Methods for U-Pb LA-ICP-MS Analysis

Calcite U-Pb dating was performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on polished thick sections. The analyses were conducted at ETH Zürich using an ASI RESOlution laser ablation system with a 193 nm excimer (ArF) laser source and a two-volume Laurin Technic S-155 ablation cell coupled to a Thermo Element XR sector-field ICP-MS. The analytical and data reduction protocols follow Roberts et al. (2017) using NIST 614 and WC-1 primary reference materials and Guillong et al. (2020) using spot sizes of 110 and 163 µm with a matched ablation crater aspect ratio for the primary reference materials and unknowns. U-Pb ages were calculated from Tera-Wasserburg concordia lower intercepts using the IsoplotR software package (Vermeesch. 2018). All uncertainties are reported at the 95% confidence level. A long-term excess variance of 2% relative was propagated by quadratic addition to the uncertainty of the individual lower intercept dates (Guillong et al. 2020). Prior to and after the LA-ICP-MS measurements, cathodoluminescence microscopy was conducted in order to identify potential growth zonings and to identify misplaced or defective ablation spots. In addition to the samples, the two secondary reference materials ASH15D (Nuriel et al. 2020) and JT (Guillong et al. 2020) were analyzed in all sessions for validation and are reported in the Data Supplement. Correction for matrix effects with WC-1 was done with anchoring to 0.85 common-lead while samples and secondary reference materials were not anchored. No disequilibrium correction was applied. The table below shows the metadata of U-Pb analyses and data processing with reporting standards after Horstwood et al. (2016).

Laboratory and sample preparation	
Laboratory name	Department of Earth Sciences. ETH Zürich
Sample type/mineral	Calcite
Sample preparation	Polished thick sections
Imaging	CL8200 Mk5-2 Optical Cathodoluminescence System
Laser ablation system	

Make. model. and type	ASI (Resonetics) RESOlution S155
Ablation cell and volume	Laurin Technic, two-volume cell, effective volume approx. 1 cm^3
Laser wavelength	193 nm
Pulse width	25 ns
Fluence	~1.8 J cm^{-2}
Repetition rate (Hz)	5.0 or 7.4. See data for actual value
Ablation duration	40 s
Ablation pit depth / ablation rate	Variable. equivalent to 0.09-0.15 mm/pulse
Spot diameter (mm) nominal/actual	110 or 163μm. See data for actual value
Sampling mode / pattern	Static spot ablation
Carrier gas	100% He in the cell, Ar make-up gas combined in cell above ablation in funnel
Cell carrier gas flow	0.5 l min^{-1}
ICP-MS instrument	
Make. model and type	Thermo Element XR, sector-field single collector ICP-MS with high-capacity interface pump
Sample introduction	Ablated aerosol direct
RF power	1350-1550 W (optimized daily)
Make-up gas flow	0.90-1.05 l min^{-1} Ar (optimized daily), 2 ml min^{-1} N_2
Detection system	Triple (pulse counting, analog, Faraday), cross-calibrated daily with ^{238}U, fixed analogue counting factor (ACF) value, all isotopes usually in pulse-counting only (<5 Mcps)
Masses measured (amu)	202, 204, 206, 207, 208, 232, 235, 238
Integration time per peak/dwell times	11 ms (all masses) except 206, 207 (50 ms)
Total integration time per output data point	0.174 s
Sensitvity / efficiency	~ 1 % U
Dead time	25 ns
Typical oxide rate (ThO/Th)	0.18%
Typical doubly charged rate (Ba^{++}/Ba^{+})	3.50%
Data processing	

