# Supplementary Information for

# LA-ICP-MS U-Pb carbonate geochronology: strategies, progress and limitations

Nick M W Roberts1, Kerstin Drost2,Matthew S A Horstwood1, Daniel J Condon1, , David Chew2, Henrik Drake3, Antoni E Milodowski4,Noah M McLean5, Andrew J Smye6,Richard J Walker7, Richard Haslam4, Keith Hodson8, Jonathan Imber9,Nicolas Beaudoin10, Jack K Lee9

1Geochronology and Tracers Facility, British Geological Survey, Environmental Science Centre, Nottingham, NG12 5GG, UK

2Department of Geology, Trinity College Dublin, Dublin 2, Ireland

3Department of Biology and Environmental Science, Linnaeus University, 39231 Kalmar, Sweden

4British Geological Survey, Environmental Science Centre, Nottingham, NG12 5GG, UK

5Department of Geology, University of Kansas, Lawrence, KS 66045, USA

6Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA

7School of Geography, Geology, and the Environment, University of Leicester, Leicester, LE1 7RH, UK

8Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA

9Department of Earth Sciences, Durham University, Science Labs, Durham, UK

10Laboratoire des Fluides Complexes et leurs Réservoirs-IPRA, E2SUPPA, Total, CNRS, Université de Pau et des Pays de l’Adour, UMR5150, Pau, France

# Methods

## Imagery

Back-scattered electron (BSE) and charge-contrast (CCI) images were taken at the British Geological Survey (BGS, Nottingham, UK), using a FEI QUANTA 600 environmental scanning electron microscope (ESEM). Samples were prepared as resin-impregnated polished sections and imaged as uncoated samples under low-vacuum conditions (130 Pa) with a working distance of 10 mm. BSE images were recorded using a solid-state (dual-diode) electron detector, with a 20 kV electron beam accelerating voltage, and beam currents between 0.1 and 0.6 nA,. CCI images were recorded using a FEI large-field gaseous secondary electron (electron cascade) detector, with 20 kV electron beam accelerating voltage, and beam currents of 1.2 to 4.5 nA. Cathodoluminescence imaging was undertaken at the BGS using a Technosyn 8200 MkII cold-cathode luminoscope stage attached to a Nikon optical microscope with long working distance lenses, and equipped with a Zeiss AxioCam MRc5 digital camera; vacuum and electron beam voltage and current were adjusted as required to generate optimum luminescence.

## LA-ICP-MS - BGS

For Image-guided data, both U-Pb and trace element data were collected at the Geochronology and Tracers Facility, BGS, using a Nu Instruments Attom single-collector inductively coupled plasma mass spectrometer coupled to a New Wave Research (ESI) 193UC excimer laser ablation system, and follow protocols outlined in Roberts & Walker (2016) and Roberts et al. (2017). U-Pb analyses utilise the following typical ablation conditions: a 100 µm static spot, for a 30 s dwell time, with a repetition rate of 10 Hz, and a fluence of 6 to 9 J/cm2. A pre-ablation using the same conditions is used to clean the surface material using a 150 µm spot for 2-4 s. For U-Pb, NIST614 is used for normalisation of Pb-Pb ratios, followed by WC-1 calcite (Roberts et al., 2017) for U-Pb ratios. For trace elements, NIST614 is used for normalisation using 44Ca for internal standardisation assuming 40.4% Ca content in the samples. Trace element maps are created by rastering lines across the material using typical conditions of a 100 \* 100 µm square at 50 µm/s, and using Iolite v2.5 to create a map image.

### Table 1: Data Reporting Table for BGS

|  |  |
| --- | --- |
| Laboratory & Sample Preparation | |
| Laboratory name | Geochronology & Tracers Facility, NERC Isotope Geosciences Laboratory |
| Sample type/mineral | Calcite |
| Sample preparation | Chips mounted in 1 inch epoxy mounts |
| Imaging | See main paper for details. |
| Laser ablation system | |
| Make, Model & type | ESI/New Wave Research, UP193UC |
| Ablation cell & volume | NWR TV2 |
| Laser wavelength (nm) | 193 nm |
| Pulse width (ns) | 4 ns |
| Fluence (J.cm-2) | ~6-8 J/cm-2 |
| Repetition rate (Hz) | 10 Hz |
| Spot size (m) | Generally 100 μm |
| Sampling mode / pattern | Static spot for U-Pb. Line rasters for elemental maps. |
| Carrier gas | 100% He, Ar make-up gas from DSN-100 combined using a Y-piece 50% along sample line. |
| Ablation duration (secs) | 30 secs for U-Pb spots generally. |
| Cell carrier gas flow (l/min) | 0.6 l/min |
| ICP-MS Instrument | |
| Make, Model & type | Nu Instruments, Attom, SC-ICP-MS |
| Sample introduction | Ablation aerosol |
| RF power (W) | 1300 W |
| Make-up gas flow | 0.7 l/min Ar |
| Detection system | Single Mascom SEM |
| Masses measured | 202, 204, 206, 207, 208, 232, 238 |
| Integration time per peak (ms) | Dwell times of 200 μs to 1000 μs per peak |
| Total integration time per reading (secs) | 0.35 sec  (should represent the time resolution of the data) |
| Sensitvity / Efficiency (%, element) | ~0.2% U |
| IC Dead time (ns) | 15 ns |
| Data Processing | |
| Gas blank | 60 second on-peak zero subtracted |
| Calibration strategy | NIST614 as primary reference material for Pb-Pb ratios, WC-1 carbonate standard for matrix matching of 206Pb/238U, DuffBrown carbonate for QC (only some sessions) |
| Reference Material info | NIST614 (concentration data Jochum et al., 2011; Pb isotopes Baker et al., 2004)  WC-1 (Roberts et al., 2017)  DBT (Hill et al., 2016) |
| Data processing package used / Correction for LIEF | In-house spreadsheet data processing after initial signal integration using Nu Instruments TRA software. No LIEF correction (mean of uncorrected ratios used). |
| Mass discrimination | Standard sample bracketing |
| Common-Pb correction, composition and uncertainty | None applied. Ages calculated from regressions used in Tera-Wasserburg plots. |
| Uncertainty level & propagation | Ages are quoted at 2sigma absolute, propagation is by quadratic addition. Excess variance of reference material propagated into sample data. Systematic uncertainties include age uncertainty of reference material. |
| Other information | |

