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Supplement of

Regional-scale paleofluid system across the Tuscan Nappe–Umbria–Marche Apennine Ridge (northern Apennines) as revealed by mesostructural and isotopic analyses of stylolite–vein networks

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Supplementary data

U-Pb Geochronology

Methodology of the batch at the IPREM (Pau, France)

Calcite U-Pb geochronology was conducted via a LA-ICPMS isotope mapping approach at the Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IPREM, Pau, France). All the samples were analysed with a 257 nm femtosecond laser ablation system (Lambda3, Nexeya, Bordeaux, France) coupled to an HR-ICPMS Element XR (ThermoFisher Scientific, Bremen, Germany) fitted with the Jet Interface. The method is based on the construction of isotopic maps of the elements of interest for dating (U,Pb,Th) from ablation along lines, with ages calculated from the pixel values (Hoareau et al., in review). The ablation was made in a helium atmosphere (600 mL min^{-1}), and 10 mL min^{-1} of nitrogen was added to the helium flow before mixing with argon in the ICPMS. Measured wash out time of the ablation cell was ~500 ms for helium gas based on the 99% criterion. The fs-LA-ICP-MS coupling was tuned on a daily basis, and the additional Ar carrier gas flow rate, torch position and power were adjusted so that the U/Th ratio was close to 1 +/- 0.05 when ablating the glass SRM NIST612. Detector cross-calibration and mass bias calibration were checked daily. The laser and HR-ICPMS parameters used for U-Pb dating are detailed in Annex A.

Two types of isotopic maps were produced. The first one was designed to rapidly identify the areas with highest U/Pb, over a large surface of the 29 samples analysed. Samples were ablated along lines of 1.7 to 9.3 mm length at a repetition rate of 300 Hz. The lines of 50 µm width were spaced by 100 µm and were ablated using a stage movement rate of 100 $\mu m.s^{-1}$, corresponding to 17 to 94 s of analysis per line, followed by 15 seconds of break between the lines. The number of lines was of 14 to 90, making 10 to 94 minutes for a surface comprised between 3.2 and 46.2 mm^2. Only ^{238}U and ^{206}Pb were selected, with a mass sweep of 500 ms. The second one was designed to date the samples selected after the first step (n = 2). They consisted in linear scans of 0.68 to 1.47 mm length at a repetition rate of 500 Hz. These lines of 25 µm width, separated by a distance of 25 µm, were obtained with a stage movement rate of 25 $\mu m.s^{-1}$, corresponding to 27 to 59 s of analysis per line, followed by 15 seconds of break. The number of lines was of 32 to 59, resulting in a total analysis time ranging from 22.5 to 78 minutes for a surface of 0.54 to 2.16 mm^2. Before analysis, the samples were pre-cleaned with the laser using a stage movement rate of 200 $\mu m.s^{-1}$ and a lower energy (Il faut donner la valeur). Only ^{238}U, ^{232}Th, ^{208}Pb, ^{207}Pb, and ^{206}Pb were selected, reaching a total mass sweep times of about ~60 ms.

The 2 selected unknowns were bracketed with the glass SRM NIST612 for lead ratios, followed by the WC1 calcite standard (Age 254.4 ± 7 Ma; Roberts et al. (2017)) for the U/Pb ratio, based on Roberts et al. (2017). The standards were analysed in conditions similar to the unknowns, except that the isotopic maps were of smaller surface (~0.2 mm^2), corresponding to an analysis time of ~5 minutes. The Duff Brown Tank limestone (Age 64.04 ± 0.67; Hill et al., 2016) was used as a secondary standard. The normalized pixel ratio Pb-Pb and U-Pb values were plotted in Tera-Wassurburg (TW) concordia, 86 Tera-Wasserburg (86TW) concordia ($^{208}Pb_{common}/^{206}Pb$ versus $^{238}U/^{206}Pb$; Parrish et al., 2018) and $^{206}Pb/^{208}Pb_{common}$ versus $^{238}U/^{208}Pb_{common}$ isochron plots. To calculate the age, a MM-robust linear regression was then applied to the pixels in the three types of plots (Hoareau et al., in review). The goodness-of-fit to the data was assessed by the calculation of the residual standard error of the regression (RSE), by the calculation of a MSWD on discretized data ('pseudo-ellipses') and by similar ages (within uncertainty) obtained for the different plots. The calculated ages have uncertainties quoted as age ± x/y, where x corresponds to the confidence interval of the regression and y is with (i) additional analytical uncertainties (on $^{238}U/^{206}Pb$ of glass SRM NIST612) and (ii) systematic uncertainties (on decay constant of ^{238}U (0.05%, 1s), on $^{238}U/^{206}Pb$ ratio of WC1 as estimated by Roberts et al. (2017) (1.35%, 1s), and long-term excess uncertainty (1.25%, 1s)).

