



# New analytical and data evaluation protocols to improve the reliability of U-Pb LA-ICP-MS carbonate dating

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#### Abstract

We document that the reliability of carbonate U-Pb dating by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is improved by matching the aspect ratio of the LA single hole drilling craters and propagating of long-term excess uncertainty and systematic uncertainties. We investigated the impact of different matrices and ablation crater geometries

- 10 using U-Pb isotope analyses of one primary (WC-1) and two secondary reference materials (RMs). Validation RMs (VRM) include a previously characterized (ASH-15D) and a new candidate (JT), characterized by ID-TIMS (intercept age: 13.797  $\pm$  0.031 Ma) with excellent agreement to pooled LA-ICP-MS measurements (13.81  $\pm$  0.11  $\pm$  0.30 Ma), U concentration of approx. 1 µg/g and <sup>238</sup>U/<sup>206</sup>Pb ratios from 5 to 460, well defining the isochron. Differences in ablation crater depth to diameter ratios (aspect ratio) introduce an offset due to downhole fractionation and/or matrix effects. This effect can be observed either when
- 15 the crater size between U-Pb RM and sample changes or when the ablation rate for the sample is different than for the RM. Observed deviations are up to 20% of the final intercept age depending on the degree of crater geometry mismatch. The long-term excess uncertainty was calculated to be in the range of 2% (ASH-15D) to 2.5% (JT), and we recommend propagating this uncertainty into the uncertainty of the final results. Additionally, a systematic offset to the ID-TIMS age of 2-3% was observed for ASH-15D but not for JT. This offset might be due to different ablation rates of ASH-15D compared to the primary RM or
- 20 remaining matrix effects, even when chosen aspect ratios are similar.

# **1** Introduction

Recent improvements in the sensitivity of ICP-MS instruments coupled to a laser ablation system allows not only to date very young zircons by the U-Pb method (Guillong et al., 2014), but also minerals with very low U concentrations, typically of several ppb to tens of ppm, and even lower concentrations of radiogenic Pb, such as carbonates (Li et al., 2014;Methner et al.,

25 2016;Roberts and Walker, 2016;Nuriel et al., 2017). Additionally, carbonates often incorporate variable amounts of initial (common) Pb during crystallisation from aqueous fluids, so that age determination relies on the use of regression lines (isochrons) in the Tera-Wasserburg isotopic space (<sup>207</sup>Pb/<sup>206</sup>Pb vs. <sup>238</sup>U/<sup>206</sup>Pb) (Li et al., 2014). Importantly, this also entails that there is no available carbonate reference material (RM) yielding a concordant U-Pb age. Therefore, accurate U-Pb dating of carbonates requires a two-step data reduction approach (Roberts et al., 2017) consisting of (1) <sup>207</sup>Pb/<sup>206</sup>Pb mass bias





- 30 correction based on a homogeneous reference material (typically glass); and (2) U/Pb inter-element fractionation correction based on the lower intercept in the Tera-Wasserburg concordia diagram using a matrix-matched RM. With this method, carbonates can be dated by LA-ICP-MS with the advantage of easy availability, high sample throughput, high spatial resolution allowing to resolve large differences in U-Pb ratio and cost effectiveness. Within a day, 300-600 single points can be analysed and a minimum number of 20-30 points per sample is suggested (Beaudoin et al., 2018;Godeau et al., 2018;Yokoyama et al., 2018), although the appropriate number is strongly sample-specific and depends on the variability of the initial to radiogenic
- Pb ratios. To maximize the variation of the initial to radiogenic Pb ratios and improve the isochrone, new approaches in the acquisition of data by imaging and data pooling were introduced and look promising (Drost et al., 2018). Previous studies of dating carbonates, mostly calcite, focused either directly on the analytical method development (Li et al., 2014;Roberts et al., 2017;Drost et al., 2018;Yokoyama et al., 2018) or a range of applications from dating fault activity to
- directly dating early-diagenetic cements in ammonites (Coogan et al., 2016;Methner et al., 2016;Burisch et al., 2017;Drake et al., 2017;Goodfellow et al., 2017;Nuriel et al., 2017;Hellwig et al., 2018;Walter et al., 2018;MacDonald et al., 2019;Scardia et al., 2019). Only recently, secondary RMs were routinely analysed (Beaudoin et al., 2018) with data reporting standards following more or less the community derived standards suggested for zircons (Horstwood et al., 2016). However, no actual data on the long term excess variance is given as not many secondary RMs are available and as the number of sessions including
- 45 these was limited (Beaudoin et al., 2018). In this work, we introduce a new secondary RM and aim at investigating the longterm excess variance of U-Pb LA-ICP-MS carbonate dates. In addition, we investigate potential matrix effects influencing the accuracy of such dates, which have been largely overlooked so far. In particular, we document that changes in laser crater aspect ratios between primary RMs and samples may result in significant inaccuracy of U-Pb LA-ICP-MS carbonate dates and propose new analytical strategies to minimize this effect.

