JAAS

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Cite this: J. Anal. At. Spectrom., 2017, 32, 1359

Received 15th March 2017 Accepted 25th May 2017 DOI: 10.1039/c7ja00095b

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1. Introduction

U-Th-Pb age dating relies on the accurate and precise determination of a set of isotope ratios (e.g. ²³⁸U/²⁰⁶Pb, ²³²Th/²⁰⁸Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb). Three main techniques are widely used to obtain such data:¹ (i) isotope dilution thermalionisation mass spectrometry (ID-TIMS) that is an absolute method, (ii) secondary ion mass spectrometry (SIMS/SHRIMP) and (iii) laser-ablation inductively-coupled-plasma massspectrometry (LA-ICP-MS) that both are relative methods. ID-TIMS is the most precise way to determine the above mentioned isotope ratios.2 However, modern ID-TIMS U-Th-Pb geochronology focuses on single accessory crystals (mostly <300 µm in diameter) or fragments of single crystals.² This strongly limits the use of ID-TIMS techniques to analyze natural samples because chemical and isotopic zonation is common, e.g., the presence of <50 µm sized inherited cores. In situ analysis techniques such as SIMS and LA-ICP-MS are suitable to analyse

Non-matrix-matched standardisation in LA-ICP-MS analysis: general approach, and application to allanite Th–U–Pb dating[†]

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To make use of the full geochronological potential of accessory minerals such as zircon, allanite, monazite, and titanite, high spatial resolution isotopic analysis of the Th-U-Pb system is required. Laser ablation ICP-MS techniques are increasingly applied for this purpose, yet the matrix-dependence of analysis and the paucity of high-guality standards for most of these minerals impose major limitations - as for all in situ microbeam analytical techniques. A novel approach for LA-ICP-MS data reduction is presented here that allows for non-matrix-matched external standardization while yielding highly accurate isotopic ratios and age data. The matrix-dependent downhole fractionation during laser ablation is empirically quantified and corrected; hence, well constrained reference materials (here: Plesovice zircon) can be employed as primary standards for the analysis of rare yet petrologically essential minerals (here: SISS, CAP, and TARA allanite). Using laser beam sizes of 32 and 24 µm, transient isotope ratio data show systematic differences between zircon and allanite; these are attributed to matrix effects and are combined to correct for the temporal evolution of the matrix-dependent downhole fractionation. The new data reduction technique was tested on three allanite standard reference materials demonstrating analytical accuracy at precisions equal to those achieved by ion probe and LA-ICP-MS rastering. The analytical procedures presented here could be applied to any combination of two different matrices (calibration standard and sample), thus greatly mitigating dependence on precisely characterized calibration materials, and contribute to establishing universally applicable LA-ICP-MS dating protocols that can be applied to a much broader range of minerals and chronometers.

small sample masses (0.5–10 ng) and to resolve heterogeneities within single grains, notably in their textural context observed in CL images of polished thin sections of a rock sample. However, *in situ* techniques are relative (except possibly the 207 Pb/ 206 Pb age) and thus rely on accurate external standardisation.³

Ideal standards for U-Th-Pb dating are chemically and isotopically homogeneous.^{4,5} So far, mineral-matrix matched standards have been deemed a must for highly accurate age dating via LA-ICP-MS.6 It has been demonstrated recently, however, that non-matrix-matched calibration employing a twovolume ablation cell (Laurin Technic Pty S-15), robust plasma conditions7 and a procedure of low ablation rate maintaining high laser crater diameter/depth ratio can yield accurate 193 nm ns-LA-ICP-MS age data8,9 when accepting much reduced analytical sensitivity and thus spatial resolution. Calibration standard concentrations in U, Th, and Pb need to be high enough to provide high-intensity calibration signals and, ideally, are comparable to unknowns. Standards commonly used so far for U-Th-Pb dating are of natural origin. A significant fraction of the Pb isotopes in these calibration materials is therefore derived from the decay of U and Th (radiogenic Pb, referred to as Pbrad). However, some minerals incorporate Pb



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also during their growth (initial Pb or common Pb, referred to as Pb_c). The primary quality requirement of natural reference materials used as standards is homogeneity in age. However, natural reference materials all show minor chemical and isotopic heterogeneity, and it is of major concern to take these properly into account. Based on the *in situ* analytical precisions now achieved, available reference materials can be subdivided into two classes according to their quality: (i) reference materials with known chemical heterogeneities, but constant 238 U/²⁰⁶Pb and 232 Th/²⁰⁸Pb ratios (*i.e.*, no common lead, as in zircon and most monazite samples), and (ii) reference materials with a fixed age, but variable isotopic ratios due to the incorporation of variable amounts of common lead.

