Supplementary Information for

LA-ICP-MS U-Pb carbonate geochronology: strategies, progress, and application to fracture-fill calcite

Nick M W Roberts[1], Matthew S A Horstwood[1], Daniel J Condon[1], Kerstin Drost[2], David Chew[2], Henrik Drake[3], Antoni E Milodowski[4], Noah M McLean[5], Andrew J Smye[6], Richard J Walker[7], Richard Haslam[4], Keith Hodson[8], Jonathan Imber[9], Nicolas Beaudoin[10]

1Geochronology and Tracers Facility, British Geological Survey, Environmental Science Centre, Nottingham, NG12 5GG, UK
[2]Department of Geology, Trinity College Dublin, Dublin 2, Ireland
[3]Department of Biology and Environmental Science, Linnaeus University, 39231 Kalmar, Sweden
[4]British Geological Survey, Environmental Science Centre, Nottingham, NG12 5GG, UK
[5]Department of Geology, University of Kansas, Lawrence, KS 66045, USA
[6]Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA
[7]School of Geography, Geology, and the Environment, University of Leicester, Leicester, LE1 7RH, UK
[8]Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA
[9]Department of Earth Sciences, Durham University, Science Labs, Durham, UK
[10]Laboratoire des Fluides Complexes et leurs Réservoirs-IPRA, E2SUPPA, Total, CNRS, Université de Pau et des Pays de l’Adour, UMR5150, Pau, France

Methods

1. 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.

2. LA-ICP-MS - BGS

For Image-guided data (Examples A-C and G), 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 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/cm^2. 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 ^{44}Ca 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 $^{206}Pb/^{238}U$, 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	

3. 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/cm^2. 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 $^{206}Pb/^{238}U$ 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	polished rock slab (BH06), polished 25mm mount
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/cm^2
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), Ar make-up gas (0.65 l/min) and N_2 (8 ml/min)
Ablation duration (secs)	BH6: 15 x 243s, 1511: 30 x 145s BM18: 30 x 160s, BH11: 3x11 x 153s

Cell carrier gas flow (l/min)	0.23 l/min in the cell and 0.13 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)	0.65 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 and 238, 30ms for 207, 20ms for 208, 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	≥9 s 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 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. Lower intercept age uncertainty and excess uncertainty derived from anchored (0.85 ± 0.04, Roberts et al., 2017) Tera-Waserburg regression of WC-1 carbonate reference material is propagated for ^{238}U/^{206}Pb ratios and excess uncertainty derived from ^{207}Pb and ^{208}Pb counting statistics is propagated for ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios, respectively, by quadratic addition. The uncertainty value for lower intercept ages and isochron ages includes systematic uncertainties (uncertainty on WC-1 reference age, decay constant uncertainties).
Quality control / Validation	Duff Brown Tank limestone gave a lower intercept age of 63.89 ± 0.73/1.8 Ma (2s, MSWD = 0.65) over the course of session 1 and 62.96 ± 0.77/1.8 Ma (2s, MSWD = 0.49) over session 2.
Other information	

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. 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.

11. 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.