# 50 1 Instrumentation, methods and samples

#### 1.1 LA-ICP-MS analyses

The LA-ICP-MS analyses were carried out at ETH Zürich, using a Resolution laser ablation system with a 193 nm excimer (ArF) laser source and a two-volume, Laurin Technic S-155 ablation cell. To investigate possible matrix effects and the influence of the ablation crater geometry, we used variable crater sizes and repetition rates of the laser producing laser ablation

55 craters with aspect ratios (crater depth / crater diameter) ranging from 0.08 to 1.3. Crater geometries (depth and diameter) were measured using a Keyence Digital Microscope VHX-6000.

The ablated aerosol was mixed in the ablation cell with carrier gas consisting of helium (0.5 L.min<sup>-1</sup>) and make-up gas consisting of argon (ca. 1 L.min<sup>-1</sup>) and nitrogen (2 mL min<sup>-1</sup>). The aerosol was then homogenized by a squid smoothing device and introduced in the plasma of the Thermo Element XR ICP-MS. This single collector sector field MS is equipped with a

60 high capacity (80 m<sup>3</sup> h<sup>-1</sup>) interface pump to achieve, in combination with jet sampler and normal H-skimmer cones, a detection efficiency in the range of 2% (based on U in a single spot ablation of NIST SRM612 glass). Detailed instrumentation and data





acquisition parameters are summarized in Table A1. A measurement session consists of several samples (20-50 points analyses each), matrix-matched primary RM (WC-1; n = 20-40), two validation RMs (ASH-15D (Mason et al., 2013;Vaks et al., 2013) and JT; n=15-30) and a homogenous glass RM (NIST614 or NIST 612; n = 10-20). RMs are distributed over the whole sequence to monitor and if necessary, to correct for instrumental drift.

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# 1.2 LA-ICP-MS data reduction

The data reduction methods follow largely the one described in Roberts et al. (Roberts et al., 2017) and are described here shortly focusing on differences and some observations. The raw data (time-resolved intensities) from the spectrometer are loaded into the Iolite v.2.5 data reduction software (Paton et al., 2011) and processed using the VisualAge data reduction scheme (Petrus and Kamber, 2012;Paton et al., 2010), to calculate gas blank corrected intensities, raw ratios, and their uncertainties. The integration intervals of both reference materials and samples are subsequently adjusted to optimize the spread along the isochron line. All further data reduction uses an in-house spreadsheet based on Microsoft Excel. The <sup>238</sup>U/<sup>206</sup>Pb ratio is drift corrected using the glass RM, e.g. NIST 614. Due to the low <sup>207</sup>Pb count rate on some of the samples and RMs, the <sup>207</sup>Pb/<sup>206</sup>Pb ratio is calculated as ratio of the mean count rate for each integration interval and not the mean of the ratios of