A correction for common lead is needed in order to calculate the exact ${}^{238}\text{U}/{}^{206}\text{Pb}$, ${}^{232}\text{Th}/{}^{208}\text{Pb}$, ${}^{235}\text{U}/{}^{207}\text{Pb}$, and ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ radiogenic isotope ratios of standards. 10,11 Different common lead correction schemes rely on four sets of variables: (i) age, (ii) common lead fractions, (iii) initial Pb-isotope ratios, and (iv) isotopic composition of a sample at present time. 12 Prior knowledge of two sets of variables allows for the complete determination of the system of variables given concordance in the U and Th systems. Consequently, reference materials with known age and given initial Pb isotope composition can be used for standardisation in *in situ* analysis techniques. 11

Allanite is an example of a promising petrochronological mineral12-18 with limitations in U-Th-Pb age dating due to the quality of available reference materials that all contain variable amounts of common lead. Reference materials so far employed are chemically heterogeneous, and high Th/U ratios make allanite ages especially prone to ²⁰⁶Pb_{excess}.¹⁹ Age heterogeneity is documented for several reference materials within and among grains, and various data reduction procedures are employed,13,20 all of which complicates the definition of "true" reference ages. We thus developed a fully calibrated procedure for non-matrix matched standardisation in quadrupole LA-ICP-MS using zircon as a standard for U-Th-Pb dating of allanite. SRM610 from NIST was not considered in the present study as reference material for U-Th-Pb age dating because of heterogeneities in trace element concentrations notably for Pb;21 hence, isotope ratios involving U/Pb and Th/Pb may unpredictably vary in the calibration material, thus adding additional procedural uncertainty. The calibration procedures are documented in full detail, as they can be employed for any other non-matrix-matched pair of standard and unknown, provided the instrumental setup employed for dating is properly calibrated. We also evaluate the suitability of the three most often used allanite reference materials BONA, CAP, and TARA, and conclude that TARA is the most suitable matrix-matched standard reference material for allanite available to date.

2. Reference materials

Several natural standard reference materials for allanite are being used by the community; data for these rely on various analytical methods, summarized in Gregory *et al.*¹³ and Smye *et al.*²⁰ The present work utilizes the data reported in these studies for the three standard reference materials BONA, CAP and TARA. Careful examination of primary analytical data for these materials (from different labs and different techniques) indicates that minor chemical differences exist among some of the materials running under the same name. However, the available data set is insufficient to determine whether small systematic differences also exist in the relevant isotopic ratios. For sake of clarity, the allanite separates used in the present study are specifically labelled (BONA^b, CAP^b). BONA^b and CAP^b were separated from newly collected samples. TARA used in this study was separated from blocks of granodiorite (obtained from D. Rubatto) collected at the site of the original material; hence, we use the same acronym for our data.

2.1 TARA

TARA allanite (from a granodiorite of the Berridale Batholith, SE Australia) was introduced as a reference material by Gregory et al.13 whose SHRIMP analyses gave a ²³²Th/²⁰⁸Pb-age of 414.3 \pm 3.3 Ma (2 σ) and a ²⁰⁷Pb-corrected weighted mean 238 U/ 206 Pb-age of 419.3 \pm 7.7 Ma (2 σ , 24 analyses). Common lead fractions vary between 0.5 to 1.0% for ²⁰⁸Pb and 12 to 25% for ²⁰⁶Pb. LA-ICP-MS data^{12,13} are in agreement with the SHRIMP ages; however, averaged ²³²Th/²⁰⁸Pb single spot ages are older than the reference age originally used by Williams et al.22 who had interpreted their K-Ar and Ar-Ar data on hornblende (412 \pm 1.4 Ma, 2 σ) to represent the emplacement age of this intrusion. ID-TIMS data by Smye et al.20 indicate complications in TARA allanites: two of five single grain analyses in the ²³²Th/²⁰⁸Pb system give younger apparent ages, whereas ²⁰⁴Pb-corrected ²³⁸U/²⁰⁶Pb data show a large spread, between 407 and 431 Ma (\pm 4 Ma). Zircon from a TARA sample yields a weighted mean $^{238}\text{U}/^{206}\text{Pb-age}$ of 418 \pm 4.2 Ma. 23 In view of the complex magmatic history documented for the Berridale complex,²² it is difficult to relate the age data for the different minerals and isotopic systems to one another. This is discussed further in Section 6. As used by Gregory et al.,13 the 412 \pm 1.4 Ma age of Williams *et al.*²² is taken here as preliminary reference age.

2.2 CAP

CAP allanite (named after the Permian Cima d'Asta pluton, northern Italy) was investigated and first dated by Barth et al.24 by ID-TIMS to 275 \pm 1.5 Ma (2 σ , weighted mean of four ²³²Th/²⁰⁸Pb allanite analyses from individual grains). A Triassic stage of regional hydrothermal alteration was recognized in the area,²⁴ but it seems not to have affected the Th-U-Pb system of CAP allanite; two of four analyses show concordance in the Th-Pb and U-Pb age data. The first study to use SIMS for spot dating of allanite25 reproduced the TIMS reference age, but the individual spot data show a wide spread in ages. Common Pbcorrected (based on ²⁰⁷Pb) ²³²Th/²⁰⁸Pb age data obtained by SHRIMP13 show much less scatter and are concordant with their ²³⁸U/²⁰⁶Pb ages. LA-ICP-MS analyses agree with the SHRIMP age data, but two out of 27 spots analyzed do indicate an effect of hydrothermal alteration.13 The data set as a whole shows larger uncertainties in Th/Pb data and yields slightly older apparent ages. Common lead fractions vary between 0.7-1.0% for ²⁰⁸Pb and 13–21% for ²⁰⁶Pb.

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For the present study CAP^b allanite was separated from a granodiorite sample collected at the location indicated by Barth *et al.*²⁴ (p. 151). However, three small granodioritic stocks are discernible in the field, and the Barth's study did not report the chemical composition of allanite and gave insufficient detail to be sure which intrusive body had been sampled. These differ slightly in grain size and visible alteration; the one showing least alteration was sampled, and all CAP^b allanite grains used in the present study were separated from sample CAP-1202. Their chemical compositions are very similar to those reported by Gregory *et al.*¹³ CAP^b allanite grains show some altered peripheral domains, and locally these are intergrown with the dominant clean allanite.²⁴ Tiny inclusions of zircon and monazite were occasionally detected, the age of which is not known. No ID-TIMS data exist for CAP^b.