## LA-ICP-MS - TCD

For image-based data (Examples D-F), analyses were performed at the Geology Department of Trinity College Dublin using a Photon Machines Analyte Excite 193 nm ArF excimer laser ablation system coupled to an Agilent 7900 quadrupole ICP-MS. Analytical protocol and data processing routine are described in Drost et al. (2018). Samples were ablated along successive linear rasters with a spot size of 95µm, a repetition rate of 50Hz, a scan speed of 30 µm/s, and a fluence of 2J/cm2. NIST614 is used as the primary reference material for both the U-Pb data and the elemental data (concentration data of Jochum et al., 2011; Pb isotopes of Baker et al., 2004). In addition WC-1 carbonate standard (Roberts et al., 2017) is used for matrix matching of 206Pb/238U and Duff Brown Tank lacustrine limestone (Hill et al., 2016) was analysed as a quality control. Data processing was conducted using Iolite V3.6 (Paton et al., 2010, 2011) with the Trace Elements and VisualAge\_UcomPbine data reduction schemes (Chew et al., 2014; Petrus & Kamber, 2012), Monocle (Petrus et al., 2017) and an in-house spreadsheet with the Isoplot add-on (Ludwig, 2012).

### Table 2: Data Reporting Table for TCD

|  |  |
| --- | --- |
| **Laboratory & Sample Preparation** |  |
| Laboratory name | Department of Geology, Trinity College Dublin |
| Sample type/mineral | calcite veins |
| Sample preparation | 25mm round mount (NR1511) - session 1, polished rock slabs (BH11, BM18) - session 2 |
| Imaging | scans of polished rock slabs only |
| **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) | 2.0 J/cm2 |
| Repetition rate (Hz) | 50 Hz |
| Spot size (µm) | 95 µm square, except DBT: 80µm round |
| Sampling mode / pattern | linear rasters, 1 pass, 30 µm/sec scan speed |
| Carrier gas | 100% He in the cell (0.36 l/min [session 1], 0.4 l/min [session 2]), Ar make-up gas (0.65 l/min) and N2 (8 ml/min) |
| Ablation duration (secs) | session 1: NR1511: 30x 145s  session 2: BM18: 30 x 160s, BH11: 3x11 x 153s |
| Cell carrier gas flow (l/min) | session 1: 0.23 l/min in the cell and 0.13 l/min in the cup  session 2: 0.25 l/min in the cell and 0.15 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 |
| Make-up gas flow (l/min) | 0.65 l/min Ar |
| Detection system | Dual-mode discrete dynode electron multiplier |
| Masses measured | 25, 43, 55, 57, 63, 71, 85, 88, 137, 140, 202, 204, 206, 207, 208, 232, 238 |
| Integration time per peak (ms) | 2.5ms for masses 25 to 204, 20ms for 206, 208 and 238, 30ms for 207, 15ms for 232 |
| Total integration time per reading (secs) | 171 ms / 1.026 s after averaging |
| Sensitvity / Efficiency (%, element) | 0.02% U |
| IC Dead time (ns) | 38ns |
| **Data Processing** |  |
| Gas blank | ≥10 s on-peak zero subtracted |
| Calibration strategy | NIST614 as primary reference material, WC-1 carbonate standard for matrix matching of 206Pb/238U, DBT carbonate for QC |
| Reference Material info | NIST614 (concentration data Jochum et al., 2011; Pb isotopes Baker et al., 2004)  WC-1 (Roberts et al., 2017)  DBT (Hill et al., 2016) |
| Data processing package used / Correction for LIEF | Iolite V3.6 & Monocle & 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. |
| Uncertainty level & propagation | Ratios and ages are quoted at 2s. Error propagation was carried out using the recommendations of Horstwood et al. (2016) with the modifications suggested in this paper. 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 (if applicable). The second uncertainty additionally includes systematic uncertainties such as the uncertainty on the reference age of WC-1, uncertainty on the 238U decay constant and a laboratory-specific long-term reproducibility based on the results of the QC material. |
| Quality control / Validation | Duff Brown Tank limestone gave lower intercept ages of 63.70 ± 0.54/2.1 Ma (2s, MSWD = 1.22) in session 1 and 62.89 ± 0.71/2.1 Ma (2s, MSWD = 0.69) over the course of session 2 |
| **Other information** | All reference materials and samples were cleaned with ethanol followed by sonication in DIW. Potentially remaining surface contamination was removed during a preablation of all ablated sites. Details on the general analytical protocol are given in Drost et al. (2018). |

