



Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Applications of the LA-ICP-MS image mapping approach to U-Pb carbonate dating : from far-field tectonism to pedogenic nodules

Thesis Dissertation for Doctor of Philosophy
School of Natural Sciences
Department of Geology

by

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Annexes

Part 1: Supplementary documents and figures



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

Laboratory & Sample Preparation	U-Pb geochronology of calcite vein systems in southwestern Ireland: constraints on the post-Variscan tectonic evolution
Laboratory name	Dept of Earth Science, Trinity College Dublin
Sample type/mineral	Calcite veins and Calcite crystals from brachiopod shells
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)	all: 2.2 J/cm ² except 30-Nov-2022/ 01-Dec-2022: 2.5 J/cm ² except 10-Oct-2023/11-Oct-2023/16-Oct-2023 : 2 J/cm ²
Repetition rate (Hz)	all : 50 Hz except 10-Oct-2023/11-Oct-2023/16-Oct-2023 : 55 Hz
Spot size (µm)	all: 85 µm square except 17-Feb-2020/05-Mar-2020/ 19-May-2021: 80 µm round
Sampling mode / pattern	line raster, 1 pass, 30 µm/sec scan speed
Carrier gas	optimized daily: 100% He in the cell (0.30-0.40 l/min), Ar carrier gas (0.58-0.65 l/min) and N ₂ (7-12 ml/min ¹) added at ARIS adaptor
Ablation duration (secs)	17-Feb-2020 : 21x60s [NIST614], 21x35s [WC-1], 21x60s [Duff Brown Tank], VMF3:30x95s, VMF6:30x120s 05-Mar-2020 : 21x60s [NIST614], 21x35s [WC-1], 21x60s [Duff Brown Tank], VMF7: 56x60s 19-May-2021 : 18x60s [NIST614], 18x46s [WC-1], 18x57s [Duff Brown Tank], VMF2: 30x122s, VMF5b : 30x132s 19-Sept-2022 : 24x70s [NIST614], 24x70s [WC-1], 8x180s [Duff Brown Tank], VMB10: 36x120s 20-Sept-2022 : 18x70s [NIST614], 18x70s [WC-1], 6x180s [Duff Brown Tank], VMB6: 36x30s 14-Oct-2022 : 21x66s [NIST614], 21x66s [WC-1], 7x180s [Duff Brown Tank], VMB7: 90x37s 30-Nov-2022 : 21x70s [NIST614], 21x70s [WC-1], 7x180s [Duff Brown Tank], VMB16: 40x70s 01-Dec-2022 : 18x70s [NIST614], 18x70s [WC-1], 6x180s [Duff Brown Tank], VMB14: 40x150s 10-Oct-2023 : 21x65s [NIST614], 21x65s [WC-1], 7x180s [Duff Brown Tank], VMB21: 50x35s, VMB29: 50x45s 11-Oct-2023 : 15x65s [NIST614], 15x65s [WC-1], 5x180s [Duff Brown Tank], VMB31: 45x126s, VMB35: 45x140s 16-Oct-2023 : 21x65s [NIST614], 21x65s [WC-1], 7x180s [Duff Brown Tank], VMB20: 60x106s, VMB36: 60x60s

Cell carrier gas flow (l/min)	optimized daily: 0.25-0.40 l/min in the cell and 0.08-0.20 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)	0.58-0.65 l/min Ar
Detection system	Dual-mode discrete dynode electron multiplier
Masses measured and [Integration time per peak (ms)]	17-Feb-2020 and 05-Mar-2020 : 25 [2.5], 43 [2.5], 51 [2.5], 55 [2.5], 57 [2.5], 63 [2.5], 66 [2.5], 71 [2.5], 85 [2.5], 88 [2.5], 137 [2.5], 140 [2.5], 202 [2.5], 204 [2.5], 206 [17.5], 207 [22.5], 208 [15], 232 [10], 238 [17.5] 19-May-2021 : 25 [1.5], 43 [3], 51 [2], 55 [1.5], 57 [1.5], 63 [2], 66 [2], 71 [2], 85 [2], 88 [1.5], 137 [2], 140 [2], 202 [1], 204 [1], 206 [40], 207 [100], 208 [40], 232 [15], 238 [40] 19-Sept-2022/ 20-Sept-2022 : 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 [20], 207 [40], 208 [20], 232 [20], 238 [20] 14-Oct-2022/ 30-Nov-2022/ 01-Dec-2022/ 10-Oct-2023/ 11-Oct-2023/ 16-Oct-2023 : 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)	17-Feb-2020 : 300 ms / 1500 ms after averaging 05-Mar-2020 : 300 ms / 1800 ms after averaging 19-May-2021 : 300 ms / 1500 ms after averaging 19-Sept-2022 : 200 ms / 1000 ms after averaging 20-Sept-2022 : 200 ms / 1000 ms after averaging 14-Oct-2022 : 300 ms / 1500 ms after averaging 30-Nov-2022 : 300 ms / 1500 ms after averaging 01-Dec-2022 : 300 ms / 1500 ms after averaging 10-Oct-2023 : 300 ms / 1500 ms after averaging 11-Oct-2023 : 300 ms / 1500 ms after averaging 16-Oct-2023 : 300 ms / 1500 ms after averaging
Sensitivity / Efficiency (% , element)	0.02% U
IC Dead time (ns)	38ns
Data Processing	
Gas blank	17s to 21s 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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> 17-Feb-2020 : Lower Intercept Age = $63.30 \pm 1.00 / 2.28 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7003 \pm 0.020$ (2s, MSWD = 1.8) 05-Mar-2020 : Lower Intercept Age = $64.45 \pm 0.81 / 2.22 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7115 \pm 0.017$ (2s, MSWD = 0.60) 19-May-2021 : Lower Intercept Age = $65.10 \pm 1.30 / 2.48 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7167 \pm 0.025$ (2s, MSWD = 1.0) 19-Sept-2022 : Lower Intercept Age = $64.05 \pm 0.69 / 2.18 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7264 \pm 0.013$ (2s, MSWD = 0.61) 20-Sept-2022 : Lower Intercept Age = $65.00 \pm 1.00 / 2.33 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7120 \pm 0.020$ (2s, MSWD = 0.73) 14-Oct-2022 : Lower Intercept Age = $65.92 \pm 0.53 / 2.20 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7295 \pm 0.007$ (2s, MSWD = 1.3) 30-Nov-2022 : Lower Intercept Age = $63.20 \pm 0.79 / 2.19 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7043 \pm 0.013$ (2s, MSWD = 0.82) 01-Dec-2022 : Lower Intercept Age = $63.01 \pm 0.75 / 2.17 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7176 \pm 0.013$ (2s, MSWD = 1.13) 10-Oct-2023 : Lower Intercept Age = $64.90 \pm 1.30 / 2.47 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7362 \pm 0.018$ (2s, MSWD = 0.94) 11-Oct-2023 : Lower Intercept Age = $65.20 \pm 1.00 / 2.54 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7364 \pm 0.014$ (2s, MSWD = 0.63) 16-Oct-2023 : Lower Intercept Age = $65.30 \pm 1.20 / 2.43 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7502 \pm 0.020$ (2s, MSWD = 0.74)
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., 2014, U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb: *Chemical Geology*, v. 363, p. 185-199.

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- Woodhead, J. D., and Hergt, J. M., 2001, Strontium, Neodymium and Lead Isotope Analyses of NIST Glass Certified Reference Materials: SRM 610, 612, 614: *Geostandards Newsletter*, v. 25, no. 2-3, p. 261-266.

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

Laboratory & Sample Preparation	U-Pb direct dating on calcite paleosol nodules by LA-ICP-MS mapping: first absolute age constraints on the Miocene continental succession of the Paris Basin
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)	01-Dec-2022: 2.5 J/cm ² 27-Mar-2023: 2.5 J/cm ² 30-Mar-2023: 2.5 J/cm ²
Repetition rate (Hz)	01-Dec-2022: 50 Hz 27-Mar-2023: 50 Hz 30-Mar-2023: 50 Hz
Spot size (µm)	all: 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)	01-Dec-2022: 18x70s NIST614, 18x70s WC-1, 6x180s Duff Brown, P00: 59x35s 27-Mar-2023: 18x65s NIST614, 18x65s WC-1, 6x180s Duff Brown, P01: 62x35s, P14: 62x35s 30-Mar-2023: 21x65s NIST614, 21x65s WC-1, 7x180s Duff Brown, P02: 77x35s, P04: 52x35s
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)]	all: 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)	01-Dec-2022: 301 ms / 1505 ms after averaging 27-Mar-2023: 301 ms / 1505 ms after averaging 30-Mar-2023: 301 ms / 1505 ms after averaging

Sensitivity / Efficiency (% element)	0.02% U
IC Dead time (ns)	38ns
Data Processing	
Gas blank	17s to 22s on-peak zero subtracted
Calibration strategy	NIST614 as primary reference material, WC-1 carbonate standard for matrix matching of $^{206}\text{Pb}/^{238}\text{U}$, 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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> 01-Dec-2022: 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) 27-Mar-2023: Lower Intercept Age = $65.7 \pm 2.2 / 3.1 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7040 \pm 0.043$ (2s, MSWD = 0.66) 30-Mar-2023: Lower Intercept Age = $68.3 \pm 3.3 / 4.0 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7870 \pm 0.068$ (2s, MSWD = 1.4)
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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- 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*, v. 36, no. 3, p. 247-270.
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- Woodhead, J. D., and Hergt, J. M., 2001, Strontium, Neodymium and Lead Isotope Analyses of NIST Glass Certified Reference Materials: SRM 610, 612, 614: *Geostandards Newsletter*, v. 25, no. 2-3, p. 261-266.

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

Laboratory & Sample Preparation	Ballinalack carbonate hosted ore from DeBrit thesis (DeBrit, 1989)
Laboratory name	Dept of Earth Science, Trinity College Dublin
Sample type/mineral	Calcite veins
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)	all: 2.0 J/cm ² except 15-Sept-2022: 2.2 J/cm ²
Repetition rate (Hz)	all : 65 Hz except 15-Sept-2022: 50 Hz
Spot size (µm)	all: 80 µm square except 08-Jul-2022: 80 µm round
Sampling mode / pattern	line raster, 1 pass, 30 µm/sec scan speed
Carrier gas	optimized daily: 100% He in the cell (0.30-0.40 l/min), Ar carrier gas (0.58-0.65 l/min) and N ₂ (7-12 ml/min ¹) added at ARIS adaptor
Ablation duration (secs)	08-Jul-2022 : 18x65s [NIST614], 18x60s [WC-1], 6x180s [Duff Brown Tank], P12994 : 35x180s 13-Jul-2022 : 18x65s [NIST614], 18x60s [WC-1], 6x180s [Duff Brown Tank], P12994 : 50x75s 14-Jul-2022 : 18x65s [NIST614], 18x60s [WC-1], 6x180s [Duff Brown Tank], P15012 : 20x219s, P15024 : 40x205s 23-Aug-2022 : 18x65s [NIST614], 18x60s [WC-1], 6x180s [Duff Brown Tank], P12851 : 38x120s 24-Aug-2022 : 21x65s [NIST614], 21x60s [WC-1], 7x180s [Duff Brown Tank], P12981 : 40x163s, P14981 : 50x61s 15-Sept-2022 : 16x65s [NIST614], 16x65s [WC-1], 4x180s [Duff Brown Tank], P15027 : 30x63s
Cell carrier gas flow (l/min)	optimized daily: 0.25-0.40 l/min in the cell and 0.08-0.20 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)	0.58-0.65 l/min Ar
Detection system	Dual-mode discrete dynode electron multiplier

Masses measured and [Integration time per peak (ms)]	all : 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 [20], 207 [40], 208 [20], 232 [20], 238 [20] except 15-Sept-2022: 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)	08-Jul-2022 : 200 ms / 1000 ms after averaging 13-Jul-2022 : 200 ms / 1000 ms after averaging 14-Jul-2022 : 200 ms / 1000 ms after averaging 23-Aug-2022 : 200 ms / 1000 ms after averaging 24-Aug-2022 : 200 ms / 1000 ms after averaging 15-Sept-2022: 300 ms / 1500 ms after averaging
Sensitivity / Efficiency (% , element)	0.02% U
IC Dead time (ns)	38ns
Data Processing	
Gas blank	17s to 21s on-peak zero subtracted
Calibration strategy	NIST614 as primary reference material, WC-1 carbonate standard for matrix matching of $^{206}\text{Pb}/^{238}\text{U}$, 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 ± 0.67 Ma / 0.738 ± 0.010)</i> 08-Jul-2022 : Lower Intercept Age = 64.18 ± 0.48 / 2.14 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.711 \pm 0.007$ (2s, MSWD = 0.84) 13-Jul-2022 : Lower Intercept Age = 64.18 ± 0.93 / 2.28 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.694 \pm 0.012$ (2s, MSWD = 1.7) 14-Jul-2022 : Lower Intercept Age = 64.85 ± 0.45 / 2.15 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.719 \pm 0.006$ (2s, MSWD = 1.04) 23-Aug-2022 : Lower Intercept Age = 65.0 ± 1.30 / 2.48 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.713 \pm 0.027$ (2s, MSWD = 0.95) 24-Aug-2022 : Lower Intercept Age = 65.1 ± 1.0 / 2.3 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.700 \pm 0.020$ (2s, MSWD = 0.97) 15-Sept-2022 : Lower Intercept Age = 64.0 ± 2.0 / 2.3 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.724 \pm 0.042$ (2s, MSWD = 2.00)
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).

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Applications of the LA-ICP-MS image mapping approach to U-Pb carbonate dating : from far-field tectonism to pedogenic nodules

Thesis Dissertation for Doctor of Philosophy
School of Natural Sciences
Department of Geology

by

Vincent Monchal

2024

Annexes

Part 2: Publications and Abstracts



Precise U-Pb dating of incremental calcite slickenfiber growth: Evidence for far-field Eocene fold reactivation in Ireland

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ABSTRACT

The Variscan orogen in southern Ireland and Britain is characterized by an intensely deformed, E-W-trending fold-and-thrust belt. Farther north in Ireland, the Carboniferous North Dublin Basin exhibits tight chevron folds and kinematically linked en echelon vein sets, along with bedding-parallel veins with slickenfibers. This deformation is assumed to be Variscan in age, despite lying 150 km north of the supposed Variscan “front.” The laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) U-Pb dating of these calcite veins undertaken for this study showed that relict Variscan U-Pb ages are very poorly preserved. Instead, late Eocene ages were obtained from many calcite veins, including fold hinge breccias and bedding-parallel slickenfiber veins associated with N-S shortening (flexural slip). Also, U-Pb ages from one bedding-parallel vein showed protracted flexural slip over ~5 m.y. during late Eocene times. Detection of the growth domains within this vein was facilitated by the imaging approach to LA-ICP-MS U-Pb dating adopted in this study, which can identify age-homogeneous domains by integrating spatial U-Pb isotopic information with maps of petrogenetically diagnostic major and trace elements. The late Eocene fold reactivation phase was hitherto undetected on the Irish mainland, but regional Cenozoic N-directed shortening has been documented in Mesozoic–Cenozoic sequences of the southern Irish Sea, Celtic Sea, southern England, and the Paris Basin. We attribute late Eocene fold reactivation to far-field, N-directed shortening associated with the Alpine/Pyrenean orogenies. It is likely that many Variscan or Caledonian folds, particularly in southern onshore Ireland, were reactivated during Eocene–Oligocene shortening, which has not been recognized to date because of the lack of post-Variscan markers (e.g., dikes, Mesozoic–Cenozoic cover sequences).

INTRODUCTION

The Variscan-Alleghanian-Ouachita orogen is a long (~10,000 km) mountain belt ranging from the Urals to the Ouachita Mountains (Nance et al., 2010). This mountain system formed between 480 and 250 Ma because of the convergence of Laurussia with Gondwana along with the amalgamation and incorporation of several microcontinents (Matte, 2001). Ireland lies in the northern Variscan foreland (Fig. 1A), where the Variscan orogeny primarily reworked preexisting Caledonian structures. This interaction created an E-W-trending fold-and-thrust belt and an orogenic front, the significance and location of which in the south of Ireland are still debated (e.g., Graham, 2009). Constraining the timing of Variscan deformation in Ireland is challenging because fabrics, particularly

north of the Variscan “front,” formed under very low-grade metamorphic conditions. Even in the south of Ireland, the low metamorphic grade does not easily allow for dating of synkinematic minerals directly related to Variscan processes (e.g., Quinn et al., 2005). Hence, indirect dating techniques have been employed, such as ⁴⁰Ar–³⁹Ar dating of phlogopite in syn-, late-, and post-kinematic trachytic dikes (Quinn et al., 2005), which constrain Variscan deformation in the south of Ireland to ca. 315–300 Ma. Additionally, post-Variscan cover sequences are almost completely lacking, so relative age constraints on Variscan and potential post-Variscan deformation processes cannot be ascertained.