2.3 BONA

The original BONA allanite from Bergell granodiorite (named after the sample location Valle di Bona) was dated by von Blanckenburg,¹⁹ who analyzed multigrain fractions by ID-TIMS and obtained a Common-Pb corrected (based on ²⁰⁷Pb) ²³²Th/²⁰⁸Pb-age of 30.1 ± 0.25 Ma (2 σ) and a ²³⁸U/²⁰⁶Pb-age of 36.49 ± 0.59 Ma (2 σ). Zircon from the same rock gives a complex age pattern with ²³⁸U/²⁰⁶Pb-ages of 26.3 to 30.7 Ma (*ca.* ±0.15 Ma, 2 σ). Allanite crystals from the same grain fraction as the original allanite used for ID-TIMS in von Blanckenburg,¹⁹ were analyzed by Gregory *et al.*¹³ (²³²Th/²⁰⁸Pb-age: 30.5 ± 0.4 Ma) using SHRIMP. Smye *et al.*²⁰ reported only the ²³⁸U/²⁰⁶Pb-ages from their ID-TIMS study (using single grain allanite), and these are highly variable (22 to 60 ~ ±4 Ma, uncorrected for ²⁰⁶Pb_{excess}).

BONA^b was collected from a petrographically similar granodiorite, but not at the same outcrop as the original sample (BONA1, von Blanckenburg,¹⁹ p. 21). Regarding the complexity reported in previous studies and the fact that we are not studying the exact same sample, we classified our material as an unknown in the first instance. BONA^b allanite shows very similar, complex zonation, chemical composition, and heterogeneity within grains and fractures as described in the previous work for the original BONA allanite grains. Darling *et al.*¹² analyzed BONA^b and obtained a ²³²Th/²⁰⁸Pb-age: 30.6 ± 0.3 Ma using LA-ICP-MS. Their ²³⁸U/²⁰⁶Pb-ages, as in Smye *et al.*²⁰ were generally older and highly variable (16 to 100 Ma), and common lead fractions vary between 14–22% for ²⁰⁸Pb and 65–85% for ²⁰⁶Pb.

2.4 Plesovice

Plesovice zircon was characterized and proposed as a zircon standard by Slama *et al.*⁵ It is of particular interest because its Th concentration is higher than in other zircon standard reference materials and approaches the typically high Th concentrations in allanite. Thus it is well suited as a primary standard for allanite-dating and was successfully used,¹² minimizing matrix sensitivity by dynamic (raster) ablation. The reference age of Plesovice zircon is 337.13 \pm 0.37 Ma (ID-TIMS, 95% confidence limits, including tracer calibration

uncertainty⁵). Slama *et al.*⁵ limited their characterization of Plesovice zircon to the U–Pb system, but Darling *et al.*¹² concluded from their analysis that the Th–Pb system is also concordant.

3. Experimental

LA-ICP-MS Th–U/Pb analysis of allanite was performed at the Institute of Geological Sciences, University of Bern. A GeoLas Pro 193 nm ArF excimer laser ablation system (Lambda Physik, Germany) is combined with an ELAN DRC-e quadrupole ICP-MS (QMS). The instrumental setup and operating conditions employing robust plasma conditions are reported in Table 1, the data acquisition procedure is summarized in Fig. 1 (left column) and addressed below in detail.

Ablation experiments were carried out in single spot mode under fixed laser operating conditions (9 Hz repetition rate and 2.5 J cm⁻² fluence producing 12 µm deep craters in 40 seconds). Operating conditions (gas flow rates, torch parameters, ionlenses and acceleration voltage) on the QMS were optimized prior to each analytical session by ablation of the standard glass NIST SRM610 with a 44 µm beam size, a repetition rate of 10 Hz and a fluence of 6 J cm⁻². Criteria to be met are maximum sensitivity at robust plasma conditions (S(U) = S(Th)) with an oxide production rate ThO⁺/Th⁺ well below 0.5% and low plasma aerosol mass load.²⁶

The isotopes ²⁷Al, ²⁹Si, ¹³⁹La, ²⁰²Hg, ²⁰⁴(PbHg), ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, ²³⁵U, and ²³⁸U were measured in peak hopping mode. Longer dwell times (ms in brackets) were chosen for ²⁰⁴Pb (10), ²⁰⁶Pb (20), ²⁰⁷Pb (30), ²⁰⁸Pb (30), ²³²Th (20), and ²³⁸U (20) isotopes relevant for dating in order to improve measurement precision. ²⁷Al, ²⁹Si and ¹³⁹La (5) were measured to monitor composition, whereas ²⁰²Hg (5) was used to correct the gross 204 signal (10) for ²⁰⁴Hg interference on ²⁰⁴Pb (assuming common Hg isotopic abundances). ²⁰⁴Pb was only measured to ensure that ²⁰⁴Pb common lead correction is not relevant.

