Exploring the advantages and limitations of *in situ* U-Pb carbonate geochronology using speleothems

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Abstract

The recent development of methods for *in situ* U-Pb age determination in carbonates has found widespread application but the benefits and limitations of the method over bulk analysis (isotope dilution - ID) approaches have yet to be fully explored.

10   Here we use speleothems – cave carbonates such as stalagmites and flowstones - to investigate the utility of *in situ* dating methodologies for 'challenging' matrices with typically low U and Pb contents, and predominantly late Cenozoic ages. Using samples for which ID data have already been published, we show that accurate ages can be obtained for many speleothem types by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA- ICPMS). Consideration of our own and literature data suggests that most carbonates with >1ppm Uranium and a few hundred ppb of Pb should be good

15   targets for *in situ* methodologies, regardless of age. *In situ* analysis often provides a larger spread in U/Pb ratios which can be advantageous for isochron construction but isochron ages rarely achieve the ultimate precision of ID analyses conducted on the same samples. LA analysis is faster than ID and thus will play a significant role in reconnaissance studies. The major advantage of the *in situ* methodology appears to be the potential for successful dating outcomes in sample types requiring high spatial resolution analysis.

20   **1 Introduction**

The U-Pb decay scheme has played a key role in the chronology of carbonate rocks for more than three decades (e.g., Moorbath et al., 1987, Jahn and Cuvellier, 1994, Rasbury and Cole, 2009) utilizing predominantly ID (i.e. bulk sample) methods. Recent years, however, have seen a revolution in the field with the emergence of *in situ* analysis techniques employing LA-ICPMS offering the prospect of direct determination of U-Pb ages on the scale of a few hundred microns.

25   Although still in its infancy, this method has already been applied to the chronology of marine cements (Li et al., 2014), vein calcites associated with faulting (Roberts and Walker, 2016; Hansman et al., 2018; Parrish et al., 2018), and the alteration of oceanic crust (Coogan et al., 2016).

To date, a thorough exploration of the utility of *in situ* techniques to speleothem (secondary cave calcite such as stalagmites and flowstones) research has not been conducted although U-Pb dating of speleothems is widely used in studies

30 of climate change (e.g. Vaks et al., 2013; Sniderman et al., 2016), human evolution and migration (e.g., Walker et al., 2006; Pickering et al. 2011, 2019), bio-diversity and ecosystem change (e.g. Woodhead et al., 2016), and tectonics and landscape evolution (e.g. Lundberg, 2000; Polyak et al., 2008; Meyer et al., 2011; Woodhead, 2019). Speleothems offer a variety of unique analytical challenges for *in situ* analysis - not least because of their highly variable and often very low levels of radiogenic Pb, but also the fact that most samples of interest are also relatively young - predominantly Neogene or early

35 Quaternary. As such they actually form a useful test of the limitations of the *in situ* carbonate dating methodology more generally. Here we explore the utility of *LA-ICPMS* techniques as applied to speleothems not only to highlight important new research avenues but also to explore both the benefits and limitations of the method.

We first compare LA-ICPMS (hence forth 'LA') ages for a variety of speleothem samples for which bulk, solution multi-collector-ICPMS, ID U-Pb age data have already been published as a benchmark against which to judge the reliability of our

40 *in situ* analyses. We then explore the advantages and limitations of LA-methodologies in this context and make recommendations for the optimal use of both technologies.

2 Materials and Methods

2.1 Overview

Samples for analysis were prepared either as polished slabs or Epofix™ resin mounts. While a polished surface is not an

45 essential prerequisite for LA studies it significantly enhances the ability to view the sample clearly with the reflected light microscopes widely employed in LA systems. Mounts were cleaned in ultra-pure water in an ultrasonic bath, and dried under nitrogen prior to loading into the sample cell.

We used the 'freeform' sample holder available in the S155 large-format ablation cell of an Australian Scientific Instruments (now Applied Spectra) RESOlution-LR ablation system, based around a Lambda Physik Compex 110 excimer

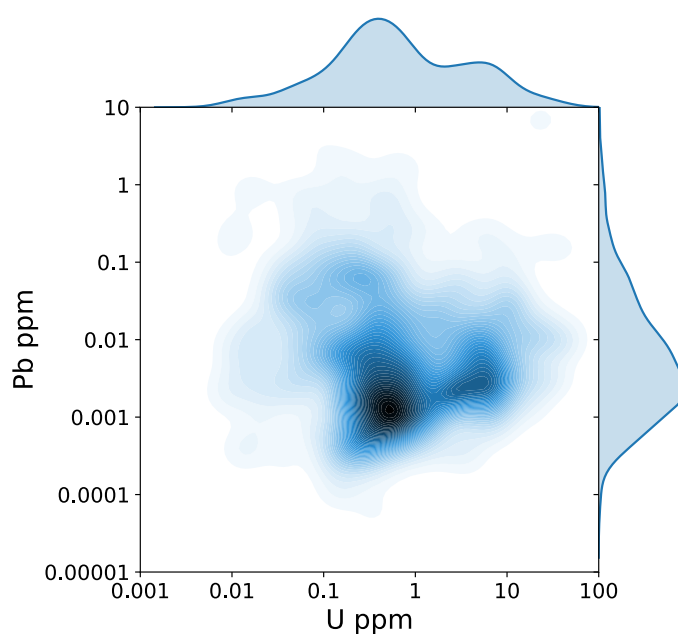
50 laser, operating at 193nm wavelength, and coupled to a Nu Instruments Attom-ES high resolution magnetic sector ICPMS.