## Datasets

### Table 3 - Common lead composition of vein calcite

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **ID** | **Location A** | **Location B** | **Type** | **Sample** | **Age (Ma)** | **2s** | **Y-Int.** | **2s** |
| 1 | Czech | Prague Basin | Frac.-fill | 160B | - | - | 0.777 | 0.023 |
| 2 | Czech | Prague Basin | Frac.-fill | 160A | - | - | 0.950 | 0.250 |
| 3 | England | Cleveland Basin | Frac.-fill | NR1623 | 29.2 | 3.4 | 0.775 | 0.037 |
| 4 | England | Cleveland Basin | Frac.-fill | JL1808 | 32.4 | 2.3 | 0.808 | 0.005 |
| 5 | England | Cleveland Basin | Frac.-fill | JL1812 | 24.4 | 3.0 | 0.806 | 0.008 |
| 6 | England | Cleveland Basin | Frac.-fill | JL1815 | 44.4 | 1.9 | 0.805 | 0.022 |
| 7 | England | Cleveland Basin | Frac.-fill | JL1932 | 39.7 | 1.3 | 0.802 | 0.006 |
| 8 | England | Cleveland Basin | Frac.-fill | JL1934 | 44.4 | 2.7 | 0.811 | 0.012 |
| 9 | England | Cleveland Basin | Frac.-fill | JL1939 | 42.2 | 1.5 | 0.785 | 0.021 |
| 10 | England | Cleveland Basin | Frac.-fill | NR1501 | 34.4 | 2.1 | 0.845 | 0.042 |
| 11 | England | Cleveland Basin | Frac.-fill | NR1503 | 32.3 | 1.4 | 0.837 | 0.002 |
| 12 | England | Cleveland Basin | Frac.-fill | NR1504 | 35.2 | 3.4 | 0.822 | 0.049 |
| 13 | England | Cleveland Basin | Frac.-fill | NR1505 | 33.4 | 3.5 | 0.792 | 0.037 |
| 14 | England | Cleveland Basin | Frac.-fill | NR1604 | 35.3 | 1.8 | 0.822 | 0.011 |
| 15 | England | Cleveland Basin | Frac.-fill | NR1609 blocky | 37.6 | 1.6 | 0.800 | 0.012 |
| 16 | England | Cleveland Basin | Frac.-fill | NR1609 fibrous | 37.5 | 1.3 | 0.822 | 0.006 |
| 17 | England | Cleveland Basin | Frac.-fill | NR1612 | 32.8 | 4.6 | 0.790 | 0.048 |
| 18 | England | Cleveland Basin | Frac.-fill | NR1615 | 32.3 | 2.6 | 0.822 | 0.028 |
| 19 | England | Cleveland Basin | Frac.-fill | NR1617 | 26.6 | 2.2 | 0.790 | 0.110 |
| 20 | England | Cleveland Basin | Frac.-fill | NR1619 | 28.8 | 1.2 | 0.827 | 0.004 |
| 21 | England | Cleveland Basin | Frac.-fill | NR1620 | 31.0 | 1.1 | 0.836 | 0.002 |
| 22 | England | Cleveland Basin | Frac.-fill | NR1621 | 31.7 | 3.6 | 0.830 | 0.005 |
| 23 | England | Flamborough | Frac.-fill | NR1708 | 63.4 | 1.8 | 0.807 | 0.011 |
| 24 | England | Flamborough | Frac.-fill | NR1707 | 63.9 | 2.1 | 0.812 | 0.041 |
| 25 | England | Flamborough | Frac.-fill | NR1901 | 58.8 | 1.4 | 0.833 | 0.033 |
| 26 | England | Flamborough | Frac.-fill | NR1709 | 56.2 | 1.6 | 0.837 | 0.006 |
| 27 | England | Flamborough | Frac.-fill | CJ1 | 56.7 | 1.4 | 0.846 | 0.120 |
| 28 | England | in confidence | Frac.-fill | in confidence | 246.0 | 3.3 | 0.823 | 0.016 |
| 29 | England | in confidence | Frac.-fill | in confidence | 21.0 | 6.3 | 0.829 | 0.007 |
| 30 | England | in confidence | Frac.-fill | in confidence | 259.2 | 3.4 | 0.844 | 0.009 |
| 31 | England | in confidence | Frac.-fill | in confidence | 153.0 | 14.0 | 0.846 | 0.005 |
| 32 | England | in confidence | Frac.-fill | in confidence | 100.0 | 6.3 | 0.846 | 0.004 |
| 33 | England | in confidence | Frac.-fill | in confidence | 258.0 | 2.1 | 0.848 | 0.012 |
| 34 | England | in confidence | Frac.-fill | in confidence | 253.3 | 3.0 | 0.850 | 0.003 |
| 35 | England | in confidence | Frac.-fill | in confidence | 200.7 | 2.1 | 0.850 | 0.003 |
| 36 | England | in confidence | Frac.-fill | in confidence | 274.0 | 2.3 | 0.853 | 0.007 |
| 37 | England | in confidence | Frac.-fill | in confidence | 239.0 | 5.4 | 0.855 | 0.010 |
| 38 | England | in confidence | Frac.-fill | in confidence | 177.2 | 19.0 | 0.868 | 0.029 |
| 39 | England | in confidence | Frac.-fill | in confidence | 31.8 | 3.7 | 0.878 | 0.035 |