As U concentrations in allanite are commonly low, ²³⁵U can approach its analytical limit of detection where measurement uncertainty thus increases for ²⁰⁷Pb/²³⁵U ratios. Since the variation in ²³⁵U/²³⁸U is negligibly small at our analytical precision in accessory minerals to be dated,²⁷ we calculate the ²⁰⁷Pb/²³⁵U ratio from the measured ²³⁸U: ²⁰⁷Pb/²³⁵U = (²⁰⁷Pb/²⁰⁶Pb) × (²⁰⁶Pb/²³⁸U) × 137.9.²⁸

Hand-picked mineral grains were mounted and polished. BSE images were acquired to ensure precise location of measurement spots for chemically zoned crystals. Grains in the mount were arranged in the ablation cell near the central axis of gas flow (Table 1).

The output of a single LA-ICP-MS spot analysis is a timeresolved sequence of measurements for different isotopes reported in counts per second (cps). A single analysis includes 60 s background, 5 s pre-ablation, 15 s pre-wash-out, 40 s of ablation and 15 s of final wash-out. Spot analyses are grouped in analytical blocks of one hour, which include analyses on the SRM610 glass, the zircon standard, a secondary allanite standard, and the samples to be dated (Fig. 1). The system

Laboratory and sample preparation

Laboratory name Sample type/mineral Sample preparation

Imaging

Laser ablation system

Make, model and type Ablation cell and volume

Laser wavelength (nm) Pulse width (ns) Fluence (J cm⁻²) Repetition rate (Hz) Ablation duration (s) Ablation pit depth/ablation rate

Spot diameter (µm) Sampling mode/pattern Carrier gas

Cell carrier gas flow ($L \min^{-1}$)

ICP-MS Instrument

Make, model and type RF power (W) Make-up gas flow (L min⁻¹) Detection system Masses measured Integration time per peak/dwell times (ms); quadrupole settling time between mass jumps Total integration time per output data point (s)

IC dead time (ns)

Data Processing Gas blank

Calibration strategy Reference material info Data processing package used/correction for LIEF Common-Pb correction, composition and uncertainty Uncertainty level and propagation

GeoLasPro (Compex 102; Lambda Physics) In-house built rectangle cell brought down to a round base area, volume *ca*. 21 cm³ 193 nm ArF excimer laser 15 ns 2.5 J cm^{-2} 9 Hz 40 s 12 mm pit depth, measured using an optical microscope, equivalent to 35 nm per pulse 24 µm/32 µm Static spot ablation He (1.000 L min⁻¹) and H₂ (0.008 L min⁻¹) cell gas flow, Ar make-up gas combined using a Y-piece 50% along the sample transport line to the torch 1.008 Lmin^{-1}

Elan DRC-e (Perkin Elmer) ICP-QMS 1550 W 0.65–0.70 L min⁻¹ Ar Dual (cross-calibrated pulse/analog modes) 27, 29, 202, 204, 206, 207, 208, 232, 235, 238 See text

Dwell time: 180 ms sweep⁻¹ 222 sweeps acquired per spot 55 ns

60 s on-peak zero subtracted Plešovice as primary standard Plešovice (Slama *et al.* 2008) In-house package (see text) Common-Pb correction applied to the data (see text) Ages are quoted at 2s absolute. Age uncertainty of reference material and common-Pb composition uncertainty are propagated where appropriate

performance was checked by measuring an allanite reference material prior dating unknowns.

4. A procedure for non-matrix matched standardisation in quadrupole LA-ICP-MS analysis

The analytical protocol is presented here for the case of U–Th– Pb dating of allanite by LA-ICP-MS measurements standardized on zircon, but in principle the method can be applied to any other combination of sample mineral – reference material. The procedure described below is divided into two parts: (i) definition of the strategy for non-matrix matched standardisation (Fig. 2) and empirical quantification of LA-ICP-MS setupspecific correction parameters for the pair zircon (standard) + allanite (unknown) to be dated, and (ii) establishing the data reduction and age calculation scheme (flow chart shown in Fig. 1). The development of this method was done before the publication of community-derived guidelines;²⁷ nevertheless, the recommended procedures are consistent with those presented in this work. Notably the total systematic uncertainty (S_{sys}) is evaluated by measurement in this study for the magmatic allanite reference materials presented, S_{sys} constituting a prominent fraction of the total uncertainty of an age determination for unknowns.²⁷

A MATLAB©-based program with the graphical user interface TRINITY was built to perform analytical data processing (Fig. 1)

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Fig. 1 Flow diagram of LA-ICP-MS allanite age dating. The general dating procedure consists of three steps displayed in columns: (i) data acquisition, (ii) data reduction, and (iii) common lead correction. The downhole fractionation (DF) evolution needs to be quantified for each LA-ICP-MS analytical setup individually. Subroutines of TRINITY, the MATLAB©-based data reduction and associated in-house age-calculation program, are indicated. DHFM: DF model.

and is used to (i) quantify the data reduction variables, (ii) perform data reduction, (iiia) correct for common lead, and (iiib) calculate ages.

4.1 Fractionation of isotopic ratios in LA-ICP-MS

Three factors may cause LA-ICP-MS signal ratios to deviate from their true values:²⁹ matrix effects, instrumental mass bias, and isobaric interferences. The concept of 'matrix effects' includes all material-dependent effects that cause deviations of measured data from true values. Matrix effects are subdivided into three groups:³⁰ (i) *Intensity variability*: laser sampling may result in drastically variable amounts of material being delivered to the ICP-MS. This affects absolute concentrations, but cancels out if isotopic ratios are used, unless plasma mass load effects become significant. (ii) *Elemental fractionation*: laser

sampling, material transport, ICP vaporisation, atomization, and ionisation are thought to play key roles in elemental fractionation, but it is still a matter of debate how these processes are linked and how much each of them may contribute to the problem (see *e.g.*, Sylvester,³⁰ for more details). (iii) *Instrumental mass bias.*³¹ Instrumental mass bias is due to the slight increase in sensitivity with increasing mass. For Pb this amounts to about 0.1% per amu. (atomic mass unit); hence, measured ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁷Pb ratios are overestimated by about 0.1%. Finally, (iv) *intra-element isotopic fractionation* during laser ablation and aerosol transport can also occur.