In the North Dublin Basin (Fig. 1B), calciturbidites of the late Visean Loughshinny Formation exhibit chevron folds and related calcite vein systems traditionally assumed to be associated with the Variscan orogeny (e.g., Johnston, 1993). Recent advances in U-Pb dat-

ing of carbonate veins and slickenfibers open new opportunities to date deformation and faulting (e.g., Ring and Gerdes, 2016; Roberts et al., 2021; Roberts and Holdsworth, 2022). We investigated how the calcite U-Pb system in the external Variscan foreland has recorded deformation, including potential younger events, using an imaging approach to U-Pb calcite geochronology (Drost et al., 2018; Roberts et al., 2020; Chew et al., 2021). Our results revealed that Variscan U-Pb ages are rare and poorly preserved, while late Eocene calcite formation and recrystallization ages prevail.

GEOLOGICAL CONTEXT

In southern Ireland, the Variscan orogeny is associated with between ~30% and 42% NNW-directed shortening and low-grade metamorphism (>300 °C based on vitrinite reflectance measurements and conodont alteration indices), with the maximum amount of shortening in the West Munster Basin (Graham, 2009). The intensity of Variscan deformation and the metamorphic grade decrease northward. Intense deformation ascribed to the Variscan orogeny is locally seen north of the Variscan “front,” including spectacular chevron folding and related vein systems (Figs. 1 and 2) that deform the Loughshinny Formation in the North Dublin Basin (Figs. 1A and 1B). The Loughshinny Formation is composed of late Visean (Brigantian, ca. 336–330 Ma; Aretz et al., 2020) calciturbidites interbedded with thin black shales with pyrite and chert (Nolan, 1986). Vertical dextral en echelon vein sets trending NW (Fig. 1E) are associated with right-stepping fold arrays (fold axes trending ENE; fold arrays trending E) and a clockwise-transecting cleavage (trending E). Subordinate sinistral vein sets (vertical and trending N) are associated with left-stepping fold arrays (fold axes trending ESE; fold arrays trending ENE) and are transected in a counterclockwise sense by the E-trending cleavage (Johnston, 1993). Where dextral and sinistral vein arrays

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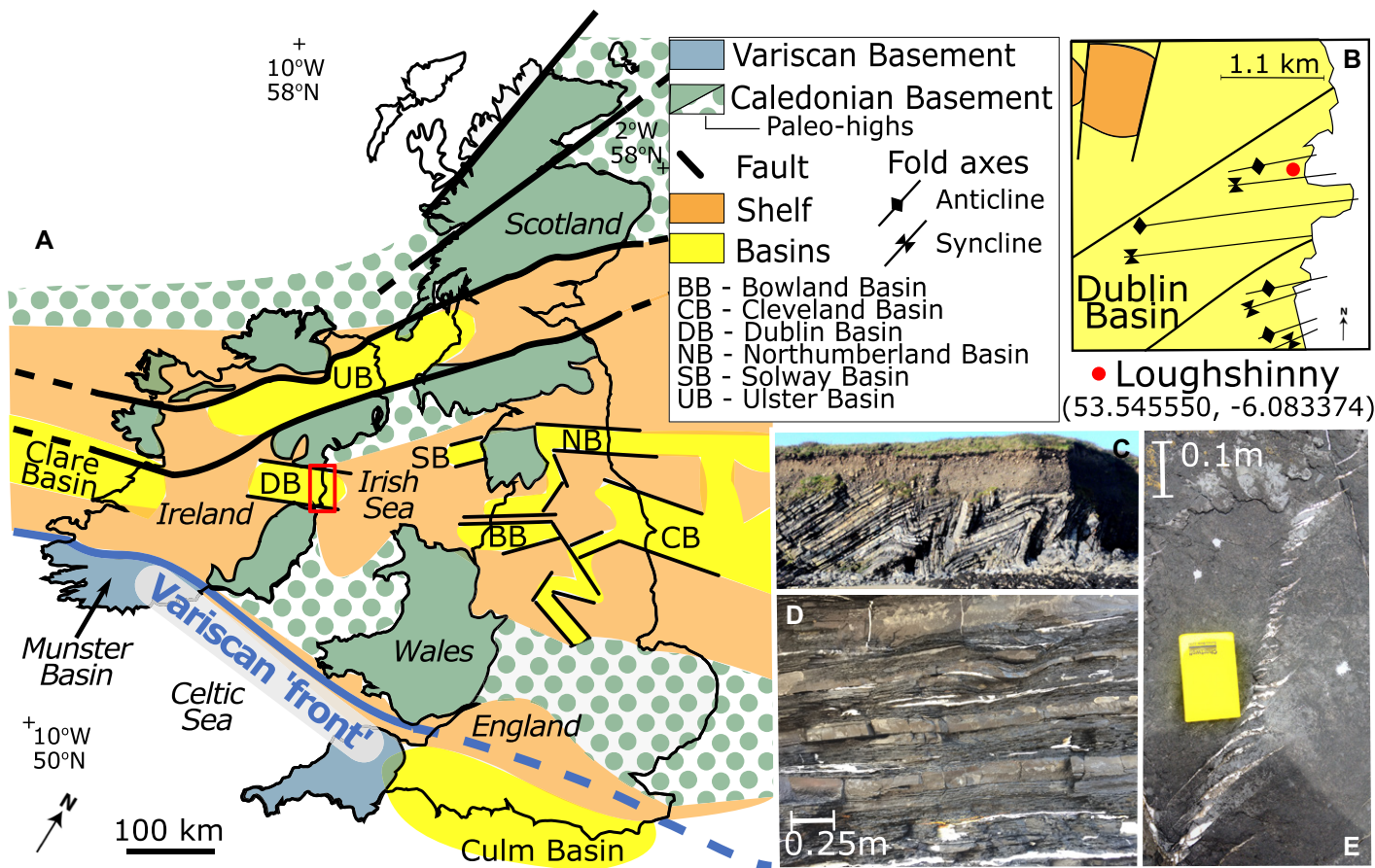


Figure 1. (A) Carboniferous paleogeography of Ireland and Britain (from Graham, 2009). (B) Schematic geology of Carboniferous North Dublin Basin with sampling location (Loughshinny) denoted by red circle. (C) Chevron folds in ~10-m-high cliff outcrop, looking W. (D) Bedding-parallel carbonate veins. (E) Dextral en echelon vein sets.

occur together, they are at a low angle to each other, sometimes $<10^\circ$, and their acute bisector trends NNW. Abundant evidence for flexural slip is provided by bedding-parallel carbonate veins, which dip shallowly SSW with slickenfibers that plunge shallowly SSW (Figs. 1D and 2B). Vein sets increase in abundance close to chevron fold

hinges that plunge shallowly E or W (Fig. 2B), and they often exhibit complex vein geometries, including brecciated veins that sometimes cross-cut earlier folded veins (Shelton et al., 2019).

Given the paucity of direct age constraints on Variscan deformation in Ireland, particularly north of the Variscan "front," U-Pb calcite dating was

employed to directly constrain the evolution of Variscan structures (synkinematic vein systems) and their potential later reactivation in Ireland.

METHODS

Laser ablation (quadrupole)-inductively coupled plasma-mass spectrometry (LA[Q]-

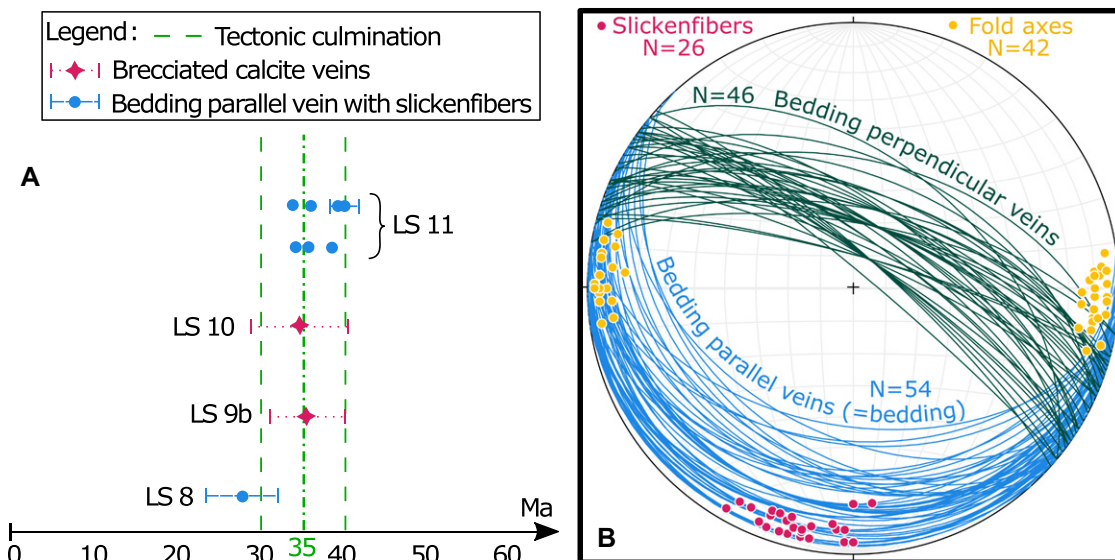


Figure 2. (A) Summary of geochronological results with ages and vein type illustrated. Age uncertainty bars are indicated by dashed lines, and 35 ± 5 Ma time window (tectonic culmination) is added for reference. (B) Stereonet of studied area.

ICP-MS) U-Pb dating was performed at Trinity College Dublin using a Photon Machines Analyte Excite 193 nm ArF excimer LA system coupled to an Agilent 7900 Q-ICP-MS, primarily employing the U-Pb imaging technique of Drost et al. (2018). Additionally, we performed U-Pb spot analysis dating on veins that were too narrow (<1 mm) for the mapping protocol, or when U-Pb imaging revealed disturbed U-Pb systematics, for which the origin (e.g., mixing of growth domains or resetting) can sometimes be hard to discern on maps due to the pooling. The mapping approach employed selection of pixels from two-dimensional (2-D) maps and pooling of data into “pseudo-analyses” using a channel that reflects parent U versus initial Pb and thus maximizes the spread of data points on isochron diagrams. In this study, $^{238}\text{U}/^{208}\text{Pb}$ was the pooling channel because the samples were typically low in Th and Th/U; employing $^{207}\text{Pb}/^{235}\text{U}$ as the pooling channel yielded dates within uncertainties. Details on the analytical and data processing protocol (e.g., selection criteria, regions of interest [ROIs], map dimensions) are given in the Supplemental Material.¹ Dates were derived from unanchored regression in Tera-Wasserburg (TW) space. Uncertainties on dates in text and figures are given as X/Y Ma, where X is a session-wide estimate, and Y includes systematic uncertainties (e.g., the uncertainty on the reference age of WC-1; see Supplemental Material). Uncertainties are quoted at a 2σ or 95% confidence level, respectively.

Twenty-six samples of different calcite vein geometries were analyzed: en echelon vein sets, veins from fold hinge breccias, and veins either parallel or perpendicular to bedding (with local slickenfiber development). These samples were collected at different locations ~700 m across strike, but they all were kinematically linked to folding of assumed Variscan age. Eight samples did not contain enough U to yield reliable U-Pb age data (<10 ppb). Thirteen samples yielded insufficient spread on TW concordia, and we thus focus on the five samples providing robust dates that can be interpreted as ages.

RESULTS

A Paleogene event (ca. 35 Ma) was detected in our sample suite (Fig. 2A), most noticeably in discontinuous bedding-parallel veins with slickenfibers (LS8, LS11), and in brecciated fold hinges (e.g., LS9b, LS10). Some of the veins (e.g., LS8d [bedding parallel], LS21 [bedding perpendicular]) yielded evidence for an older (ca. 300 Ma) Variscan age, with the data forming a wedge-shaped topol-

ogy on TW concordia bounded by Variscan and Paleogene discordia intercepts (Fig. 3).

The LA-ICP-MS mapping approach is ideally suited to unraveling the spatial (e.g., spread

in U-Pb ratios) and temporal (e.g., U-Pb age zoning) complexity inherent in the U-Pb carbonate system. Sample LS11 yielded at least three distinct U-Pb age zones ($38.72 \pm 0.78/1.3$ Ma;

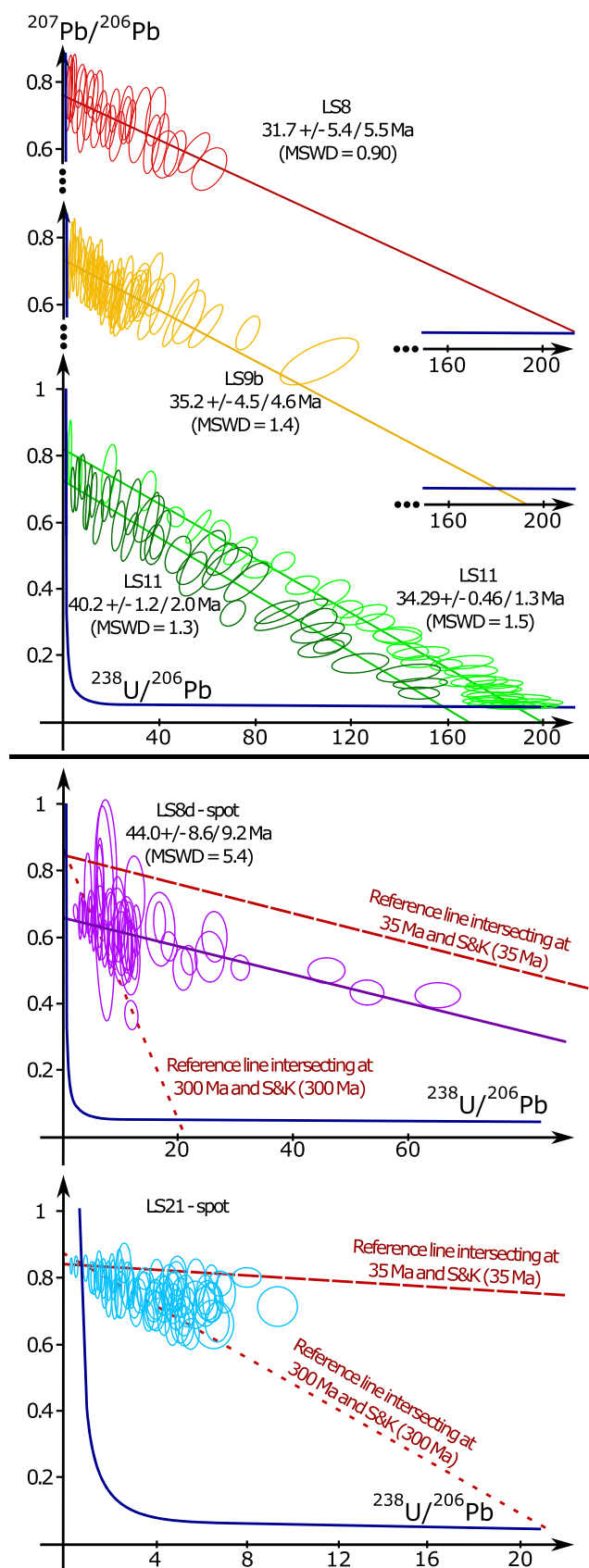


Figure 3. Tera-Wasserburg concordia curves of key samples. See text and Supplemental Material (text footnote 1) for sample descriptions. Spot analysis demonstrated an open U-Pb system. S&K—Stacey and Kramers (1975) terrestrial model Pb composition; MSWD—mean square of weighted deviates.

¹Supplemental Material. Details on the electron backscatter diffraction (EBSD) analyses, analytical setup, and LA-ICP-MS operating conditions. Analytical data are provided in Tables S1 to S5 (U-Pb LA-ICP-MS) and Tables S6 and S7 (EBSD). Please visit <https://doi.org/10.1130/GEOL.S.22661563> to access the supplemental material, and contact editing@geosociety.org with any questions.

