Dear editor,

We thank you for the positive feedback on our paper and for the opportunity to revise our manuscript following the constructive suggestions of both reviewers. We accepted all of their comments as described in details below. Please note that line numbers refer to the final PDF revised paper.

The main changes in the revised manuscript include:

1) We changed discussion on the minor differences between previous and new ID data which are indeed largely overlapping within uncertainties.
2) We included footnotes for all supplementary tables (S1-S8)
3) We included some new LA-MC-ICPMS data from 2018-2020 in Fig. 4b and Table S5.
4) We included new figure 8 and section 4.5 dedicated to discussion on U-Pb concentrations of available standards and comparison to concentrations in carbonate material.

Sincerely,

Perach Nuriel, on behalf of all co-authors

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Reviewer answer letter

"The use of ASH-15 flowstone as a matrix-matched reference material for laser-ablation U-Pb geochronology of calcite"

AC1

Fernando Corfu (Referee)
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Received and published: 14 August 2020

The paper reports the results of a calibration of carbonate to be used as reference material. Measurements were done with various ICP instruments and operators, and by two ID-TIMS laboratories. The data are good and important, considering the type of material and the very young age of the samples, and considering the purpose of the study. I find the fundamental elements of the paper to be correct. At the same time, some of the terms used and descriptions of the material and sample targets are confusing and I recommend that the authors consider using better terms and correct some of the confusing parts.

We greatly appreciate the reviewer's comments and good suggestions that helped to improve this contribution. Please see our specific answers to each comment.

Comment: There is a terms' growth bands' which I first assumed to mean growth zones (line in an onion) only to find out that it designated zones perpendicular to growth zones. Then there are two transects for ICP spot analyses, the two being perpendicular to each other. Even enlarging Fig. 2 I can only see a row of spots, so I cannot really understand where the layer-parallel transect would be. Eventually after reading to the end one gets the idea, but it would simplify matters if the text and figures would not create confusion in the first place.

Answer: We agree and we corrected this confusing terms to 'spots array along growth zone' and 'along growth direction'. We also improve Figure 2 with a new XPL image showing nicely growth direction and a new close-up image of the two spot arrays.

Comment: I have made some suggestions and comments in the text.

Answer: all suggestions are corrected in the revised paper, many thanks for thorough reading.

Comment: The data are reported in sheets of an excel file, which is fine. The ID-TIMS data are given in great detail, and have good footnotes explaining the nature of all the entries. By contrast the ICP tables have essentially no explanations. They seem to be working table just thrown in without bothering to format them properly, explaining what the data mean and how/where they were treated and produced. I suppose this is all evident for the authors. The readers do not count? Please make sure the tables are well prepared and informative.

Answer: We included footnotes in all tables in the supplementary file (S1-S8).

AC2

Jon Woodhead (Referee)
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Received and published: 28 August 2020

Comment: The in-situ carbonate U-Pb chronometer is an exciting development finding a host of new applications across a range of Geoscience disciplines. The main impediment to its use remains the dearth of suitable (moderate U, Pb, homogeneous) calcites that can be utilised as reference materials. Most practitioners are now using the WC-1 calcite (Roberts et al) as a primary calibrant and employing analytical strategies to compensate for its non-homogeneous characteristics but there remains an urgent need for the development of further reference materials. This manuscript takes a step along this path providing accurate ID data for the ASH-15 speleothem material which is used by many labs as a secondary standard.

The analytical procedures documented in the manuscript appear rigorous and the close correspondence between data from different laboratories is very encouraging. Notably the scatter about the ASH-15 isochron is considerably less than that observed for WC-1 suggesting that ASH-15 could be adopted as a primary calibrant, offering more precise age determinations. As such I think this is a valuable contribution to Geochronology and should be published with minor modifications.

Answer: We greatly appreciate the reviewer's comments and good suggestions that helped to improve this contribution. Please see our specific answers to each comment.

Comment: my main concern with the manuscript stems from the comparison with previous ID determinations for the ASH-15 material (primarily Vaks et al., 2013, Mason et al., 2013, although see later discussion). At the outset (line 35) the authors note that the new ID-TIMS ages are '1.3-1.5% younger than previously suggested' and later (lines 388 onwards) in the manuscript there is considerable discussion surrounding an observation that the literature ages are 'systematically older' and that the 'origin of this bias should be investigated'. In fact (as the authors themselves note) the new and literature ages for the individual determinations by each lab are all within uncertainty of each other and so, as far as I can see, they must therefore be statistically indistinguishable? Once the grand mean for the current study is employed the overlap in uncertainties is admittedly minor but, at that point, any statistical comparison is invalidated because data from two different labs have already been combined.

Answer: Indeed there is overlap within uncertainties and we have revised the text as suggested (lines 388-391):

"These ages are largely overlapping within uncertainty with our new ID-TIMS age of 2.965 ± 0.011 Ma (Fig. 7; and data in Table S7 in the supplements). The apparent minor systematic offset towards slightly older ages is attributed to the lower number of aliquots in the MC-ICPMS datasets combined with the heterogeneous initial Pb isotope composition."

Comment: In addition, no mention is made of the University of Leeds determination (Vaks et al, Supplementary table 3) which is from yet another lab and is also in agreement with all of these numbers.

Answer: Unfortunately, we forgot to point on the data from the University of Leeds in Figure 7 (although shown on the RHS). We have now revised Figure 7 to indicate in which lab each date was obtained.

Comment: So, as far as I can see, the existing data from 5 different labs - all using slightly different analytical approaches - are all statistically identical? No biases required. Of course a case can be mounted that the new data are based on more aliquots and therefore may be more robust (in terms of common Pb intercept, for example) but I do not see any justification for looking for a bias here when, in fact, the statistics tell us that there is very little evidence of such. I think that it would be far more honest to simply say that the new data are 'statistically indistinguishable from the literature values but considerably more precise'.

Answer: We accept this comment and we revised this part as suggested (see lines 388-391 above).

A few more minor points:

Comment: 1. Lines 320, 329 what is the justification for the common Pb anchor of 0.8315? The TIMS data seem to show intercepts ranging from 0.814 to 0.832 and all show minor heterogeneity in 207/206 initial. Is this value a weighted mean of the ID TIMS data?

Comment: 2. Also, it might be worth processing LA data with slightly different value – that might explain the slightly younger age of the LA data cf TIMS?

Answer: To avoid changing the common-lead value for each TW plot we did not use anchoring in age calculations in the revision.

Comment: 3. Re. the discussion at lines 383-393 alluded to above:
Why were ages the literature recalculated? Is this due to differences in error handling between Isoplot and Isoplot-R?

Answer: Indeed. We wanted to calculate all the data with the exact same settings: same decay constant, with the same anchoring or no anchoring, without disequilibrium correction and without propagating external uncertainties.

Comment: Figure 7 shows two different fields for 'ASH15D (Vaks et al)' which are quite different. What is the lower one (RHS), not mentioned in the text?

Answer: This is the missing data from Leeds lab, we now indicate it in the revised Figure 7.

Comment: The use of EarthTime reference materials (line 396) is not unique to the current study as suggested here and this argument should not be used in an attempt to cast doubts on the literature data. The Supplementary information for Vaks et al. (2013) clearly states 'sample solutions were spiked, using a 233U-205Pb tracer, calibrated against EarthTime U-Pb normals'. Similarly (lines 397-398), although double spiking may well be important for control of mass bias effects in TIMS, the relatively stable mass bias of plasma instruments means that the bias correction is actually a very small component of the uncertainty budget for ID-MCICPMS. As noted above the main advantage of the current study is undeniably the larger number of analyses contributing to lower uncertainty. I think that most of the other arguments posited in lines 389-398 are probably illusory.

Answer: We removed 'compared to previous bulk analyses' from this sentence.

Comment: Lines 24, 354 etc refer to 'high precision ID TIMS'. I may be mistaken but I don't think that there is really such a thing these days as 'low precision ID TIMS' (!) so the words 'high precision' are unnecessary hyperbole.

Answer: We removed 'high-precision' from these lines.

Comment: Line 185 to what does the term 'dosage' refer? Is this something specific to the ARIS laser sample introduction system?

Answer: We added a short explanation after the word 'dosage' in the text in line 186-187: "(10 overlapping pulses per spot size which amount to a scanning speed of 588 $\mu m s^{-1}$)"

Comment: Finally, I think that the manuscript would benefit from some discussion of the relative merits of an ideal calcite reference material. While extreme homogeneity seems an almost impossible goal, there are also clearly 'sweet spots' for both U and Pb content when using different instruments/analysing different samples and it would be beneficial to explore this trade-off here – as an aid to the general reader. ASH15 appears to have about half the U content of WC-1 but it also has very low Pb content requiring relatively large spot sizes compared to WC-1. This is alluded to in the last line of the conclusions, but it would be nice to see both WC-1 and ASH-15 plotted relative to the range of calcites commonly encountered e.g. by using the plots from Roberts et al 2020 (Geochronology) Fig 5. Then we can visually determine how well suited they are as standards for the analysis of such materials and indeed where we should be looking for the next standard (in terms of U and Pb content).