Laboratory & Sample Preparation		
Laboratory name	Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux (IPREM), UPPA, Pau (France)	
Sample type/mineral	Calcite	
Sample preparation	In situ in polished blocks	
Imaging	Screening (n = 29) and for dating (n = 2)	
Laser ablation system		
Make, Model & type	Lambda 3, Nexeya (France)	
Laser wavelength (nm)	257 nm	
Pulse duration (fs)	360 fs	
Fluence ($J.cm^{-2}$)	5-8 $J.cm^{-2}$	
	Screening	***Isotope dating maps***
Repetition rate (Hz)	300 Hz	500 Hz
Gas blank (s)	No	27 s to 59 s per image (1 line)
Ablation duration (s)	10 min to 94 min	22.5 min to 78 min
Washout and/or travel time in between analyses (s)	Wash out time: 500 ms. 15 s of break between lines to allow data processing	
Spot diameter (µm)	17 µm	
Sampling mode / pattern	Ablation lines (50 µm-width) made by combining laser beam movement across the surface (10 mm/s) and stage movement (100 µm/s). 100 µm between lines.	Ablation lines (25 µm-width) made by combining laser beam movement across the surface (5 mm/s) and stage movement (25 µm/s). 25 µm between lines.
Cell Carrier gas (L/min)	He = 0.650 L/min	
ICP-MS Instrument		
Make, Model & type	ICPMS Thermo Fisher Element XR Jet Interface	
RF power (W)	1100 – 1200 W	
Cooling gas flow rate	16 L min^{-1}	
Auxiliary gas flow rate	1 L min^{-1}	
Nebuliser gas flow rate	0.55 L min^{-1}	
Isotopes	206,238	206, 207, 208, 232, 238
Samples per peak	40	30
Mass window	50 %	10 %
Sample time	12.5 ms	3 ms
Settling time	1 ms	1 ms
Mass sweep	502 ms	50 ms
Number of averaged acquisition points per pixel	2	8
Resolution	300	
Data Processing		
Calibration strategy	No	Calibration by standard bracketing with NIST612 for Pb-Pb and WC-1 calcite for Pb-U
Reference Material info	No	Primary: NIST612 - Woodhead and Hergt (2001) WC-1 254 ± 6 Ma (2s) - Roberts et al., 2017 Secondary: Duff Brown 64.04 +/- 0.67 Ma (2s) - Hill et al., 2016
Data processing package used / Correction for LIEF	Element XR acquisition software, data processing with in-house Python code and ImageJ software	
Common-Pb correction, composition and uncertainty	No	No common Pb correction. Unanchored robust regressions in Tera-Wasserburg, 86TW plot (Parrish et al., 2018) and $^{206}Pb/^{208}Pb_{common}$ versus $^{238}U/^{208}Pb_{common}$ isochron plots.

		Ages in the data table are quoted at 95% absolute uncertainties and include systematic uncertainties, propagation is by quadratic addition.
Quality control / Validation	No	1 analysis of Duff Brown (anchored to common Pb value of 0.738) gave age of 66.87 ± 2.48 Ma

Methodology of the batch at the BGS (Keyworth, UK)

U-Pb and trace element maps were generated at the Geochronology and Tracers Facility, British Geological Survey, UK, using a Nu Instruments Attom single collector inductively coupled plasma mass spectrometer coupled to a NWR193UC laser ablation system fitted with a TV2 cell. Both methods followed those previously described by Roberts & Walker (2016) and Roberts et al. (2017).

Trace elements

Trace elements were measured in linkscan mode on the SC-ICP-MS, which provides non-adjustable dwell times per mass, and a fixed cycle time of 200 ms. The following masses were measured: ^{24}Mg, ^{44}Ca, ^{51}V, ^{55}Mn, ^{57}Fe, ^{63}Cu, ^{88}Sr, ^{89}Y, ^{95}Mo, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{149}Sm, ^{153}Eu, ^{157}Gd, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{172}Yb, ^{175}Lu, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{238}U. Normalisation was achieved using NIST614 glass and assuming a stoichiometric Ca content of 40.4 %. Tuning was adjusted to achieve low oxides, with ThO/Th <0.3% and UO/U <0.1%.