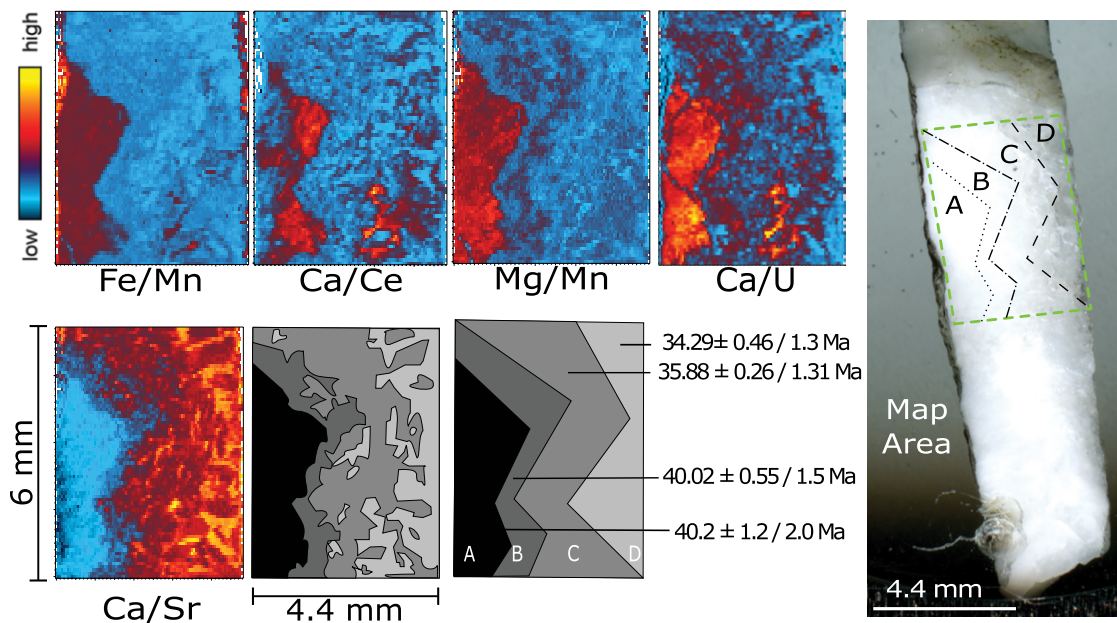


Figure 4. Macroscopic image of sample LS11 with mapped area and growth zones indicated and results of mapping experiments showing elemental ratio zoning interpreted as four generations of successive vein calcite growth (labeled A–D from oldest to youngest).

35.83 ± 0.36/1.0 Ma; 34.50 ± 0.43/1.1 Ma; see Supplemental Material). The dates were extracted from the same map, and the age differences between the zones are temporally distinct (session-wide uncertainty estimate). We applied a Ca filter to isolate calcite from other minerals (e.g., quartz/dolomite/opaque phases; ~5% of the map pixels) and a filter for $^{238}\text{U}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ (both >0) to exclude pixels (~1%) corresponding to nondetection of ^{207}Pb and/or ^{208}Pb and to spikes in the time-resolved data. The ROIs were then defined using Ca/Sr ratios, which increased from left to right in the map and revealed a decrease in U-Pb age from left to right (Fig. 4, zones A–D). This zoning was also reflected in the macroscopic optical zoning seen in the sample, with the older, low-Ca/Sr zone (Fig. 4, zone A) appearing opaque and bright white, and the younger, high-Ca/Sr zone (Fig. 4, zone D) appearing transparent and colorless. The intermediate zones were opaque and dull white (Fig. 4, zone B) and moderately opaque and colorless (Fig. 4, zone C), respectively. A second, larger map undertaken using similar analytical conditions yielded four dates with similar age and Ca/Sr zoning (40.2 ± 1.2/2.0 Ma; 40.02 ± 0.55/1.5 Ma; 35.88 ± 0.26/1.3 Ma; 34.29 ± 0.46/1.3 Ma; Figs. 3 and 4; Supplemental Material), demonstrating a reproducible ~5 m.y. age difference related to incremental vein opening. The two older ages are identical within internal uncertainty, but they are differentiated because of their distinct initial $^{207}\text{Pb}/^{206}\text{Pb}$ and elemental compositions (Fig. 4).

INTERPRETATION

While evidence for a relict late Variscan (ca. 300 Ma) age component was found in some bedding-perpendicular veins, spot analyses on such samples showed wedge-shaped patterns

of the data points and indicated open U-Pb system behavior (Fig. 3). However, the sample suite yielded robust Paleogene ages clustering around 35 Ma (Figs. 2 and 3), and the tectonic significance of these results is discussed here. A regional pulse of early Cenozoic exhumation is documented in the Irish Sea region (E Ireland, Wales, NW England, and SW Scotland). It initiated between ca. 65 and 60 Ma and lasted for ~10 m.y. (Cogné et al., 2016), with evidence including an apatite fission-track age of 70.2 ± 30.4 Ma from a Carboniferous sandstone in Loughshinny (Allen et al., 2002). Similarly, the vast majority of (U-Th)/He apatite ages (closure temperature of ~40–80 °C) in the Irish Sea region are older than ca. 50 Ma (Cogné et al., 2016). This pulse of early Cenozoic exhumation preceded the ca. 35 Ma U-Pb ages revealed by our data set. A model of passive-margin tectonism for the fracture-fill calcite (cf. Amidon et al., 2022) is also excluded because the vein geometries are associated with flexural-slip folding under N-directed shortening (Figs. 1 and 2B). New mineral growth associated with this shallow, low-temperature folding mechanism is restricted to synkinematic carbonate veins, and hence the ca. 35 Ma deformation phase cannot be dated by other geochronometers. Hillis et al. (2008) documented late Paleogene–Neogene tectonic inversion in the southern Irish Sea region, similar to the timing of middle Eocene–Miocene shortening in the Celtic Sea (Rodríguez-Salgado et al., 2019). Two phases of Cenozoic (early Paleocene/early Oligocene) regional strike-slip faulting are consistent with the kinematics of N-S shortening identified in the north of Ireland (Anderson et al., 2018), while Cenozoic U-Pb calcite vein ages from S England (34–31 Ma tectonic culmination; Parrish et al., 2018) and the eastern Paris

Basin (most ages between ca. 50 and 30 Ma; Blaise et al., 2022) have been attributed to far-field propagation of Pyrenean horizontal stress.

There is therefore abundant regional evidence for Cenozoic N-directed shortening (of variable intensity) in the Mesozoic–Cenozoic sequences of the southern Irish Sea, the Celtic Sea, southern England, and the Paris Basin. The kinematics of the ca. 35 Ma structures in this study (Fig. 2) are compatible with this regional Cenozoic N-directed shortening, and they are similarly attributed to far-field (>1000 km) propagation of horizontal stress from the Pyrenean or Alpine orogeny. We therefore envision that the North Dublin Basin experienced Variscan deformation (chevron folding) that was reactivated during Eocene shortening, with tightening of folds and associated vein development (bedding-parallel slickenfibers, vein sets, breccias). Relict Variscan ages are found in vein sets that were suitably orientated so as to be not entirely erased by later Eocene shortening (i.e., bedding-perpendicular veins in limestone).

The respective importance of low-temperature deformation versus fluid flow at ca. 35 Ma in our data set is difficult to assess, but field evidence shows that the late Eocene samples (e.g., fold breccias/slickenfibers) could not have formed without a contractional kinematic component. Recent studies have highlighted the complexity of interpreting U-Pb data in carbonate vein systems. Roberts et al. (2021) showed that slickenfibers linked to a discrete deformation event can be affected by later fluid ingress, resulting in significant data dispersion on TW concordia. Slickenfiber ages can record the youngest phases of fault slip or the timing of fluid ingress, or potentially mixtures between these two age components (Roberts et al., 2021; LS8d and LS21 in Fig. 3), and hence detailed

petrography (trace-element mapping, optical and electron backscatter diffraction [EBSD] imaging; Fig. 4; Supplemental Material) is required. Importantly, no older or younger age components were identified in our Eocene slickenfiber data (Fig. 2), all of which yielded acceptable mean square of weighted deviate (MSWD) values and did not show U and Pb mobility. Our image-based approach to LA-ICP-MS U-Pb calcite geochronology can also precisely constrain complex polyphase histories and resolve tectonic events closely spaced in time, such as incremental vein opening and fold reactivation (cf. Craddock et al., 2021), with at least three phases of vein opening recorded during an ~5 m.y. time interval.

CONCLUSIONS

Our LA-ICP-MS mapping approach to geochronology incorporated complementary elemental and textural information and produced detailed (for carbonate at the tens of microns scale) maps of isotope (including U-Pb age data) and element distributions. When applied to carbonate vein systems north of the Variscan “front” in Ireland, results showed that the assumption that the deformation is solely of Variscan age is not tenable. Instead, several calcite veins (e.g., bedding-parallel slickenfibers related to flexural slip) yielded late Eocene ages, representing a folding phase hitherto undetected on the Irish mainland (where the lack of synkinematic mineral growth precludes application of other geochronometers), which we interpret as regional Cenozoic far-field (>1000 km) Pyrenean or Alpine N-directed shortening. The data also show the strength of our approach because they demonstrate that incremental flexural slip took place over ~5 m.y. during late Eocene times. We speculate that many Variscan or Caledonian folds, particularly in southern onshore Ireland, were tightened or reactivated during Eocene–Oligocene shortening. While fault reactivation is extensively documented in the literature, evidence for fold reactivation is more difficult to determine and has relied on detecting folded layers overlain by (folded) unconformity surfaces, with the unconformity surface used as a structural marker (e.g., Alonso, 1989). U-Pb carbonate dating of mesostructures related to fold tightening (Lacombe et al., 2021) is a unique way to constrain the initiation, duration, and rate of folding, and it is the only feasible approach to detecting fold reactivation when younger structural markers (e.g., dikes, cover sequences) are absent.

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Supplementary material summary

Supplementary Figure S1..... 1

Detailed view of the spatial relations of age zones in the first map of LS11 containing the mapped locations on the sample image, relevant element maps, the area covered by each age zone and their respective TW plots.

Supplementary Figure S2..... 2

Detailed view of the spatial relations of age zones in the second map of LS11 containing the area covered by each age zone and their respective TW plots.

Supplementary Figure S3..... 3

Summary of EBSD data for sample LS11 containing Inverse Pole Figures (IPF) (X and Z) and the area covered by EBSD analysis on a sample photo.

Methods..... 4

Supplementary details on the analytical method and analytical setup employed in the paper for both maps and spot analyses. The two tables describing the analytical setup include QC results and information on the standards employed and corresponding literature references.

EBSD data..... 12

Presentation and interpretation of the EBSD analysis. Includes detailed description of the EBSD analysis on samples LS8 and LS11 including images, EBSD setup, phase fractions and the results of the analysis.

LS8 data Excel Table 1

Includes field and sample images, GPS location, selected pixels, criteria of selection, map dimensions, relevant elemental maps and processed data for the three isotopic systems employed in the study along with QC material data.

LS9b data Excel Table 2

Includes field and sample images, GPS location, selected pixels, criteria of selection, map dimensions, relevant elemental maps and processed data for the three isotopic systems employed in the study along with QC material data.

LS10 data Excel Table 3

Includes field and sample images, GPS location, selected pixels, criteria of selection, map dimensions, relevant elemental maps and processed data for the three isotopic systems employed in the study along with QC material data.

LS11-first map data Excel Table 4

Includes field and sample images, GPS location, selected pixels, criteria of selection, map dimensions, relevant elemental maps and processed data for the three isotopic systems employed in the study along with QC material data.

LS11-second map data Excel Table 5

Includes field and sample images, GPS location, selected pixels, criteria of selection, map dimensions, relevant elemental maps and processed data for the three isotopic systems employed in the study along with QC material data.

LS8d and LS21 spot analysis data Excel Table 6

Includes field and sample images, GPS location, photomicrograph of the ablated area, spot ablation locations, number of spots and processed data for the three isotopic systems employed in the study along with QC material data.

EBSD dataset LS8 Excel Table 7

Raw data of the EBSD analysis for LS8.

EBSD dataset LS11 Excel Table 8

Raw data of the EBSD analysis for LS11.

Figure S1 : Spatial relations of age zones in LS11

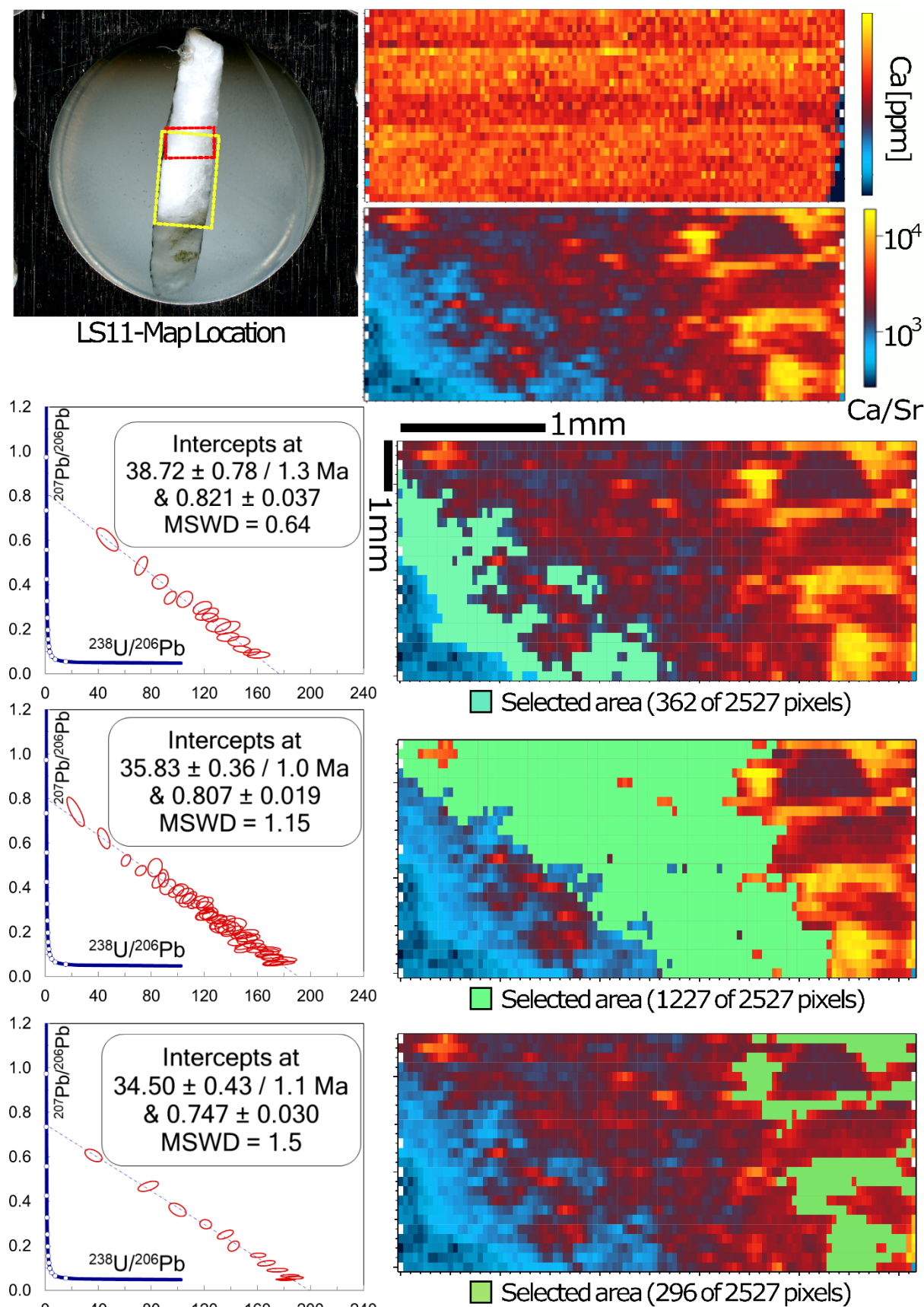


Figure S1 – Tera-Wasserburg concordias and corresponding Ca/Sr maps from which the U-Pb data were extracted (green pixels) of a bedding-parallel carbonate vein (LS11). Area mapped is the red rectangle on the 25 mm mount in the top left-hand corner of the figure. Maps are constructed using Monocle with 25 rasters corresponding to an area of 4.75 mm x 3.6 mm. Uncertainties are quoted at 2s or 95% conf. respectively.