Answer: We thank the reviewer for this suggestion and we added in the revised manuscript figure (Figure 8) that shows concentrations comparison of WC1, ASH15 and JT reference materials as well as different carbonate material. We also included a whole section (4.5, lines 410-431) that elaborate on these issues:

"4.5. Calcite reference material

The U and Pb concentrations of carbonate materials vary greatly. Data compilation by Roberts et al. (2020; this issue) combined hundreds of carbonate samples from different origin such as diagenetic, biogenic, speleothem, and vein-fill. This compilation indicates several orders of magnitude differences in U and Pb concentrations of the different types of carbonate and the heterogeneity of spot analysis within each type or even a single sample. A modified representation of their data, excluding calcite vein-fill, which vary throughout the entire compositional range, is shown together with the currently available calcite reference materials (Fig. 8; and full data in Table S8 in the supplement). Note that both ASH15 and JT, display much larger heterogeneity when measured by LA-ICPMS (small symbols) relative to ID-TIMS (large symbols). Despite the high compositional heterogeneity of each of the reference material, they show minimal overlap and together they cover most of the compositional range of the presented carbonate material. WC1 (Roberts et al., 2017) with relatively high U and Pb concentrations can easily be measured on single collector ICPMS (including quadrupole instruments) and is most appropriate to be used for dating vein-fill and diagenetic carbonates. In contrast, the ASH15 flowstone, with relatively low Pb and high U concentration that are better measured on sector-field (MC)-ICPMS is most appropriate for dating speleothem type carbonates. Finally the JT (Guillong et al., 2020), with moderate U and Pb concentration can be used on both single- and multi-collector sector field ICPMS instruments and for all types of carbonate samples. Reference material with high Pb and low U or both low U and Pb concentrations will further help to cover the full compositional range of carbonate material but may introduce analytical challenges."

The use of ASH-15 flowstone as a matrix-matched reference material for laser-ablation U-Pb geochronology of calcite

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Abstract

Latest advances in laser ablation inductively coupled plasma mass spectrometer (LA-ICPMS) allow for accurate *in-situ* U-Pb dating of carbonate material, with final age uncertainties usually >3% 2σ. Cross-laboratory reference materials (RMs) used for sample-bracketing are currently limited to WC1 calcite with an age of 254.4 ± 6.5 (2σ). The minimum uncertainty on any age determination with the LA-ICPMS method is therefore ≥ 2.5%, and validation by secondary RMs ~~are~~ is usually performed on in-house standards. This contribution present a new reference material, ASH-15, a flowstone that is dated here by i~~I~~sotope d~~D~~ilution (ID) TIMS analysis using ~~36~~ 37 sub-samples, 1-7 mg each. Age results presented here are slightly younger compared to previous ID-IRMS U-Pb ~~dating~~ dates of ASH-15, but within uncertainties and in agreement with *in-situ* analyses ~~(~~using WC1 as the primary~~a~~ RM~~)~~. We provide new correction parameters to be used as primary or secondary standardization. The suggested $^{238}U/^{206}Pb$ apparent age, not corrected for disequilibrium and without common-lead anchoring, is 2.965 ± 0.011 Ma (2σ). The new results could improve the propagated uncertainties on the final age with a minimal value of 0.4%, which is approaching the uncertainty of typical ID analysis on higher-U materials~~, for example,~~ such as zircon ~~(<1% 2s)~~. We show that although LA-ICPMS spot analyses of ASH-15 exhibit~~s~~ significant scatter in their isotopic ratios, the down-hole fractionation of ASH-15 is similar to that of other reference materials. This high-U (~1 ppm) and low Pb (<0.01 ppm) calcite is most appropriate as a reference material for other speleothem-type carbonates but requires sensitive sector-field ICP-MS instruments. Reference materials with high Pb and low U or both low U and Pb compositions are still needed to fully cover the compositional range of carbonate material but may introduce analytical challenges. ~~For LA work, we recommend the use of the new ID-TIMS ages that are 1.3-1.5% younger than previously suggested, because of the lower uncertainties (0.4%), the large number of sub-samples (n=36), the use of the EARTHTIME isotopic tracers, and the small aliquots (1-7 mg) that are more representative of laser-ablation spot analysis.~~

Introduction

Recent advances in laser ablation techniques applied to multi-phase carbonates allow for accurate dating of a variety of sample types, including calcite cements (Li et al., 2014; Godeau et al., 2018; Anjiang et al., 2019; Holdsworth et al., 2019), hydrothermal veins (Coogan et al., 2016; MacDonald et al., 2019; Piccione et al., 2019), fault-related veins, breccia cement, and slickenfibers (Ring and Gerdes, 2016; Roberts and Walker, 2016; Goodfellow et al., 2017;

Nuriel et al., 2017; Hansman et al., 2018; Parrish et al., 2018; Nuriel et al., 2019), and speleothems (Woodhead and Petrus, 2019). With increasing attention ~~on~~ to climatic, seismic, and environmental events in the geological record, there is a growing need for dating techniques that can be accurate~~ly~~ and easily implemented ~~to~~ for samples at the sub-millimeter scale. This newly emerging technique has the potential to contribute to our understanding of the duration, rate, and extent of these important events in the geological record.

The *in-situ* approach has a great research potential for studying texturally complex samples because it can resolve problems of age mixing of different phases or averaging of continuous growth at the sub-millimeter scale, and thus increase the overall accuracy of the dated material. While the precision of traditional isotope-dilution (ID) U-Pb analyses is still favorable (<1% 2σ) (Woodhead and Petrus, 2019), the increasing analytical development of the LA-ICPMS method indicates the potential for improving the currently reported uncertainties (usually >3% 2σ). Finding the right matrix-matched reference material (RM) is a major hurdle for LA analyses of carbonates because of the variety of mineralogy (calcite, dolomite, and aragonite), textures, composition (e.g. high-magnesium calcite, high common-lead), and ages (e.g. low radiogenic lead in young samples). Textural differences such as microcrystalline, fine- and coarse-grained material, between the unknown and RMs can contribute to high uncertainties due to differences in ablation efficiency, down-hole fractionation, and differences in crater morphology (e.g. Guillong et al., 2020 and Elisha et al, 2020, this issue). Observed deviations are potentially up to 20% of the final intercept age depending on the degree of crater geometry mismatch and are related ~~to~~ either to downhole fractionation and/or matrix effects (Guillong et al., 2020).

Currently, the most commonly used procedure for mass-bias correction in the LA method, is by standard-sample bracketing. For this, the $^{238}U/^{206}Pb$ LA-age of the RMs is corrected to the true RM's $^{238}U/^{206}Pb$ apparent age (not corrected for disequilibrium) as measured independently by an ID-IRMS method (~~e.g.~~ ID-TIMS or ID-MC-ICPMS). The RMs are measured throughout each session along with the unknown samples, and a normalization factor is applied to correct both the RMs and the unknowns. Uncertainty propagation onto the age of the unknowns includes the uncertainties of the 'true' RM age. As a result, the accuracy of the LA analyses can only be as good as the uncertainties on the age of the RMs which is by itself subjected to analytical challenges due to natural heterogeneities, impurities, and textural complexities at the sub-millimetre scale. It is therefore essential that the 'true age' of the reference material will reflect these complexities while maintaining minimal uncertainties.

Currently, several in-house standards are being used as reference materials, including Duff Brown Tank (64 Ma; Hill et al., 2016), and JT (13.797 ± 0.031 Ma; Guillong et al., 2020). The only well-characterized reference material that is distributed across laboratories is the WC1 calcite with an age of 254.4 ± 6.5 2s (2.5%) (Roberts et al., 2017). The use of WC1 alone for mass-bias correction has several disadvantages. First, it is highly recommended with all in situ U-Th-Pb geochronology to use secondary RMs to validate any correction parameters that are being used, and to appropriately propagate uncertainties. Second, the relatively high uncertainty (2.5%) on the age of WC1 sets a minimal uncertainty on any LA U-Pb age determination. Finally, the quantity of the WC1 sample that is currently available for future work is limited and is likely to not fully meet the growing demands of the LA scientific community; although~~,~~ we note here that there is a potential for further sample collection from the original site.