4. Datasets

Table 3 - Common lead composition of vein calcite

Identifier	Location A	Location B	Sample	Age (Ma)	2s (Ma)	Y-Intercept	2s
1	Czech	Prague Basin	160B	-	-	0.777	0.023
2	Czech	Prague Basin	160A	-	-	0.950	0.250
3	England	Cleveland Basin	NR1623	29	3.4	0.775	0.037
4	England	Cleveland Basin	JL1808	32	2.3	0.808	0.005
5	England	Cleveland Basin	JL1812	24	3.0	0.806	0.008
6	England	Cleveland Basin	JL1815	44	1.9	0.805	0.022
7	England	Cleveland Basin	JL1932	40	1.3	0.802	0.006
8	England	Cleveland Basin	JL1934	44	2.7	0.811	0.012
9	England	Cleveland Basin	JL1939	42	1.5	0.785	0.021
10	England	Cleveland Basin	NR1501	34	2.1	0.845	0.042
11	England	Cleveland Basin	NR1503	32	1.4	0.837	0.002
12	England	Cleveland Basin	NR1504	35	3.4	0.822	0.049
13	England	Cleveland Basin	NR1505	33	3.5	0.792	0.037
14	England	Cleveland Basin	NR1604	35	1.8	0.822	0.011
15	England	Cleveland Basin	NR1609 blocky	38	1.6	0.800	0.012
16	England	Cleveland Basin	NR1609 fibrous	38	1.3	0.822	0.006
17	England	Cleveland Basin	NR1612	33	4.6	0.790	0.048
18	England	Cleveland Basin	NR1615	32	2.6	0.822	0.028
19	England	Cleveland Basin	NR1617	27	2.2	0.790	0.110
20	England	Cleveland Basin	NR1619	29	1.2	0.827	0.004
21	England	Cleveland Basin	NR1620	31	1.1	0.836	0.002
22	England	Cleveland Basin	NR1621	32	3.6	0.830	0.005
23	England	Flamborough	NR1708	63	1.8	0.807	0.011
24	England	Flamborough	NR1707	64	2.1	0.812	0.041
25	England	Flamborough	NR1901	59	1.4	0.833	0.033
26	England	Flamborough	NR1709	56	1.6	0.837	0.006
27	England	Flamborough	CJ1	57	1.4	0.846	0.120
28	England	in confidence	in confidence	246	3.3	0.823	0.016
29	England	in confidence	in confidence	21	6.3	0.829	0.007
30	England	in confidence	in confidence	259	3.4	0.844	0.009
31	England	in confidence	in confidence	153	14.0	0.846	0.005
32	England	in confidence	in confidence	100	6.3	0.846	0.004
33	England	in confidence	in confidence	258	2.1	0.848	0.012
34	England	in confidence	in confidence	253	3.0	0.850	0.003
35	England	in confidence	in confidence	201	2.1	0.850	0.003
36	England	in confidence	in confidence	274	2.3	0.853	0.007
37	England	in confidence	in confidence	239	5.4	0.855	0.010
38	England	in confidence	in confidence	177	19.0	0.868	0.029
39	England	in confidence	in confidence	32	3.7	0.878	0.035