Laser fluence was typically adjusted to ~2-3 Jcm^{-2} and we used a laser repetition rate of 5Hz, allowing the potential for depth resolution if required (see below). Analyses were conducted with either a 154μm or 228μm spot; we aimed to achieve maximum ^{207}Pb counts, without taking ^{238}U into attenuated mode (the first attenuation mode trip on our instrument was set to 3 million cps for this study). A brief pre-ablation using a larger spot size was conducted prior to every analysis. 30 seconds

55 of baseline measurement were followed by 40 seconds acquisition during each spot ablation. The masses measured and dwell times used are documented in Table 1, together with other instrumental parameters. Laser gas flows and instrument settings were optimised primarily for highest sensitivity: for a 40μm spot under these conditions on a NIST glass we see around 25-35,000 cps/ppm. Although oxide levels are generally low (^{248}ThO/^{232}Th<<1), and Th/U ratios close to unity, we have observed no relationship between variation in these parameters and data quality, and do not tune to optimize these

60 values. Table 2 lists the samples used in these experiments and the publications in which original ID data for these materials can be found.

2.2 Analytical Strategies

Natural speleothems display a remarkably wide range of U and Pb concentrations – Fig.1 shows data generated for over 2000 speleothem calcite aliquots analysed at the University of Melbourne by ID methods over a 10-year period following
65   rigorous sample cleaning protocols to remove Pb contaminants derived from initial processing (e.g. Woodhead et al., 2012). The majority of samples contain ~0.1-10 ppm U and generally very low Pb concentrations, typically ~1-100 ppb. These traits provide very challenging conditions for LA analysis.

70   **Figure 1: Speleothem U and Pb concentrations.** 2D Kernel density plot of U and Pb concentration data obtained by ID methods in our laboratory over the past decade, representing over 2000 sample aliquots. All samples were leached briefly in dilute HCl prior to dissolution to remove any blank Pb that may have been introduced during sample handling (e.g. Woodhead et al., 2012). The small hotspot to the right of the main array is dominated by the Corchia site in Italy, from which we have analysed many samples. The vast majority of other speleothems, however, have 0.1-1 ppm U and ~1ppb Pb.

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      The primary concern for any samples of this type, and particularly when measuring by LA, is the obvious potential for contamination with environmental ('blank') Pb during analysis. Although LA rastering and extraction of age information from the resulting isotopic images has shown great promise for dating limestones with relatively high Pb abundances (Drost
80   et al., 2018), the same approach cannot be easily implemented in speleothems where Pb contents are often in the low ppb

range and thus where each spot analysis may be measuring total Pb amounts in the low femtogram range. For this reason, in this study, we have used spot analyses and perform a clean pre-ablation with a larger spot size before analysis. In addition, we also discard the first few seconds (and often more – see below) of each analysis to avoid any remaining blank Pb contaminants.

85   A variety of different calibration strategies for *in situ* carbonate U-Pb analysis are currently in use. The major problem facing analysts is that, to date, no suitable, homogeneous carbonate reference material has been identified. Most studies therefore use the heterogeneous, but well-characterised calcite WC-1 (Roberts et al., 2017) and employ a variety of strategies in order to compensate for its heterogeneous nature. For example, Roberts & Walker (2016) use a NIST glass to correct for any bias in $^{207}Pb/^{206}Pb$ ratios and then take a session mean of values for the WC-1 reference material to correct the $^{238}U/^{206}Pb$

90   ratio of unknowns. They do not perform any downhole fractionation corrections but simply use means of each ablation. Conversely, Hansman et al. (2018) use the NIST glass for correction to both the $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$ ratios and then apply external correction factors to account for matrix-induced variation in U/Pb ratio between NIST and calcite and downhole fractionation effects.

Although we have confirmed that there are no observable matrix effects on the $^{207}Pb/^{206}Pb$ ratio when ablating NIST 614

95   glass relative to calcite, we see no immediate advantage in using a NIST glass in this way and therefore simply use the WC-1 reference material as the primary calibrant. The VizualAge UcomPbine data reduction scheme (DRS; Chew et al., 2014) for iolite (a popular ICPMS data processing software package; Paton et al., 2011) is designed to allow the use of heterogeneous reference materials (ie. those with variable amounts of common Pb) such as WC-1 but assumes no $^{207}Pb/^{206}Pb$ fractionation. The time-resolved reference material data from a single spot analysis exhibit shifts in $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron ('Tera-