This contribution introduces a new carbonate reference material that can be widely used for *in-situ* dating of calcite as primary or as cross-reference material with other available standards. We characterise the reference material at various resolutions using a combination of (1) laser ablation imaging (20 µm square beam); (2) LA spot analysis, ~80-110 µm in diameter, conducted on both multi-collector (MC) and single collector inductively coupled plasma mass spectrometer (ICPMS); and (3) ID-TIMS analyses of ~~36~~ 37 sub-samples (~1-7 mg aliquots). We discuss several key issues related to the use of ASH-15 sample as a RM, including down-hole fractionation, heterogeneities, and previous bulk analyses~~, and the possible effect of samples size and blank corrections~~, to provide the best correction parameters and suggested protocols for users of the LA scientific community.

1. The ASH-15 flowstone

The ASH-15 flowstone was found in Ashalim Cave, a karstic cave in the central Negev Desert (30°56′36.2″ N, 34°44′22.5″ E), southern Israel, which is part of the northern margin of the Saharan–Arabian desert belt. The cave entrance is located at an elevation of 414 m above sea level and 67 km SE from the Mediterranean Sea coast. The cave is a three-dimensional hypogene maze with a total length of 540 m, situated in Turonian limestone rock strata, at depths of 0-31 m below the surface. The cave is richly decorated with vadose speleothems, such as stalagmites, stalactites and flowstone, which are not active today because of the aridity of the climate in the area (Vaks et al, 2010, 2018), but periods of their deposition correspond to past episodes of wet climate in present-day desert. The thickness of the speleothems varies from several cm to a few tens of cm. The soil above the cave is silicate loess, originated mainly from aeolian dust (Crouvi et al., 2010) and the present day vegetation is composed of sparse xeric shrubs with <10% vegetation cover.

The vadose speleothems of Ashalim Cave are composed of low-Mg calcite, and are divided into a relatively thick Pliocene Basal layer, and thinner Pleistocene layers above it. The Basal layer varies from 5 to 25 cm in thickness and comprises c. 90% of the speleothem volume in the cave. It is composed of massive yellow calcite crystals (Fig. 1a-b), often showing continuous growth in stalagmites and flowstone, suggesting deposition from continuously dripping water. In all speleothems the Basal layer is terminated at its top by a <1 mm layer of microcrystalline calcite, evaporite minerals and reddish clays (Fig. 1a), that is interpreted as a hiatus (growth break) separating the Basal Pliocene layer and Quaternary layers above it (Vaks et al., 2013). The thickness of Pleistocene top layers varies from several mm to 17 cm, but usually does not exceed a few cm, comprising about 10% of the speleothem volume in the cave. It is composed of alternating layers of brown calcite, with the youngest top layer (where found) composed of yellow calcite. Several variably colored layers <1 mm thick of microcrystalline calcite, evaporite minerals and reddish clays are found within the columnar crystalline structure, suggesting hiatuses in speleothem deposition (Vaks et al., 2013).

The youngest periods of speleothem deposition in several Ashalim Cave speleothems were dated by the ^{238}U-^{230}Th method and occurred from 221 ka to 190 ka and from 134 to 114 ka (Vaks et al, 2010). Earlier periods of deposition were dated by the U-Pb method on ASH-15 flowstone ~~and are dated to~~at 1.272 ± 0.018 Ma (ASH-15-C), and the Basal layer of ASH-15 flowstone (layers D-K) ~~dated to~~at c. ~3.1 Ma (Fig 1a). These layers have been dated in three different labs following several protocols for ID analysis (Vaks et al., 2013; Mason et al., 2013). The U concentrations in speleothem calcite range between 1.9 and 19.7 µg/g and the amounts of non-radiogenic Th are negligible (Vaks et al., 2010).

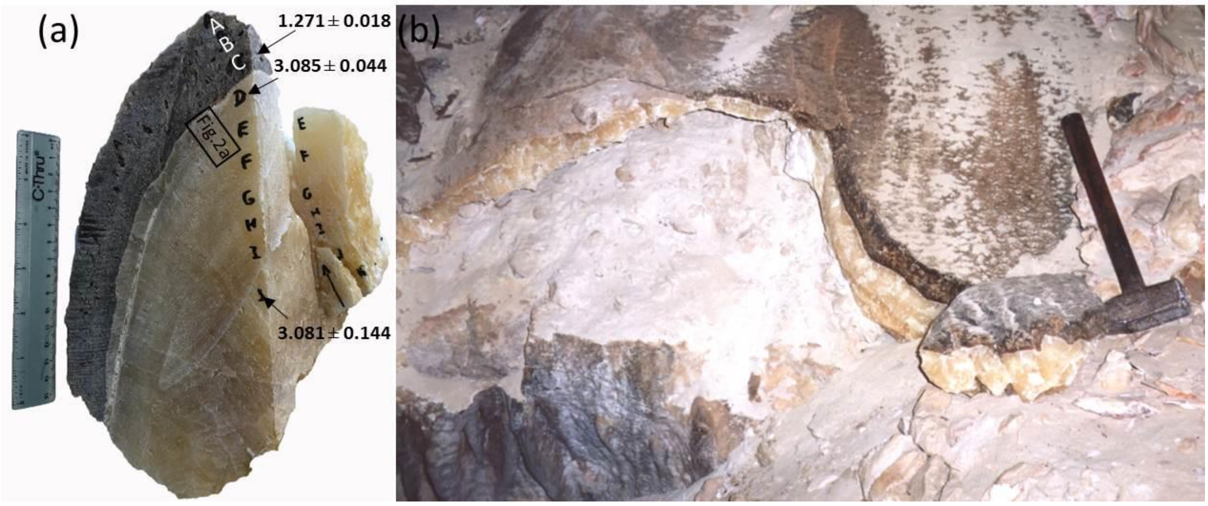

Figure 1. Sample ASH-15 from Ashalim Cave. (a) ~5 kg block of sample ASH-15 flowstone consisting of the massive Pliocene yellow Basal layer (>2 cm calcite crystals; section D–K) and the brown Quaternary layer (top section, A–C), the thin layer between the two stratigraphic members represents a growth break (hiatus). The main U-Pb ages of Vaks et al., 2013 are indicated; ~~.~~ (b) In-situ flowstone within Ashalim Cave from which ASH-15 was sampled, showing the large reservoir of this flowstone.

2. Sample ASH-15 textural characterization

The ASH-15 thin-section includes section D and E ~~of the ASH-15 sample~~ (see location in Fig.1a). Overall the thin-section examination indicates that the original texture is preserved with consistent growth direction, no observed hiatus, and no indications for dissolution and recrystallization. A spot analysis array, 85 µm in diameter, targeted along growth ~~bands~~ zone and ~~perpendicular to~~along -growth direction ~~are~~ is visible in Fig. 2a-c. The ASH-15 sample shows no luminescence under cathodoluminescence light (Fig. 2c), suggesting formation under oxidising conditions. The slight bright luminescence observed within grain boundaries, discontinuities, and veins (arrows in Fig. 2b-c) may suggest ~~for~~ the presence of fluid inclusions, textural differences, or some local replacement within these areas. These areas should be avoided if possible during spot analysis. The relatively homogenous low luminescence may suggest for a single-phase continuous calcite growth, whereby precipitation occurred relatively rapid from the same fluid source (e.g. with consistent Mn^{2+} Fe^{2+} composition) and/or under similar precipitation redox conditions. This 15 cm thick, ~3 Ma Pliocene layer (section D-K) is essentially of the same age. For this reason, previous dating of this sample also considered a similar initial $^{234}U/^{238}U$ activity ratio for disequilibrium correction (Mason et al., 2013; Vaks et al., 2013). The ASH-15 reference material consists of the whole Pliocene section that terminates with a sharp transition to the darker Pleistocene layers above it (section A-C; see Fig. 1b). About 3 kg of ASH-15 sample are excavated from the Ashalim Cave (Fig. 1a), and potentially much more can be sampled in the future (we estimate more than 10 kg of sample; Fig. 1b). The ASH-15 flowstone is therefore a good candidate for a reference material because of its large volume, high U concentrations, and potentially homogenous age which will be examine next.