| 40 | England | in confidence | Frac.-fill | in confidence | 32.9 | 1.5 | 0.830 | 0.011 |
| 41 | England | in confidence | Frac.-fill | in confidence | 3.8 | 1.8 | 0.833 | 0.016 |
| 42 | England | in confidence | Frac.-fill | in confidence | 34.1 | 1.8 | 0.837 | 0.003 |
| 43 | England | in confidence | Frac.-fill | in confidence | 52.8 | 1.5 | 0.838 | 0.005 |
| 44 | England | in confidence | Frac.-fill | in confidence | 47.5 | 1.3 | 0.838 | 0.005 |
| 45 | England | in confidence | Frac.-fill | in confidence | 183.2 | 2.3 | 0.849 | 0.011 |
| 46 | England | in confidence | Frac.-fill | in confidence | 315.6 | 1.3 | 0.891 | 0.044 |
| 47 | England | in confidence | Frac.-fill | in confidence | 324.0 | 2.4 | 0.894 | 0.046 |
| 48 | England | in confidence | Frac.-fill | in confidence | 31.7 | 5.9 | 0.731 | 0.010 |
| 49 | England | in confidence | Frac.-fill | in confidence | 40.0 |  | 0.789 | 0.023 |
| 50 | England | in confidence | Frac.-fill | in confidence | 34.0 | 51.0 | 0.807 | 0.037 |
| 51 | Faroe Islands | Faroe Islands | Frac.-fill | TJN-2-1 | 16.6 | 2.3 | 0.835 | 0.025 |
| 52 | Faroe Islands | Faroe Islands | Frac.-fill | TJN-0-1 | 44.8 | 1.1 | 0.862 | 0.007 |
| 53 | Faroe Islands | Faroe Islands | Frac.-fill | Mol-1-2 | 45.4 | 2.1 | 0.870 | 0.088 |
| 54 | Faroe Islands | Faroe Islands | Frac.-fill | Mol-1-1 | 41.4 | 3.4 | 0.874 | 0.012 |
| 55 | Faroe Islands | Faroe Islands | Frac.-fill | TOR-1-1 | 41.2 | 1.8 | 0.881 | 0.086 |
| 56 | Faroe Islands | Faroe Islands | Frac.-fill | TJN-1-3 | 37.7 | 2.5 | 0.887 | 0.059 |
| 57 | Faroe Islands | Faroe Islands | Frac.-fill | LEY-2-1 | 11.4 | 2.3 | 0.901 | 0.034 |
| 58 | in confidence | in confidence | Frac.-fill | in confidence | 19.1 | 2.5 | 0.667 | 0.048 |
| 59 | in confidence | in confidence | Frac.-fill | in confidence | 18.2 | 5.5 | 0.715 | 0.009 |
| 60 | in confidence | in confidence | Frac.-fill | in confidence | 14.0 | 5.6 | 0.762 | 0.027 |
| 61 | in confidence | in confidence | Frac.-fill | in confidence | 18.1 | 5.4 | 0.840 | 0.120 |
| 62 | Scotland | Arran | Frac.-fill | JM5 T7-8 | 386.0 | 11.4 | 0.844 | 0.020 |
| 63 | Scotland | Arran | Frac.-fill | AR08 | 218.4 | 1.9 | 0.845 | 0.005 |
| 64 | Scotland | Arran | Frac.-fill | JF7a | 291.0 | 2.1 | 0.851 | 0.005 |
| 65 | Scotland | in confidence | Frac.-fill | in confidence | 240.0 | 3.0 | 0.817 | 0.005 |
| 66 | Scotland | in confidence | Frac.-fill | in confidence | 28.3 | 2.3 | 0.840 | 0.011 |
| 67 | Scotland | in confidence | Frac.-fill | in confidence | 368.0 | 1.3 | 0.845 | 0.001 |
| 68 | Sweden | COSC-1 | Frac.-fill | COSC-9 | 494.4 | 2.0 | 0.798 | 0.022 |
| 69 | Sweden | in confidence | Frac.-fill | in confidence | 576.0 | 22.0 | 0.494 | 0.031 |
| 70 | Sweden | in confidence | Frac.-fill | in confidence | 464.0 | 0.1 | 0.582 | 0.013 |
| 71 | Sweden | in confidence | Frac.-fill | in confidence | 37.7 | 0.9 | 0.689 | 0.019 |
| 72 | Sweden | in confidence | Frac.-fill | in confidence | 39.2 | 2.1 | 0.751 | 0.010 |
| 73 | Sweden | in confidence | Frac.-fill | in confidence | 39.3 | 10.1 | 0.758 | 0.014 |
| 74 | Sweden | in confidence | Frac.-fill | in confidence | 506.0 | 24.0 | 0.772 | 0.013 |
| 75 | Sweden | in confidence | Frac.-fill | in confidence | 80.3 | 3.0 | 0.786 | 0.011 |
| 76 | Sweden | in confidence | Frac.-fill | in confidence | 25.2 | 6.5 | 0.805 | 0.007 |
| 77 | Sweden | in confidence | Frac.-fill | in confidence | 62.0 | 6.2 | 0.817 | 0.022 |
| 78 | USA | Bighorn Basin | Frac.-fill | R135B | 86.3 | 2.5 | 0.551 | 0.018 |
| 79 | USA | Bighorn Basin | Frac.-fill | BM18 | 59.5 | 2.5 | 0.590 | 0.012 |
| 80 | USA | Bighorn Basin | Frac.-fill | R135A | 89.7 | 4.8 | 0.606 | 0.013 |
