**Far-field brittle deformation record in the eastern Paris Basin (France)**

***Original Article – Special issue “****Faults and fractures in rocks: mechanics, occurrence, dating, stress history and fluid flow”*

Thomas Blaise\*1, Sid Ahmed Ali Khoudja1, Cédric Carpentier2, Benjamin Brigaud1, Yves Missenard1, Xavier Mangenot3, Philippe Boulvais4, Philippe Landrein5, Jean Cochard5

1 Université Paris-Saclay, CNRS, GEOPS, 91405, Orsay, France.

2 Université de Lorraine, CNRS, GeoRessources, 54500 Nancy, France

3 Caltech, Geological and Planetary Sciences, 91106, Pasadena, CA, USA

4 Géosciences Rennes, CNRS, Univ Rennes, UMR 6118, F-35000, Rennes, France

5 Agence Nationale pour La Gestion des Déchets Radioactifs (ANDRA), Centre de Meuse/Haute-Marne, RD 960, 55290 Bure, France

\*corresponding author: thomas.blaise@universite-paris-saclay.fr

**Supplementary Material 1**

**U-Pb GEOCHRONOLOGY**

***Analytical Protocol***

U-Pb analyses were conducted using a Thermo ScientificTM Sector Field Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS) ELEMENT XR (ThermoFisher Scientific, Waltham, USA) coupled to a 193 nm ArF Laser Ablation System (Photon Machines Teledyne, Thousand Oaks, USA) at the Géosciences Paris-Saclay (GEOPS) laboratory at the University of Paris-Saclay.

WC-1(Roberts et al., 2017) was used as primary reference material to correct for 206Pb/238U fractionation. NIST614 glass standard was used to correct 207Pb/206Pb mass bias and to evaluate the instrumental drift during analytical sessions. Duff Brown Tank (DBT) (Hill et al., 2016) and B6 (Pagel et al., 2018) were measured as secondary reference materials to ensure accuracy.

A "prescan" consisting in making 6 to 10 spots in each sample (random location when the calcites are homogeneous in reflected light and cathodoluminescence, or, if not, determined location according to the different zones distinguished) was carried out to select the most favourable areas. Once the samples selected and the ablation spots placed, the automatic analysis was started for several hours (12-13h) with the operating conditions listed in Table S1.

The laser beam diameter for calcite unknowns and calcite reference materials (WC-1, B6 and DBT) was 150 μm. Calcite crystals (including reference materials) were ablated at a frequency of 8 Hz and a fluence of 1 to 2 J.cm-2. Glass reference materials NIST612 and NIST614 (Jochum et al., 2011) were ablated at a frequency of 10 Hz, a fluence of 6.25 J.cm-2 and a beam size of 40 μm for NIST612 and 110 μm for NIST614.

Each analysis consists of 30 s background acquisition followed by 30 s of sample ablation and 30 s washout. Prior to analysis, each sample spot was pre-ablated during 3 s at a frequency of 8 Hz and with a fluence of 2 J.cm-2 over an area larger than the beam diameter to clean the surface (155 μm) and remove potential surface contamination. The laser-induced aerosol was carried by helium (lage volume at 0.5 L.min-1 and inner cup at around 0. 3 L.min-1) from the sample cell to a mixing funnel in which the sample and He are mixed with 0.950 to 1 L.min-1 Ar and 0.8 to 1.5 mL.min-1 N2 to stabilize the aerosol input to the plasma. Signal strength of the ICP-MS was tuned for maximum sensitivity while keeping Th/U between 0.97 and 1.03 and ThO/Th below 0.4 % on NIST612. Isotopes 206Pb, 207Pb, 208Pb, 232Th and 238U were acquired with integration time per peak (ms) of 10 ms for 208Pb and 232Th, of 20 ms for 238U , of 35 ms for 206Pb and of 45 ms for 207Pb by 750 runs.