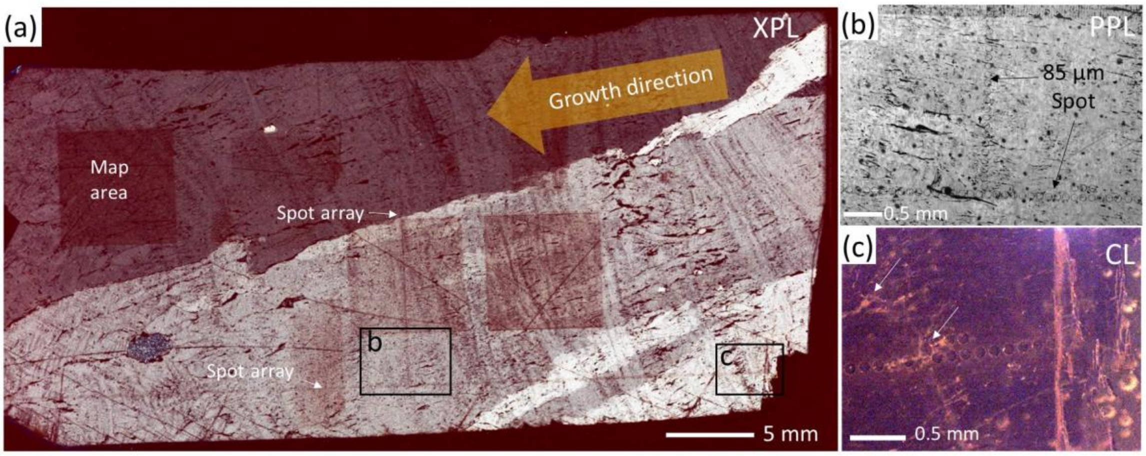

Figure 2. ASH-15D-E thin-section. (a) cross-polarized (XPL) scan ~~of ASH-15D-E thin-section~~, 36 mm long, showing continuous growth (no hiatus), and consistent growth direction (indicated with yellow arrow). Spot analyses are targeted either sub-parallel to growth ~~band~~ zone or ~~perpendicular~~ sub-parallel to growth direction; (b) close-up on spot array analyses (location is shown in a) with 85 µm diameter; (c) CL image ~~of the same area~~ showing no luminescence ~~and~~ except for some bright luminescence within grains boundaries and veins (arrows).

3. Methods

3.1. Elemental mapping

The sample ASH-15 was cut perpendicular to the growth ~~bands~~ zone of section D and E (see Fig.1b) in order to examine heterogeneities across growth ~~bands~~ zone and within. Thin-sections were then examined under plane- and cross-polarized light (XPL/PPL), and cathodoluminescence (CL) microscopy (Fig. 2). The central part of the thin-section was also analyzed for elemental distribution of selected elements. The elemental maps were measured via LA-ICPMS, carried out on a 193 nm ArF excimer laser ablation system (Analyte G2 Teledyne Photon Machines Inc., Bozeman MT) coupled to an ICP-QMS (Agilent 7900, Agilent Technologies, Santa Clara CA). The laser was equipped with a Photon Machines HelEx II ablation chamber and an Aerosol Rapid Introduction System (ARIS). The experiments were carried out using acquisition parameters (both on the ICP and on the laser) modelled using the approach of van Elteren et al (2019; 2018) to avoid artefacts (e.g., aliasing, smear, blur). All images (500x500 pixels) were acquired using a 20 µm square beam, fluence of 3.5 Jcm^{-2}, 294 Hz repetition rate and dosage of 10 (10 overlapping pulses per spot size which amount~~ing~~ to a scanning speed of 588 μms^{-1}). The masses monitored were ~~^{24}Mg, ^{55}Mn, ^{63}Cu, ^{85}Rb~~ ^{88}Sr, ^{137}Ba, ^{206}Pb, ^{208}Pb, ^{232}Th, and ^{238}U and the images were constructed using Photon Machines' HDIP data reduction software (van Malderen, 2017).

3.2. LA-MC-ICPMS spot analyses

A thin section of ASH-15 was dated by U-Pb laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) following the method described in Nuriel et al. (2017). A Nu Plasma 3D was employed in conjunction with a Photon Machines Excite 193nm Excimer laser equipped with a HelEex two volume cell. The laser was fired for 15 s during analysis, using a ~~rep~~repetition rate of 10 Hz, a spot size of 85 µm, and a fluence of approx. 1 J/cm^2. The Nu Plasma 3D allows for the simultaneous acquisition of ^{238}U, ^{235}U, ^{232}Th, ^{208}Pb, ^{207}Pb, ^{206}Pb, ^{204}Pb(+Hg), and ^{202}Hg, where ^{238}U-^{232}Th are measured on Faraday detectors and the low-side masses are measured on Daly detectors. Instrumental mass-bias was corrected using a two-step approach: both the ^{207}Pb/^{206}Pb and ^{206}Pb/^{238}U ratios were first corrected to NIST-614 glass reference material in *Iolite 3* using the geochronology reduction scheme (Paton et al., 2010) to account for both mass-bias (^{207}Pb/^{206}Pb) and instrumental drift (^{207}Pb/^{206}Pb and

^{206}Pb/^{238}U). The Tera-Wasserburg data, output from *Iolite*, was then plotted and ^{206}Pb/^{238}U ratios of all RMs and unknowns were adjusted such that the primary calcite reference material—WC-1—yielded an age of 254 Ma (Roberts et al., 2017). This resulted in accurate dates for both our secondary calcite RM:, Duff Brown Tank at -66.8 ± 3.4 Ma (previously reported 64 Ma; Hill et al., 2016) and a a ^{207}Pb/^{206}Pb date of zircon RM at 566.0 ± 2.8 Ma (previously reportedSri Lanka, 564 Ma; Gehrels et al., 2008), of 66.8 ± 3.4 Ma and a ^{207}Pb/^{206}Pb date of a 566.0 ± 2.8 Ma. Uncertainty propagation of individual ratios was assessed by reproducibility of the NIST614 and SL RMs (n=44 in both cases) and added in quadrature such that the MSWD of each weighted average is ≤1 and that the uncertainty is no better than 2% (long-term reproducibility); this resulted in propagated uncertainties of 2.5% and 2% for the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ratios, respectively. Given that the typical uncertainties of the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ratios of the unknowns was >10% and >3%, respectively, the uncertainty propagation on individual ratios had little effect on the calculation of the final date of ASH-15. The thin section of ASH-15 was measured both parallel to the length of section (303 spots, and perpendicular to it (101 spots). Data are plotted using Isoplot (Ludwig, 1998).

3.3. LA-ICPMS spot analyses

Analyses were conducted at the Geochronology and Tracers Facility, British Geological Survey (Nottingham, UK). The instrumentation comprised a New Wave Research 193UC excimer laser ablation system fitted with a TV2 cell, coupled to a Nu Instruments Attom single collector inductively coupled plasma mass spectrometer (ICP-MS). The method follows the protocols described in Roberts and Walker (2016) and Roberts et al. (2017). Laser parameters varied slightly per session, but typically involve a pre-ablation cleaning spot of 150 µm, fired at 10 Hz with a fluence of ~6 J/cm^2 for 2 seconds, and ablation conditions of 80-100 µm spots, fired at 10 Hz with a fluence of ~6-8 J/cm^2 for 25-30 seconds. A 60 second background is taken before every set of standard-bracketed analyses, and a 5 second washout is left between each ablation. Normalization of Pb-Pb ratios is achieved using NIST614 glass (values of Woodhead and Hergt, 2001), and WC-1 carbonate for Pb-U ratios (Roberts et al., 2017). Data reduction uses the Time Resolved Analysis function of the Nu Instruments Attolab software, and an excel spreadsheet, with uncertainty propagation following the recommendations of Horstwood et al. (2016).

3.4. ID-TIMS U-Pb geochronology

Isotope dilution thermal ionization mass spectrometry (ID-TIMS) U-Pb geochronology was performed at the Institute of Geochemistry and Petrology of ETH Zurich (ETHZ) and at the Department of Earth Sciences of the University of Geneva (UNIGE). Millimeter-sized chips of the ASH-15-D and ASH-15-K calcite were extracted using stainless steel tools. Larger chips were further sub-divided resulting in ~1-7 mg aliquots. Individual chips were transferred into 3 ml Savillex beakers and repeatedly ultrasonically cleaned in ultrapure acetone and water. Cleaned sampled were transferred into pre-cleaned 3 ml Savillex beakers, spiked with ~5-10 mg EARTHTIME (^{202}Pb-)^{205}Pb-^{233}U-^{235}U tracer solution (Condon et al., 2015) and dissolved in 6N HCl at 120°C on a hotplate for ~30 minutes to assure complete dissolution and sample-spike equilibration. Dissolved samples were dried down and redissolved in 1N HBr. Uranium and Pb were separated using a single-column (50 µl, AG1-X8 resin) HBr-HCl anion exchange chemistry. The Pb fraction was dried down with a drop of H_3PO_4 after a single column pass. Uranium was dried down, redissolved in 3N HCl and further purified with a HCl-based second column pass before drying it down with a drop of H_3PO_4. Uranium and Pb were loaded on outgassed single Re filaments with ~1 µl of Si-gel emitter for thermal ionization mass spectrometry. Uranium and Pb isotope ratios were measured on a Thermo TRITON Plus at ETHZ and a Thermo TRITON at UNIGE. Lead isotopes were measured on the axial secondary electron multiplier employing dynamic peak-hopping routine collecting masses (202), 204, 205, 206, 207 and 208. Measured Pb isotope ratios were corrected for mass fractionation either using the double spike (ETHZ) or using a mass fractionation factor of 0.15 ± 0.03 %/amu for single Pb spiked samples (UNIGE). Uranium isotope ratios were measured as uranium-oxide (UO_2) employing a static measurement routine with Faraday cups connected to amplifiers with 10^{13} ohm feedback resistors (von Quadt et al., 2016; Wotzlaw et al., 2017). Isotope ratios were corrected for isobaric interferences from minor UO_2 isotopologues (Wotzlaw et al., 2017) and for mass fractionation using the double spike assuming a $^{238}U/^{235}U$ ratio of 137.818 ± 0.045 (Hiess et al., 2012) for sample and blank. Total procedural Pb blanks for the HBr-based chemistry at ETHZ are consistently between 0.2 and 0.4 pg. We therefore attribute up to 0.4 pg to laboratory blank with the remaining common Pb being attributed to initial common Pb. Total procedural blanks measured at UNIGE yielded an average of 1.15 pg that was taken as the laboratory blank contribution. Data reduction and uncertainty propagation was performed using Tripoli and an Microsoft Excel-based spreadsheet that uses the algorithms of Schmitz and Schoene (2007). Isochron calculations were performed using IsoplotR (Vermeesch, 2018). All uncertainties are reported at 95% confidence ignoring systematic uncertainties associated with the tracer calibration and decay constants unless otherwise stated.