Figure S2 : Spatial relations of age zones in LS11 (second map)

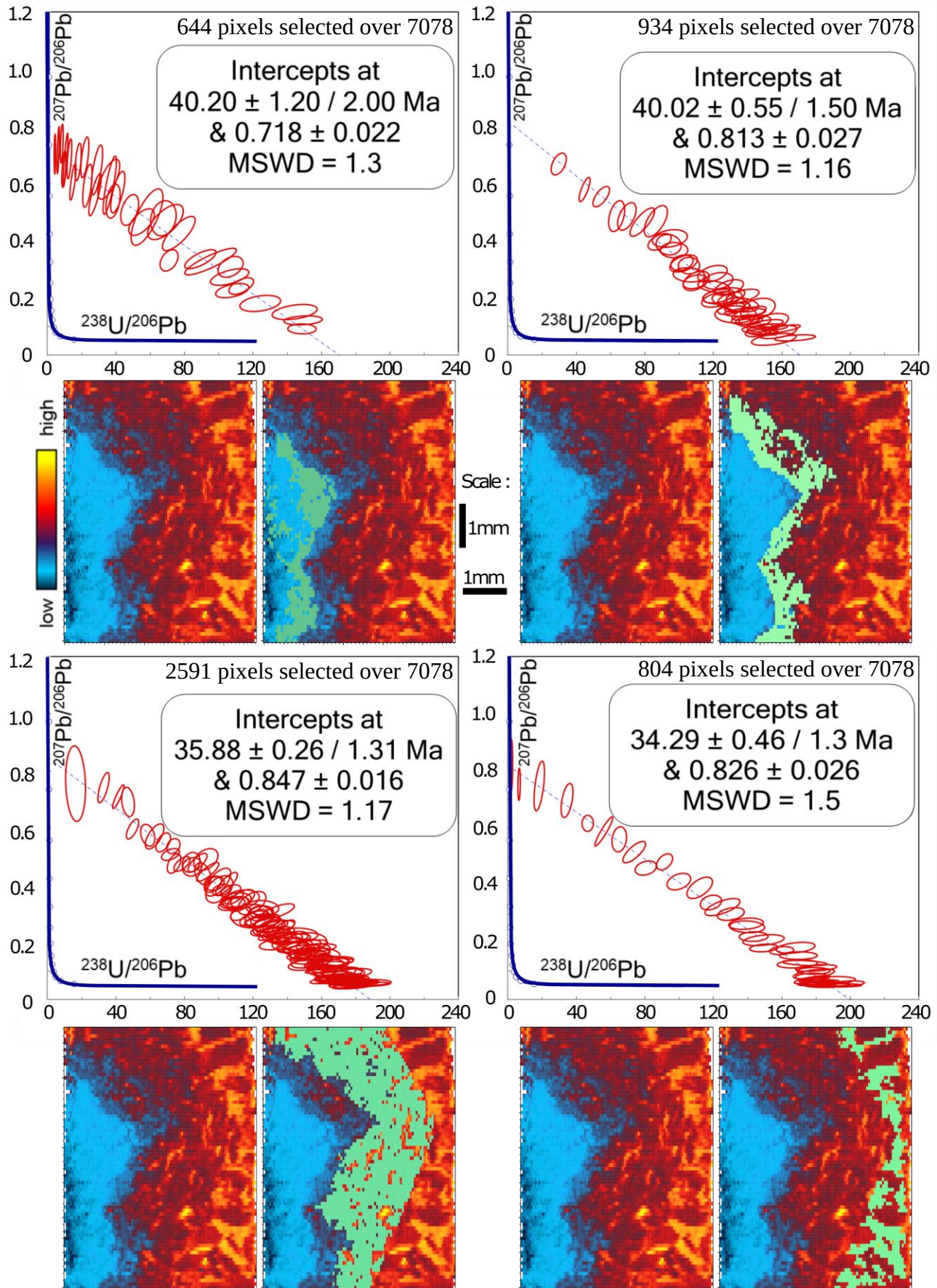


Figure S2. Results from the replicate mapping experiment performed on sample LS11.

Tera-Wasserburg concordias and corresponding Ca/Sr maps from which the U-Pb data were extracted (green pixels) of a bedding-parallel carbonate vein (LS11). Area mapped is the yellow rectangle on Fig. S1. Maps were constructed using Monocle with 75 rasters corresponding to an area of 6 mm x 4.4 mm. Uncertainties are quoted at 2s or 95% conf. respectively.

Figure S3 : Summary of EBSD results for LS11

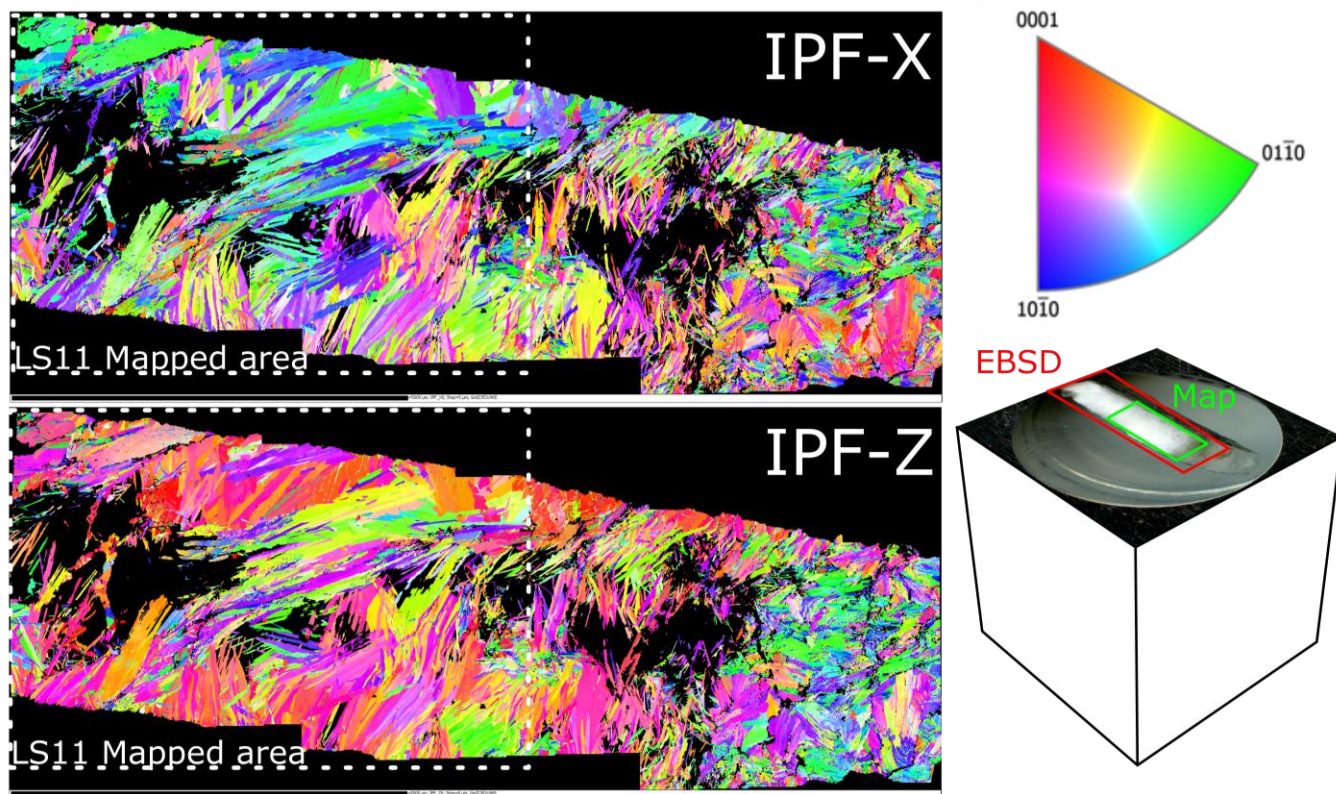


Figure S3. Inverse Pole Figures (IPF) from EBSD mapping of the top surface (Face 1) of sample LS11. The IPF X and Y axes lie within the plane of the thin section, while Z is perpendicular to the plane of section. Crystals are colored according to their orientation relative to the respective axis for each IPF map. Red is parallel to the respective IPF axis while a green or blue color indicates growth in a different direction (see key). The LS11 mapped area is represented by a white dashed box on the IPF maps.

Methods

Laser ablation Q-ICP-MS U-Pb dating was performed at the Geology Department of Trinity College Dublin using a Photon Machines Analyte Excite 193 nm ArF excimer LA system coupled via an aerosol rapid introduction system (ARIS) to an Agilent 7900 Q-ICP-MS and employing the imaging technique described in Drost et al. (2018). Additionally, two samples were analysed using spot analyses to better illustrate incomplete resetting of the U-Pb system in samples of assumed Variscan initial age. Specific instrument settings and operating conditions used for the samples shown in figures and in supplementary figures are given below. Spot analyses were performed using a condensed analyte menu and signal smoothing via a variable volume mixing device (c. 10ml). The mapping approach performed on the remaining samples employed ablation of successive linear rasters that were compiled into element, element ratio and isotope ratio maps in which one pixel represents one time-slice of the time-resolved signal. For this study, major and minor elements are measured (Mg, Ca, Mn, Fe) to identify potential changes of mineralogy, different generations of crystallization or any transformations on the mineral scale. Trace elements are included in the element menu (typically: V, Cu, Zn, Ga, Rb, Sr, Ba, Ce, Th, U) to highlight redistribution of elements, fluid interactions, detrital material or inclusions in carbonates. The isotopes ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th and ^{238}U are used for U-Pb geochronology on growth zones identified by elemental maps. Dwell times and masses measured can vary from one session to another (please see tables below for detailed analytical setup and operating conditions).

Raw data processing and map compilation was carried out in Iolite 3.6 (Paton et al., 2011) with the add-on Monocle (Petrus et al., 2017). Filtering of the data associated with the pixels in the maps was undertaken by applying a combination of specific geochemical criteria and manually drawn regions of interest to separate pixels from chemically and texturally different domains and to only include data with baseline corrected U and Pb isotope signals greater than zero counts per second. We first applied a Ca filter to isolate clean calcite from other minerals (e.g. quartz, dolomite, opaque phases), cracks and epoxy. This removed c. 5% of the pixels on the map. Then a filter for $^{238}\text{U}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ was employed to exclude pixels corresponding to non-detection of ^{238}U , ^{207}Pb and/or ^{208}Pb and to spikes in the time-resolved data discarding less than 1% of the pixels. These filters mainly rejected outliers and did not significantly modify the calculated age. Further chemical criteria were then used to isolate domains that are likely homogeneous in age (e.g., the Ca/Sr ratio in sample LS11) and initial Pb composition (e.g., LS8 Ga<0.05ppm to exclude trapped detrital particles). The selected pixels were then pooled into “pseudo-analyses” by using the empirical cumulative distribution function (ECDF) of the $^{238}\text{U}/^{208}\text{Pb}$ ratio and plotted into isochron diagrams. We used the $^{238}\text{U}/^{208}\text{Pb}$ ratio as pooling channel due to typically low concentrations of Th and U in our samples. Details on selection criteria, regions of interest, map dimensions and time-equivalents of selected pixels and pseudo-analyses are given in the supplementary data tables 1 to 6.

Matrix matching of the $^{206}\text{Pb}/^{238}\text{U}$ ratio and uncertainty propagation were carried out in an Excel spread sheet. The dates reported in this study were derived from unanchored regression in Tera-Wasserburg (TW) space. 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. This session wide uncertainty can be used to compare different age domains within the same map acquired during a single analytical session. 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. Furthermore, dates derived from regression of the data points in $^{206}\text{Pb}_{\text{total}}/^{208}\text{Pb}_{\text{common}}$ vs $^{238}\text{U}/^{208}\text{Pb}_{\text{common}}$ and in 86TW (Parrish et al., 2018) plots are given in Supplementary Tables 1 to 6. These are identical within uncertainty to the dates derived from Tera-Wasserburg regression demonstrating consistency of the data set.

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

Laboratory & Sample Preparation	Mapping technique
Laboratory name	Dept of Earth Science, Trinity College Dublin
Sample type/mineral	calcite veins
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)	16-Mar-2021: 2.0 J/cm ² 13-Oct-2020: 2.2 J/cm ² 08-Jan-2020: 2.2 J/cm ² 06-Jan-2020: 2.0 J/cm ²
Repetition rate (Hz)	16-Mar-2021: 51 Hz 13-Oct-2020: 50 Hz 08-Jan-2020: 51 Hz 06-Jan-2020: 50 Hz
Spot size (µm)	all: 80 µm round except 06-Jan-2020: 95 µm square
Sampling mode / pattern	linear raster, 1 pass, 30 µm/sec scan speed
Carrier gas	optimized daily: 100% He in the cell (0.35-0.40 l/min), Ar carrier gas (0.58-0.65 l/min) and N ₂ (7-12 ml/min ¹) added at ARIS adaptor
Ablation duration (secs)	16-Mar-2021: 18x64s NIST614, 18x34s WC-1, 18x61s Duff Brown, LS11(2 nd): 75x147s 13-Oct-2020: 21x55s NIST614, 21x48s WC-1, 14x90s Duff Brown, LS9b: 17x230s 08-Jan-2020: 18x59.2s NIST614, 18x36.5s WC-1, 18x56.7s Duff Brown, LS8: 35x57.7s, LS10: 15x185s 06-Jan-2020: 13x56.5 s NIST614, 12x31s WC-1, 12x56.7s Duff Brown, LS11: 25x127.7s
Cell carrier gas flow (l/min)	optimized daily: 0.25-0.40 l/min in the cell and 0.08-0.20 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)	0.58-0.65 l/min Ar
Detection system	Dual-mode discrete dynode electron multiplier

Masses measured and [Integration time per peak (ms)]	16-Mar-2021: 25 [2], 43 [3], 51 [2], 55 [2], 57 [2], 63 [2], 66 [2], 71 [2], 85 [2], 88 [2], 137 [2], 140 [2], 202 [1], 204 [1], 206 [35], 207 [63], 208 [35], 232 [15], 238 [35] 13-Oct-2020: 25 [1.5], 43 [3], 51 [2], 55 [1.5], 57 [1.5], 63 [2], 66 [2], 71 [2], 85 [2], 88 [1.5], 137 [2], 140 [2], 202 [1], 204 [1], 206 [30], 207 [75], 208 [30], 232 [20], 238 [30] 06-Jan-2020 and 08-Jan-2020: 25 [2.5], 43 [2.5], 51 [2.5], 55 [2.5], 57 [2.5], 63 [2.5], 66 [2.5], 71 [2.5], 85 [2.5], 88 [2.5], 137 [2.5], 140 [2.5], 202 [2.5], 204 [2.5], 206 [17.5], 207 [22.5], 208 [15], 232 [10], 238 [17.5]
Total integration time per reading (secs)	16-Mar-2021: 250 ms / 1500 ms after averaging 13-Oct-2020: 250 ms / 1500 ms after averaging 08-Jan-2020: 210 ms / 1260 ms after averaging 06-Jan-2020: 207 ms / 1242 ms after averaging
Sensitivity / Efficiency (% , element)	0.02% U
IC Dead time (ns)	38ns
Data Processing	
Gas blank	17s to 21s on-peak zero subtracted
Calibration strategy	NIST614 as primary reference material, WC-1 carbonate standard for matrix matching of $^{206}\text{Pb}/^{238}\text{U}$, 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 $^{207}\text{Pb}/^{206}\text{Pb}$ 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 ± 0.67 Ma / 0.738 ± 0.010)</i> 16-Mar-2021: Lower Intercept Age = 65.95 ± 0.78 / 2.5 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7149 \pm 0.0099$ (2s, MSWD = 0.76) 13-Oct-2020: Lower Intercept Age = 65.27 ± 0.74 / 2.3 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7174 \pm 0.0138$ (2s, MSWD = 0.71) 08-Jan-2020: Lower Intercept Age = 65.0 ± 1.1 / 2.1 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.7261 \pm 0.0190$ (2s, MSWD = 0.32) 06-Jan-2020: Lower Intercept Age = 62.36 ± 0.94 / 1.9 Ma, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.6882 \pm 0.0160$ (2s, MSWD = 1.7)
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 veins
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)	2.0 J/cm ²
Repetition rate (Hz)	12 Hz
Spot size (µm)	160 µm round
Sampling mode / pattern	spots, 420 shots, 35s each
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 (secs)	27x35s NIST614, 27x35s WC-1, 27x35s Duff Brown, LS8d: 100x35s, LS21: 100x35s
Cell carrier gas flow (l/min)	0.175 l/min in the cell and 0.225 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)	0.70 l/min Ar
Detection system	Dual-mode discrete dynode electron multiplier
Masses measured and [Integration time per peak (ms)]	24-Aug-2020 : 25 [1.5], 43 [3], 51 [2], 55 [1.5], 57 [1.5], 85 [2], 88 [1.5], 140 [2], 202 [1], 204 [1], 206 [50], 207 [125], 208 [50], 232 [25], 238 [50]
Total integration time per reading (secs)	350 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, 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) & in-house spreadsheet; no LIEF correction
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 negligible and was therefore modelled using a linear correction ($y=a+bx$) with zero slope ($b=0$). 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. 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. 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: $64.04 \pm 0.67 \text{ Ma} / 0.738 \pm 0.010$) Lower Intercept Age = $63.6 \pm 2.1 / 2.9 \text{ Ma}$, $^{207}\text{Pb}/^{206}\text{Pb}_{\text{initial}} = 0.714 \pm 0.0047$ (2s, MSWD = 0.87)
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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EBSD data

Electron Backscatter Diffraction (EBSD) analysis is a microstructural crystallographic analytical technique that measures the orientation of individual crystals and any change of orientation inside a crystal (Valcke et al., 2006). In this study, EBSD analysis was conducted on key samples in the MEA (Microscopie Électronique et Analytique) platform, Montpellier University (France) with a CamScan Crystal Probe X500FE. The specific settings for each sample are listed below (p.14-27).