- 75 each replicate. The <sup>207</sup>Pb/<sup>206</sup>Pb ratio is corrected for mass bias using the mass bias factor determined from the homogenous glass RM. The drift-corrected <sup>238</sup>U/<sup>206</sup>Pb ratios and the mass bias-corrected <sup>207</sup>Pb/<sup>206</sup>Pb ratios of all analyses of the WC-1 calcite RM are subsequently plotted in a Tera-Wasserburg concordia diagram, using IsoplotR (Vermeesch, 2018). An isochron is calculated by linear regression through the resulting dataset and anchoring to the initial <sup>207</sup>Pb/<sup>206</sup>Pb of 0.85 (Roberts et al., 2017). The ratio between the lower intercept age obtained thereby and the reference age of 254.4 Ma (Roberts et al., 2017) is
- 80 used as the correction factor for the <sup>238</sup>U/<sup>206</sup>Pb ratio throughout the sequence. This correction factor would encompass matrix effects, including laser-induced (i.e. downhole) element fractionation, and ICP-related U/Pb inter-element fractionation, including mass bias.

#### 1.3 ID-TIMS

For the characterization of the candidate secondary RM JT we used isotope dilution thermal ionization mass spectrometry methods equivalent to those described in (Nuriel et al., in prep). Seven calcite chips of 1.3 to 3.7 mg were sampled from the JT calcite vein using a stainless-steel needle. Individual chips were loaded in 3 ml Savillex beakers and repeatedly cleaned in ultrapure acetone and water. Cleaned aliquots were spiked with 4-8 mg of the EARTHTIME <sup>202</sup>Pb-<sup>205</sup>Pb-<sup>233</sup>U-<sup>235</sup>U tracer solution and dissolved in 6N HCl at 120°C for 30 minutes. Dissolved samples were dried down and re-dissolved in 1N HBr for anion exchange chromatography. U and Pb were separated using a HBr-HCl based anion exchange chemistry employing

90 AG1-X8 resin in 50 μl Teflon columns. The U and Pb fractions were collected separately in 7 ml Savillex beakers and dried down with a drop of 0.02 M H<sub>3</sub>PO<sub>4</sub>. U and Pb were loaded on outgassed Re filaments with a Si-Gel ion emitter for thermal ionization mass spectrometry and analyses were performed using a Thermo TRITON plus instrument at ETH Zürich. Pb isotope ratios were measured on the axial secondary electron multiplier and U was measured as UO<sub>2</sub> employing a static routine





with Faraday cups connected to amplifiers with 10<sup>13</sup> ohm resistors(Wotzlaw et al., 2017). Data reduction and uncertainty
 propagation was done using Tripoli, an excel-based spreadsheet that employs algorithms of (Schmitz and Schoene, 2007) and
 isochron calculations were performed using IsoplotR (Vermeesch, 2018). U-Pb data were not corrected for <sup>234</sup>U and <sup>230</sup>Th
 disequilibria. Uncertainties are reported at the 95% confidence level without systematic uncertainties associated with tracer
 calibration and decay constants unless otherwise indicated.

# 1.4 New validation reference material JT

100 JT is a sparry vein calcite that originates from a deep borehole within the Molasse Basin of Northern Switzerland and is hosted by a micritic limestone of the Middle Triassic Muschelkalk group. JT is part of a dense network of calcite veins located in the footwall of a secondary thrust fault of the basal décollement of the thrusted Alpine foreland and Jura fold-and-thrust belt. It is one of the samples ("K") which were used to date the decoupling of the Swiss Molasse basin from its basement and the formation of the thin-skinned Jura fold-and-thrust belt (Looser et al., in prep).

#### 105 2 Results and discussion

All LA-ICP-MS and ID-TIMS data can be found in the supplementary information Table S1(LA-ICP-MS) and S2 (ID-TIMS).