100   Wasserburg': Tera and Wasserburg, 1972) space primarily from encountering variable common Pb and/or experiencing downhole Pb/U fractionation. UcomPbine corrects each time-slice of background subtracted data for the reference material based on its known common and radiogenic Pb compositions using a ^{204}Pb-, ^{207}Pb-, or ^{208}Pb-based approach. This allows the time-resolved radiogenic Pb/U signals to be combined with the ablation depth (or a proxy, such as time since laser on) to correct for downhole Pb/U fractionation as described by Paton et al. (2010). Drift correction is carried out as usual in iolite

105   by fitting a function (in this case a smoothing spline) to the reference material analyses that bracket unknowns. For this study, the ^{207}Pb-based correction of UcomPbine was employed. Note that the data presented here include only the internal uncertainty for each measurement. The propagated error of Pb/U ratios can be calculated by UcomPbine using the 'pseudo-secondary' approach iolite uses for its built in U-Pb geochronology DRS (i.e. Paton et al., 2010), but UcomPbine's ^{207}Pb-based correction precludes calculating excess error on $^{207}Pb/^{206}Pb$ this way. We typically find propagated Pb/U errors 1.25

110   times the internal error and expect that this factor would be smaller for $^{207}Pb/^{206}Pb$. To properly assess the $^{207}Pb/^{206}Pb$ excess error, a true secondary reference material could be employed. The long-term reproducibility of this methodology is still being evaluated.

We prefer to correct for any downhole elemental fractionation effects, which will be exacerbated with smaller spot sizes. Provision of a downhole correction capacity conveys an important advantage for this type of work in so much as it allows

115   selection of only the most advantageous areas in a single spot ablation for use, knowing that an appropriate correction for downhole effects has been made at each point in the ablation profile: in other words, the downhole correction allows depth resolution within each individual analysis. This can be a significant benefit in avoiding areas with spurious common Pb content which are invariably encountered in the analysis of most carbonates (Fig.2) or, alternatively, maximizing data spread in Tera-Wasserburg space. In addition, this methodology allows us to maximise the use of 'good' data e.g. by trimming only

120   those analyses required at the start of a run to remove surface contamination rather than employing a blanket crop of several seconds for every spot analysis. Although the downhole correction profile obtained by iolite from multiple analyses of a heterogeneous reference material is not as robust as that which might be obtained from a homogeneous standard, in practice the large numbers of standard analyses included in any given run (at least 16 for propagation of excess uncertainty) usually produce well-characterised downhole U/Pb profiles when using the UcomPbine DRS.

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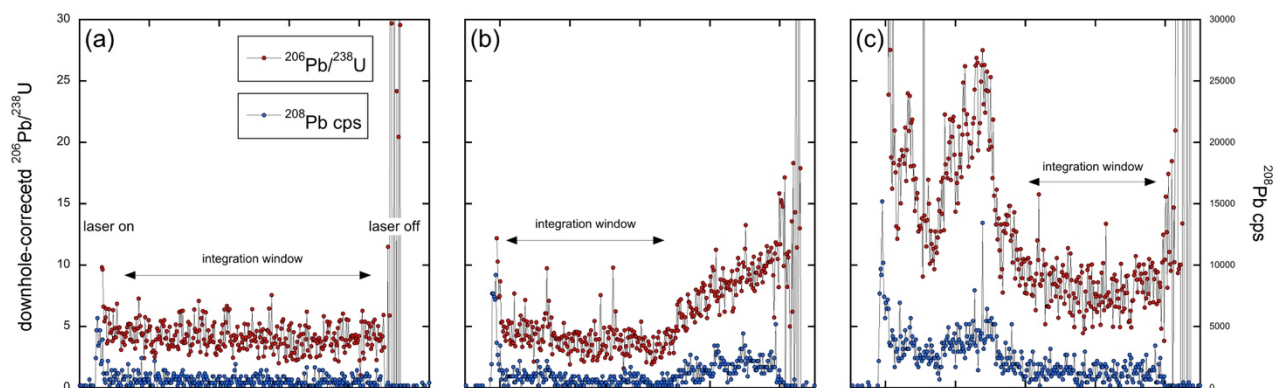


Figure 2: The importance of downhole correction. Panels (a) – (c) show examples of the complex compositional behaviour seen in many carbonates - these are all single ablations of the same sample. In panel (a) a relatively simple structure is observed and, with the

130   exception of a small amount of (surface-contamination) common Pb at the start of the analysis, almost all of the data collected can be used. Panel (b) shows a grain with more complex structure and a zone of intrinsic common Pb (high $^{206}Pb/^{238}U$ and ^{208}Pb cps) encountered towards the end of the ablation while in (c) more common Pb is seen in the first half of the ablation. In complex cases such as these the analyst can focus on the most radiogenic parts of the analysis, as indicated, as long as the data are downhole corrected.