| 81 | USA | Bighorn Basin | Frac.-fill | 24M | 2.4 | 5.1 | 0.617 | 0.007 |
| 82 | USA | Bighorn Basin | Frac.-fill | 21M C | 65.5 | 3.0 | 0.617 | 0.027 |
| 83 | USA | Bighorn Basin | Frac.-fill | R84(a) | 14.5 | 10.5 | 0.636 | 0.009 |
| 84 | USA | Bighorn Basin | Frac.-fill | 47T | 5.6 | 7.4 | 0.643 | 0.014 |
| 85 | USA | Bighorn Basin | Frac.-fill | R84(B) | 27.9 | 3.2 | 0.646 | 0.008 |
| 86 | USA | Bighorn Basin | Frac.-fill | 21M A | 72.0 | 3.6 | 0.658 | 0.010 |
| 87 | USA | Bighorn Basin | Frac.-fill | 24M B | 1.8 | 52.0 | 0.684 | 0.015 |
| 88 | USA | Bighorn Basin | Frac.-fill | LSM3 | 75.3 | 3.2 | 0.725 | 0.002 |
| 89 | USA | Bighorn Basin | Frac.-fill | BH12 | 56.6 | 2.4 | 0.727 | 0.005 |
| 90 | USA | Bighorn Basin | Frac.-fill | SMA1 | 45.4 | 1.9 | 0.729 | 0.002 |
| 91 | USA | Bighorn Basin | Frac.-fill | BH11 | 53.5 | 2.0 | 0.729 | 0.006 |
| 92 | USA | Bighorn Basin | Frac.-fill | BH14 | 63.1 | 1.6 | 0.731 | 0.001 |
| 93 | USA | Bighorn Basin | Frac.-fill | R17 | 60.5 | 3.0 | 0.761 | 0.007 |
| 94 | USA | Bighorn Basin | Frac.-fill | R157 | 66.9 | 2.1 | 0.764 | 0.002 |
| 95 | USA | Bighorn Basin | Frac.-fill | R155 | 58.5 | 2.7 | 0.766 | 0.002 |
| 96 | USA | Bighorn Basin | Frac.-fill | R152 | 45.9 | 0.3 | 0.773 | 0.001 |
| 97 | USA | Bighorn Basin | Frac.-fill | R153 | 58.4 | 1.5 | 0.773 | 0.001 |
| 98 | USA | Bighorn Basin | Frac.-fill | R98 | 53.7 | 2.5 | 0.799 | 0.008 |
| 99 | USA | Bighorn Basin | Frac.-fill | BH6 | 59.6 | 3.5 | 0.820 | 0.006 |
| 100 | USA | Bighorn Basin | Frac.-fill | 20M | 37.2 | 2.7 | 0.878 | 0.041 |
| 101 | USA | Bighorn Basin | Frac.-fill | R93 | 34.4 | 5.5 | 0.892 | 0.024 |
| 102 | USA | Moab Fault | Frac.-fill | KH18 | 41.0 | 23.0 | 0.756 | 0.007 |
| 103 | USA | Moab Fault | Frac.-fill | KH08 | 52.0 | 41.0 | 0.761 | 0.006 |
| 104 | Turkey | Travertine | Frac.-fill | MQ | 12.2 | 0.5 | 0.805 | 0.097 |
| 105 | Turkey | Travertine | Frac.-fill | Pal | 1.2 | 0.6 | 0.832 | 0.006 |
| 106 | in confidence | in confidence | Diagenetic | in confidence | 149.0 | 10.8 | 0.850 | 0.003 |
| 107 | in confidence | in confidence | Diagenetic | in confidence | 79.0 | 12.2 | 0.851 | 0.005 |
| 108 | in confidence | in confidence | Diagenetic | in confidence | 86.2 | 3.6 | 0.852 | 0.009 |
| 109 | in confidence | in confidence | Diagenetic | in confidence | 118.0 | 12.4 | 0.853 | 0.003 |
| 110 | in confidence | in confidence | Diagenetic | in confidence | 148.2 | 8.5 | 0.855 | 0.007 |
| 111 | in confidence | in confidence | Diagenetic | in confidence | 84.3 | 3.0 | 0.860 | 0.006 |
| 112 | in confidence | in confidence | Diagenetic | in confidence | 83.4 | 5.2 | 0.861 | 0.004 |
| 113 | in confidence | in confidence | Diagenetic | in confidence | 87.4 | 4.6 | 0.910 | 0.210 |
| 114 | China | Xuhai | Diagenetic | SX117 | 1008.0 | 31.6 | 0.746 | 0.007 |
| 115 | China | Xuhai | Diagenetic | SX106 | 1047.0 | 31.0 | 0.882 | 0.002 |
| 116 | England | Cleveland Basin | Diagenetic | Ammonite | 128.0 | 11.5 | 0.641 | 0.029 |
| 117 | England | Cleveland Basin | Diagenetic | Ammonite | 161.0 | 8.2 | 0.785 | 0.021 |
| 118 | England | Cleveland Basin | Diagenetic | Ammonite | 161.0 | 11.8 | 0.832 | 0.003 |
| 119 | England | Cleveland Basin | Diagenetic | Ammonite | 144.0 | 25.3 | 0.833 | 0.003 |
| 120 | Finnmark | Gaisa Nappe | Diagenetic | Cone-in-cone | 475.0 | 25.0 | 0.847 | 0.002 |
| 121 | Finnmark | Gaisa Nappe | Diagenetic | Cone-in-cone | 418.0 | 23.0 | 0.848 | 0.001 |
| 122 | Finnmark | Gaisa Nappe | Diagenetic | Spherulites | 563.0 | 70.0 | 0.849 | 0.004 |
| 123 | Finnmark | Gaisa Nappe | Diagenetic | Fibres | 486.0 | 161.0 | 0.853 | 0.002 |

