

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

| Laboratory & Sample Preparation | Maps |
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| 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 (µm) | 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 |
| Sensitivity / 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 |

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| 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $^{206}\text{Pb}/^{238}\text{U}$ ratios of QC and unknowns |
| 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 | <i>DBT (Hill et al., 2016: $64.04 \pm 0.67 \text{ Ma} / 0.738 \pm 0.010$)</i> Lower Intercept Age = $63.01 \pm 0.75 / 2.18 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7176 \pm 0.013$ (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 (µm) | 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 |
| Sensitivity / 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 |

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| 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 $^{206}\text{Pb}/^{238}\text{U}$ ratios of QC and unknowns Except WC-1: Anchored regression in TW using an initial $^{207}\text{Pb}/^{206}\text{Pb}$ 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 $\text{Pb}_{\text{initial}}$ anchor. |
| 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 | <i>WC-1 (Roberts et al., 2017: $254.4 \pm 6.4 \text{ Ma} / 0.85 \pm 0.04$)</i> 23-May-24: Lower Intercept Age = $250.0 \pm 4.4 / 7.1 \text{ Ma}$, Anchored (2s, MSWD = 2.5) 13-June-24: Lower Intercept Age = $253.4 \pm 7.3 / 9.2 \text{ Ma}$, Anchored (2s, MSWD = 2.7) 20-June-24: Lower Intercept Age = $250.6 \pm 6.4 / 8.5 \text{ Ma}$, 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

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