Gas blank	20 s
Calibration strategy	NIST614 glass standard as primary reference material for drift and $^{207}Pb/^{206}Pb$ ratios (see Roberts et al. 2017); WC-1 carbonate reference material for matrix matching of $^{206}Pb/^{238}U$ (anchored to initial Pb composition of 0.85, see Roberts et al. 2017); ASH-15D (Nuriel et al. 2020) and JT (Guillong et al. 2020) calcite validation reference materials for assessing accuracy and repeatability.
Reference material info	NIST614 (concentration data Jochum et al. 2011, Pb isotopes Baker et al. 2004); WC-1 (Roberts et al. 2017); ASH-15D (Nuriel et al. 2020); JT (Guillong et al. 2020)
Data processing package used	Iolite 2.5, VisualAge for integration, interval selection, and gas blank correction only. In-house spreadsheet data processing. IsoplotR (Vermeesch 2018) for isochrons, intercept ages, and initial Pb compositions
Correction for LIEF	No separate LIEF correction. $^{238}U/^{206}Pb$ corrected to primary RM assumed to have similar LIEF as samples.
Mass discrimination	Normalized to reference material (sample-standard bracketing)
Common-Pb correction. composition and uncertainty	Not applied. Ages calculated by linear regressions in Tera-Wasserburg concordia plots using the IsoplotR software package (Vermeesch. 2018)
Uncertainty level and propagation	Lower intercept ages are quoted at 2σ absolute, propagation is by quadratic addition. Counting statistics uncertainties are propagated to the $^{207}Pb/^{206}Pb$ ratios, together with the uncertainty of the primary RM value and the uncertainty of repeated measurements. The uncertainty value for lower intercept isochron ages includes uncertainties from the primary RM and unsystematic uncertainties, estimated in this work to be 2 %. Decay constant uncertainties are neglected.
Quality control / Validation	ASH-15-D: Weighted mean of $^{206}Pb/^{238}U$ intercept ages: 2.769 ± 0.144 Ma (2σ, MSWD = 0.97, n = 4, including weighted average uncertainty (internal) and 2% total external uncertainty) Pooled measurements for 4 sessions: 2.894 ± 0.092 Ma (2σ, MSWD = 2.2, n = 107, including internal and 2% total external uncertainty)
	JT: Weighted mean of $^{206}Pb/^{238}U$ intercept ages: 13.340 ± 0.680 Ma (2σ, MSWD = 2.31, n = 4, including weighted average uncertainty (internal) and 2% total external uncertainty) Pooled measurements for 4 sessions: 13.385 ± 0.367 Ma (2σ, MSWD = 2.2, n = 112, including internal and 2% total external uncertainty)
	Systematic uncertainty for propagation is 2% (2σ)

Metadata of U-Pb analyses and data processing. Reporting standards after Horstwood et al. (2016).

References

Guillong, M., Wotzlaw, J., Looser, N., and Laurent, O., 2020, Evaluating the reliability of U – Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) carbonate geochronology : matrix issues and a potential calcite validation reference material: Geochronology, v. 2, p. 155–167, doi:10.5194/gchron-2-155-2020.

Horstwood. M.S.A. et al.. 2016. Community-Derived Standards for LA-ICP-MS U-(Th-)Pb Geochronology – Uncertainty Propagation. Age Interpretation and Data Reporting: Geostandards and Geoanalytical Research. v. 40. p. 311–332. doi:10.1111/j.1751-908X.2016.00379.x.

Nuriel, P., Wotzlaw, J.-F., Ovtcharova, M., Vaks, A., Stremtan, C., Šala, M., Roberts, M.W., and Kylander-Clark, R.C., 2020, The use of ASH-15 flowstone as a matrix-matched reference material for laser-ablation U-Pb geochronology of calcite: Geochronology, v. Preprint.

Roberts. N.M.W.. Rasbury. E.T.. Parrish. R.R.. Smith. C.J.. Horstwood. M.S.A.. and Condon. D.J.. 2017. A calcite reference material for LA-ICP-MS U-Pb geochronology: Geochemistry. Geophysics. Geosystems. v. 18. p. 2807–2814. doi:10.1002/2016GC006784.

Vermeesch. P.. 2018. IsoplotR: A free and open toolbox for geochronology: Geoscience Frontiers. v. 9. p. 1479–1493. doi:10.1016/j.gsf.2018.04.001.