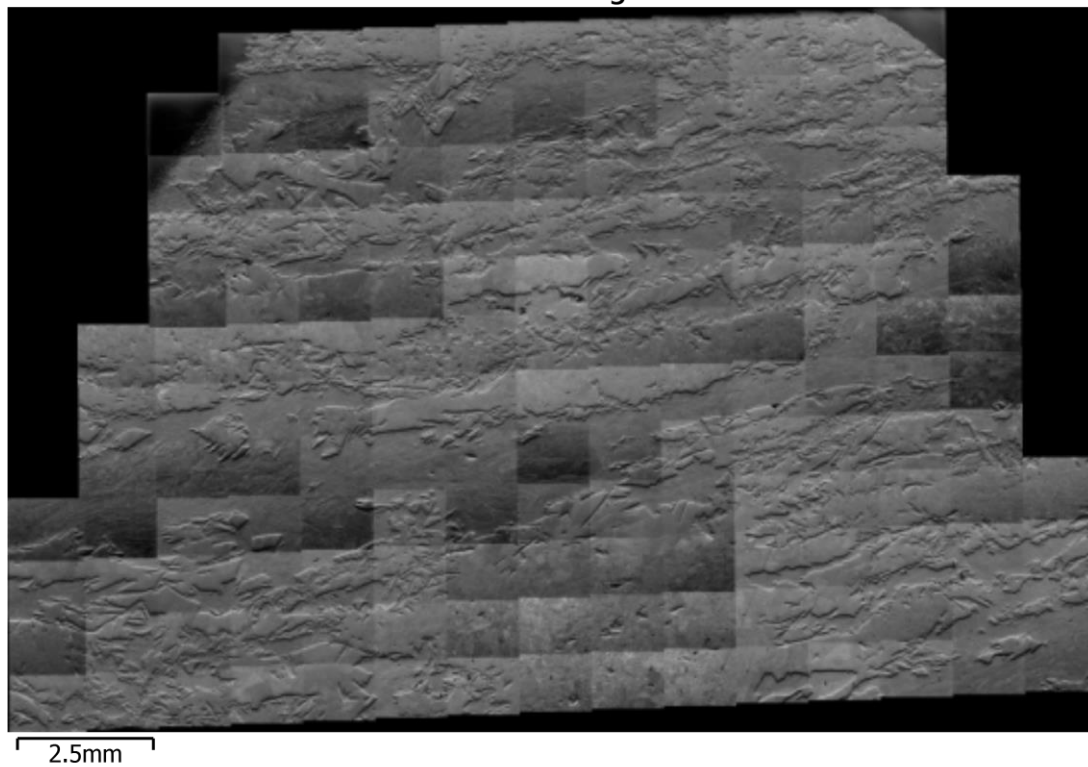
The EBSD images for sample LS11 show that the crystals have grown in a preferential direction but that is neither parallel nor perpendicular to any axes of the EBSD analysis (Fig. S3). However, no apparent pattern mimicking the Ca/Sr zoning is visible. The crystal structure of LS8 preferentially follows an axis perpendicular to the surface of the puck (Z on EBSD), and is therefore perpendicular to the plane containing the slickenfibers. The grain orientation spread (GOS) is an index corresponding to relative differences of orientation inside a given crystal, which can reveal if the crystals have been deformed or dynamically recrystallized (and potentially during what stage of the deformation) (Hadadzadeh et al., 2018). The GOS is $>3^\circ$ for c. 22% of the calcite grains in both samples of Eocene age, indicating that they have recrystallized during an early deformation stage while the remainder of the calcite grains have a low GOS ($<2^\circ$), either late in the deformation history or possibly associated with subsequent recrystallization during recovery (Valcke et al., 2006).

References

Hadadzadeh, A., Mokdad, F., Wells, M. A. and Chen, D. L., 2018, A new grain orientation spread approach to analyze the dynamic recrystallization behavior of a cast-homogenized Mg-Zn-Zr alloy using electron backscattered diffraction, *Materials Science and Engineering, ser. A*, v. 709, p. 285-289, <https://doi.org/10.1016/j.msea.2017.10.062>.

Valcke, S. L. A., Pennock, G. M., Drury, M. R. and De Bresser J. H. P., 2006, Electron backscattered diffraction as a tool to quantify subgrains in deformed calcite, *Journal of Microscopy*, v.224, p. 264-276, <https://doi.org/10.1111/j.1365-2818.2006.01698.x>

FSD Mixed Image 158



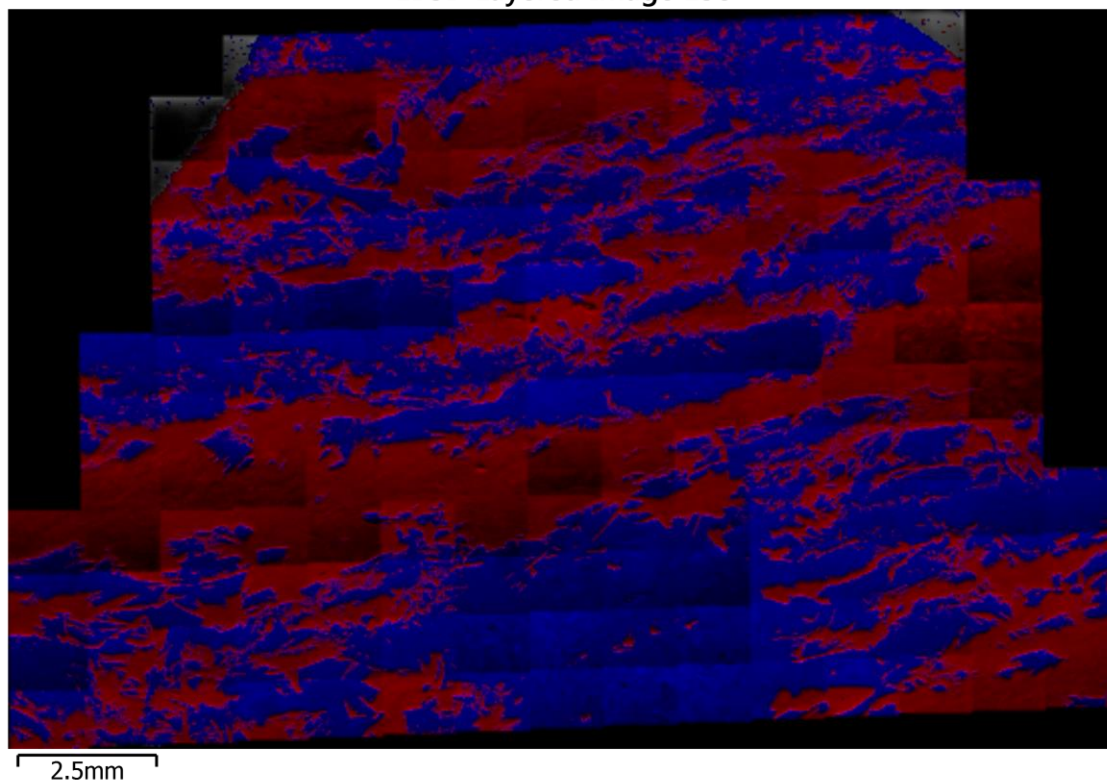
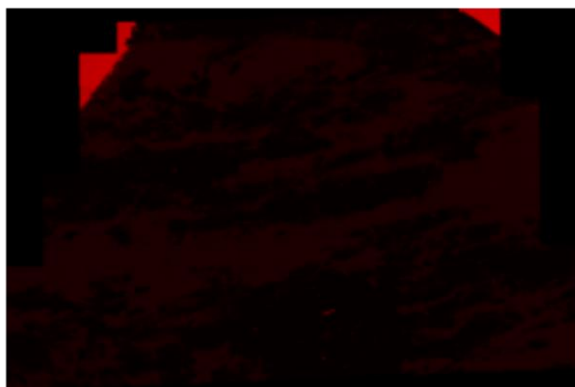
Settings

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Specimen Tilt (degrees)	70.00 °
Hit Rate	94.55 %
Speed of Acquisition	313629.20 Hz

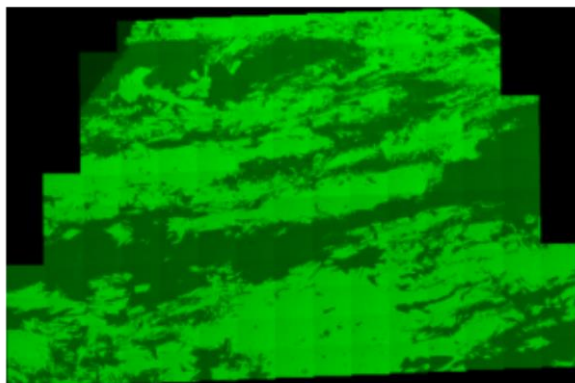
Phases for Acquisition

Phase	a	b	c	Alpha	Beta	Gamma	Space Group	Database
Calcite	4.99 Å	4.99 Å	17.06 Å	90.00 °	90.00 °	120.00 °	0	HKL
Quartz-new	4.91 Å	4.91 Å	5.50 Å	90.00 °	90.00 °	120.00 °	152	HKL