#### 2.1 Characterisation of JT as a validation reference material

We characterized the vein calcite JT both by ID-TIMS and LA-ICPMS (all data provided in the supplementary file). The ID-TIMS analyses yielded an isochron, lower intercept age of 13.797  $\pm$  0.031 Ma (n=6, 1 outlier excluded; MSWD=3.6), and a (<sup>207</sup>Pb/<sup>206</sup>Pb)<sub>0</sub> of 0.8394  $\pm$  0.0025 (Fig. 1a). Both the intercept age of pooled LA-ICP-MS data from n sequences with a total of 474 single point analyses (13.75  $\pm$  0.11 Ma respectively 13.75  $\pm$  0.36 Ma including  $\epsilon$ `, MSWD of 2.0 and a (<sup>207</sup>Pb/<sup>206</sup>Pb)<sub>0</sub> of 0.8473  $\pm$  0.008, as shown in Fig. 1b) and the mean of the intercept ages from n sequences (13.695  $\pm$  0.157 Ma, respectively 13.70  $\pm$  0.37 Ma including  $\epsilon$ `, n=16, Fig. 2a) agree well with the ID-TIMS intercept age. U concentrations of JT vary between ~0.1 and ~4 µg/g with a mean of ~1 µg/g and the <sup>238</sup>U/<sup>206</sup>Pb ratio varies between ~5 and ~460 (Fig. 1b).





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Figure 1: Tera-Wasserburg concordia plot of JT analyses by (a) ID-TIMS (n=6) and (b) LA-ICP-MS (n=474).

#### 2.2 Long-term excess variance

- The validation RMs JT and ASH-15D were analysed 16 and 30 times in 9 and 16 sessionsrespectively, sometimes with 120 different laser parameters, each yielding an intercept age with uncertainty. Fig. 2 shows the sorted intercept ages with 120 uncertainties both without (white) propagation of the long-term (inter sessions) excess variance (ε`) and with propagation (green). The MSWD of the original data sets are 1.57 for JT and 1.26 for ASH-15D. Assuming ideal behaviour of these validation RMs (homogeneous age, cogenetic character of all analysed domains and closed system behaviour) a MSWD of ~1 is expected. To obtain an MSWD of ~1, a long term (inter sessions) excess variance (ε`) of 2.5 % (JT) and 2.0 % (ASH-15D)
- 125 needs to be propagated by quadratic addition to the intercept uncertainty of the individual sequences (Fig. 2). For this calculation, only VRM measurements with similar aspect ratio as the primary RM were considered. This excess variance is slightly larger than for zircons (Horstwood et al., 2016), probably reflecting the difference in age calculation, greater heterogeneity and matrix differences.







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Figure 2: Sorted intercept ages for JT (a: white) of n=16 with an MSWD of 1.57 and ASH-15D (b: white) of n=30 with an MSWD of 1.26 for the estimation of the long-term excess variance ( $\epsilon$ ) to be propagated and the same data including  $\epsilon$  (green). Also presented is the superpopulation mean, mean with  $\epsilon$  and reference age from ID-TIMS. Uncertainties are 95% confidence levels with overdispersion (white) respectively 95% confidence levels with overdispersion and excess long-term variance (green).

# 135 **2.3 Influence of the ablation crater aspect ratio on data accuracy**

#### 2.3.1 Results on tests based on WC-1, JT and ASH-15D

During 15 sequences of carbonate dating, we have measured the validation RM with different crater sizes and repetition rates, matching the need of sufficient signal on the samples with generally low U contents. We varied the crater diameter and repetition rate from 110  $\mu$ m and 5 Hz for the primary RM WC-1 up to 250  $\mu$ m and 5-10 Hz for validation RM and samples.