4. Results

All analyses were performed on ASH-15-D-K yellow Pliocene layer, abbreviated here as "ASH-15" unless specification of ASH-15-D, E etc. is indicated. The ASH-15-A-C brown Pleistocene layer is not part of the ASH-15 suggested reference material.

4.1. LA elemental mapping

Elemental mapping for ^{88}Sr, ^{137}Ba, ^{206}Pb, ^{208}Pb, ^{238}U and $^{238}U/^{206}Pb$ ratio shows that the distribution of most elements is relatively homogeneous (Fig.3), and in good accordance with the luminescence data. Higher intensities for ^{238}U and ^{88}Sr were observed along grain boundaries and discontinuities, whereas Pb and the rest of the trace elements are more homogeneously distributed, arguing for steady environmental conditions ~~that have kept steady~~ during the deposition. Ten random regions of interest (ROI) were selected throughout the sample to mimic 10 spot analysis carried out at 85-90 microns spot size – just like one would do for U-Pb geochronology~~, for example~~. These ROIs were generated by drawing on the map circular regions with the radius of 85 or 90 microns in diameter. The pixels comprising each ROI were pooled together as representing the equivalent of a single spot analysis. The statistical data for each cluster (data are given in supplementary file) ~~was~~ were compared. The average values for all pixel data ~~is~~ are within 2 standard errors and in good agreement, indicating that, at least based on the elemental distribution we measured, the sample is relatively homogeneous for a natural sample. To further investigate the chemical homogeneity of the sample, a random transect through one of the growth zones was drawn and the signal intensities for ^{238}U were extracted. The transect data also indicate that ^{238}U variations are within 2 standard errors of the average value~~.~~ (full data is avilable in Table S1 in the supplement).

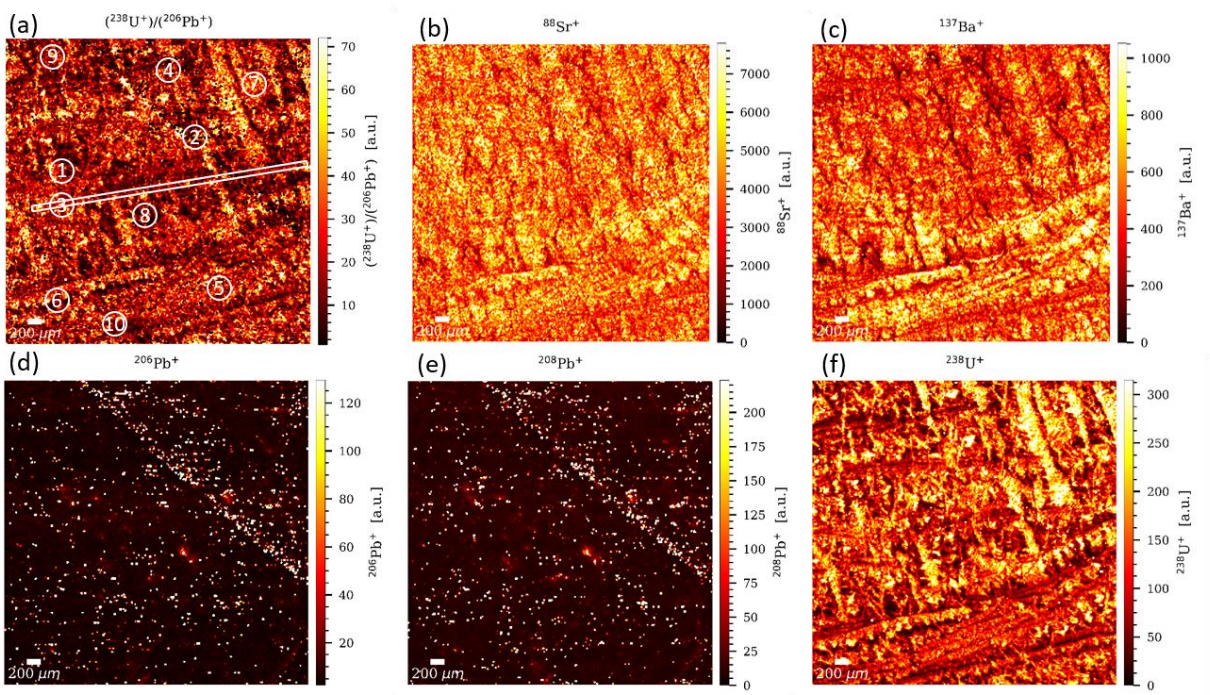

Figure 3. Signal intensity maps of ASH-15. for $^{238}U/^{206}Pb$, ^{88}Sr, ^{137}Ba, ^{206}Pb, ^{208}Pb, and ^{238}U (a-d). The plotted signal was corrected for blank and analytical drift of the instrumentation. Note that each distribution map has its own signal intensity scale. The position of the regions of interest and transect is shown in (a). The circles designating the location of the regions of interest are not at scale. (data is available in Table S1 in the supplement).

4.2. LA-MC-ICPMS spot analyses

Data and calculated ages for the LA-ICPMS transects are shown in Tera-Wasserburg space in Fig. 4 (n = 379 of 412 total spots). Analyses rejected from the age calculation include those with $^{207}Pb/^{206}Pb$ uncertainties larger than 0.1% (n = 2) and those with high common-Pb contents (^{208}Pb cps >5000; n = 17). A further 14 spots plotted below the array; these data were represent the first 1–2 mm of spots of the lengthwise transect (lower right in Fig. 2a), and suggest that a small percent of ASH-15 may behave differently during ablation and/or may have been subsequently modified after crystallization; upon inspection, this portion of the section contains more pore space and impurities than the majority of the section. The remaining 379 define a normally distributed array with a lower intercept age of 2.952 ± 0.043 Ma (MSWD = 2.5), which is well within uncertainty of the new ID-TIMS data presented herein (full data is avilable in Table S2 in the supplement)and the scatter observed in the LA data (i.e., MSWD > 1) is lower compared with scatter observed in the ID-TIMS data. The calculated upper intercept of each transect is equivalent and within 1% of the common Pb composition calculated from the ID-TIMS data. Not surprisingly, the lengthwise transect reveals a larger spread in common/radiogenic Pb ratios; this transect crosses more growth zones and has a higher probability of sampling a variety of concentrations of both Pb and U. Conversely, the more limited spread in common/radiogenic Pb ratios appears to reflect the limited sampling of growth zones, and would suggest that individual growth zones contain a relatively limited range of concentrations in U and Pb. The slightly higher MSWD for the lengthwise transect

(2.7) relative to the growth zone transect (2.5) could also reflect these inherited compositional differences during growth history, and a resulted “mixing” or “averaging” of different growth phase along calcite continuous growth.

Variations of ASH-15 ages during 20 different runs (with 5-30 spot analysis in each) using both single (ICPMS) and multi-collector (MC-ICPM) are shown in Fig. 4b (full data is avilable in Tables S3-S5 in the supplement). The ages are calculated using IsoplotR, not anchored to ~~0.8315~~specific common-lead, and are not corrected for disequilibrium. Although there is a large scatter in the ages of the different runs the average ages (marked ~~in~~ with black box~~thick lines~~) ~~are~~ plot~~ted~~ close to the new ID-TIMS ages, or are slightly younger in age.