From a practical point of view, two types of correction need to be distinguished, *i.e.* for isotopic ratios of the same element (*e.g.* 207 Pb/ 206 Pb, see Fig. 3), and for isotopic ratios of different elements (208 Pb/ 232 Th or 206 Pb/ 238 U, notation used for practical purposes, see Fig. 4). The first case refers to mass bias effects



Fig. 2 Conceptual sketch of downhole fractionation (DF) evolution and its correction. (a) The transient raw ratio of a given analysis (blue signal) with the specific DF model obtained from analysis of reference materials of identical matrix and analytical conditions. This model is adjusted to the unknown by the factor Y = X(unknown)/X(model). (b) The adjusted DF model (light blue) is used to correct the DF in order to get an essentially time-invariant signal ratio (green signal). (c) Timeinvariant signal ratios of different matrices (*i.e.*, sample allanite and standard zircon) show an offset to their respective true isotope ratios, defining their respective *k*-factors that are matrix-dependent (general case).

sensu stricto. Evolution of ²⁰⁷Pb/²⁰⁶Pb during ablation was studied by averaging 20 Plesovice zircon signal ratios from four analytical sessions (Fig. 3a). The average evolution shows no time-dependence during analytical periods of 40 s, indicating absence of Pb isotope fractionation with progressive laser drilling (*i.e.*, with time). The measured ²⁰⁷Pb/²⁰⁶Pb ratios extracted from 65 measurements of Plesovice zircon acquired over 7 sessions (Fig. 3b) are identical to the reference value, within uncertainty, demonstrating that there is no need for mass bias correction in our analytical setup. These results indicate that mass bias correction can be neglected for Pb isotope ratios measured by QMS. This is plausible since the uncertainty on the external analytical precision for isotopic ratios determined by QMS is of the order of several permil at best, thus larger than the expected 0.1% mass bias per amu.

Isotopic ratios of different elements are much more prone to complications because (a) the elemental fractionation effect is added, and (b) for larger mass differences the mass bias can be substantial. Here, two types of fractionation overlap, (i) a timedependent part known as downhole (elemental) fractionation evolution, and (ii) a time-independent part.³² Several downhole fractionation models have been proposed with the aim to correct the measured signal ratio for the time-dependent part in order to obtain time-invariant signal isotope ratios. Horn et al.33 claimed that a linear downhole fractionation (DF) correction may be sufficient to obtain (approximate) 'true' ratios from measured ratios. However, the physical background of DF^{34,35} indicates that a linear approach is a simplification; hence, more complex DF models have been introduced such as exponential functions.³⁶ In any case, once the DF evolution is quantified for a given material and for specified analytical conditions, the time-dependence of the signal can be eliminated. This is a prerequisite for matrix-matched standardisation approaches in age dating.

4.2 Downhole fractionation: matrix dependent evolution, models and correction

How DF evolves with time depends on (i) measurement parameters such as the beam size, laser frequency, fluence, gas flows, and geometry of the ablation cell, (ii) mineral parameters (chemical composition and structure), and (iii) the elements of interest. This implies that different element abundance ratios (e.g., Pb/Th or Pb/U) evolve variably with progressive laser drilling. Fixing (i) and (iii) thus allows for mineral-specific quantification of DF (ii). The approach used here to correct for DF builds on the one implemented in Iolite³⁶ which involves (a) calibration of the DF model (f(model)), which is determined on the bracketing primary standards for each analytical block, and (b) applying this model to the unknowns, which corrects for the time-dependent DF evolution. This then returns a timeindependent signal. The prerequisite for this to work is that the primary standard and the unknowns have the same DF, besides having identical intrinsic time-independent fractionation (see k-value below); hence, matrix-matched standardisation is required. In other words, the DF model determined on the bracketing standards can be transformed (scaled) via a proportionality factor into any other DF evolution of the same matrix. Paton et al.36 demonstrated that this approach yields accurate results for zircon dating with matrixmatched standardisation. However, Iolite does not allow for dating non-matrix-matched pairs of standard and sample, because they do not have the same DF evolution.

In order to evaluate DF evolution for different allanite materials and to develop the corresponding DF functions for allanite and zircon, measurements of Plesovice zircon and three different allanite types were acquired in 12 sessions over 8 months with constant measurement parameters (Table 1). These data document that DF evolution does not change from one analytical session to the next for the same material; in fact it has not significantly changed over the past 2.5 years in our lab.



Fig. 3 Transient ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ signals (a) of 20 Plesovice zircon analyses (blue lines) averaged to a mean evolution (red line); (b) background corrected ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ratios of 65 Plesovice zircon analyses. Uncertainties are 2σ . The reference value of 0.0532 is from Slàma *et al.* (2008).