- 140 We observe that analyses performed with larger diameter ablation craters show a systematic offset towards higher <sup>238</sup>U/<sup>206</sup>Pb ratios, corresponding to younger isochron intercept ages. This suggests an influence of the crater geometry on the offset between measured and real values, which is problematic when the unknowns and primary RM are measured with different crater sizes and/or repetition rates, as sometimes done in carbonate U-Pb dating by LA-ICP-MS.
- Therefore, we further measured a single sequence (190130) analysing WC-1 not only as primary RM with the standard parameters of 110 µm ablation crater diameter and 5 Hz repetition rate, but also with 163 µm, 3 Hz; 110 µm, 10 Hz, 74 µm, 10 Hz and 51 µm 15 Hz, to systematically investigate the influence of ablation crater aspect ratio. These parameters result in extreme difference of crater aspect ratios (crater depth / crater diameter) between ~0.08 (flat crater, 163 µm, 3 Hz) and ~1.3 (deep crater, 51 µm, 15 Hz). The U-Pb isotopic data, corrected only for <sup>207</sup>Pb/<sup>206</sup>Pb mass bias, yield intercept ages between 226 Ma (flat crater) and 267 Ma (deep crater) as shown in Fig. 3 and Fig. A1. Plotting the aspect ratio miss match (armm,
- aspect ratio of the sample / aspect ratio of the primary RM) vs. the age offset relative to the accepted age, a linear correlation is given not only for WC-1 (Fig. 4a) but also for the validation RM JT (Fig. 4b) and ASH-15D (Fig. 4c).







Figure 3: Tera-Wasserburg concordia plot of WC-1 analyses, corrected only for <sup>207</sup>Pb/<sup>206</sup>Pb mass bias, ablated with different ablation crater aspect ratios. The deeper the crater the older the age. Intercept ages are: ~ 270, 246, 239, 234, 228 Ma. Ellipses are 95% confidence level. Individual plots including regression and intercept statistics are shown in Fig. A1.







160 Figure 4: Linear correlation between aspect ratio offset (aspect ratio of the sample / aspect ratio of the primary RM) and intercept age. (a): WC-1 where the coloured rectangles represent the cross section of the crater (not to scale). (b): JT validation RM including the ID-TIMS reference age. (c) ASH-15D validation RM including the ID-TIMS reference (Nuriel et al., in prep) age Error bars are 95% confidence including overdispersion.





### 2.3.2 Variable ablation efficiency for different carbonates

- 165 Due to the observed age offset depending on the LA crater geometry (Fig. 4), the ablation rate between RM and unknown sample must be very similar when using identical laser parameters (energy density, crater size and repetition rate) to get the same ablation crater aspect ratio. As the ablation efficiency of an unknown sample is not known prior to ablation, we measured ablation rates of various carbonates with differences in mineralogy (calcite, dolomite, aragonite), crystal size (micritic, sparry), and purity (turbid, clear), relative to the ablation rate of WC-1 (ablation rate of ~120 nm per laser pulse at energy density of 2
- 170 J cm<sup>-2</sup>) as shown in figure 5, to estimate the ablation rate of a "unknown" carbonate. Regardless of their occurrence (i.e. sparry, micritic, etc.), calcite matrices show ablation rates that vary within <14% relative to WC-1. In turn, the corresponding armm if WC-1 is used as primary RM would result in an offset of the lower intercept date of 1% or less (Fig. 4), which is identical or smaller to the minimum uncertainty on such dates based on our assessment of the excess variance. By contrast, dolomite shows higher ablation efficiencies than calcite and much larger variations, from 105 to 160% relative to WC-1 (Fig. 5). The</p>
- 175 only aragonite sample tested in this compilation had an even faster ablation rate than dolomite and almost twice as fast as WC-1 (Fig. 5). These differences in ablation rates would result in significant age offsets of 4-8 % for dolomite (160 % ablation rate compared to WC-1, calculated based on the linear regressions as shown in figures 4a-d) and 6-11 % for aragonite (200 % ablation rate of WC-1). In addition, the large spread for dolomite and the small number of tested aragonite makes the estimation of the ablation rate unpredictable for these matrices. These results highlight that matrix-matched standardization is required
- 180 for accurate LA-ICPMS U-Pb geochronology of different carbonates and dolomite/aragonite dates obtained using WC-1 calcite as primary RM are prone to systematic errors.



Figure 5: Ablation rate variation relative to WC-1 for different calcite, dolomite and an aragonite sample.