EBSD Layered Image 158

C K α 1_2

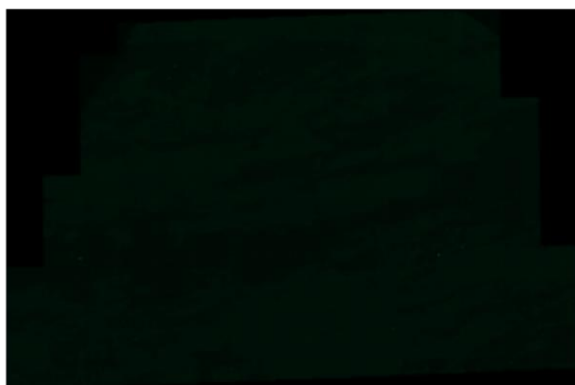
2.5mm

O K α 1

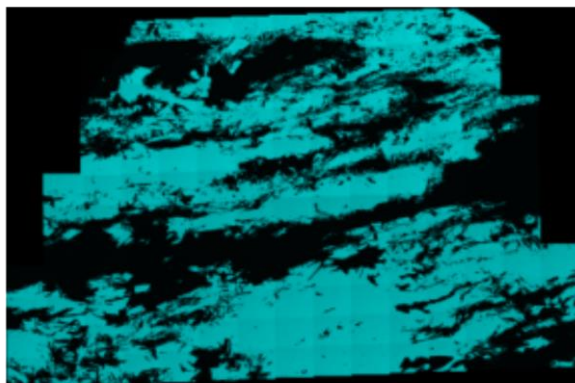
2.5mm

Mg K α 1_2

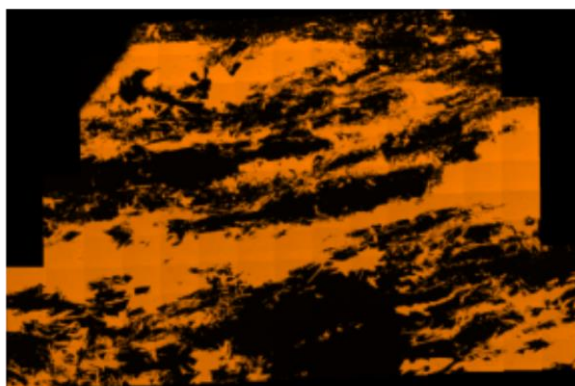
2.5mm

Al K α 1

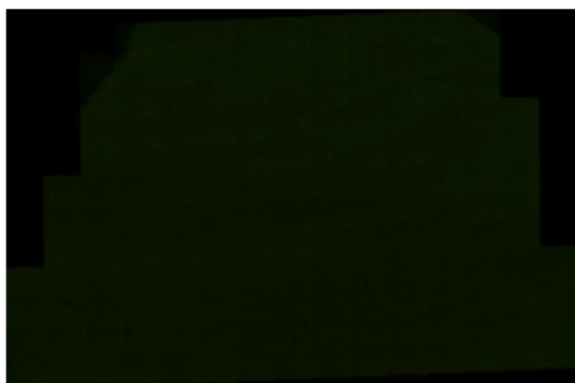
2.5mm

Si K α 1

2.5mm

Ca K α 1

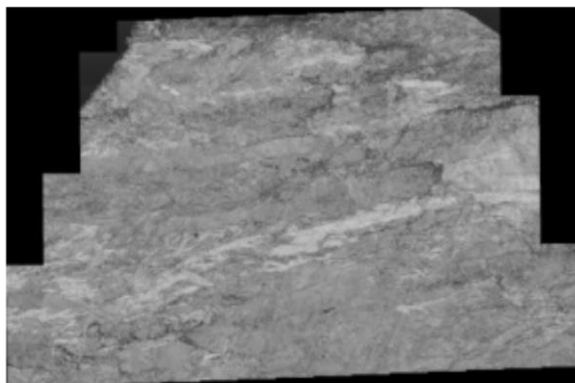
2.5mm

Fe K α 1

2.5mm

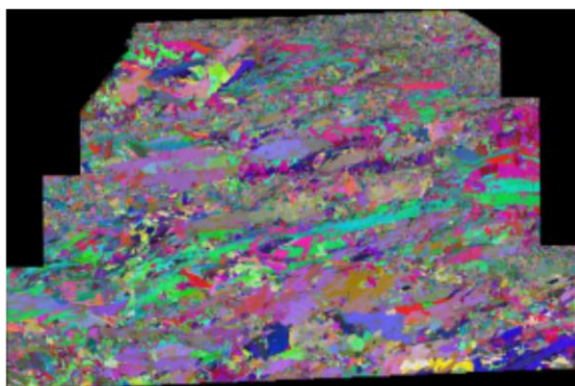
Band Contrast 158

BC



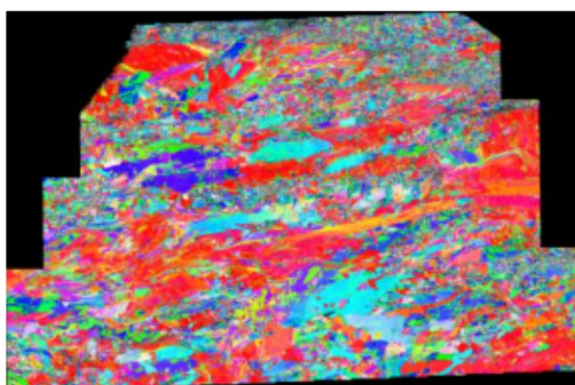
2.5mm

Euler Color 158

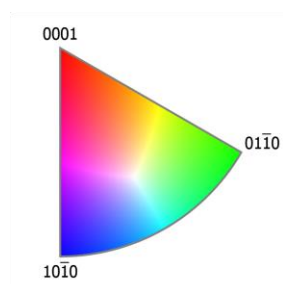
 $\phi 1$ Φ $\phi 2$ 

2.5mm

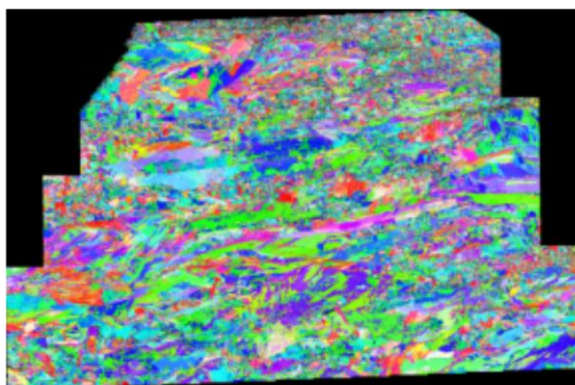
IPF Z Color 158



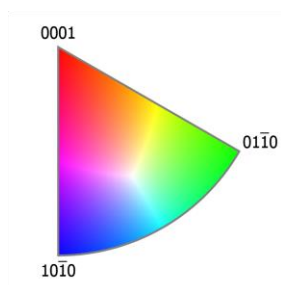
2.5mm



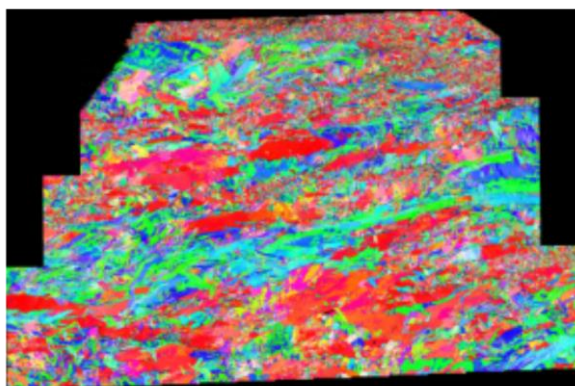
IPF Y Color 158



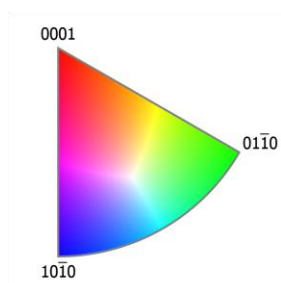
2.5mm



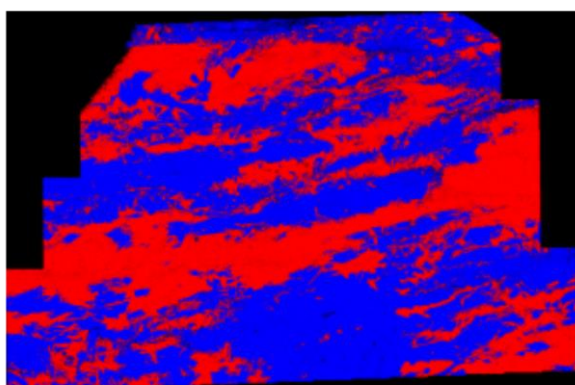
IPF X Color 158



2.5mm



Phase Color 158



2.5mm

Calcite Quartz-new

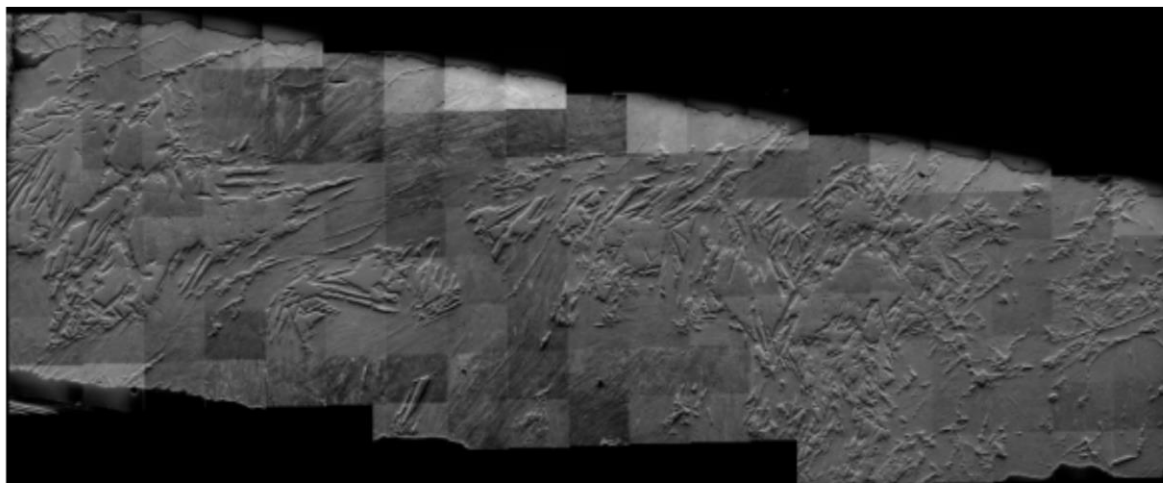
EBSD settings and results for LS8

09/11/2021

Phase Fraction

Phase Name	Phase Fraction (%)	Phase Count	Mean Band Contrast	Standard Deviation Band Contrast	Min Band Contrast	Max Band Contrast	Mean MAD	Standard Deviation MAD	Min MAD	Max MAD
Calcite	43.14	1101402	148.50	31.13	26.00	231.00	0.55	0.26	0.07	2.00
Quartz-new	51.40	1312286	135.11	23.97	24.00	227.00	0.57	0.22	0.09	2.00
Zero Solutions	5.45	139214	58.63	27.36	0.00	254.00				

FSD Mixed Image 143



1mm

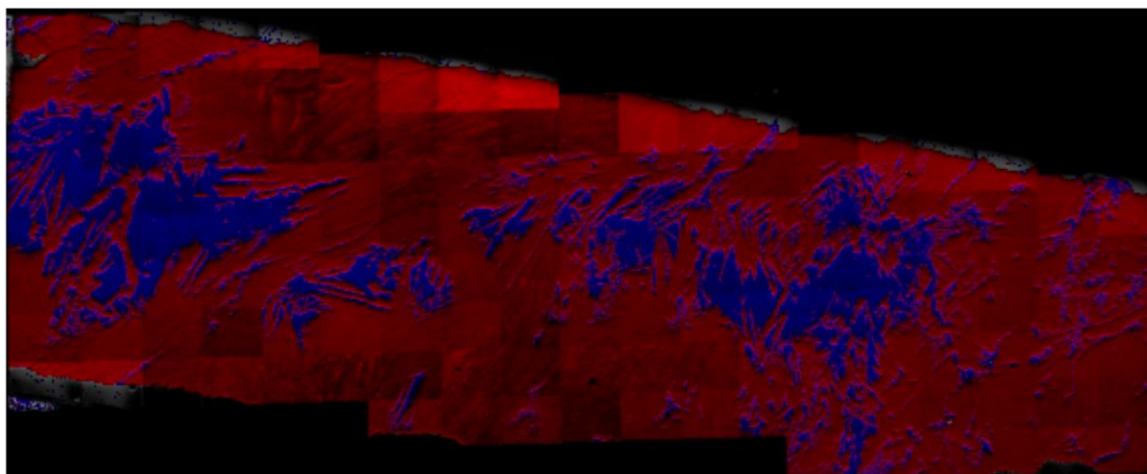
Settings

Accelerating Voltage	20.00 kV
Specimen Tilt (degrees)	70.00 °
Hit Rate	92.32 %
Speed of Acquisition	353756.40 Hz

Phases for Acquisition

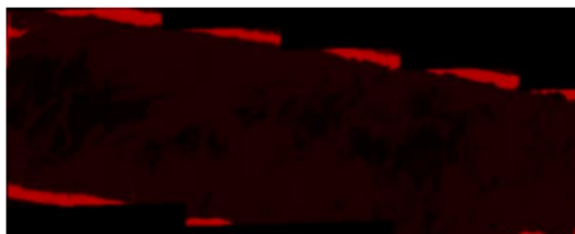
Phase	a	b	c	Alpha	Beta	Gamma	Space Group	Database
Calcite	4.99 Å	4.99 Å	17.06 Å	90.00 °	90.00 °	120.00 °	0	HKL
Quartz-new	4.91 Å	4.91 Å	5.50 Å	90.00 °	90.00 °	120.00 °	152	HKL

EBSD Layered Image 142

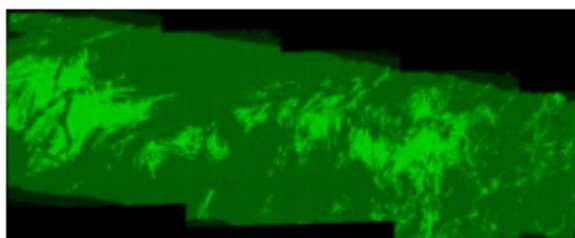


1mm

C K α 1_2



1mm

O K α 1

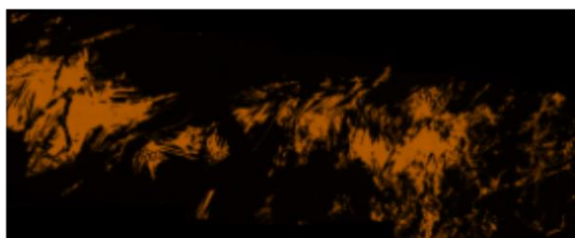
1mm

Mg K α 1_2

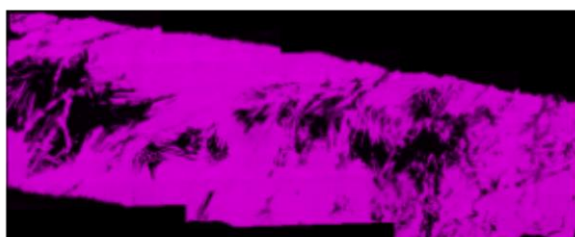
1mm

Al K α 1

1mm

Si K α 1

1mm

Ca K α 1

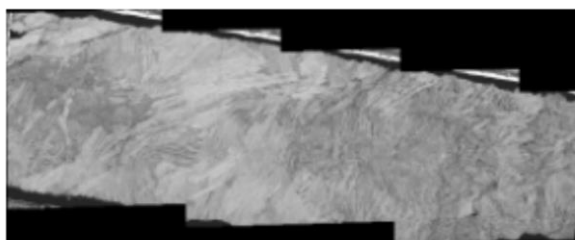
1mm

Fe K α 1

1mm

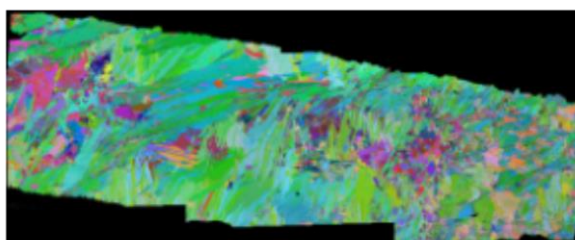
Band Contrast 142

BC



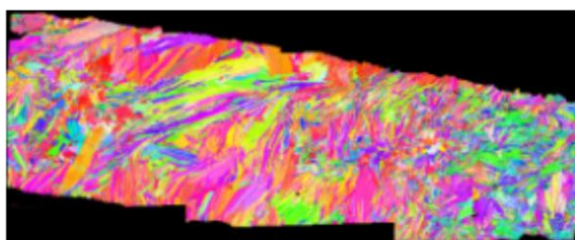
1mm

Euler Color 142

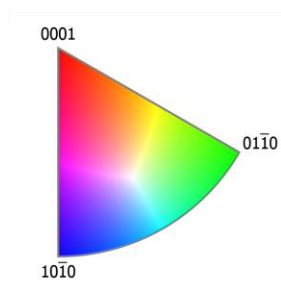
 $\phi 1$ Φ $\phi 2$ 

1mm

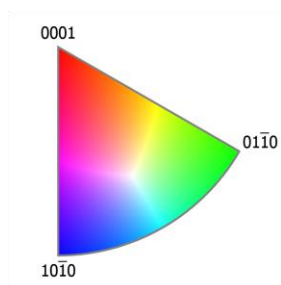
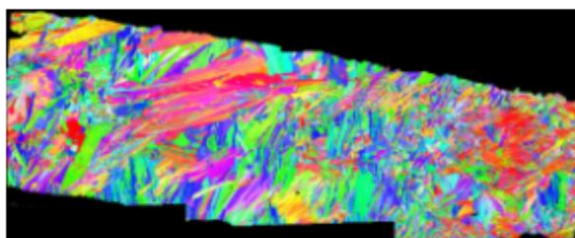
IPF Z Color 142



1mm

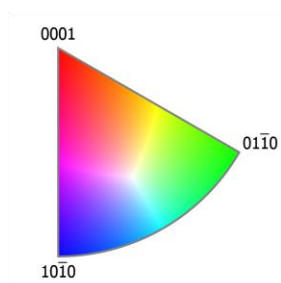
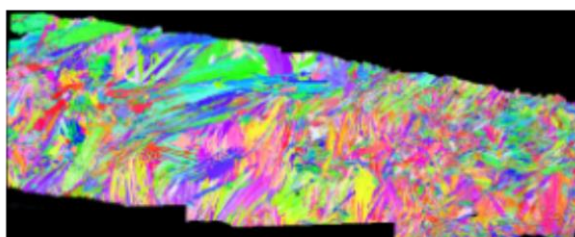


IPF Y Color 142



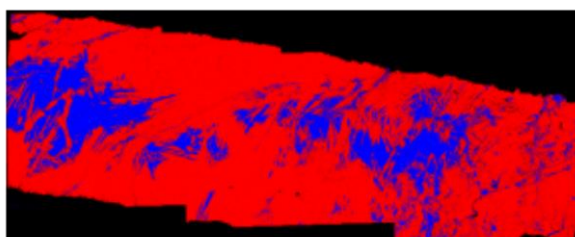
1mm

IPF X Color 142



1mm

Phase Color 142

Calcite Quartz-new

1mm

EBSD settings and results for LS11**09/11/2021**

Phase Fraction

Phase Name	Phase Fraction (%)	Phase Count	Mean Band Contrast	Standard Deviation Band Contrast	Min Band Contrast	Max Band Contrast	Mean MAD	Standard Deviation MAD	Min MAD	Max MAD
Calcite	73.21	1890043	164.70	28.64	28.00	255.00	0.40	0.16	0.09	2.00
Quartz-new	19.11	493233	135.74	22.95	24.00	255.00	0.53	0.17	0.11	2.00
Zero Solutions	7.68	198248	77.14	64.39	18.00	255.00				



Shallow deformation kinematic history, a new insight from carbonates U-Pb direct dating by LA-ICP-MS imaging technique.

Vincent Monchal, Kerstin Drost, and David Chew
Trinity College Dublin, Geology, Ireland (monchalv@tcd.ie)

This project aims to refine direct dating of carbonates by the U-Pb system, using a new LA-ICP-MS imaging technique that incorporates complementary element and textural analysis information. The direct dating of carbonates in deep time has been considered desirable for decades (e.g. Jahn and Cuvellier, 1994) given their ubiquity in the Earth system, and carbonates are a key phase for dating geological processes such as brittle-ductile deformation in carbonate successions. This new method facilitates detailed (on the scale of tens of microns) mapping of U-Pb isotope and element distributions (cf Drost et al., 2018), and is here applied to carbonate vein dating to constrain local and regional histories of deformation or fluid activity.

In this presentation we focus on a sample from the Carboniferous North Dublin Basin, Ireland. The basin has been affected by deformation that led to tight chevron folds and kinematically-linked dextral en-echelon vein sets. Additionally bedding-parallel veins and slickenfibres are common. The deformation has been conventionally assumed to be of Variscan age, and some Variscan U-Pb ages are recorded in this study. However many calcites analysed yield late Eocene ages, a deformation phase that is hitherto undetected on the Irish mainland. Our data indicate repeated fault slip over a period of at least c. 4 my during late Eocene times and, thus, demonstrate the ability of the LA-ICP-MS imaging approach to not only unravel complex polyphase deformation histories in carbonates but also to resolve processes on fine temporal and spatial scales.

DROST, K., CHEW, D., PETRUS, J. A., SCHOLZE, F., WOODHEAD, J. D., SCHNEIDER, J. W. & HARPER, D. A. T. 2018. 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.

JAHN, B.-M. & CUVELLIER, H. 1994. Pb-Pb and U-Pb geochronology of carbonate rocks: an assessment. *Chemical Geology*, 115, 125-151.

An image mapping approach to U-Pb LA-ICP-MS carbonate dating applied to far-field Pyrenean compression in Ireland

ORAL PRESENTATION

Presented by David M Chew



Tuesday, 11 July 2023



14:15 - 14:30



R8 (Building A, Level -2, Lyon Congress Center)

Session: 4aO1 - What's next for high precision geochronology? (Session in honor of Urs Schaltegger)

Symposium Session: 4a - What's next for high precision geochronology? (session in honor of Urs Schaltegger)

Theme: Theme 4: Crust: magmatism, metamorphism and metasomatism

Abstract

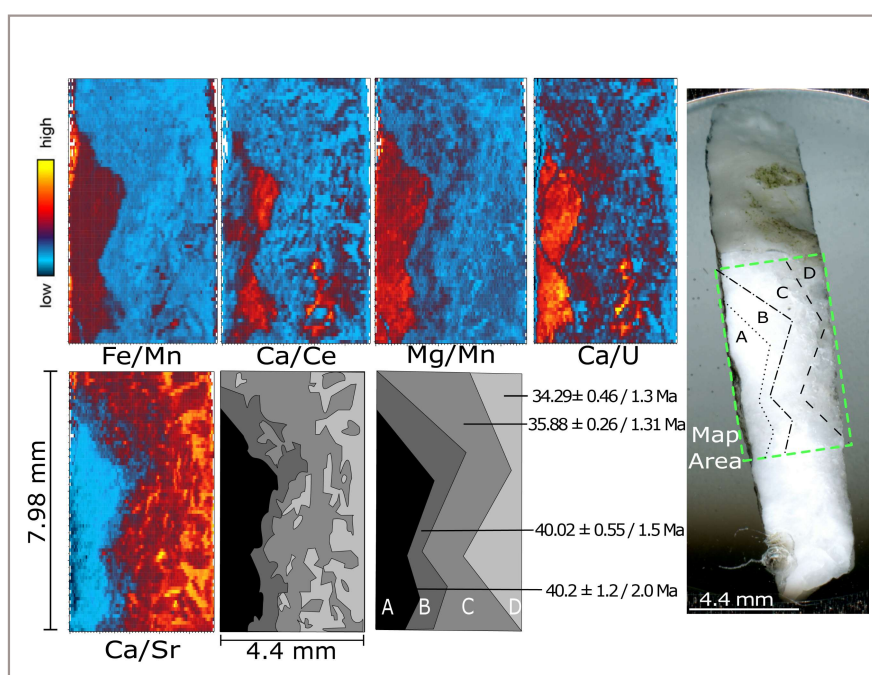
LA-ICP-MS mapping produces spatially resolved, quantitative trace element and isotopic analyses in geo-materials at the ppm level across nearly the entire mass range of the periodic table. Dating calcite by the U-Pb method is challenging as it contains very low U and/or high amounts of initial Pb, but opens up many exciting avenues in geochronology, including dating calcite veins in orogens, fossil-free ancient limestones in the geological record and ore-bearing vein systems. A U-Pb image mapping approach [1] can circumvent limitations of the U-Pb calcite system, as pixels on a U-Pb age map can be pooled into “analyses” based on elemental or isotopic ratio distributions to produce a spread in $^{238}\text{U}/^{204}\text{Pb}$ ratio (μ) on concordia. Simultaneous imaging of diagnostic trace elements allows identification and exclusion of zones representing chemically different generations of carbonate or detrital components. Rapid data acquisition is possible using a combination of high-repetition rates ($>100\text{Hz}$) and low-dispersion LA cells.