Fig. 4 Downhole fractionation (DF) evolutions of 208 Pb/ 232 Th and 206 Pb/ 238 U ratios for 32 µm beam for BONA allanite and Plesovice zircon are averaged (red lines) from single-spot analyses (n = 20; blue lines). Residuals of the DF models (black lines in lower boxes of (a)–(d)) show no time-dependency. Reference values for Plesovice from Slàma *et al.* (2008) and for BONA from Smye *et al.* (2014).

$$f(t) = a + b \times epx(c \times t)$$
(1)

with a, b, and c representing empirically calibrated parameters, derived by fitting the DF model to the measurements. It needs to be stressed that these data are specific for every analytical setup used for age dating. DF evolution of allanite (BONA^b) and zircon (Plesovice) are evaluated for two different beam sizes (32 and 24 µm; Fig. 4 and 5, respectively) while keeping everything else constant. Some 20 single spot analyses obtained during 6 analytical sessions were averaged to obtain the parameters describing the DF evolution (red curves in Fig. 4 and 5). In contrast to the case of isotopic ratios of the same element (Fig. 3), a continuous change in the ratios with progressive ablation is observed; ²⁰⁸Pb/²³²Th and ²⁰⁶Pb/²³⁸U values increase exponentially with time (Fig. 4). Consequently, the extent of deviation from the reference ratios of Plesovice and BONA^{b5,20} also varies with time. 208Pb/232Th and 206Pb/238U ratios are generally overestimated. For the smaller beam size (24 µm),

deviations from the true values are larger (Fig. 5), and patterns of the DF evolution are steeper. This is expected since for a small beam the aspect ratio of the ablation crater (depth/ diameter) increases faster with time. After correction for the averaged DF evolution based on the empirically determined exponential models, residuals are centered at zero and show no time-dependent patterns; the residuals indicate a good quality of fit (Fig. 4 and 5).

Material-dependent (*i.e.* matrix-dependent) differences of the DF evolution are documented in Fig. 4 and 5. To investigate in more detail the differences in the DF evolution between allanite materials of different compositions, exponential DF models were determined for magmatic allanite BONA^b, TARA, CAP^b and for a metamorphic allanite from Gran Paradiso massif in the Western Alps; results are reported in Fig. 6. For a beam size of 32 μ m, nearly asymptotic behavior is observed for allanite already ~20 seconds after ablation start (Fig. 6a), while for zircon this is attained only at *ca.* 30 s. To relate the different evolutions to one another, normalization is required. The 32 μ m beam size DF models were normalized to the value of their asymptote (given by eqn (1), once the material-specific



Fig. 5 DF evolutions of 208 Pb/ 232 Th and 206 Pb/ 238 U ratios for 24 μ m spot size for BONA allanite and Plesovice zircon are averaged (red lines) from single-spot analyses (n = 15; blue lines). Residuals of the DF models (black line) show no time-dependency. Reference values for Plesovice from Slàma *et al.* (2008) and for BONA from Smye *et al.* (2014).



Fig. 6 Normalized DF models used to compare DF evolution (see text) of different allanite and zircon materials for (a) 32 μm and (b) 24 μm spot size. Dashed lines represent the 3% uncertainty envelope. The first 4 s are emphasized by a grey band. This variable part of the signal involves complex ablation behavior and is not used in the derivation of the DF correction.

parameters *a*, *b*, *c* were determined). The 24 μ m beam size DF models are normalized to their average value between 25 and 35 seconds after the ablation started because of the absence of asymptote (Fig. 6). For a given beam size, the DF models determined for different allanite samples agree well, *i.e.* to within 3% uncertainty (for 32 μ m, Fig. 6a; for 24 μ m, Fig. 6b). For 32 μ m beam size the DF models of magmatic and metamorphic allanite (with different compositions) agree to within 0.5% uncertainty after 10 seconds of ablation. For both cases (*ø*: 24 and 32 μ m) Plesovice zircon shows a DF evolution that consistently differs from that of allanite (Fig. 6).

Data in Fig. 6 imply that a single proportionality factor (Y) is sufficient to transform the ${}^{208}\text{Pb}/{}^{232}\text{Th}$ and ${}^{206}\text{Pb}/{}^{238}\text{U}$ DF function of the allanite standard BONA (in the following used as the model DF for allanite) to any given allanite sample analysis with different ${}^{208}\text{Pb}/{}^{232}\text{Th}$ and ${}^{206}\text{Pb}/{}^{238}\text{U}$ ratios. This proportional factor is defined as:

$$Y = \frac{X(\text{sample})}{X(\text{model})} \tag{2}$$

where X is the average isotope intensity ratio on a defined interval of the time-dependent signal of the allanite sample (=unknown) and of the model DF (derived from BONA allanite), respectively (Fig. 2a). This results in a DF model for the unknown:

$$f(t)_{\text{unknown}} = Y \times f(t)_{\text{model}}$$
(3)

In selecting the signal interval to derive the proportionality factor *Y*, care needs to be taken (i) to avoid potential problems of early signal sections (*e.g.* due to surface contamination, large aerosol particles prone to incomplete ionisation, spiky signals), and (ii) to be representative of the shallow part of the ablation crater (corresponding to the crater depth interval from 2 to 9 μ m below surface), so as to relate the age to the microstructural

context resolved by imaging techniques obtained prior to ablation. To meet these two criteria, a time interval between 10 and 15 s after ablation start is set to determine the proportionality factor, which then allows data reduction and thus to calculate final isotope ratios (Fig. 2a).