#### 2.3.3 Strategies for matching aspect ratios

- The results showed in Figure 4 suggest that carbonate U-Pb dating by LA-ICP-MS is only accurate when the laser ablation 185 crater aspect ratio is similar between RM and unknown sample. If the crater geometry varies, an artificial and significant age offset can be introduced (>10% relative in extreme cases; Fig. 4). This can be a problem because U contents in carbonates vary by orders of magnitude so that it is not ideal to use one single crater size and repetition rate for all unknowns and RMs. We suggest therefore a two-step strategy to account for this issue: (1) estimating the U content of all unknowns to be dated in a
- 190 specific sequence, via a short, pre-sequence test run; and (2) apply a crater diameter to each unknown, inversely proportional to its U content, and adjust the repetition rate as to match the aspect ratio of the craters in the primary RM. Based on this suggestion, it is possible to use larger spot sizes for lower-U samples than used for the RM to improve the counting and precision, as long as the repetition rate is increased accordingly.

It is possible to measure the crater depth and aspect ratios of the analysed samples and RMs post ablation and if necessary,

- 195 apply a correction (based on the linear relationship between aspect ratio miss-match and age offset as shown in Fig. 4) to improve accuracy, especially when dealing with different carbonate minerals. However, this correction will have to be based on measurements with different aspect ratios for both primary and secondary RM ideally within the same session, as it seems likely that both the ablation rate and age offsets are dependent on the actual laser ablation and ICP-MS parameters. A detailed study on how to best apply this correction if necessary is beyond the scope of this work, and we suggest for a more robust data 200 reduction to always use similar aspect ratios.

#### 2.4<sup>207</sup>Pb/<sup>206</sup>Pb correction

NIST 614 has been proposed as RM for the mass bias correction of the <sup>207</sup>Pb/<sup>206</sup>Pb ratio (Roberts et al., 2017) due to the similar Pb concentration to many carbonates. We investigated several homogeneous and well characterized glass RMs (NIST 610, NIST 612, NIST 614, GSD-1G and KL2G) on two different days to be used for this correction and we found no significant

205 influence from different LA parameters, notably ablation crater diameter, and Pb concentration of the RM (Fig.6). Only the smallest spot size of 13 microns on the highest Pb concentration glass (NIST 610) produced a small offset (within uncertainty) compared to the other glasses.







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Figure 6: Correction factor of the <sup>207</sup>Pb/<sup>206</sup>Pb ratio based on different RM glasses and crater size show no variation. Error bars are 2 SE.

#### 2.5 WC-1 heterogeneity

To investigate the homogeneity of our aliquot of WC-1, in one sequence (190405) we specifically targeted the brighter, vein-215 like, sparry zone, in addition to the normal sampling strategy aiming at the darker, more homogeneous material as shown in figure 7. While the darker zones yielded the usual results, the brighter zone in comparison exhibited more initial Pb or had lost some U and yielded significantly younger ages. The analyses show a larger scatter and no well-defined isochrone can be fitted to the data, possibly due to mixing between the two materials. This finding demonstrates that WC-1 is not single-phased and heterogeneous in age. Accordingly, the locations for analysis have to be chosen carefully and the data has to be screened for

220 outliers to avoid additional scatter and a bias towards younger ages of the RM, finally resulting in older ages for the unknown samples.







Figure 7: Tera-Wasserburg concordia plot of WC-1 analyses in two different regions of the sample as indicated in the inserted image. The darker part (green) gives good results while the brighter vain like part (red) gives more scatter and younger ages.

#### 225 3 Summary and conclusion

We report LA-ICP-MS U-Pb data for previously and newly characterised calcite reference materials. We introduce the JT vein calcite as a potential validation RM due to its homogeneity and very good spread in relative radiogenic to initial Pb contents. The ID-TIMS U-Pb data for JT yielded an isochron intercept date of  $13.797 \pm 0.031$  Ma, consistent with a LA-ICP-MS isochron intercept date of  $13.81 \pm 0.30$  Ma (relative to WC-1).