We used NIST614 to correct for 207Pb/206Pb fractionation (Woodhead, Horstwood & Cottle, 2016; Roberts et al., 2017). For mass-bias correction of the measured 238U/206Pb ratios, we used the calcite reference material WC-1, (Roberts et al.,(2017), dated by thermal ionization mass spectrometry (TIMS) after isotope dilution at 254.4±6.4 Ma. To ensure accuracy, we analyzed two secondary calcite reference materials during the analytical session: Duff Brown Tank (DBT) calcite, dated at 64.0±0.7 Ma by U-Pb ID-TIMS (Hill et al., 2016), and B6, a calcite breccia dated at 43.0±1.0 Ma (Pagel et al., 2018) by LA-ICP-MS. Internal secondary reference calcite B6 comes from the Gondrecourt graben (Eastern Paris Basin), part of the European Cenozoic Rift System, and is routinely analyzed at GEOPS (University Paris-Saclay). Measurements have been made by sequences composed of 7 reference material analyses (2 NIST612, 1 NIST614, 1 DBT, 2 B6 and 1 WC-1), 10 to 15 spots on unknown calcite, 5 reference material analysis (1 NIST614, 1 DBT, 2 B6 and 1 WC-1), 10 to 15 spots on unknowns calcite, etc., ending with 7 reference material analysis (2 NIST612, 1 NIST614, 1 DBT, 2 B6 and 1 WC-1). Data were acquired in fully automated mode overnight in sequences of max. 400 analyses the 24th of June, 25th of June, 28th of June, 1st of July and 8th of July 2021.

Data was reduced in Iolite© using NIST614 glass as the primary reference material to correct for baseline and for Pb isotope mass bias over the sequence time (Paton et al., 2011; Lawson et al., 2018). No down-hole fractionation correction is applied in Iolite© (Nuriel et al., 2017). The approach to data reduction was to define the largest time window (>25 s if possible) within the data profile and average the ratios. The two standard errors in 207Pb/206Pb and 206Pb/238U ratios measured on NIST614 during each analytical session (instrumental drift) was propagated to the final age uncertainty of calcite samples by quadratic addition. During the sessions, NIST614 two sigma standard error of the 207Pb/206Pb was max. 0.4 % and was max. 1.5 % for 206Pb/238U (Table S2). Each reduced data is plotted in a Tera-Wasserburg 238U/206Pb *versus* 207Pb/206Pb graph using the online version of IsoplotR© (Vermeesch, 2019). An isochron is drawn and the isochron age is deduced by the intersection on the concordia. For each sequence, the age and uncertainty of WC-1 was calculated without further normalization using a Tera-Wasserburg intercept age calculated from the raw 206Pb/238U and NIST614-normalized 207Pb/206Pb ratios. Following the analytic run, we applied a linear correction factor to correct the 206Pb/238U such that WC-1 yields the correct intercept age (*i.e.*, 254.4±6.4 Ma, Roberts et al. (2017)). We anchored the initial 207Pb/206Pb ratio at 0.85 when we calculated the Tera-Wasserburg intercept age on WC-1. On unknown calcite samples, Tera-Wasserburg intercept ages are calculated by plotting each spot from a single sample (or a single calcite type) and by applying the linear correction factor obtained from WC-1 during the session to correct the 206Pb/238U ratios. When data are spreading along a single regression line, this spread is interpreted as an isochron and an age is calculated from the IsoplotR© software without any constraint on the initial 207Pb/206Pb value. Error ellipses of each spots and the error on the Tera-Wasserburg intercept age are 2σ. In each Tera-Wasserburg graph, two age uncertainties are given. The first uncertainty does not take into account error propagation, except the errors related to the decay constants of 235U and 238U using IsoplotR©. A second age uncertainty is given, by propagating the systematic uncertainty of primary reference material WC-1 age (2.6 %), and the two sigma standard errors of the 207Pb/206Pb and 206Pb/238U of the corresponding analytical session by quadratic addition. The uncertainty related to the systematic long-term excess-variance was not propagated in this study. Following this description, calculated ages for secondary reference materials analyzed during the sequence are indicated in Figure S3, without anchoring 207Pb/206Pb at the origin.