## References for 234U/238U disequilibria

### Groundwater and Brines

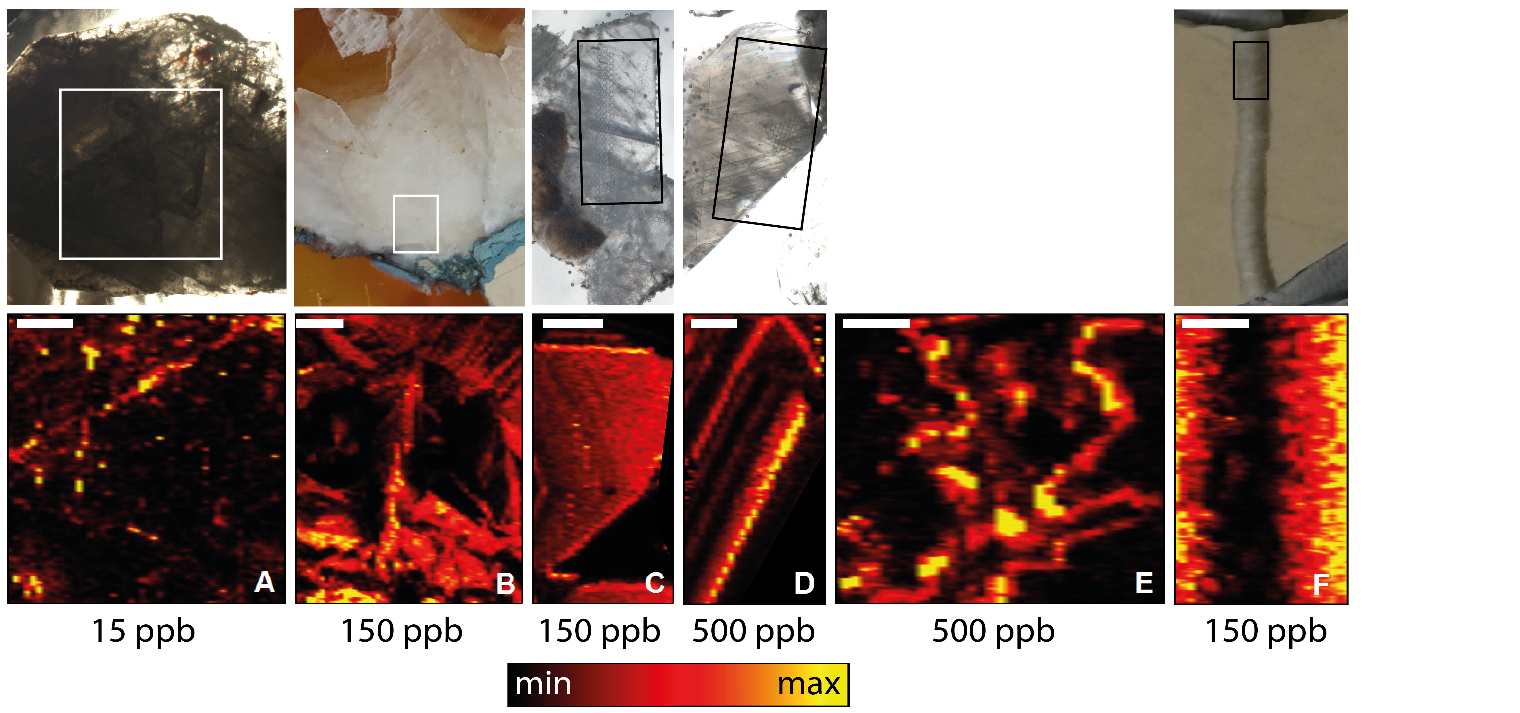
1. Ammar, F.H., Chkir, N., Zouari, K. and Azzouz-Berriche, Z., 2010. Uranium isotopes in groundwater from the “Jeffara coastal aquifer” (southeastern Tunisia). *Journal of environmental radioactivity*, *101*(9), pp.681-691.
2. Chkir, N., Guendouz, A., Zouari, K., Ammar, F.H. and Moulla, A.S., 2009. Uranium isotopes in groundwater from the continental intercalaire aquifer in Algerian Tunisian Sahara (Northern Africa). *Journal of environmental radioactivity*, *100*(8), pp.649-656.
3. Chkir, N. and Zouari, K., 2007. Uranium isotopic disequilibrium for groundwater classification: first results on complexe terminal and continental intercalaire aquifers in Southern Tunisia. *Environmental geology*, *53*(3), pp.677-685.
4. [Osmond, J.H. and Cowart, J.B., 1992](https://www.sciencedirect.com/science/article/pii/0016703794901937#bBIB23). Groundwater. In: Ivanovich, M. and Harmon, R. (Eds.), Uranium Series Disequilibrium: Applications to Environmental Problems (2nd Ed.), Clarendon Press, pp. 290-333.
5. Kaija, J., 1998. The hydrogeochemical database of Palmottu, Version 1998. The Palmottu Natural Analogue Project Technical Report 98-08.
6. Lidman, F., Peralta-Tapia, A., Vesterlund, A. and Laudon, H., 2016. 234U/238U in a boreal stream network—Relationship to hydrological events, groundwater and scale. *Chemical Geology*, *420*, pp.240-250.
7. Paces, J.B. and Wurster, F.C., 2014. Natural uranium and strontium isotope tracers of water sources and surface water–groundwater interactions in arid wetlands–Pahranagat Valley, Nevada, USA. *Journal of hydrology*, *517*, pp.213-225.
8. Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H., Vuorinen, U., 1999. Geochemical modeling of groundwater evolution and residence time at the Olkiluoto site. Posiva 98-10, 184 p.
9. Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H., Vuorinen, U., 2001. Geochemical modeling of groundwater evolution and residence time at the Hästholmen site. Posiva 2001-01, 175 p.
10. Pitkänen, P., Partamies, S., Luukkonen, A., 2004. Hydrogeochemical interpretation of Baseline groundwater conditions at the Olkiluoto site. Posiva 2003-07, 159 p.
11. Pitkänen, P., Snellman, M., Vuorinen, U., Leino-Forsman, H., 1996. Geochemical modelling study on the age and evolution of the groundwater at the Romuvaara site. Posiva 96-06, 120.
12. Reyes, E. and Marques, L.S., 2008. Uranium series disequilibria in ground waters from a fractured bedrock aquifer (Morungaba Granitoids—Southern Brazil): Implications to the hydrochemical behavior of dissolved U and Ra. *Applied Radiation and Isotopes*, *66*(10), pp.1531-1542.
13. Rodrigo, J.F., Casas-Ruiz, M., Vidal, J., Barbero, L., Baskaran, M. and Ketterer, M.E., 2014. Application of 234U/238U activity ratios to investigations of subterranean groundwater discharge in the Cádiz coastal area (SW Spain). *Journal of environmental radioactivity*, *130*, pp.68-71.
14. Suksi, J., Rasilainen, K., Casanova, J., Ruskeeniemi, T., Blomqvist, R. and Smellie, J.A.T., 2001. U-series disequilibria in a groundwater flow route as an indicator of uranium migration processes. *Journal of contaminant hydrology*, *47*(2-4), pp.187-196.
15. Tullborg, E.L., Smellie, J.A. and MacKenzie, A.B., 2003. The use of natural uranium decay series studies in support of understanding redox conditions at potential radioactive waste disposal sites. *MRS Online Proceedings Library Archive*, *807*.