230 Repeated LA-ICP-MS analyses of this new validation RM and the existing calcite RM ASH-15D over an extended time period show that excess variance of 2 - 2.5% should be propagated in the obtained, individual lower intercept dates. This estimate of the long term excess variance is larger than for other LA-ICP-MS geochronological methods such as U-Pb in zircon U-Pb (Horstwood et al., 2016).

We also document that a mismatch in the ablation crater aspect ratio between the primary RM and unknowns result in

235 significant age offsets. This offset can be minimized by matching ablation crater geometry by using the same diameter and repetition rate for standards and unknowns. This may not always be possible, especially if the U content is significantly different in unknowns compared to the reference material, in which case the ablation crater aspect ratio of the primary RM can be matched by increasing laser repetition rate with increasing crater diameter on unknowns. While the correction of the U/Pb



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ratio is very sensitive to laser ablation parameters, the <sup>207</sup>Pb/<sup>206</sup>Pb correction is very insensitive and it is possible to use almost any well-characterized material with well characterized Pb isotopic composition.

The offset of 2-3% (usually within the uncertainty) of LA-ICP-MS results for ASH-15D compared to ID-TIMS results remains, while the results for JT are in very good agreement. This offset cannot be explained completely by differences in ablation rate and may be an additional matrix effect to be investigated in detail in future work.

Furthermore, we show differences in ablation rate between different types of calcites (<14 % relative to WC-1) and, overall,</li>
different carbonate minerals (up to + 60% for dolomite and up to + 90% for aragonite, relative to WC-1). While the expected age offset on calcite is negligible, this introduces additional systematic errors when using non-matrix matched standardization, i.e. using WC-1 calcite as primary RM to date dolomite or aragonite. The latter observation calls for characterization of further carbonate standards including various calcites, dolomites and aragonites. This will significantly increase the accuracy and possible applications of carbonate U-Pb geochronology by LA-ICPMS.

#### 250 4 Data availability

All data used in this manuscript is available from the supplementary files.

#### 5 Sample availability

Sample JT is available on request in limited quantities from the author: guillong@erdw.ethz.ch.