135   **3 Results and Discussion**

3.1. The accuracy of the method

In order to assess the accuracy of the method for relatively low concentration samples we have analysed a number of speleothems for which we have already produced and published ages by solution ID methods (Table.2); these display a wide

range of radiogenic:common Pb ratios but, in all cases, have U in the low ppm range and Pb in the low ppb range, typical of
140   many speleothems. In all of these cases the ID data were obtained using a ^{233}U-^{205}Pb isotopic tracer calibrated against EarthTime (http://www.earth-time.org) reference solutions, and accuracy was constantly monitored by reference to EarthTime synthetic zircon solutions run concurrently. The new LA data, together with the pre-existing ID data for the same speleothem sample, are presented in the familiar ^{238}U/^{206}Pb-^{207}Pb/^{206}Pb isochron 'Tera Wasserburg' construction – see Fig.3.

     It is immediately clear that the LA and ID generated data are of quite different character – laser data have inherently large
145   uncertainties resulting from the minute quantities of material being analysed and also show little, if any, error correlation. MSWD values are in the range of 2-4. In contrast ID data have far smaller individual uncertainties and usually show a high degree of error correlation which is common to many unradiogenic samples plotted in such diagrams. Because of the larger uncertainties shown by the LA data, many more analyses are required in order to constrain an isochron – a feature explored in later discussion.

150   In all cases shown in Figure 3 the LA-derived ages fall within uncertainty of the ID-derived data. In addition, for many samples, the LA data show a wider range in U/Pb ratios than the ID data although not consistently more or less radiogenic. There also appear to be subtle difference in slope of the isochrons resulting from the two methods: the LA data often (but not always) seem to have a steeper slope and the common-Pb intercepts are not always within uncertainty of each other. We have explored many explanations for this apparent isochron 'rotation', including potential inaccuracies in the assumed
155   common Pb and radiogenic Pb end members for WC-1 and inaccuracies in calculated deadtime used on our instrument but find no consistent theme in these studies. We currently believe that this effect is likely attributable to a minute (femtogram) blank contribution from the surface of some samples which is not captured in the baseline (gas blank) measurement and thus cannot be adequately corrected for nor indeed readily measured.

     It is also clear from these experiments that the LA generated isochrons rarely attain the high precision of ID datasets
160   although in some cases they certainly approach those values. As such ID generated data can still be considered the benchmark for high precision speleothem applications.