40	England	in confidence	in confidence	33	1.5	0.830	0.011
41	England	in confidence	in confidence	4	1.8	0.833	0.016
42	England	in confidence	in confidence	34	1.8	0.837	0.003
43	England	in confidence	in confidence	53	1.5	0.838	0.005
44	England	in confidence	in confidence	48	1.3	0.838	0.005
45	England	in confidence	in confidence	183	2.3	0.849	0.011
46	England	in confidence	in confidence	316	1.3	0.891	0.044
47	England	in confidence	in confidence	324	2.4	0.894	0.046
48	England	in confidence	in confidence	32	5.9	0.731	0.010
49	England	in confidence	in confidence	40		0.789	0.023
50	England	in confidence	in confidence	34	51.0	0.807	0.037
51	Faroe Islands	Faroe Islands	TJN-2-1	17	2.3	0.835	0.025
52	Faroe Islands	Faroe Islands	TJN-0-1	45	1.1	0.862	0.007
53	Faroe Islands	Faroe Islands	Mol-1-2	45	2.1	0.870	0.088
54	Faroe Islands	Faroe Islands	Mol-1-1	41	3.4	0.874	0.012
55	Faroe Islands	Faroe Islands	TOR-1-1	41	1.8	0.881	0.086
56	Faroe Islands	Faroe Islands	TJN-1-3	38	2.5	0.887	0.059
57	Faroe Islands	Faroe Islands	LEY-2-1	11	2.3	0.901	0.034
58	in confidence	in confidence	in confidence	19	2.5	0.667	0.048
59	in confidence	in confidence	in confidence	18	5.5	0.715	0.009
60	in confidence	in confidence	in confidence	14	5.6	0.762	0.027
61	in confidence	in confidence	in confidence	18	5.4	0.840	0.120
62	Scotland	Arran	JM5 T7-8	386	11.4	0.844	0.020
63	Scotland	Arran	AR08	218	1.9	0.845	0.005
64	Scotland	Arran	JF7a	291	2.1	0.851	0.005
65	Scotland	in confidence	in confidence	240	3.0	0.817	0.005
66	Scotland	in confidence	in confidence	28	2.3	0.840	0.011
67	Scotland	in confidence	in confidence	368	1.3	0.845	0.001
68	Sweden	COSC-1	COSC-9	494	2.0	0.798	0.022
69	Sweden	in confidence	in confidence	576	22.0	0.494	0.031
70	Sweden	in confidence	in confidence	464	0.1	0.582	0.013
71	Sweden	in confidence	in confidence	38	0.9	0.689	0.019
72	Sweden	in confidence	in confidence	39	2.1	0.751	0.010
73	Sweden	in confidence	in confidence	39	10.1	0.758	0.014
74	Sweden	in confidence	in confidence	506	24.0	0.772	0.013
75	Sweden	in confidence	in confidence	80	3.0	0.786	0.011
76	Sweden	in confidence	in confidence	25	6.5	0.805	0.007
77	Sweden	in confidence	in confidence	62	6.2	0.817	0.022
78	USA	Bighorn Basin	R135B	86	2.5	0.551	0.018
79	USA	Bighorn Basin	BM18	60	2.5	0.590	0.012
80	USA	Bighorn Basin	R135A	90	4.8	0.606	0.013
81	USA	Bighorn Basin	24M	2	5.1	0.617	0.007
82	USA	Bighorn Basin	21M C	66	3.0	0.617	0.027
83	USA	Bighorn Basin	R84(a)	15	10.5	0.636	0.009
84	USA	Bighorn Basin	47T	6	7.4	0.643	0.014
85	USA	Bighorn Basin	R84(B)	28	3.2	0.646	0.008
86	USA	Bighorn Basin	21M A	72	3.6	0.658	0.010
87	USA	Bighorn Basin	24M B	2	52.0	0.684	0.015
88	USA	Bighorn Basin	LSM3	75	3.2	0.725	0.002
89	USA	Bighorn Basin	BH12	57	2.4	0.727	0.005

90	USA	Bighorn Basin	SMA1	45	1.9	0.729	0.002
91	USA	Bighorn Basin	BH11	54	2.0	0.729	0.006
92	USA	Bighorn Basin	BH14	63	1.6	0.731	0.001
93	USA	Bighorn Basin	R17	61	3.0	0.761	0.007
94	USA	Bighorn Basin	R157	67	2.1	0.764	0.002
95	USA	Bighorn Basin	R155	59	2.7	0.766	0.002
96	USA	Bighorn Basin	R152	46	0.3	0.773	0.001
97	USA	Bighorn Basin	R153	58	1.5	0.773	0.001
98	USA	Bighorn Basin	R98	54	2.5	0.799	0.008
99	USA	Bighorn Basin	BH6	60	3.5	0.820	0.006
100	USA	Bighorn Basin	20M	37	2.7	0.878	0.041
101	USA	Bighorn Basin	R93	34	5.5	0.892	0.024
102	USA	Moab Fault	KH18	41	23.0	0.756	0.007
103	USA	Moab Fault	KH08	52	41.0	0.761	0.006

U-Pb and trace element data

As the examples in this paper are meant as demonstrations of the approach, and the interpretation of the data is not a focus of the paper, the full datasets are not provided. However, the full datasets generated during the current study are available from the corresponding author on reasonable request.

5. References for $^{234}U/^{238}U$ 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. 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., Fórizs, 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.