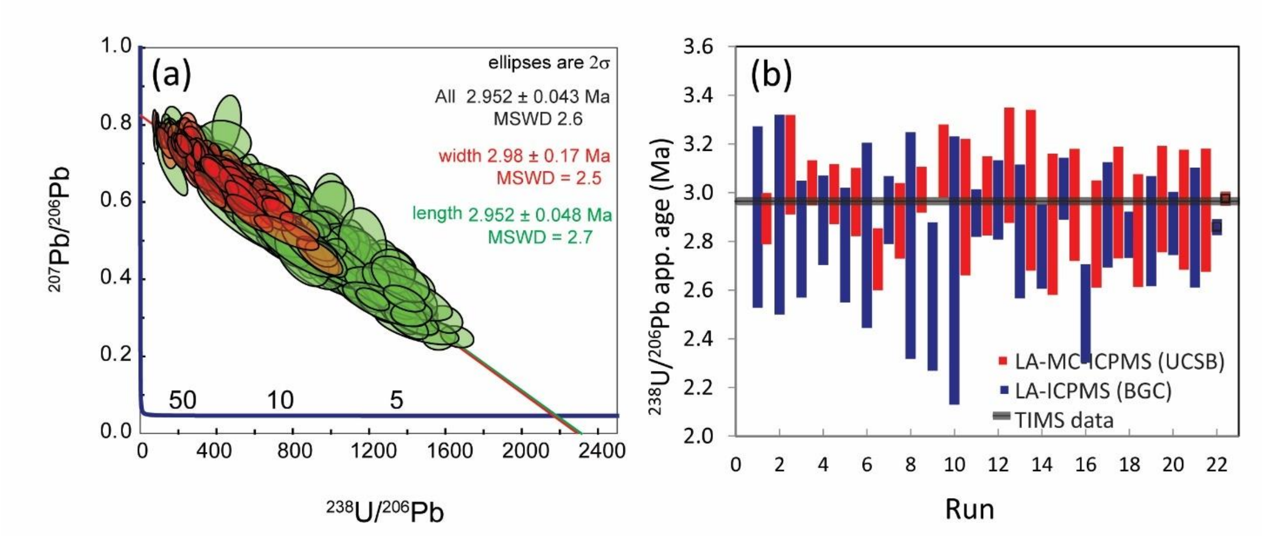

Figure 4. LA-MC-ICPMS analyses of calcite ASH-15. (a) Tera-Wasserburg concordia space plot (n=385) for ~~(n=385). Spots~~ spots analysis within lengthwise transect (green) and along growth zone transect (red). Calculated age, 2σ error and MSWD are given for both and for all spots together; (full data is available in Table S2 in the supplement); (b) Variations of ASH-15 ages during different runs using both single and multi-collector ICPMS. Ages are calculated using WC1 as primary MS; the new ID-TIMS age is indicated with a grey line; (full data is available in Table S3-S5 in the supplement) ~~Ages are calculated using IsoplotR, anchored to 0.8315 common-lead, and are not corrected for disequilibrium~~.

4.3. Down-hole fractionation

Reference material is important for correction of both laser-induced elemental fractionation (LIEF) and ~~in~~ plasma-related ionization efficiency. Ideally, the reference material should resemble the unknown samples as much as possible in terms of its chemistry (e.g. Mg and Fe content), texture (i.e. micritic, crystalline), and age. The WC1 and ASH15 are both low-Mg calcite but they are very different in ~~their~~ textures and age. The ASH15 is a ~3 Ma, well-crystallized elongated calcite (up to 1 cm) and WC1 is a 254 Ma recrystallized botryoidal calcite, formed after aragonite. Despite these differences, both WC1 and ASH15 display a very similar down-hole fractionation pattern (Fig. 5d). Fig. 5 shows stacked integration plots of the down-hole raw ^{206}Pb/ ^{238}U ratio of different RMs including, the ASH15, WC-1, and Duff Brown Tank (Black and Gulson, 1978). The ASH15 displays much larger scatter in the raw data (Fig. 5a) in comparison to both WC1 and Duff Brown Tank (Fig. 5b-c), however, the average value yielded identical down-hole ~~patterns~~ fractionation to that of WC-1 (Fig. 5d). Duff Brown Tank is also consistent with the down-hole patterns buet less steep in comparison to WC1 and ASH15 (Fig. 5d). This comparison suggests that down-hole fractionation and laser-induced elemental fractionation (LIEF) ~~is~~ are similar among the different RMs. It is thus suggested that differences in measured and expected ^{206}Pb/^{238}U ratios ~~between measured and expected~~ in calcite material are likely to be caused mostly by plasma-ionization differences between unknown samples and RMs.

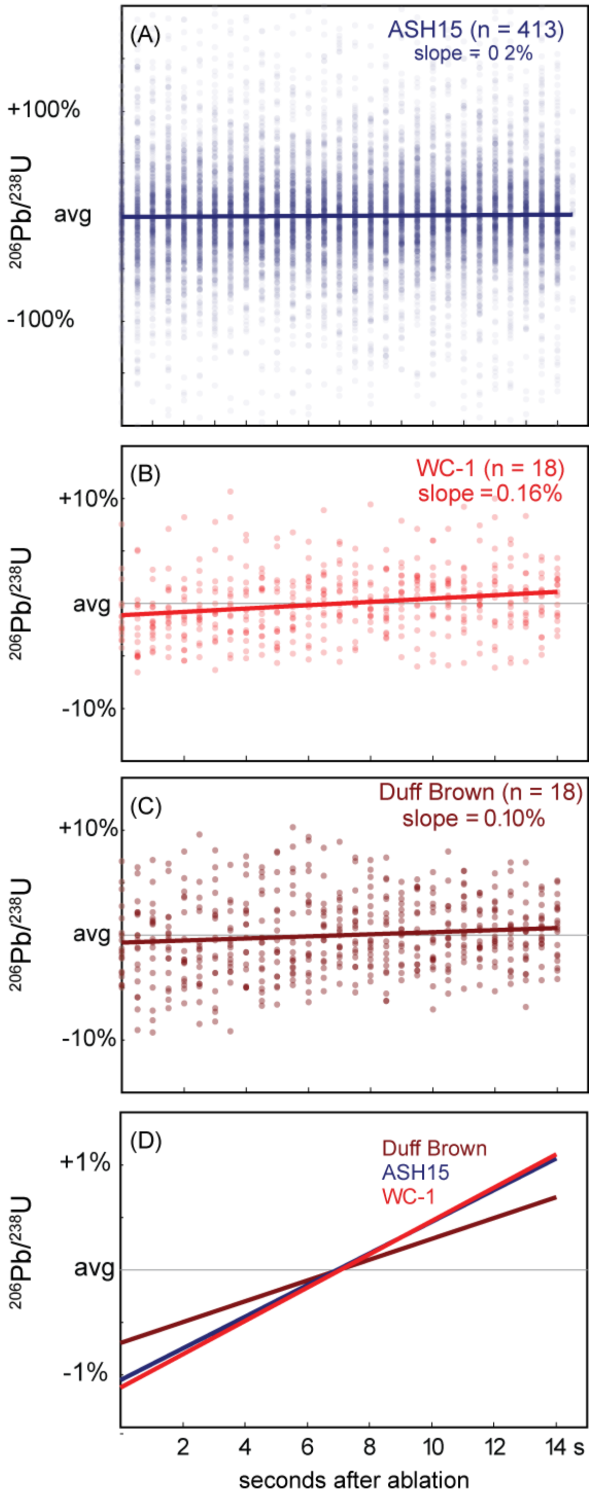

Figure 5. Stacked integration plots of raw ^{207}Pb-corrected $^{206}Pb/^{238}U$ ratios for calcite reference materials ASH-15, WC-1, and Duff Brown Tank. The low Pb concentration in ASH-15 yields more scatter, but average slopes of all RMs are similar, with 1-2% change in age over 10 seconds (100 pulses) of ablation. The results suggest ~~for~~ minimal differences in down-hole fractionation of the different RMs.