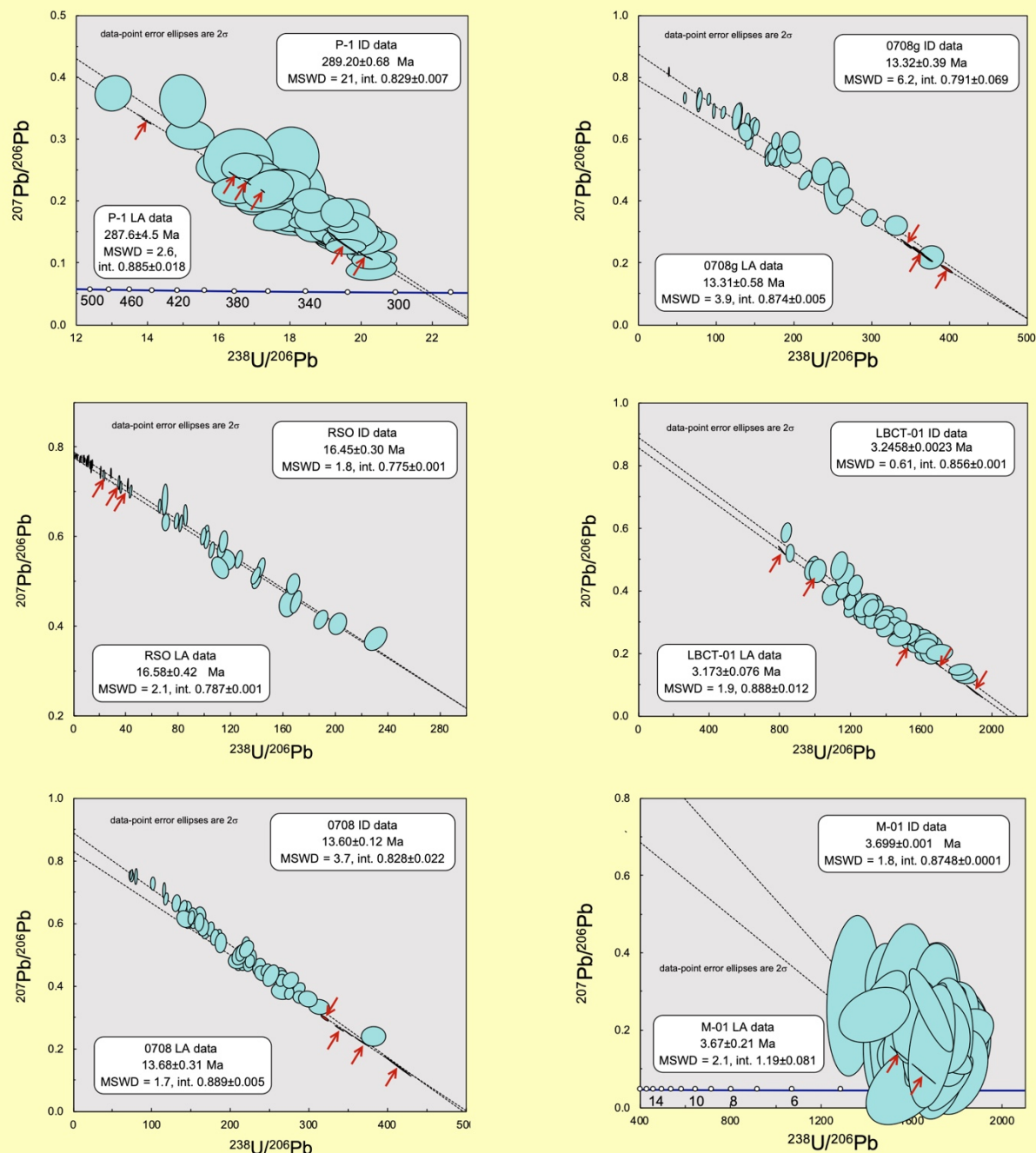



Figure 3: Comparison of ID and LA data. $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ 'Tera Wasserburg' isochron plots for key samples analysed in this study. Larger aqua symbols with low error correlations are LA data, smaller symbols with high levels of error correlation are the isotope dilution data for the same samples – in many cases these are almost invisible at this scale and their locations are therefore highlighted with red arrows. Dotted lines represent best fit isochrons for the LA and ID datasets derived from Isoplot (Ludwig, 2001).

3.2. Number of analyses required, and efficiency considerations

170 Given the relatively large uncertainties associated with each LA analysis, an important consideration in establishing an analytical protocol is the number of analyses required to form a robust age determination. In order to assess the effect of sample size on isochron quality we collected large numbers of spot analyses (up to 70) for several samples and then randomly sub-sampled this dataset, determining the age at each step. All samples show very similar behaviour and we use, as an example, results for sample P-1 in Fig.4.

175 A somewhat unexpected observation from this analysis is that relatively high accuracy and precision ages can be obtained with as few as 30 spot analyses and that any subsequently acquired data often do little to improve the analytical precision. There is, however, considerable scope for generating erroneous ages with analysis counts lower than ~30.

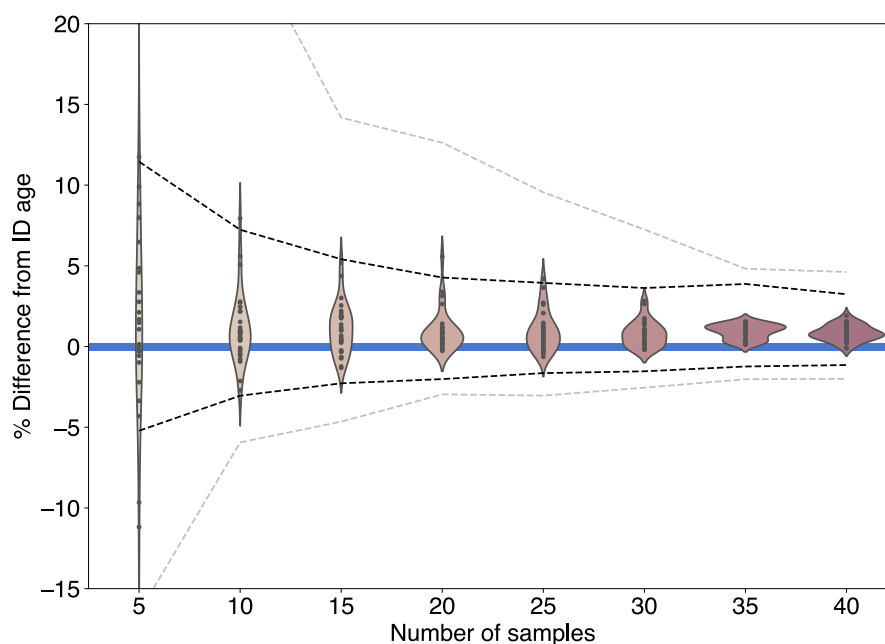
These data feed into an assessment of the potential time savings available from LA analysis compared to ID studies. If we assume 30 spot analyses 'per age' this amounts to around 40 minutes run time per sample using our analytical protocol.

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Figure 4: Sample size vs isochron quality. Percent difference of LA intercept age from ID age versus sample size when randomly subsampling the P-1 dataset. Thirty different random selections of the data were made for each sample size. The resulting intercept ages for each of the selections are represented individually as dots and collectively as a vertical kernel density estimate ('violin plot'). The ID age with uncertainty is represented by the blue bar centred on ordinate 0. The black and grey dashed lines are the median and extreme 185 uncertainties calculated for each sample size.

Once sample preparation time (slabbing and polishing or resin mounting) and other overheads (e.g. digitizing, cell stabilization after sample changes etc..) are taken into account, however, it may be hard to generate more than 10-20 age determinations per week without significant automation such as overnight running. In comparison, we tend to process
190   aliquots for ID studies in batches of 30 which routinely provides approximately 5 age determinations per week (1-day sample preparation and cleaning, 1-day spiking, 1-day chemistry and 2-days mass spectrometry), with clear scope for further expansion. There is certainly therefore a significant time saving when employing LA analysis but not necessarily a dramatic (order of magnitude) one. As such LA methods offer great potential as a rapid reconnaissance tool, largely superseding alternative methods noted by Woodhead et al. (2012).