Our image mapping approach to U-Pb carbonate dating is illustrated with a case study from the Variscan Orogen in Ireland. The field locality (Carboniferous North Dublin Basin) exhibits spectacular tight chevron folds and kinematically-linked en-échelon vein sets and bedding-parallel veins with slickenfibers clearly associated with N-S compression (flexural slip). Deformation is conventionally assumed to be Variscan, despite lying c. 150 km north of the Variscan ‘front’. LA-ICP-MS U-Pb



dating of these calcite vein samples shows relict Variscan U-Pb ages are very poorly preserved. Instead, many calcite veins yield late Eocene ages, including fold-hinge breccias and bedding-parallel slickenfiber veins. U-Pb ages from one bedding-parallel vein indicate protracted (5 myr) late Eocene flexural slip (Fig. 1). Detecting several age-homogenous growth domains within this vein was facilitated by integrating spatial U-Pb isotopic information with maps of petrogenetically-diagnostic major and trace elements. The late Eocene folding phase is hitherto undetected on the Irish mainland due to the lack of post-Variscan markers (dykes or Mesozoic-Cenozoic cover sequences), which we link to far-field Pyrenean compression. Carbonate U-Pb geochronology is often the only feasible approach to detecting compressional reactivation of basement units when younger markers are absent.

[1] Drost *et al.* (2019), *G³*. <https://doi.org/10.1029/2018GC007850>



Presenting Author



David M Chew

Trinity College Dublin

Authors



Kerstin Drost

Trinity College Dublin



Vincent Monchal

Trinity College Dublin

Applying U-Pb calcite direct dating by LA-ICP-MS mapping to investigate shallow crustal deformation histories in Ireland

V.Monchal¹, K.Drost¹ and D.Chew¹

¹TCD Department of Geology, Trinity College Dublin, Dublin 2.

Multi-mineral petrochronology of metamorphism and deformation: linking grain-scale process to lithosphere dynamics. **Oral is preferred.**

The near ubiquitous presence of carbonate in supracrustal rocks and the intimate association carbonate fracture fills with deformed carbonate successions has long made carbonate a desirable mineral phase for geochronology studies [1]. However direct dating of carbonates by the U-Pb method faces major challenges, such as unfavourable μ ($^{238}\text{U}/^{204}\text{Pb}$) ratios due to low U and/or high initial Pb along with potential later resetting by fluid ingress or neocrystallisation. This project employs a Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) mapping approach [2] to U-Pb in-situ geochronology with simultaneous acquisition of trace elemental data. The resultant 2D isotopic and elemental maps may be complemented by spatially-registered optical petrography, electron backscatter diffraction (EBSD) or scanning electron microscope (SEM) imagery. The method presented herein can potentially overcome some of the challenges inherent to U-Pb carbonate geochronology detailed above. For example when applied to calcite veins, the approach allow the isolation of small-scale growth zones with favourable μ ratios and with homogeneous chemical compositions that are likely age homogenous.

We have applied U-Pb calcite dating to structures in three regions in Ireland that are all assumed to Variscan in age, despite being north of the putative Variscan “front”. All structures have associated vein sets are developed in Lower Carboniferous limestones; the distance north of the Variscan front is also indicated: 1) chevron folds in the Carboniferous Dublin Basin (200 km), 2) the Kilfenora anticline in Co. Kerry (15 km) and 3) gentle monoclines in the Burren region, Co. Clare (110 km). In the Dublin Basin, Variscan ages are only partly preserved due to subsequent Cenozoic opening of the U-Pb system. The majority of veins (including bedding-parallel veins with slickenfibres indicative of flexural slip and N-S contraction) yield late Eocene ages, with evidence for protracted flexural slip for at least c. 4 My during late Eocene times that we interpret as related to far-field Alpine/Pyrenean tectonism [3]. At localities Fenit and the Burren in southwestern Ireland, Variscan ages are better preserved. Unequivocal evidence of Paleocene N-S contraction was provided by bedding-parallel slickenfibres veins indicative of flexural slip on the limb of the Kilfenora anticline at Fenit, which we attribute to Pyrenean shortening. A N-S trending, vertical vein set yielding Miocene ages is found at several localities in Fenit and the Burren indicative of either N-S shortening or E-W extension; the former is favoured and attributed to Miocene Alpine far-field stresses. Surprisingly, a regional trend of tectonic quiescence from the Early Permian to Early Cretaceous is revealed by the entire Irish sample set (including additional dated veins from central Ireland), with no veins growth or reactivation detected during this extended time period. Given the paucity of post-Variscan markers (e.g., dikes or sills, Mesozoic–Cenozoic cover sequences) in Ireland, calcite U-Pb geochronology represents the only feasible approach to reconstruct the post-Variscan deformation history of the Irish landmass.

References:

- [1] Jahn and Cuvellier, 1994, Chemical Geology
- [2] Drost et al., 2018, G³
- [3] Monchal et al., 2023, Geology



Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Applications of the LA-ICP-MS image mapping approach to U-Pb carbonate dating : from far-field tectonism to pedogenic nodules

Thesis Dissertation for Doctor of Philosophy
School of Natural Sciences
Department of Geology

by

Vincent Monchal

2024

Annexes
Part 3: Posters





U-Pb LA-ICP-MS dating of carbonate veins in orogenic belts : Overview and challenges

V. Monchal¹ (monchalv@tcd.ie), K. Drost¹ and D. Chew¹

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Introduction

Carbonates can form by a variety of geological or biological processes including in sedimentary or biogenic systems or as a result of hydrothermal activity or carbonatitic magmatism. Recent studies employing U-Pb LA-ICP-MS carbonate dating have confirmed many of the challenges highlighted by Rasbury and Cole (2009), namely that carbonates incorporate a small amount of U or have an unfavorable U/Pb ratio, while the U-Pb system in carbonates is prone to resetting and incorporation of other mineral phases (such as detrital material).

The majority of studies to date are on geochronology of vein carbonates (either in orogenic or hydrothermal systems); this project will primarily investigate dating such targets by U-Pb LA-ICP-MS image mapping (e.g. Drost et al., 2018). This technique circumvents incorporation of other mineral phases or zones of low U content zones by finding zones of pristine (i.e. inclusion-free), high U/Pb carbonate, leading to more accurate and precise dating of the targeted material (e.g. Roberts and Walker, 2016). Targeted samples will include carbonates from the Irish sector of the Variscan orogen, the Alps, and the Irish Zn-Pb ore field.

Picture credit : R. Bornet – <https://www.le-comptoir-geologique.com>

Targeted Samples

The two main sampling targets in this research are carbonates in orogenic settings, and Irish-type Mississippi Valley-Type (MVT) deposits. We choose those targets for the following reasons :

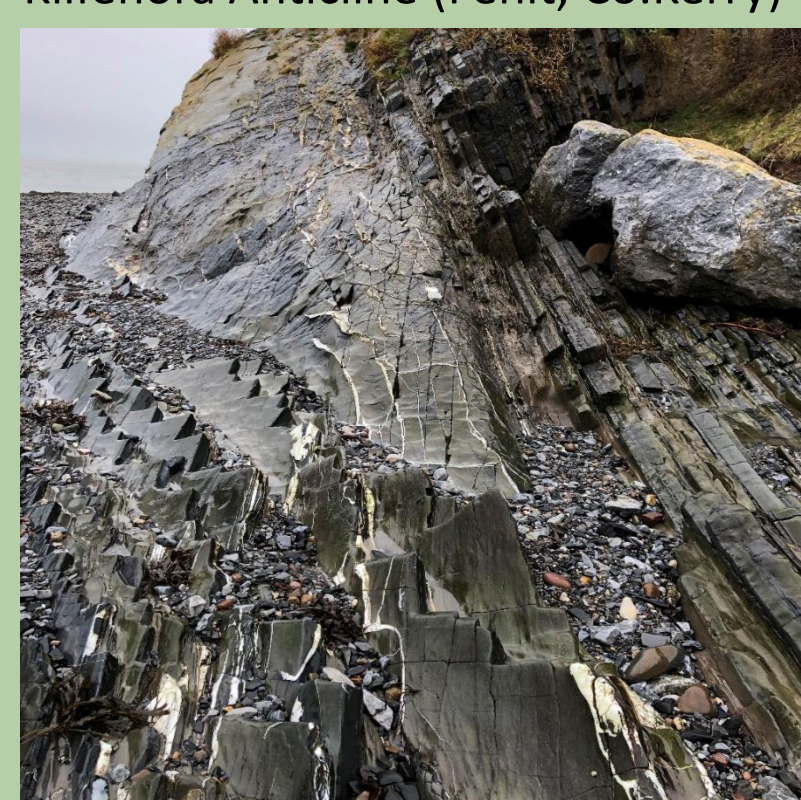
- U-Pb carbonate dating presents an ideal opportunity to directly constrain the age of Variscan structures (e.g. faults, syn-kinematic vein systems) in Ireland.
- Even if the overall regional dynamics of the Alps is well constrained, more local uncertainties in the tectonic histories remain and will be greatly benefited by U-Pb dating of vein and fracture-fill carbonates.
- A study of carbonates from Irish type MVT deposits could lead to a better understanding of the ore formation process that will refine the ore genesis models.

Carbonate samples of Irish Variscan have already been collected from Loughshinny and Fenit in this project and include :

Loughshinny folded structure



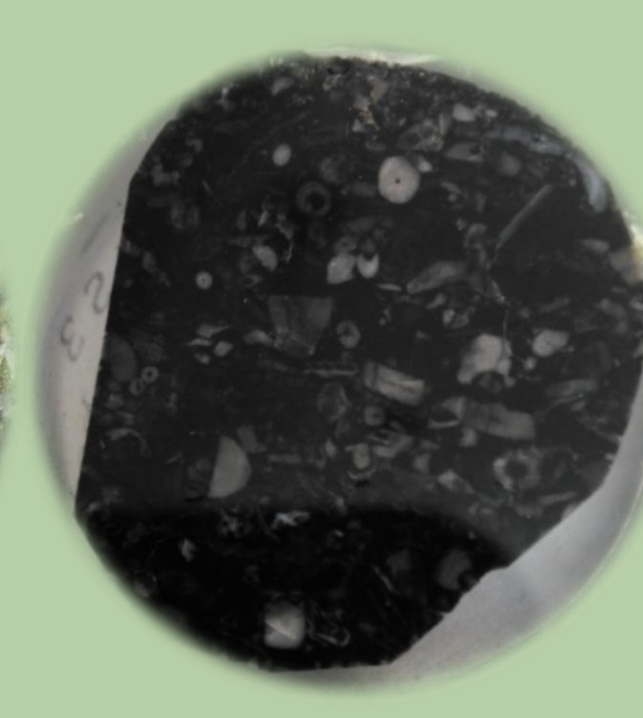
Kilfenora Anticline (Fenit, Co.Kerry)



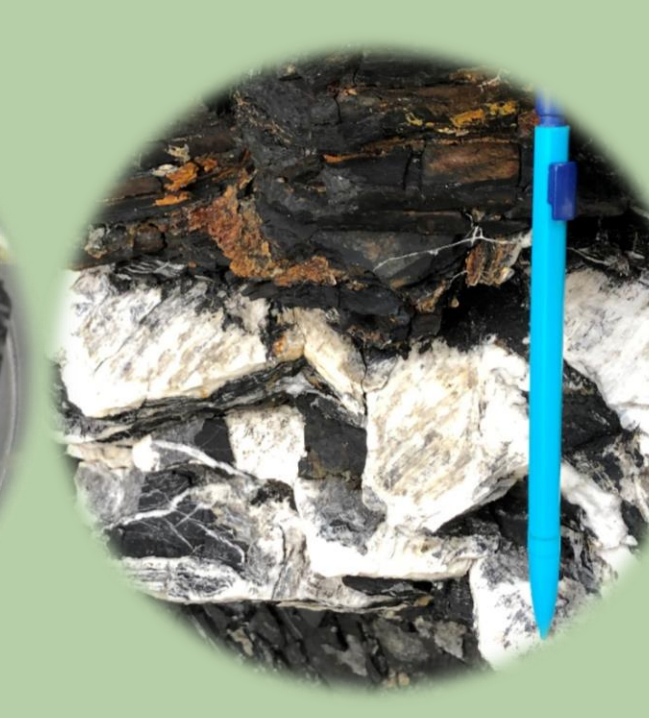
Tension gashes



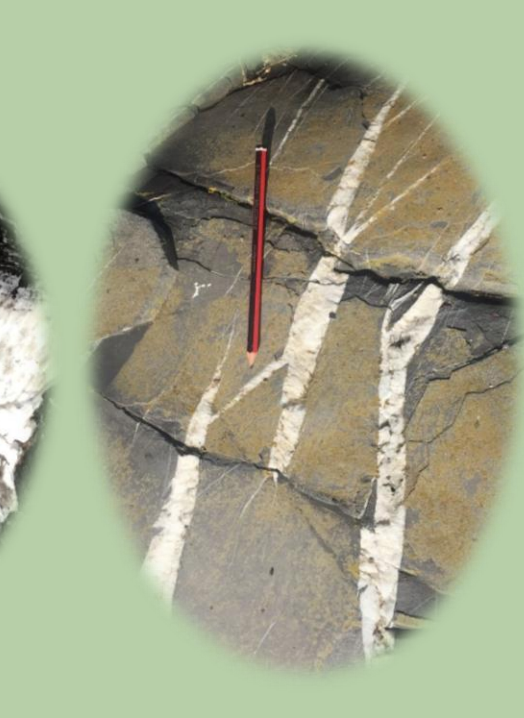
Breccia associated with folds



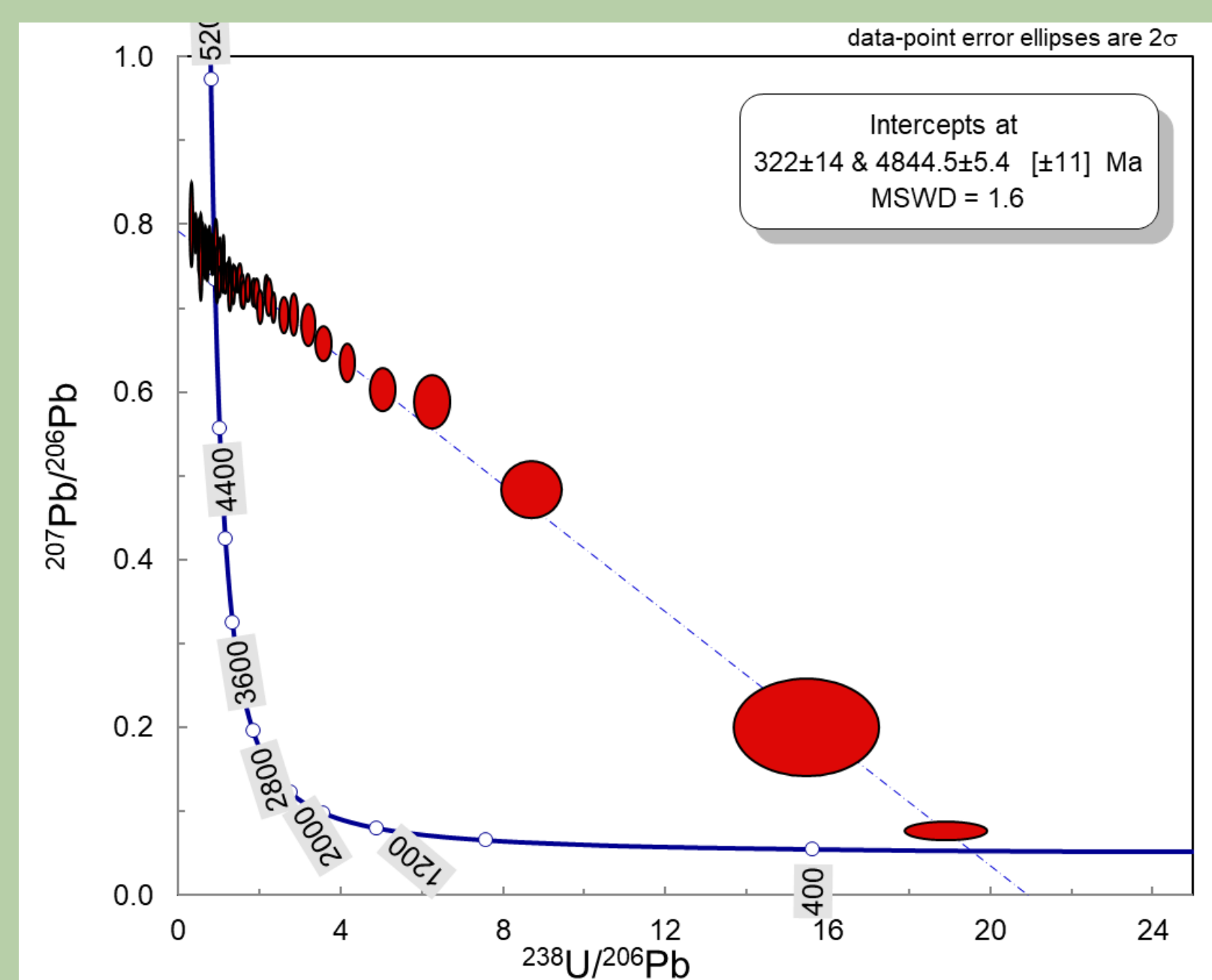
Bio-carbonates



Slickenfibres



En echelon veins



That result was obtained using a bio-carbonate in a limestone layer related to the main fold of the Kilfenora Anticline (Fenit, Co.Kerry). The limestone is known in the literature as Tournaisian (c.346.7-358.9 Ma) which is significantly distinct from the date we obtain here (322±14 Ma). More samples are currently processed, and it will be necessary to compare them before any interpretation, however this first result is promising.