4.4. ID-TIMS results

Twelve aliquots of ASH-15D analyzed at ETHZ yielded ^{238}U/^{206}Pb ratios between 1096 and 2084 and ^{207}Pb/^{206}Pb ratios between 0.0825 and 0.4403 (full data is available in Table S6 in the supplement). Plotted in Tera-Wasserburg space, ~~this~~ these data yield~~s~~ a single isochron with an initial ^{207}Pb/^{206}Pb of 0.832 ± 0.015 (uncertainties are 95% confidence intervals) and a concordia intercept age of 2.967 ± 0.022 Ma (Fig. 6a). The elevated mean square weighted deviation (MSWD) of 12 is attributed to minor heterogeneities, most likely in the initial ^{207}Pb/^{206}Pb ratio of the speleothem calcite. Twelve aliquots of ASH-15K analysed at ETHZ returned ^{238}U/^{206}Pb ratios between 723 and 2094 and ^{207}Pb/^{206}Pb ratios between 0.0720 and 0.5677. In Tera-Wasserburg space, eleven out of twelve aliquots define a isochron with an initial ^{207}Pb/^{206}Pb of 0.8314 ± 0.0040 and a concordia intercept age of 2.964 ± 0.016 Ma (Fig. 6b). A single aliquot (#5.4) plots significantly below the isochron defined by the other aliquots. The elevated MSWD of 34 together with the single outlier suggest some heterogeneities in the initial ^{207}Pb/^{206}Pb of the ASH-15K calcite. Thirteen aliquots of ASH-15K analysed at UNIGE (pink color, Fig. 6b) yielded ^{238}U/^{206}Pb ratios between 433 and 1853 and and ^{207}Pb/^{206}Pb ratios ranging from 0.1856 to 0.6660. Twelve of the thirteen analyses yield ~~define an~~best-fit ~~isochron~~~~isochron~~ line with an initial ^{207}Pb/^{206}Pb of 0.814 ± 0.019 and a Concordia intercept age of 2.947 ± 0.065 Ma. The elevated MSWD of 36 confirms the minor heterogeneity of the initial ^{207}Pb/^{206}Pb.

The excellent agreement between the ASH-15D and ASH-15K datasets ~~suggest~~ indicates that the entire speleothem growth layer between these two growth zones is of equivalent age with minor heterogeneities in the initial ^{207}Pb/^{206}Pb ratio and justifies combining the data into a single isochron regression. The combined isochron, using 35 of 37 analysed aliquots, yields an initial ^{207}Pb/^{206}Pb of 0.8306 ± 0.0033 and a concordia intercept age of 2.965 ± 0.011 Ma with a MSWD of 35 (Fig. 6c). We consider the results of the combined ~~isochron~~ regression as the best reference value for using ASH-15 as a primary reference material.

The new TIMS data provide the most extended bulk investigation analyses work of the ASH-15 sample, with a total of 37 sub-samples that are separated from bottom (K, n=25) to top (D, n=12) sections of the sample. The relatively high MSWD of 35 is suggested to reflect true heterogeneities of the dated material, possibly related to impurities that are concentrated within grain boundaries (as suggested by CL and elemental mapping). We re-calculated previously determined isochron ages of Vaks et al. (2013) and Mason et al. (2013; Fig. 7). We obtained concordia intercept ages of 3.0088 ± 0.053 Ma for ASH-15-D (MSWD=11; n=5) and 3.0153 ± 0.042 Ma for ASH-15-K (MSWD=14; n=5) of Vaks et al. (2013) and 3.0015 ± 0.029 for ASH-15-D (MSWD=2; n=5) of Mason et al. (2013). These ages are systematically older but still overlap within uncertainty withare largely overlapping within uncertainty with our new ID-TIMS age of 2.965 ± 0.011 Ma (Fig. 7; and data in Table S7 in the supplements). The apparent minor systematic offset towards slightly older ages is attributed to the lower number of aliquots in the MC-ICPMS datasets combined with the heterogeneous initial Pb isotope composition. We speculate that the small but systematic offset between previous results and our new data may be related to natural heterogeneities that are sampled differently depending on sample size but we cannot exclude analytical differences as an additional source of bias. The origin of this bias between the two techniques should be investigated more systematically in future. For laser ablation U-Pb work, we recommend the use of the new ID-TIMS age because of the large number of sub-samples (n=37), and the small aliquots (1-7 mg) that are more representative of laser-ablation spot analysis. In addition, the use of the precisely and accurately calibrated EARTHTIME tracer solutions (Condon et al., 2015) and the online mass fractionation correction provided by the double Pb and double U tracer are an important advantage of this method compared to previous bulk analyses. The excellent interlaboratory reproducibility gives us additional confidences that our ID-TIMS data provide the most accurate characterization of the U-Pb systematics of the ASH-15 calcite for use as a primary reference material.

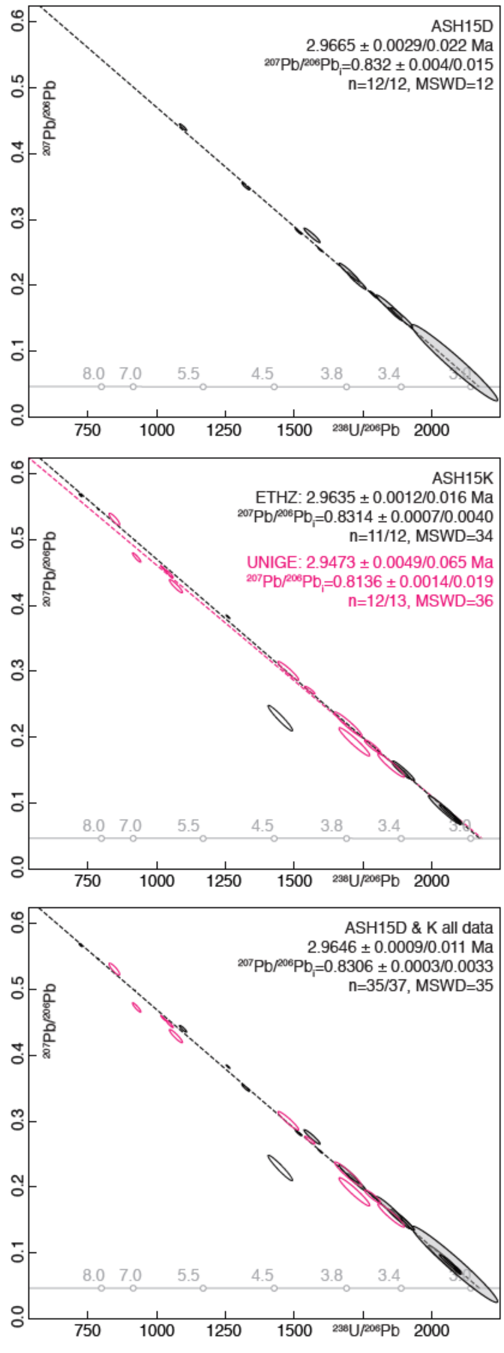

Figure 6. ID-TIMS U-Pb results for ASH-15D, ASH-15K, and for both ASH-15D–+K displayed in Tera-Wasserburg concordia space. Uncertainties on the initial $^{207}Pb/^{206}Pb$ ratios and the intercept ages are given as 2σ and as 95% confidence intervals including overdispersion (Vermeesch, 2018).

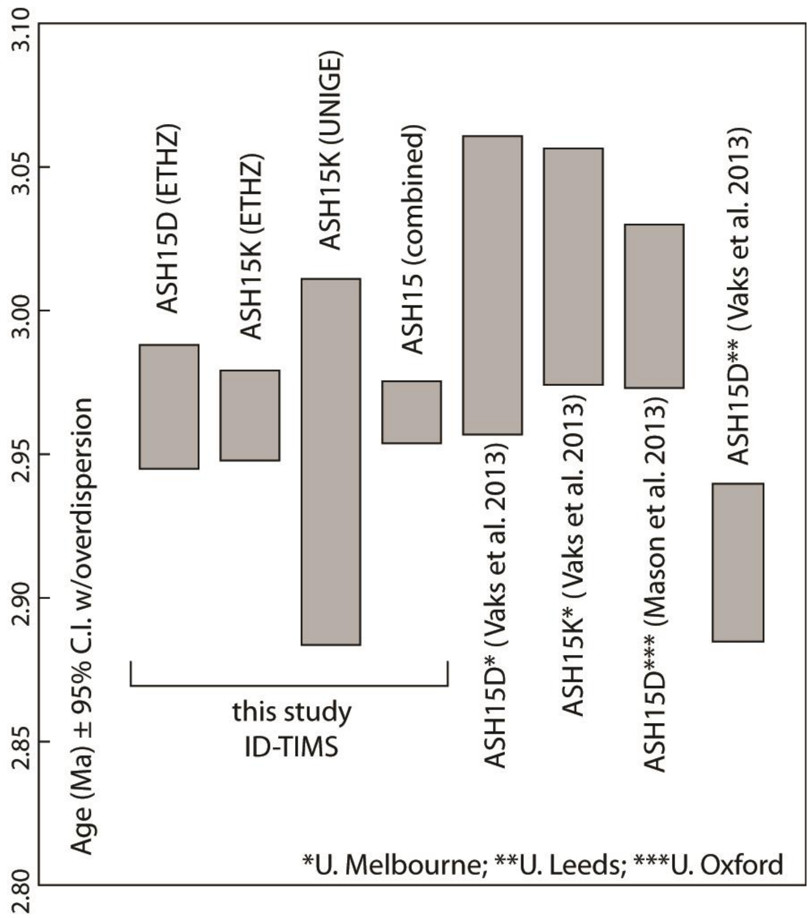

Figure 7. Previous (re-calculated) and new ages of ASH-15 from isotope-dilution U-Pb analysis. All ages are calculated using IsoplotR (Vermeesch, 2018), ~~and~~ are not corrected for disequilibrium and are not anchored to common-lead specific value (see data in Table S7 in the supplements).