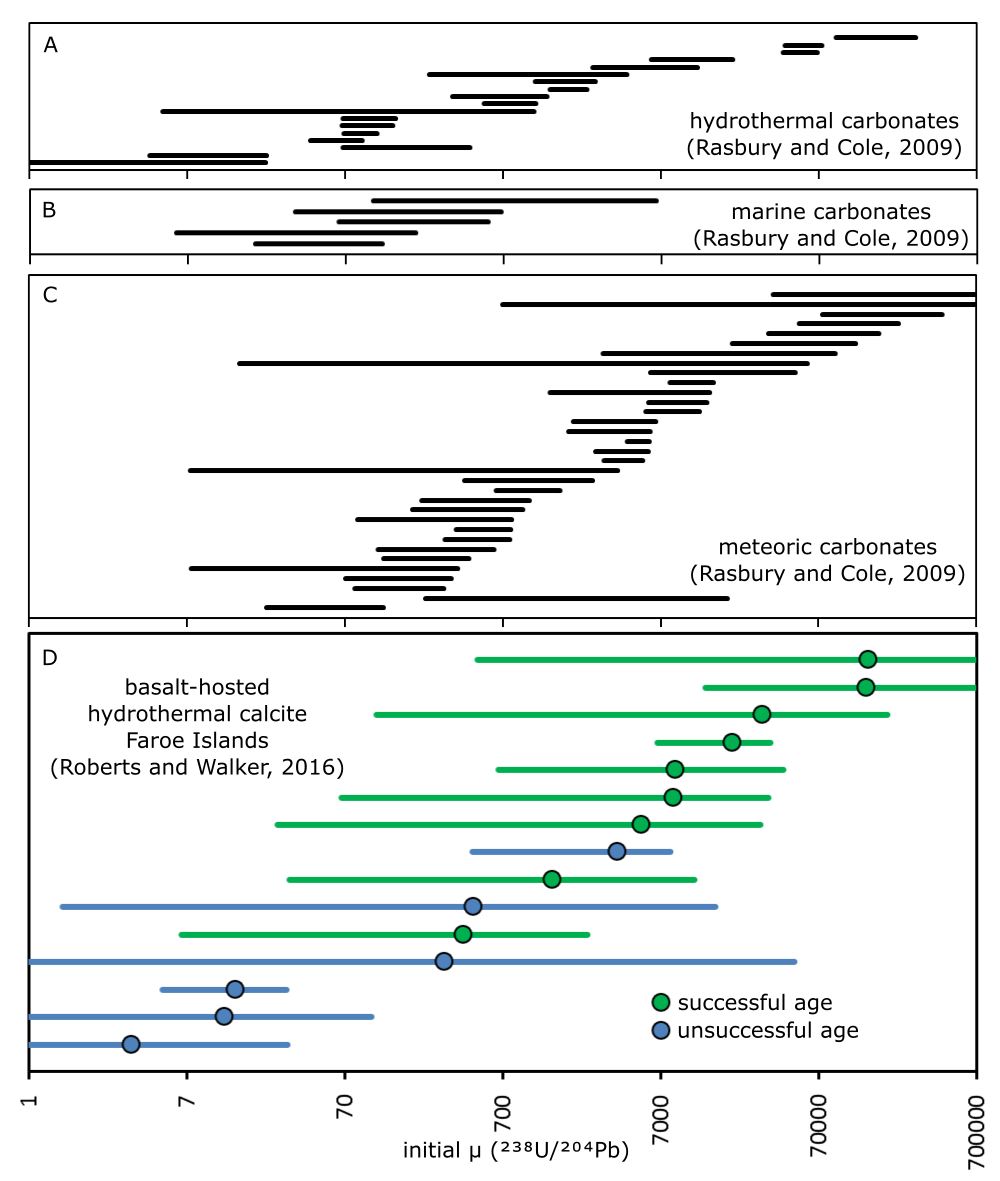
**Travertines and hydrothermal vein mineralisation**