|  |  |
| --- | --- |
| **Laboratory and Sample Preparation** |  |
| Laboratory name | Géosciences Paris-Saclay (GEOPS), University Paris-Saclay, Orsay, France |
| Sample type/mineral | Calcite |
| Sample preparation | polished fragments of calcite in epoxy mounts or thin sections |
| Imaging | Optical and cathodoluminescence microscopy |
| Laser ablation system |  |
| Make, Model and type | 193nm ArF Photon Machines (Teledyne) |
| Ablation cell | HelEx |
| Laser wavelength (nm) | 193 m |
| Pulse width (ns) | 5 ns |
| Fluence (J.cm-2) | 1 to 2 J.cm-2 for calcite, 6.25 J.cm-2 for NIST 612 and NIST614 |
| Repetition rate (Hz) | 8 Hz for calcite, 10 Hz for NIST 612 and NIST614 |
| Pre-ablation | each spot during 3 s, 155 µm for calcite, 50 µm for NIST 612 and 135 µm for NIST614 |
| Ablation duration (secs) | 30 s |
| Spot size (mm) | 150 μm for calcite, 40 µm for NIST 612 and 110 µm for NIST614 |
| Sampling mode / pattern | Static spot ablation |
| Carrier gas | He |
| Cell carrier gas flow (L.min-1) | HeliumLage volume: 0.5 L.min-1Inner cup: 0.3 L.min-1 |
| ICPMS instrument |  |
| ICPMS instrument Make, Model & type | ThermoScientific Element XR |
| Sample introduction | Ablation aerosol. Squid homogenizer placed in front of the torch  |
| RF power (W) | 1300 W |
| Make-up gas flow in ablation funnel (L.min-1) | Ar=0.950 to 1 L.min-1 , N2=0.8 to 1.5 mL.min-1 |
| Detection system | Ion counter in counting mode |
| Masses measured | 206, 207, 208, 232, 238 |
| Average gas background (cps) | 126 for 206, 107 for 207, 0 for 238 |
| Integration time per peak (ms) | 35 ms for 206, 45 ms for 207, 10 ms for 208, 10 ms for 232, 20 ms for 238 |
| Total integration time per reading (secs) | 0.12 s |
| IC Dead time (ns) | 25 ns |
| Signal strength at ICPMS tuned conditions | Th/U ̴ 1248ThO/232Th below 0.4 % |
| **Data Processing** |  |
| Data acquisition | Fully automated mode overnight in sequences of 399 analysis maximum |
| Gas blank | 30 s background, 30 s sample ablation and 30 s washout |
| Calibration strategy | NIST614 for 207Pb/206Pb, calcite WC-1 for 238U/206Pb, secondary reference material calcite Duff Brown Tank and calcite B6 |
| Reference Material info | WC-1 age: 254.4±6.4 Ma (Roberts et al., 2017), Duff Brown Tank age: 64.04 ± 0.67 Ma (Hill et al., 2016) and calcite breccia B6 age: 43 ± 1 Ma (Pagel et al., 2018) |
| Data processing package used / Correction for LIEF | Iolite to calculate uncertainties, no down-hole fractionation correction |
| Mass discrimination | 207Pb/206Pb normalization to NIST614, 206Pb/238U normalized to WC-1 |
| Common-Pb correction, composition and uncertainty | No common-Pb correction applied |
| Uncertainty level & propagation | All uncertainties at 2sigma (2σ) absolute, uncertainty propagation by quadratic addition |
| Quality control / Validation | Measurements of WC-1, Duff Brown Tank (DBT), B6 and NIST614 were done along with samples throughout the analytical session |