#### **6** Appendices

255 Table A1 : LA-ICP-MS parameters





LA-ICP-MS U-(Th-)Pb Metadata	
Laboratory and Sample Preparation	
Laboratory name	Dept of Earth Sciences, ETH Zurich
Sample type/mineral	Carbonates, mostly calcite
Sample preparation	thin sections or chips mounted in epoxy
Imaging	CL8200 Mk5-2 Optical Cathodoluminescence System
Laser ablation system	
Make, Model and type	ASI (Resonetics) Resolution S155
Ablation cell and volume	Laurin Technic, 2 volume cell, effective volume <i>ca</i> . 1 cm <sup>3</sup>
Laser wavelength (nm)	193 nm
Pulse width (ns)	25 ns
Fluence (J cm <sup>-2</sup> )	~1.8 J cm <sup>-2</sup>
Repetition rate (Hz)	variable, see data for actual value
Ablation duration (s)	40 s
Ablation pit depth /	Variable, equivalent to 0.09-0.15 µm/pulse
ablation rate	unstable one dete for extral relief
Spot diameter (µm)	variable, see data for actual value
nominal/actual	Statis spat ablation
Sampling mode / pattern	Static spot abiation
	100% He in the cell, Ar make-up gas combined in cell above ablation in runnel.
Cell carrier gas flow (I min *)	U.S I MIN
ICP-MS Instrument	Therman Flowmant VD Caster Reddicade . U. 100 Mcc. 2011 11 1
Make, Model and type	Thermo Element XR, Sector-field single collector ICP-MS, with high capacity interface pump
Sample introduction	Ablated aerosole direct
RF power (W)	1350 W - 1550W (optimized daily)
Make-up gas flow	0.90 - 1.05 l min <sup>-1</sup> Ar (optimized daily) 2 ml min <sup>-1</sup> N <sub>2</sub>
Detection system	triple (pulse counting, analog, Faraday) cross calibrated daily with U 238, fixed ACE value, all isotopes usually in pulse counting only (<5Mcps)
Masses measured (amu)	202, 204, 206, 207, 208, 232, 235, 238
Integration time per	11 ms (all masses) except: 206, 207 (50ms)
peak/dwell times (ms)	
Total integration time per	0.174 s
output data point (s)	
Sensitvity / Efficiency (%,	~1%U
element)	
Dead time (ns)	25
Typical oxide rate (ThO/Th)	0.18%
Typical doubly charged rate	3.50%
(Ba <sup>++</sup> /Ba <sup>+</sup> )	
Data Processing	
Gas blank	20 s
Calibration strategy	NIST614 glass standard as primary reference material for drift and Pb-Pb ratios; WC-1 carbonate standard for matrix matching of 206Pb/238U; ASH-15-D and JT carbonate for QC
Reference Material info	NIST614 (concentration data Jochum et al. 2011, Pb isotopes Baker et al. 2004); WC-1 (Roberts et al. 2017); ASH-15-D (Nuriel et al. 2020); JT (characterized in this work)
Data processing package	Iolite 2.5, VisualAge for integration, interval selection, and gas blank correction
used	only. In-house spreadsheet data processing. IsoplotR (Vermeesch 2018) for
	isochrons, intercept ages, and initial Pb compositions
Correction for LIEF	No LIEF correction (ratio of mean intensities 207Pb/206Pb, respectively mean of
	uncorrected ratios <sup>238</sup> U/ <sup>206</sup> Pb used)
Mass discrimination	normalised to reference material (sample standard backeting)
Common-Pb correction,	None applied. Ages calculated from regressions in TeraWasserburg concordia
composition and	plots.
uncertainty	
Uncertainty level and	Intercept ages are quoted at 2s absolute, propagation is by quadratic addition.
propagation	Counting statistics uncertainty are propagated to the 207Pb/206Pb ration,
	together with the uncerainty of the RM value and the uncertainty of repeted
	measurements. The uncertainty value for lower intercept isochron ages
	includes uncertainties from the RM, and asystematic uncertainties, estimated
Overlite energies 1 (27, 15, 1, 15, 15, 15, 15, 15, 15, 15, 15,	In this work to be 2.5%. Decay constant uncertainties are neglected.
Quality control / Validation	ASH 15D: mean of <sup>200</sup> Pb/ <sup>200</sup> U intercept ages: 2.885 ± 0.076 Ma (2s, MSWD =
	0.99, n = 30) (0.9 % Wtd ave uncert. (internal), 2.0% total external uncert.)
	JT - mean of <sup>200</sup> Pb/ <sup>230</sup> U intercept ages: 13.70 ± 0.37 Ma (2s, MSWD = 1.03, n =
	16) (1.15 % Wtd ave uncert. (internal), 2.5% total external uncert.)
	Systematic uncertainty for propagation is 2.5% (2s).

This reporting is based on a template available for download on www.Plasmage.org







Figure A1: Intercept statistics of Fig. 2. WC-1 analysed with different aspect ratios.

#### 7 Supplement link 260

#### 8 Author contribution

Marcel Guillong adapted the LA-ICP-MS methodology and data reduction, designed the LA experiments, carried out most measurements, wrote the manuscript with input from all co-authors. Jörn-Frederik Wotzlaw did the ID-TIMS measurements of JT. Nathan Looser provided the RM JT, prepared the samples, did some LA-ICP-MS and most of the ablation rate measurements. Oscar Laurent did some LA-ICP-MS measurements and was involved in the adaption of the methodology, data

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reduction process and quality control.





#### 9 Special issue statement

#### 10 Acknowledgement

Prof. Olivier Bachman and Prof. Stefano M. Bernasconi are acknowledged supporting this work. P. Nuriel is acknowledged

270 for RM ASH-15D, Nick Roberts is acknowledged for RM WC-1.

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