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U–Pb carbonate geochronology: strategies, progress, and limitations, Geochronology, 2, 33-61, 10.5194/gchron-2-33-2020, 2020.

Roberts, N. M. W., Rasbury, E. T., Parrish, R. R., Smith, C. J., Horstwood, M. S. A., and Condon, D. J.: A calcite reference material for LA-ICP-MS U-Pb geochronology, Geochemistry, Geophysics, Geosystems, 18, 2807-2814, 10.1002/2016gc006784, 2017.

Woodhead, J. D. and Hergt, J. M.: Strontium, Neodymium and Lead Isotope Analyses of NIST Glass Certified Reference Materials: SRM 610, 612, 614, Geostandards Newsletter, 25, 261-266, https://doi.org/10.1111/j.1751-908X.2001.tb00601.x, 2001.