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3.3. Limitations of the method

In addition to the small number of isochrons shown here for samples with published ID-derived ages, we have throughout the course of this study attempted to reproduce our ID-derived ages for a number of other (currently unpublished) samples of variable age and U, Pb contents. The results of these experiments, combined with comparable data gathered from literature
200   studies of non-spelean carbonates, are plotted in Fig.5. In this plot, samples are colour coded – those in purple represent successful literature age determinations by LA methodologies, whereas those in green are our own successful LA analyses. The diagram illustrates the particular challenges of analyzing speleothem materials compared with many other carbonates – sub-ppm levels of U and Pb and generally relatively young ages. Samples shown in red are those for which we have previously successfully determined ID ages but have not been able to produce isochrons using LA. These samples we
205   consider to be beyond the current limits of the LA technique due to a combination of low U and Pb contents and age.

We recognize that the results of such an entirely empirical approach are likely to show some variation between instrumentation and may ultimately change as equipment becomes more sensitive; for the moment, however, this diagram provides a first impression as to the potential limitations of the method as judged by current literature data. A relatively simple plane can be drawn to separate 'successful' from 'unsuccessful' experiments: the equation of this plane in x (U ppm)-
210   y (Pb ppm)-z (age in Ma) space is $2.25x + 10.5y + 0.42z - 3.15 = 0$. If the analyst has an independent assessment of likely U and Pb contents (e.g. from reconnaissance quadrupole ICPMS analyses) and an approximate idea of age, these values can be inserted into the equation above. Strongly positive values would suggest a high likelihood of dating success with appropriate equipment whereas negative values would suggest parameters likely to be beyond the current reach of the methodology. In broader terms any samples with >1ppm U and a few hundred ppb of Pb should be datable regardless of age. The actual range
215   of U/Pb ratios present in a sample also plays a role in the generation of isochrons but almost all carbonate materials analysed to date show some variation in this ratio at the micron scale and thus the potential for isochron construction if isotopic measurement of their U and Pb is analytically feasible.