1. Burnside, N.M., Shipton, Z.K., Dockrill, B. and Ellam, R.M., 2013. Man-made versus natural CO2 leakage: A 400 ky history of an analogue for engineered geological storage of CO2. *Geology*, *41*(4), pp.471-474.
2. Capezzuoli, E., Ruggieri, G., Rimondi, V., Brogi, A., Liotta, D., Alçiçek, M.C., Alçiçek, H., Bülbül, A., Gandin, A., Meccheri, M. and Shen, C.C., 2018. Calcite veining and feeding conduits in a hydrothermal system: Insights from a natural section across the Pleistocene Gölemezli travertine depositional system (western Anatolia, Turkey). *Sedimentary geology*, *364*, pp.180-203.
3. Çolak Erol, S., Özkul, M., Aksoy, E., Kele, S. and Ghaleb, B., 2015. Travertine occurrences along major strike-slip fault zones: structural, depositional and geochemical constraints from the Eastern Anatolian Fault System (EAFS), Turkey. *Geodinamica Acta*, *27*(2-3), pp.155-174.
4. Karabacak, V., Uysal, I.T., Ünal-İmer, E., Mutlu, H. and Zhao, J.X., 2017. U-Th age evidence from carbonate veins for episodic crustal deformation of Central Anatolian Volcanic Province. *Quaternary Science Reviews*, *177*, pp.158-172.
5. Miocic, J.M., Gilfillan, S.M., Frank, N., Schroeder-Ritzrau, A., Burnside, N.M. and Haszeldine, R.S., 2019. 420,000 year assessment of fault leakage rates shows geological carbon storage is secure. *Scientific reports*, *9*(1), p.769.
6. Neymark, L.A., Amelin, Y.V. and Paces, J.B., 2000. 206Pb–230Th–234U–238U and 207Pb–235U geochronology of Quaternary opal, Yucca Mountain, Nevada. *Geochimica et Cosmochimica Acta*, *64*(17), pp.2913-2928.
7. Nuriel, P., Rosenbaum, G., Uysal, T.I., Zhao, J.X., Golding, S.D., Weinberger, R., Karabacak, V. and Avni, Y., 2011. Formation of fault-related calcite precipitates and their implications for dating fault activity in the East Anatolian and Dead Sea fault zones. *Geological Society, London, Special Publications*, *359*(1), pp.229-248.
8. Nuriel, P., Rosenbaum, G., Zhao, J.X., Feng, Y., Golding, S.D., Villemant, B. and Weinberger, R., 2012. U-Th dating of striated fault planes. *Geology*, *40*(7), pp.647-650.
9. Özkul, M., Kele, S., Gökgöz, A., Shen, C.C., Jones, B., Baykara, M.O., Fόrizs, I., Németh, T., Chang, Y.W. and Alçiçek, M.C., 2013. Comparison of the Quaternary travertine sites in the Denizli extensional basin based on their depositional and geochemical data. *Sedimentary Geology*, *294*, pp.179-204.
10. Paces, J.B., Neymark, L.A., Whelan, J.F., Wooden, J.L., Lund, S.P. and Marshall, B.D., 2010. Limited hydrologic response to Pleistocene climate change in deep vadose zones—Yucca Mountain, Nevada. *Earth and Planetary Science Letters*, *300*(3-4), pp.287-298.
11. Priestley, S.C., Karlstrom, K.E., Love, A.J., Crossey, L.J., Polyak, V.J., Asmerom, Y., Meredith, K.T., Crow, R., Keppel, M.N. and Habermehl, M.A., 2018. Uranium series dating of Great Artesian Basin travertine deposits: Implications for palaeohydrogeology and palaeoclimate. *Palaeogeography, palaeoclimatology, palaeoecology*, *490*, pp.163-177.
12. Priewisch, A., Crossey, L.J., Karlstrom, K.E., Polyak, V.J., Asmerom, Y., Nereson, A. and Ricketts, J.W., 2014. U-series geochronology of large-volume Quaternary travertine deposits of the southeastern Colorado Plateau: Evaluating episodicity and tectonic and paleohydrologic controls. *Geosphere*, *10*(2), pp.401-423.
13. Rihs, S., Condomines, M. and Poidevin, J.L., 2000. Long-term behaviour of continental hydrothermal systems:: U-series study of hydrothermal carbonates from the French Massif Central (Allier Valley). *Geochimica et Cosmochimica Acta*, *64*(18), pp.3189-3199.
14. Ring, U., Uysal, I.T., Yüce, G., Ünal-İmer, E., Italiano, F., Imer, A. and Zhao, J.X., 2016. Recent mantle degassing recorded by carbonic spring deposits along sinistral strike-slip faults, south-central Australia. *Earth and Planetary Science Letters*, *454*, pp.304-318.
15. Uysal, I.T., Zhao, J.X., Işık, V., Shulmeister, J., Imer, A. and Feng, Y.X., 2016. CO2 outburst events in relation to seismicity: Constraints from microscale geochronology, geochemistry of late Quaternary vein carbonates, SW Turkey. *Geochimica et Cosmochimica Acta*, *187*, pp.21-40.
16. Williams, R.T., Goodwin, L.B., Sharp, W.D. and Mozley, P.S., 2017. Reading a 400,000-year record of earthquake frequency for an intraplate fault. *Proceedings of the National Academy of Sciences*, *114*(19), pp.4893-4898.

**Additional Figures**

*S1: Expansion of Figure 1 with additional optical microphotographs of samples*



*S2: A-C: Literature compilation of carbonate 238U/204Pb (µm) values, drawn from values in Rasbury & Cole (2009). D: Comparison to LA-ICP-MS-derived data* from fracture-fill hydrothermal calcite, based on study of Roberts & Walker (2016). Bars show the total range, and spots show the mean.

**References**

1. Baker, J., Peate, D., Waight, T. and Meyzen, C., 2004. Pb isotopic analysis of standards and samples using a 207Pb–204Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. Chemical Geology, 211(3-4), pp.275-303.
2. Chew, D.M., Petrus, J.A. and Kamber, B.S., 2014. U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb. Chemical Geology, 363, pp.185-199.
3. Hill, C.A., Polyak, V.J., Asmerom, Y. and P. Provencio, P., 2016. 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(4), pp.896-906.
4. Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A. and Günther, D., 2011. Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines. Geostandards and Geoanalytical Research, 35(4), pp.397-429.
5. Ludwig, K.R., 2011. Isoplot/Ex Version 4: A Geochronological Toolkit for Microsoft Excel: Geochronology Center. Berkeley, California, USA.
6. Paton, C., Hellstrom, J., Paul, B., Woodhead, J. and Hergt, J., 2011. Iolite: Freeware for the visualisation and processing of mass spectrometric data. Journal of Analytical Atomic Spectrometry, 26(12), pp.2508-2518.
7. Paton, C., Woodhead, J.D., Hellstrom, J.C., Hergt, J.M., Greig, A. and Maas, R., 2010. Improved laser ablation U‐Pb zircon geochronology through robust downhole fractionation correction. Geochemistry, Geophysics, Geosystems, 11(3).
8. Petrus, J.A., Chew, D.M., Leybourne, M.I. and Kamber, B.S., 2017. A new approach to laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using the flexible map interrogation tool ‘Monocle’. Chemical Geology, 463, pp.76-93.
9. Petrus, J.A. and Kamber, B.S., 2012. VizualAge: A novel approach to laser ablation ICP‐MS U‐Pb geochronology data reduction. Geostandards and Geoanalytical Research, 36(3), pp.247-270.
10. Rasbury, E.T. and Cole, J.M., 2009. Directly dating geologic events: U‐Pb dating of carbonates. Reviews of Geophysics, 47(3).
11. Roberts, N.M., Rasbury, E.T., Parrish, R.R., Smith, C.J., Horstwood, M.S. and Condon, D.J., 2017. A calcite reference material for LA‐ICP‐MS U‐Pb geochronology. Geochemistry, Geophysics, Geosystems, 18(7), pp.2807-2814.
12. Roberts, N.M. and Walker, R.J., 2016. U-Pb geochronology of calcite-mineralized faults: Absolute timing of rift-related fault events on the northeast Atlantic margin. Geology, 44(7), pp.531-534.