The dashed rectangle shows the map location. Then we have selected the whiter part of the rectangle. This part is made of calcite and corresponding to the recrystallization of a brachiopod shell.

VMF6

For Irish type MVT, targeted samples could be the carbonate host veins of the mineralization or carbonates from faults related to mineralization events. Sampling targets in the Apennines will likely include the ophiolite units in the Ligurian Alps which are believed to represent a fossil ocean-continent transition (OCT) zone in order to establish its exhumation history.

Pictures credit : V. Monchal and D. Chew

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Limitations

Mass Discrimination

The majority of the ions of a given isotope in a sample will never be analysed by the detector. This can be corrected by the measurement of an invariant isotope ratio (e.g. Hirata, 1996), resulting in a mass bias factor which can be applied to correct the raw data.

Laser-induced element fractionation

During the laser ablation process, the more refractory elements will tend to condensate within the ablation pits whereas the more volatile elements will be transported more easily to the plasma. This fractionation effect increases with decreasing spot size or with increasing pit depth (e.g. Chew et al., 2014).

Matrix effects

This bias arises from varying optical and chemical properties between different materials and induces fractionation between elements with strong energy bonds and elements with weak energy bonds. It can be resolved by using a matrix-matched reference material of the same mineral species as the sample target (e.g. Jackson et al., 2004).

Interferences

Interferences can be corrected for by online or offline calculations, for example using the ²⁰²Hg concentration and assuming a natural known ratio of ²⁰⁴Hg/²⁰²Hg to correct for ²⁰⁴Hg on ²⁰⁴Pb in U-Pb dating (e.g. Horstwood et al., 2003).

Common Pb

Lead not produced by *in situ* radioactive decay can still be incorporated in a material, either into the crystal lattice during crystallization or at a later stage fractures (e.g. Bruguier, 2009, Chew et al., 2014).

LA-ICP-MS

Reference Materials

Historically, a lack of suitable matrix-matched reference materials has hampered U-Pb LA-ICP-MS carbonate dating. The majority of recent studies use WC1 ('Troy') carbonate as a reference material, which is a vein calcite (a Neptunian dyke infilling a Permian reef complex in Texas) with a U-Pb TIMS age of 254.4 ± 6.4 Ma (Roberts et al., 2017).

Carbonates matrices

Despite its common chemical formula, CaCO₃ can exist as polymorphs (e.g. aragonite and calcite) with different matrices for each.

Open system behavior

The U-Pb system in carbonates is prone to open system behavior, in theory by the low diffusion temperature of Pb in carbonates (c. 440°C for calcite; Cherniak, 1997), and in a more realistic case by the high reactivity of U and C with fluids that change their stability in the carbonate lattice (e.g. Bons et al., 2012).

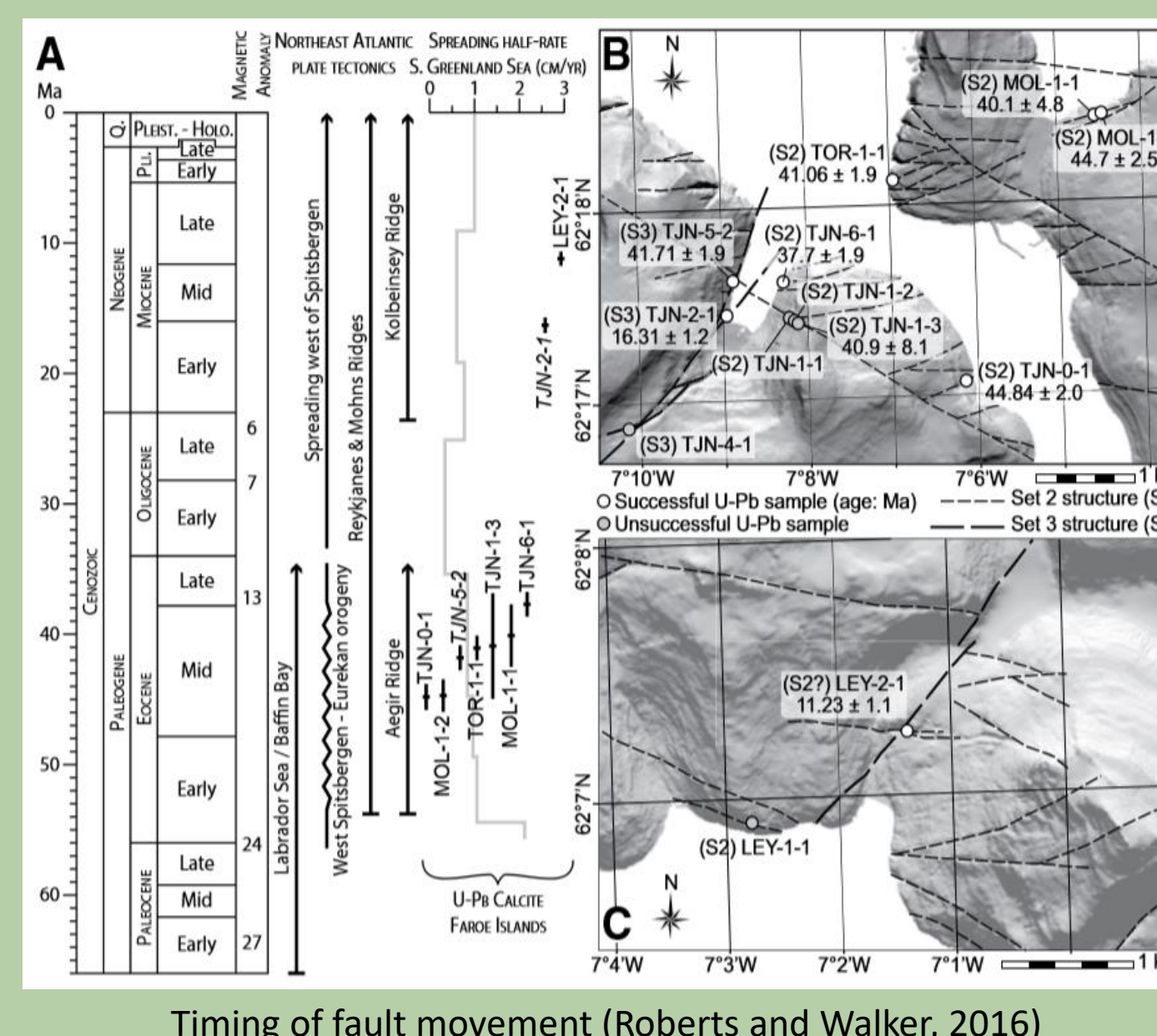
Uncertainties

The low U and Pb concentrations and often significant common Pb concentrations (and the associated assumptions on the initial common Pb composition) can result in large uncertainties on U-Pb carbonate dates (e.g. Roberts et al., 2017).

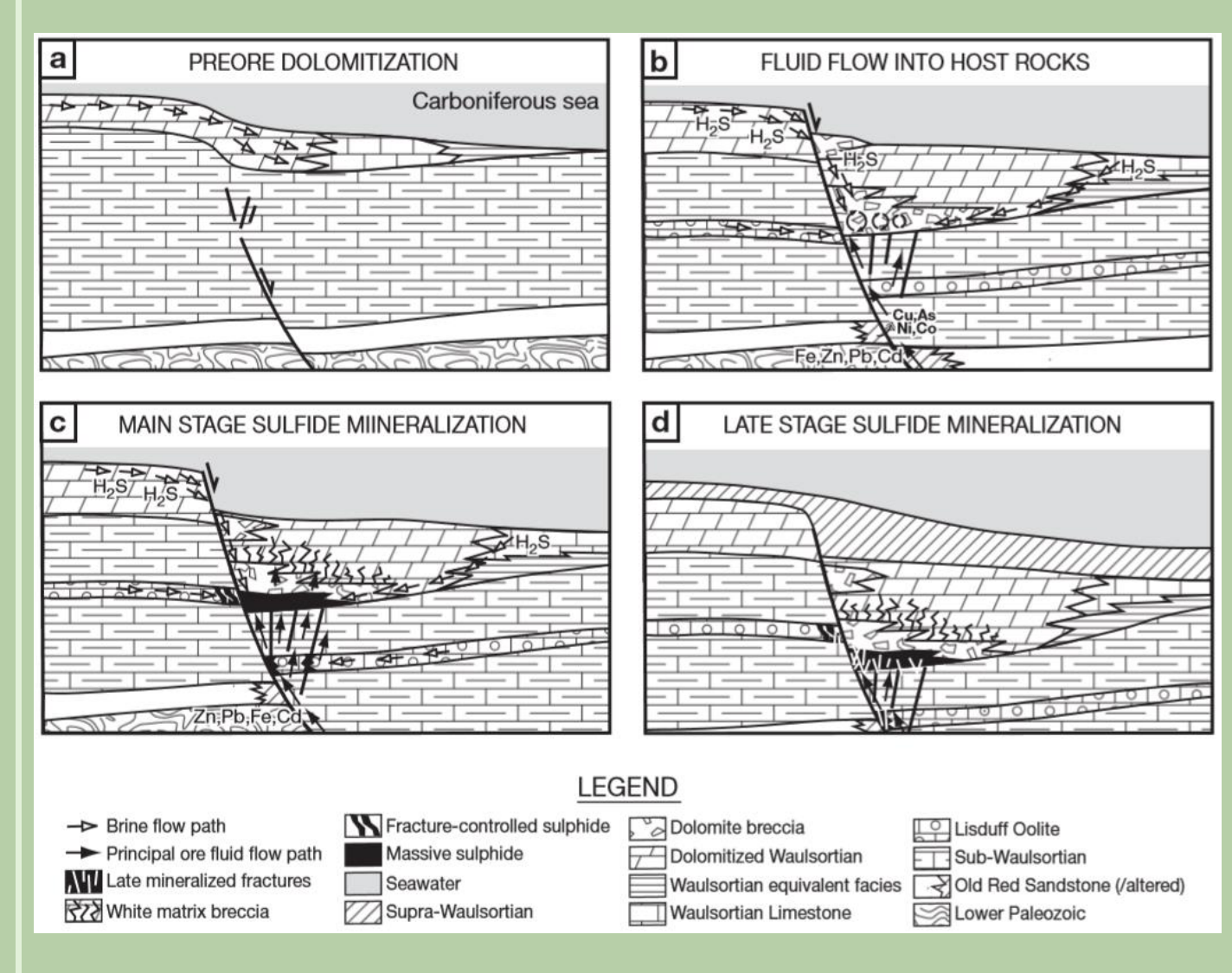
Carbonate Dating

Potential of Image mapping

In many cases carbonates are the only possible phase that can be dated in a sample, because they are the only mineral that grew during the targeted geological event (e.g. faulting; Roberts and Walker, 2016). Carbonates dating can help resolve a variety of process such as :

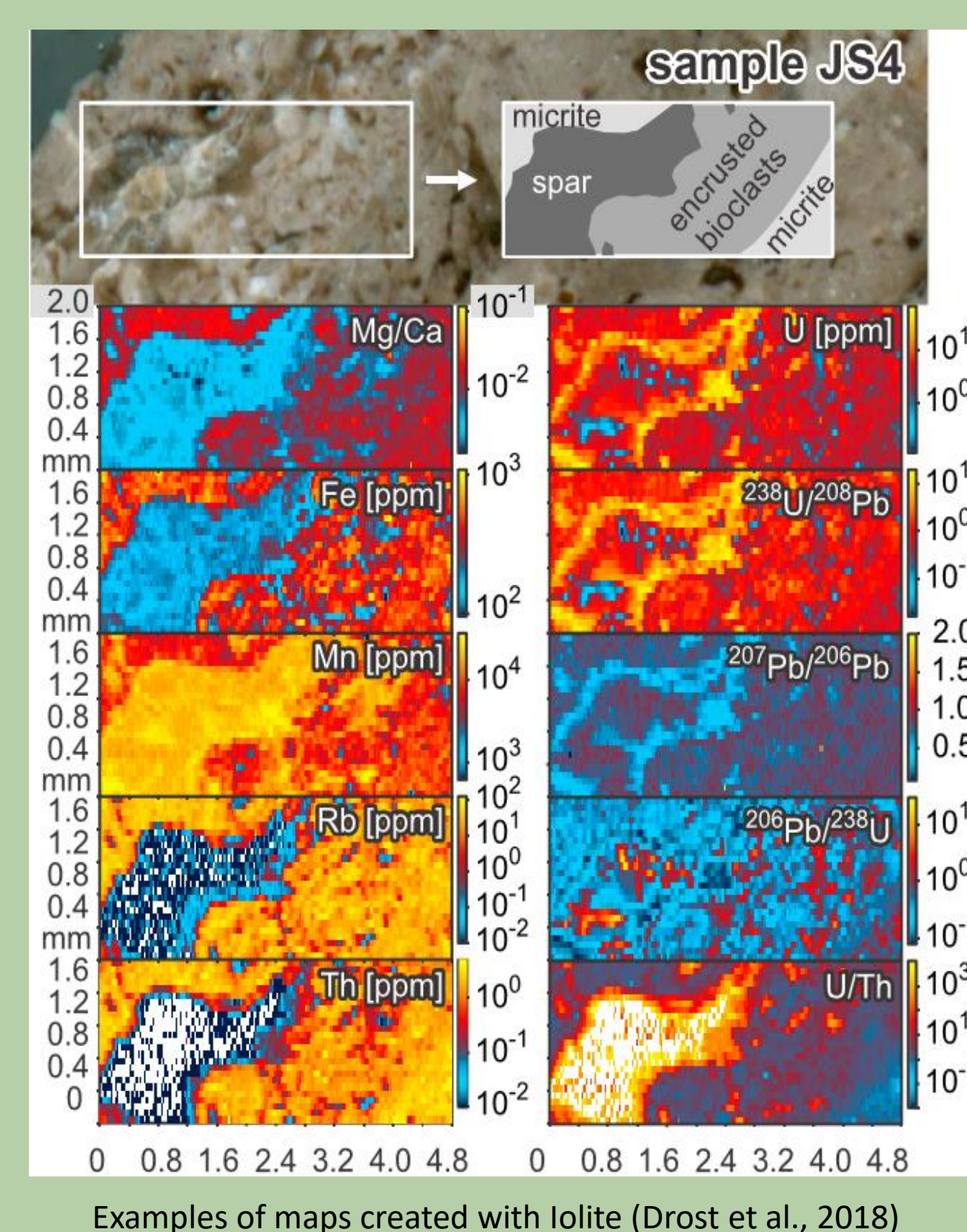


Timing of fault movement (Roberts and Walker, 2016)



Constraining stages of an ore formation (Wilkinson et al., 2005)

The recent increased of instrumental sensitivity for ICP-MS instruments improved data reduction approaches has helped develop LA-ICP-MS image mapping (e.g. Drost et al., 2018). This technique consists of ablate lines of spots (rasters) on samples, with each raster represented by a time resolved series of isotope data, that form a matrix. This method can be applied to any carbonate system (e.g. Drost et al., 2018) and could be extended to other low U minerals if they are sufficiently large (crystals on the scale of a hundred microns) and appropriate reference material(s) can be found.



Examples of maps created with Lolite (Drost et al., 2018)

This approach can help resolve some of the earlier described limitations by turning the easily-reactive behaviour of carbonates into a discrimination criterion. These elemental or isotope criteria can be combined with structural, petrographic, diagenetic or metamorphic evidence from the same ablated area to target or extract selected pixels from a map (e.g. Drost et al., 2018). U-Pb data from the selected area are then processed to produce a date (e.g. Drost et al., 2018).

In this project we will use the approach described in Drost et al. (2018) with NIST 614 glass and WC1 carbonate (Roberts et al., 2017) as primary standards and DBT carbonate (Hill et al., 2016) as a quality control material. The data reduction will be undertaken using the Lolite software (Paton et al., 2011) with the Monocle add-on (Petrus et al., 2017) for generating maps. The common Pb correction will be handled using a ²⁰⁷Pb correction by plotting all analyses of WC1 on an uncorrected Tera-Wasserburg plot. The difference between the regressed value of this plot and the accepted age of 254.4 ± 6.4 Ma (Roberts et al., 2017) yields a correction factor (e.g. Drost et al., 2018) which is then applied to unknowns.

Rialtas na hÉireann
Government of Ireland

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