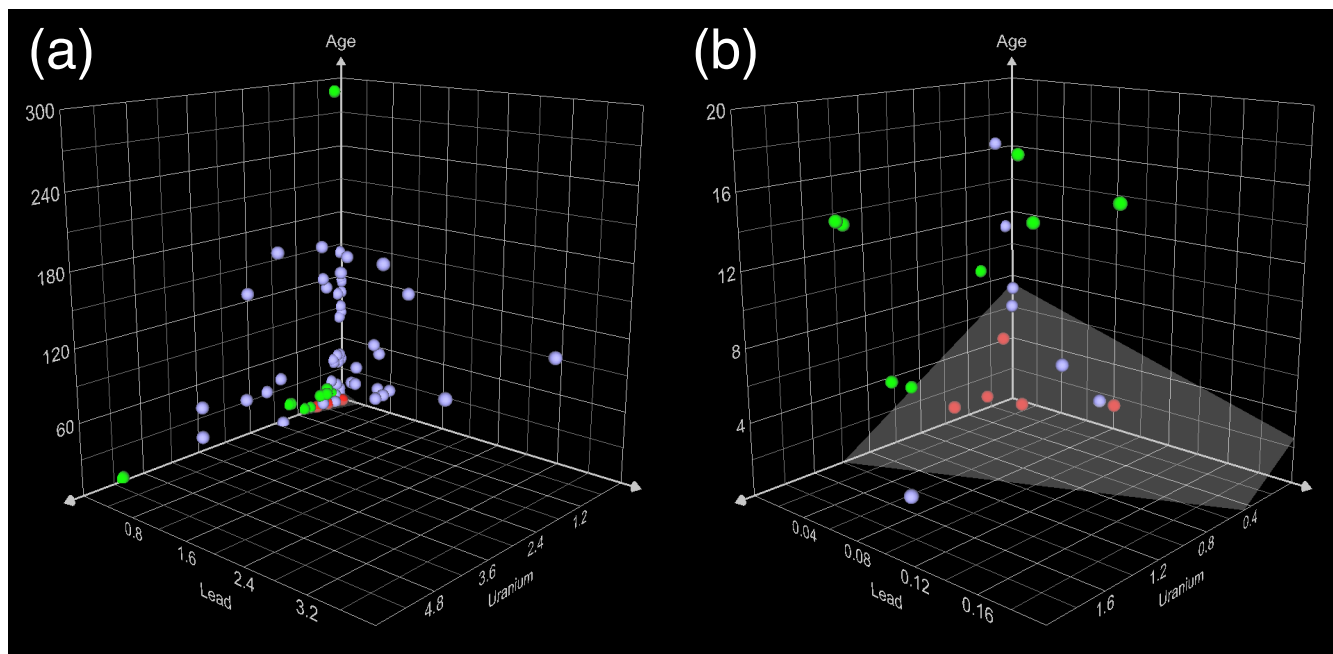



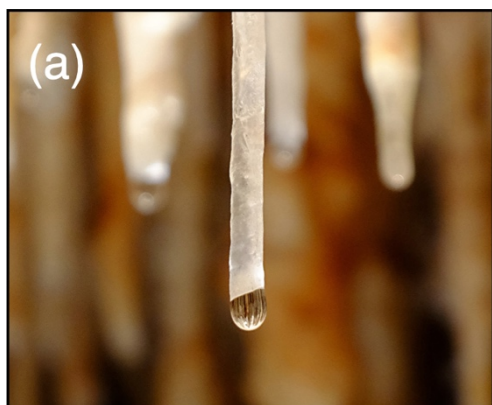
Figure 5: Limitations of the method. Plots of U and Pb contents vs age for our own samples and those literature studies from which concentration data could be extracted, with panel (b) representing a zoom view of the data shown in panel (a). Data points represent the average of concentrations reported for each sample: for our own analyses these are ID analyses but, in the case of literature samples, these are the concentration data reported from LA studies. Samples are colour coded – those in purple represent successful literature age determinations by LA methodologies, whereas those in green are our own successful LA analyses. Samples shown in red, however, are those for which we have previously successfully determined ID ages but have not been able to produce isochrons using LA. These samples we consider to be beyond the current limits of the LA technique due to a combination of low U and Pb contents and age. Data sources: this study, Li et al. (2014), Coogan et al. (2016), Ring and Gerdes, (2016), Roberts and Walker (2016), Hansman et al. (2018).

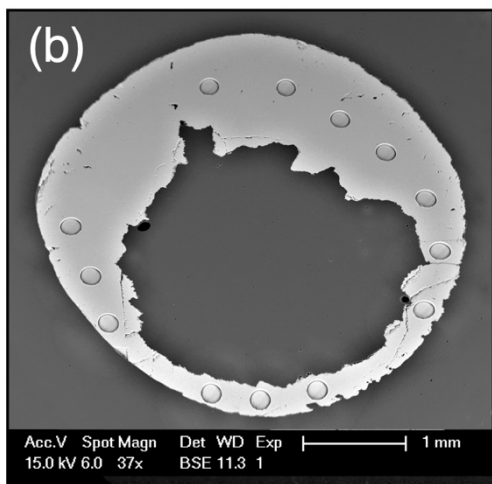
3.4. Advantages of the method

It is clear from the previous discussion that the LA methodology has some limitations in terms of working with low level or relatively young samples. In comparison, ID methods can produce useful data from samples with lower U and Pb concentrations simply because of the much larger sample sizes employed (typically 50mg for a bulk ID analysis compared with 0.005mg for a LA analysis). As a result, higher precision data can be obtained and consequently, younger samples dated – samples in the range of a few hundred thousand years are possible by ID (e.g. Richards et al., 1998), providing substantial overlap with the U-Th method in optimal circumstances.

The trade-off, however, is one of spatial resolution – LA methods offer a few hundred microns resolution compared to several millimetres (at best) using samples drilled out for ID analysis. Note in this context that it is difficult to produce sample powders for U-Pb analysis without contamination by environmental Pb and so traditional micro-milling

240 methodologies are not applicable to low level Pb samples. For this reason, in speleothem studies, complete fragments of crystalline calcite have to be removed by drilling (Woodhead et al., 2006; Woodhead et al. 2012). The power of these high spatial resolution LA approaches has already been demonstrated by previous studies e.g. analysis of single calcite fibres in vein structures (e.g. Goodfellow et al., 2017). Here we use an example from speleothem studies.

Straw stalactites – hollow, calcite cylinders that precipitate from cave drip points – are thin walled structures which are

245 plentiful in many caves and often form the nucleation point for the eventual growth of stalactites. Because of their fast-growing habit, they have been explored as short-term climate records (e.g. Paul et al., 2013) but they are also rather fragile and frequently broken off. Because of this they readily accumulate in cave sediments and have been shown to be

250 useful in the context of dating relatively young archaeological sequences at cave sites via the U-Th method (St Pierre et al., 2009). Cave straws are in fact often remarkably well preserved and so could be used to date many cave sedimentary sequences of any age but no previous attempts have been made to obtain U-Pb ages for these due to their minute size.

255 In Fig.6 we show a straw speleothem from the roof of a Nullarbor cave which has been shown to contain speleothems in the 3.1-5.6 Ma range (Woodhead et al., 2019). This sample has a total diameter of only ~5mm and a wall thickness of between 0.25 and 1.2 mm (Figure 5b). In addition, the outer regions of straws (those areas exposed to the environment) can

260 contain high levels of detrital components derived from dust. Dating of such structures would be impossible by conventional ID methods but we are able to use the laser to obtain a well-constrained isochron age of 4.91±0.33 Ma (uncorrected for initial disequilibrium). It is impossible in this case to independently confirm the validity of this age but it is well

265 within the range of nearby cave formations previously dated by ID.