4.5. Calcite reference material

The U and Pb concentrations of carbonate materials vary greatly. Data compilation by Roberts et al. (2020; this issue) combined hundreds of carbonate samples from different origin such as diagenetic, biogenic, speleothem, and vein-fill. This compilation indicates several orders of magnitude differences in U and Pb concentrations of the different types of carbonate and the heterogeneity of spot analysis within each type or even a single sample. A modified representation of their data, excluding calcite vein-fill, which vary throughout the entire compositional range, is shown together with the currently available calcite reference materials (Fig. 8; and full data in Table S8 in the supplement). Note that both ASH15 and JT, display much larger heterogeneity when measured by LA-ICPMS (small symbols) relative to ID-TIMS (large symbols). Despite the high compositional heterogeneity of each of the reference material, they show minimal overlap and together they cover most of the compositional range of the presented carbonate material. WC1 (Roberts et al., 2017) with relatively high U and Pb concentrations can easily be measured on single collector ICPMS (including quadrupole instruments) and is most appropriate to be used for dating vein-fill and diagenetic carbonates. In contrast, the ASH15 flowstone, with relatively low Pb and high U concentration that are better measured on sector-field (MC)-ICPMS is most appropriate for dating speleothem type carbonates. Finally the JT (Guillong et al., 2020), with moderate U and Pb concentration can be used on both single- and multi-collector sector field ICPMS instruments and for all types of carbonate samples. Reference material with high Pb and low U or both low U and Pb concentrations will further help to cover the full compositional range of carbonate material but may introduce analytical challenges.

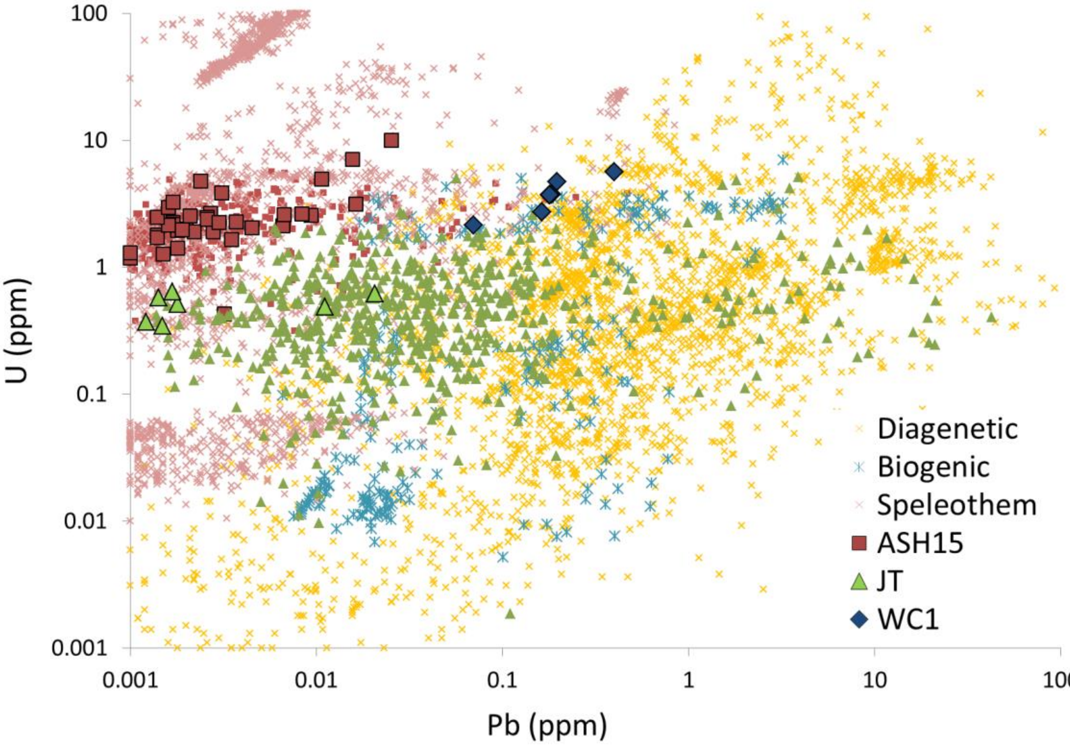

Figure 8. U and Pb concentrations of different carbonate samples and available reference materials. Large and small symbols for the reference materials indicate ID-TIMS and LA-ICPMS analyses, respectively. Note the minimal compositional overlap of the three reference materials (ASH15, WC1, and JT). Data for diagenetic, biogenic, and speleothem carbonates are from Roberts et al. (2020, this issue). Data for JT standard are from Guillong et al. (2020).

5. Conclusions

The ASH-15 speleothem calcite is characterized as a matrix matched reference material for LA-ICPMS U-Pb geochronology of calcite. ID-TIMS analyses of small 1-7 mg aliquots of two growth zones suggest sufficient homogeneity with a combined intercept age of 2.965 ± 0.011 Ma and an initial $^{207}Pb/^{206}Pb$ of 0.8315 ± 0.0026. These data are recommended as the reference values for the ASH-15 calcite reference material. The excellent agreement between the two growth zones suggest that the entire interval between the two dated layers can be used with the same reference age. Compared to other calcite reference material (e.g. WC1), ASH-15 is more homogeneous but has lower radiogenic Pb content and therefore requires more sensitive instruments (i.e. sector field rather than quadrupole mass spectrometers) to be used as a reference material.

Author's contribution

PN: data processing and writing, JFW: ID-TIMS analysis and writing, MO: ID-TIMS analysis, AV: sample collection and writing, CS: LA mapping analysis and writing, MS: LA mapping analysis. NR: LA-ICPMS, data analysis and writing. AKC: LA-MC-ICPMS, data analysis and writing.

Competing interests

The authors declare that they have no conflict of interest.

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Appendices

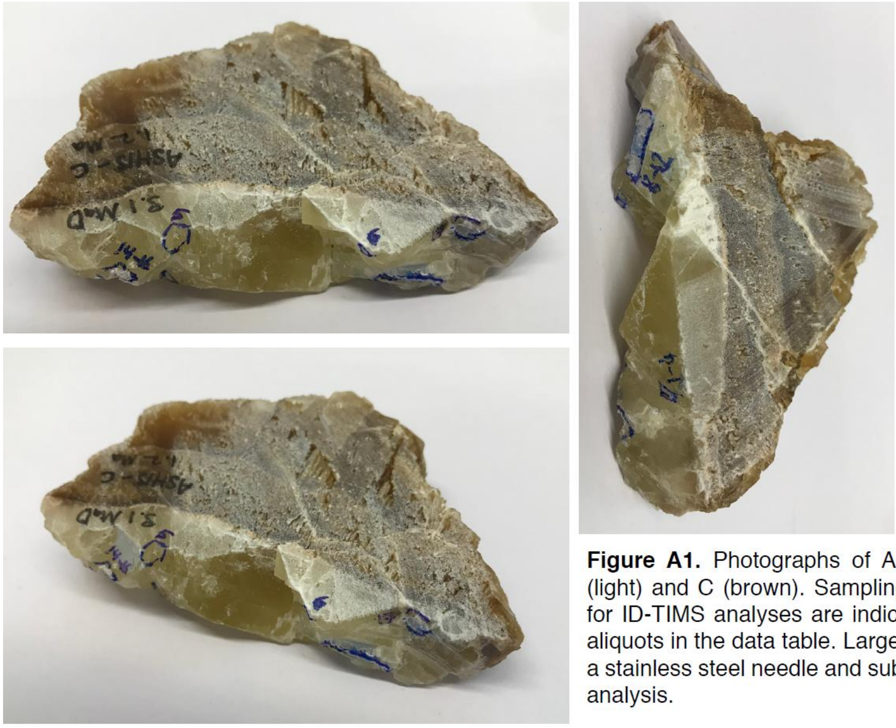

Figure A1. Photographs of ASH15 flowstone with layers D (light) and C (brown). Sampling localities of aliquots sampled for ID-TIMS analyses are indicated by numbers matching the aliquots in the data table. Larger pieces were chipped off using a stainless steel needle and subdivided into smaller aliquots for analysis.

Figure A2. Photographs of ASH15 flowstone with layers K (bottom) to D (top). Sampling localities of aliquots samples for ID-TIMS analyses within layer K are indicated with numbers (n=12) and are matching the aliquots in the data table.

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