Maps were generated by rastering 100 µm spots over the surface of the samples creating a rectangular-shaped series of lines. Rastering was conducted at 50 µm second rate of movement, with parameters of 10 Hz and a fluence of 7 J/cm^2. Maps of each element were created using Iolite v2 (Paton et al., 2011). For plotting of trace element data, the raster data were also treated as traditional analysis, equating one line as a single analysis.

U-Pb

One sample (438) was analysed using traditional static spot ablations. Laser parameters were 110 µm spots, ablated at 10 Hz for 30 seconds with a fluence of 7 J/cm^2. WC1 (Roberts et al., 2017) was used as a primary reference material for Pb/U ratios, and NIST614 for Pb/Pb ratios; no secondary reference materials were run during the session.

Additional constraints on U-Pb composition were calculated from the Pb and U masses measured during the trace element mapping. Baselines were subtracted in Iolite, and Pb/Pb and Pb/U ratios were calculated offline in excel. No normalisation was conducted, as the raw ratios are suitable accurate to assess the abundance of radiogenic lead in the samples, which is the aim of making these calculations.

Illustration of U-Pb results from the veins

The analyses of sample 438 are dominated by common lead, and no reliable age can be obtained. A few analyses yield higher U/Pb ratios, but these do not have markedly radiogenic Pb/Pb compositions; therefore, the sub-horizontal (in Tera-Wasserburg space) array may represent uranium mobility in the sample.

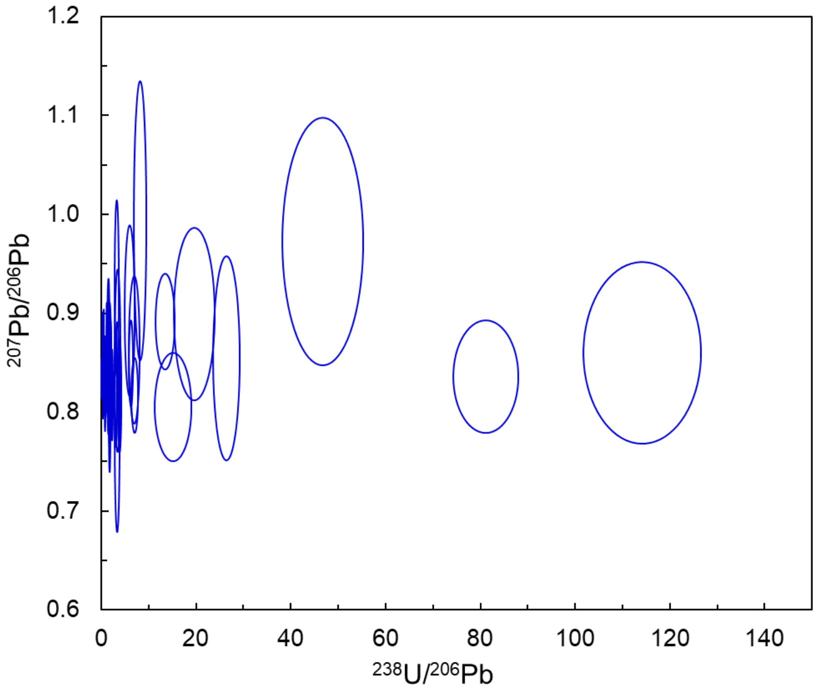

Figure S1. Tera–Wasserburg plot of U-Pb data from sample 438. No age can be obtained from the scattered sub-horizontal array.

Data from all six samples (Fig. S2) were obtained by ratioing the raw counts taken from the map rasters. All samples yielded $^{207}Pb/^{206}Pb$ ratios close to the expected Stacey & Kramers (1975) model for modern terrestrial lead, indicating a lack of radiogenic lead in the samples. The $^{238}U/^{206}Pb$ ratios were very low in most samples, also indicating a complete lack of radiogenic ingrowth of lead. Some samples had higher U/Pb ratios, but these produced sub-horizontal arrays in Tera-Wasserburg space, rather than pointing to lower intercepts on Concordia. We have found that such sub-horizontal arrays are typical of very young samples that have limited time for ingrowth of radiogenic lead, but may also indicate some U mobility, causing variable U/Pb ratios with static Pb/Pb ratios. In summary, no discernible age is obtainable from the six samples 32, 34, 49, 52, 53 and 438.