Having normalized the DF of the model to the unknown (Fig. 2a), we now need to derive time-independent isotope intensity ratios (r') as illustrated in Fig. 2b. To achieve this, each time-dependent isotope intensity ratio readout (r(t); each sweep) needs a time-specific correction (Δ_i in Fig. 2b). To this end, an arbitrary time point (t_{corr}) after ablation start is selected, which corresponds to the pivot point in the normalized DF model for the unknown (see Fig. 2 for the definition of the pivot point). Next, each isotope intensity ratio readout is corrected for its time-dependent DF by taking Δ_i at the respective t_i (Fig. 2b) as calibrated by the model DF evolution ($f(t)_{unknown}$). The result is the time-independent (*i.e.*, DF-corrected) isotope intensity ratio for the given sample spot analysis, which is required for further data processing.

The simplified equation for the time-independent isotope intensity ratio (r') is:

$$r' = Y \times (f(t_{\rm corr})_{\rm model} - f(t)_{\rm model}) + r(t)$$
(4)

where r(t) is the uncorrected signal ratio, f(t) the function of the DF model given in eqn (1), and t_{corr} the point in time (pivot point) to which the DF evolution is corrected; *Y* is defined in eqn (2).

4.3 Non-matrix-matched *versus* matrix-matched standardisation

In order to calculate accurate isotope ratios based on the time invariant isotope intensity ratios obtained above, external standardisation is required. Matrix matched standardisation involves the characterization of the offset of measured isotope intensity ratios to true isotope ratios by a so-called *k*-value, which is determined on a standard.³⁷ For the 208 Pb/ 232 Th ratio the *k*-value is calculated as:

$$k = \left(\frac{^{232}\mathrm{I}}{^{208}\mathrm{I}}\right)_{\mathrm{std}} \left(\frac{^{208}\mathrm{Pb}}{^{232}\mathrm{Th}}\right)_{\mathrm{std}}$$
(5)

where $\binom{^{232}I^{^{208}I}}{_{std}}$ is the measured isotope intensity ratio of the standard not corrected for common lead, and the $\binom{^{208}Pb^{^{232}}Th}{_{std}}$ is the reference isotope ratio of the standard. Once the *k*-value is defined, the equivalent to eqn (5) is applied to measured unknowns, to calculate their true isotope ratio. Matrix-matched standardisation thus assumes that the same *k*-value is valid for both standards and unknowns.

The situation is more complicated when the unknown mineral is chemically different from the standard, *i.e.* the two have different matrices and thus different k-values (Fig. 2c). However, k-values change with progressive ablation, and we utilize this time-dependence of k to resolve the problem of matrix difference. Specifically, to employ a standardisation on zircon for allanite dating (or indeed to use any other such pair), we need to identify the conditions at which the k-values for the two minerals are equal. For each matrix, the k-value evolves differently with progressive drilling, and for each of them the pivot point (as defined by its t_{corr}) defines the k-value (Fig. 2b). The task is thus to find a pair of pivot points for zircon and allanite with identical k-values (within error); note that $t_{corr,zrn}$ $\neq t_{\text{corr,aln}}$ because the respective DF evolutions are different (see curve shapes in Fig. 6). To identify this condition, the following procedure has been adopted: a matrix of pivot points is established, with $t_{\rm corr,zrn}$ and $t_{\rm corr,aln}$ covering the duration of the signal interval (45 seconds in our case); ²³²Th-²⁰⁸Pb apparent ages of the allanite standards CAP and TARA are calculated based on zircon standardisation (assuming 0.9% and 0.75% of ²⁰⁸Pb_c for CAP and TARA respectively; values from ref. 13). Fig. 7 illustrates that a series of pivot points exists for the zirconallanite pair that return the correct allanite ages for CAP and TARA (black line in Fig. 7a and b), thus zircon standardisation can return accurate allanite ages. This procedure calibrates which t_{corr} is suitable to determine the pivot point for allanite

for any given pivot point used for the zircon standard. Fig. 7c then illustrates that two chemically different allanites, CAP and TARA, show essentially the same pivot point relation to standard zircon. We conclude that one such calibration of pivot points is applicable to any zircon-allanite pair for dating. Fig. 7 illustrates how two matrix-dependent DF corrections link allanite to zircon. That this calibration procedure returns accurate ages for allanite is verified below.

4.4 Specific data reduction steps for a given dating session

The technically important steps for the calculation of final isotope ratios from raw signals are addressed next (Fig. 1, central column):

1. The data from spot analysis are imported, and each spot analysis is assigned to a material or standard type (*i.e.* zircon, allanite, SRM610). The starting point t_0 of the ablation signal to be used is individually set for each analysis. In a graph summing up all of the isotope intensities, t_0 is set where there is a drastic increase in signal intensity, a level that has to be maintained over at least 25 seconds (graphical control provided). This starting point t_0 of the DF evolution is used in step 4 and following.

2. The background interval is defined for each analysis and subtracted from the gross signal. Positive outliers (> 6σ ; corresponding to electronic spikes in the detector or particles reaching the plasma) are rejected from the background interval.

3. Raw intensity ratios for both standards and unknowns (R_{raw}) are calculated from the background-corrected isotope signal intensities (I):

$$r = \frac{{}^{1}I}{{}^{2}I}$$
(6)

For allanite dating, the calculated ratios are ${}^{208}Pb/{}^{232}Th$, ${}^{206}Pb/{}^{238}U$, ${}^{206}Pb/{}^{208}Pb$ and ${}^{207}Pb/{}^{206}Pb$.