**Table S1:** LA-ICP-MS calcite U-Pb geochronology parameters

***Reference materials results***

LA-ICP-MS mean background on mass 206, 207 and 238, together with the instrumental drift and the linear correction factor applied to all calcite 238U/206Pb ratios are given in Table S2.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **mean background (cps)** | **Instrumental drift (from NIST614 measurements)** | **WC-1 primary reference material** |
|  | 206Pb | 207Pb  | 238U | 207Pb/206Pb 2 S.E. (%) | 238Pb/206Pb 2 S.E. (%) | WC-1 raw age (Ma) | WC-1 raw age 2σ uncertainty (abs) | 238U/206Pb correction factor |
| **2021.06.24** | 140 | 121 | 0 | 0.08 | 1.50 | 200.7 | 2.3 | 0.7868 |
| **2021.06.25** | 145 | 126 | 0 | 0.35 | 0.42 | 202.8 | 2.0 | 0.7949 |
| **2021.06.28** | 121 | 95 | 0 | 0.28 | 1.10 | 225.1 | 3.3 | 0.8836 |
| **2021.07.01** | 144 | 123 | 0 | 0.11 | 0.90 | 218.5 | 3.3 | 0.8574 |
| **2021.07.07** | 82 | 70 | 0 | 0.39 | 1.20 | 237.7 | 2.6 | 0.9334 |

**Table S2:** Mean background, instrumental drift, and corrections on 238U/206Pb ratios applied from the analysis of WC-1 during the five analytical sessions.

Ages and propagated uncertainties of secondary reference materials B6 and DBT are given in Figure S1.



**Figure S1:** Ages and uncertainties of secondary reference materials B6 and DBT obtained during the five analytical sessions.

**REFERENCES**

Hill, C.A., Polyak, V.J., Asmerom, Y. & P. Provencio, P. 2016. Constraints on a Late Cretaceous uplift, denudation, and incision of the Grand Canyon region, southwestern Colorado Plateau, USA, from U-Pb dating of lacustrine limestone. *Tectonics* **35**, 896–906.

Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick, D.A., Günther, D. & Enzweiler, J. 2011. Determination of Reference Values for NIST SRM 610-617 Glasses Following ISO Guidelines. *Geostandards and Geoanalytical Research* **35**, 397–429.

Lawson, M., Shenton, B.J., Stolper, D.A., Eiler, J.M., Rasbury, E.T., Becker, T.P., Phillips-Lander, C.M., Buono, A.S., Becker, S.P., Pottorf, R., Gray, G.G., Yurewicz, D. & Gournay, J. 2018. Deciphering the diagenetic history of the El Abra Formation of eastern Mexico using reordered clumped isotope temperatures and U-Pb dating. *GSA Bulletin* **130**, 617–629.

Nuriel, P., Weinberger, R., Kylander-Clark, A.R.C., Hacker, B.R. & Craddock, J.P. 2017. The onset of the Dead Sea transform based on calcite age-strain analyses. *Geology* **45**, 587–590.

Pagel, M., Bonifacie, M., Schneider, D.A., Gautheron, C., Brigaud, B., Calmels, D., Cros, A., Saint-Bezar, B., Landrein, P., Sutcliffe, C., Davis, D. & Chaduteau, C. 2018. Improving paleohydrological and diagenetic reconstructions in calcite veins and breccia of a sedimentary basin by combining Δ47 temperature, δ18Owater and U-Pb age. *Chemical Geology* **481**, 1–17.

Paton, C., Hellstrom, J., Paul, B., Woodhead, J. & Hergt, J. 2011. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry* **26**, 2508.

Roberts, N.M.W., Rasbury, E.T., Parrish, R.R., Smith, C.J., Horstwood, M.S.A. & Condon, D.J. 2017. A calcite reference material for LA-ICP-MS U-Pb geochronology: calcite RM for LA-ICP-MS U-Pb dating. *Geochemistry, Geophysics, Geosystems* **18**, 2807–2814.

Vermeesch, P. 2018. IsoplotR: A free and open toolbox for geochronology. *Geoscience Frontiers* **9**, 1479–1493.

Woodhead, J.D., Horstwood, M.S.A. & Cottle, J.M. 2016. Advances in Isotope Ratio Determination by LA–ICP–MS. *Elements* **12**, 317–322.