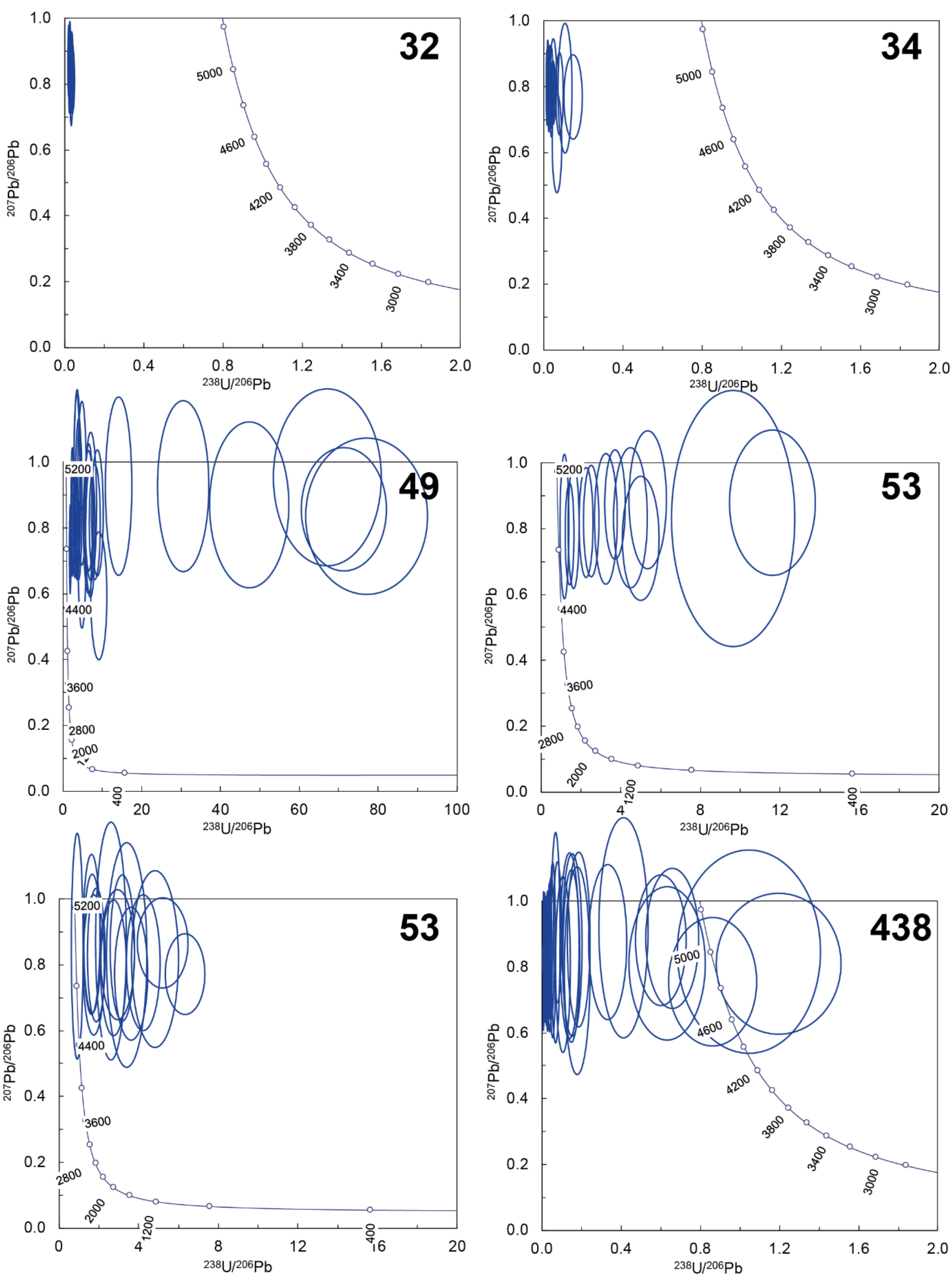

Figure S2. Tera-Wasserburg plots of U-Pb data for six samples. The data are not normalised to a reference material, but are merely the baseline-subtracted raw counts ratioed against each other.

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