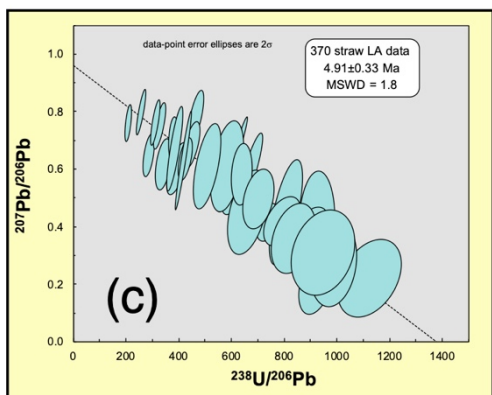



Figure 6: An example of high spatial resolution geochronology. High spatial resolution analysis of a straw speleothem from the Nullarbor Plain of SW Australia. Panel (a) shows an active straw stalactite in situ, while panel (b) is an

270 SEM cross-sectional view of the sample studied showing typical dimensions and wall thickness, together with representative laser ablation pits. Panel (c) shows the Tera-Wasserburg isochron which is within the range of other speleothems analysed from this site via ID methods (Woodhead et al., 2019).

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4 Conclusions

Laser ablation methods are capable of generating accurate U-Pb ages for speleothems (and by inference other carbonates) with moderate U contents (>1ppm), regardless of age. At lower U contents, however, the possibility of successful outcomes is also strongly dependent on Pb content and age. Together with our own studies, a compilation of successful literature

280 analyses provides a first-order test for potential dating suitability. The absolute precision obtained by LA methods can approach but rarely supersedes that of the benchmark ID method. LA conveys an advantage in speed and is thus useful as a reconnaissance tool. The overwhelming advantage of LA methods, however, remains one of high spatial resolution, allowing the dating of materials which are beyond the reach of ID methods simply because of their size.

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Author contributions. JW collected the analytical data. JW and JP both performed the data analysis and wrote the paper.

Competing interest. The authors declare that they have no conflict of interest.

295 *Data availability.* The raw Attom data and RESOlution laser log files for the LA analyses, and the iolite-3 experiments showing how they were processed can be obtained from the authors.

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300 WC-1 reference material and, together with Phil Shaw of Nu Instruments, advised on instrumental matters. Graham Hutchinson produced the SEM images. This study was funded by Australian Research Council grant FL160100028 to JW.

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Table 1. Instrumental parameters

Laser ablation system	
Manufacturer & Model	Australian Scientific Instruments (now Applied Spectra) RESOlution-LR
Ablation cell	S155 large format cell
Laser wavelength (nm)	193 nm
Pulse width (ns)	20 ns
Fluence	~2-3 J/cm^{-2}
Repetition rate (Hz)	5 Hz
Spot size (μm)	154 or 228 μm
Sampling mode / pattern	Static spot
Cell gases	Sample ablated into pure Helium but then rapidly (within 1cm) entrained into argon flow within the
Ablation conditions	30 seconds baseline measurement followed by 40 seconds ablation
Cell gas flows (l/min)	0.25 Helium, 0.8-0.9 Ar (tuned for maximum sensitivity, not low oxides)
ICP-MS Instrument	
Make, Model & type	Nu Instruments, Attom-ES high resolution ICP-MS
RF power (W)	1300W
Make-up gas flow	0.7l/min Ar
Detection system	Single Mascom SEM
Masses measured	206, 207, 208, 232, 235, 238
Integration time on peak	Dwell times of 200 μs to 2ms per peak
Time per cycle (secs)	0.125 sec
IC Dead time (ns)	17 ns
Data Processing	
Gas blank	30 second on-peak zero subtracted using Iolite smoothing spline
Calibration strategy	WC-1 carbonate
Data processing package used / Correction for LIEF	UncomPbine DRS running in Iolite providing baseline subtraction, downhole correction and calibration against the standard. The [207]Pb based common Pb method was employed.
Uncertainty level & propagation	Ages are quoted at 2sigma absolute. Data are presented with internal errors only.

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Table 2. **Samples utilised in this study.** Mean U and Pb contents are the averages of the isotope dilution data reported in the appropriate publications. In order to allow direct comparison with the LA data none of the ID ages quoted below include a correction for initial disequilibrium in the U-Pb decay chain: as such the ages shown for the two youngest samples differ slightly to those reported in the publications.

Sample ID	Location	Mean U ppm	Mean Pb ppm	I.D. Age (Ma)	Reference
P-1	Richard's Spur, Oklahoma, USA	0.206	0.016	289±1	Woodhead et al. (2010)
RSO	Riversleigh World Heritage fossil site, Queensland, Australia			16.55±0.31	Woodhead et al. (2016)
0708	Riversleigh World Heritage fossil site, Queensland, Australia	1.43	0.006	13.72±0.12	Woodhead et al. (2016)
0708g	Riversleigh World Heritage fossil site, Queensland, Australia	1.39	0.006	13.48±0.45	Woodhead et al. (2016)
LBCT-01	Nullarbor Plain, SW Australia	2.69	0.004	3.246±0.002	Woodhead et al (2019)
M-01	Nullarbor Plain, SW Australia	1.04	0.002	3.699±0.001	Woodhead et al. (2006)