4. The DF correction is applied to the ²⁰⁶Pb/²³⁸U and ²⁰⁸Pb/²³²Th raw intensity ratios. Since DF is matrix-dependent, the mineral-specific DF model (calibrated previously for the given analytical setup) is used (Fig. 2). The DF-corrected



Fig. 7 Age maps as a function of pivot points for Plesovice and allanite (CAP (a); TARA (b)) for 32 μm spot size. The thick black line of equal bias links the couple of pivot points used for accurate downhole fractionation corrections (see text). The location of pivot point is chosen between 4 and 20 seconds in order to avoid surface contamination and to be most closely related to surface imaging that guides *in situ* sampling. (c) A red area indicates the pivot point pairs (zircon–allanite) for which the calculated apparent age data for both CAP and TARA deviate less than 0.5% from their reference age.

intensity ratios (r'; Fig. 2b) are not time-dependent, *i.e.* they are constant across the integrated sample signal.

5. Based on the ²⁰⁶Pb/²³⁸U and ²⁰⁸Pb/²³²Th DF-corrected intensity ratios the integration intervals for the zircon standard spots are selected from 5 to 25 seconds. DF-corrected Plesovice intensity ratios of ²⁰⁶Pb/²³⁸U and ²⁰⁸Pb/²³²Th are then determined for each standard signal, and the mean is calculated $(\overline{r'_{\rm plz}})$. 1% outlier rejection is applied.

6. The \hat{k} -value required for obtaining the true ${}^{206}\text{Pb}/{}^{238}\text{U}$ isotope abundance ratio (Fig. 2c) is calculated:

$$k = \frac{\operatorname{Ref}_{\operatorname{value}}}{\overline{\overline{r'_{\operatorname{Ple}}}}}$$
(7)

where *k* is the *k*-value, Ref_{value} the <u>accepted</u> reference isotope ratio for the reference material, and r'_{Ple} represents the mean of the selected DF-corrected Plesovice signal ratios. The same is repeated for each isotope ratio of interest (*e.g.*, ²⁰⁸Pb/²³²Th). Specific information on estimating the uncertainty in *k*-value is given in ESI.[†]

7. The DF-corrected 206 Pb/ 238 U and 208 Pb/ 232 Th intensity ratios are converted to isotope abundance ratios by use of the *k*-value:

$$R_{\text{final}} = k \times r' \tag{8}$$

where R_{final} is the standardized, DF-corrected abundance ratio. Recall that the *k*-value is the same for standard zircon and sample allanite and for a given pivot point (Fig. 7).

8. The signal intervals for the allanite spot analyses are selected based on the individual $R_{\rm final}$ readings (*i.e.* ²⁰⁶Pb/²³⁸U, ²⁰⁸Pb/²³²Th, ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁶Pb/²⁰⁸Pb and ²³²Th/²³⁸U), again applying 1% outlier rejection. Average isotope abundance ratios and their standard errors are calculated for the selected signal intervals and combined with the uncertainty in the *k*-value.

Next, several quality control steps are performed (Fig. 1, right column). In a first step, single spot ages of the primary standard (Plesovice zircon) are calculated and compared to the true age in order to check for outliers. If outliers need to be rejected (rejection criterion: 2σ on age), the standardisation has to be repeated, using only the data of accurately analyzed primary standards. In a second step, the resulting age data of the secondary standard allanite are evaluated to ensure matrixmatching with the unknowns. This includes correction for common lead (see below). Provided that ages obtained for the secondary standard agree with the reference ages, the analytical procedure is accurate, and the isotopic data of the unknowns can now be evaluated.

4.5 Common lead correction and age calculation

Allanite incorporates variable amounts of U, Th, and Pb during growth,³⁸ therefore its total lead (Pb_{total}) consists of two types: Pb_c, incorporated during growth, and Pb_{rad} derived from *in situ* decay of U and Th. Of the four stable lead isotopes (204 Pb, 206 Pb, 207 Pb and 208 Pb) only the 204 Pb is entirely non-radiogenic, whereas the other three lead isotopes are partially radiogenic from U and Th decay. Common lead fractions

 $(f_{206} = {}^{206}\text{Pb}_{c}/{}^{206}\text{Pb}_{total} \text{ and } f_{208} = {}^{208}\text{Pb}_{c}/{}^{208}\text{Pb}_{total})$ are highly variable in allanite of different samples (magmatic allanite such as CAP compared to metamorphic common lead rich allanite such as reported in Janots & Rubatto,17), where smaller variability in common lead fraction is also often recorded from within a sample. Several approaches exist for common lead correction,12 of which those based on 204Pb (commonly employed with TIMS) and ²⁰⁷Pb (commonly employed with in situ techniques) are applicable to allanite. The ²⁰⁴Pb-based correction is mainly hampered by low precision in the ²⁰⁴Pbdata determined in situ (low natural abundance and interference correction for ²⁰⁴Hg). The ²⁰⁷Pb/²⁰⁶Pb-correction is limited by the assumption of concordance in the U-decay systems and can be biased by a possible 206Pbexcess from disequilibrium ²³⁰Th (note that our data reduction scheme does not consider ²³⁰Th correction; for a possible solution to this refer to McFarlane,⁸). The ²⁰⁸Pb/²⁰⁷Pb-based correction approach is not influenced by possible 206Pbexcess problems, but it requires knowledge of the mean ²³⁸U/²³²Th abundance ratio for each sample and assumes concordance between the uranogenic and thorogenic decay chains, both adding undue uncertainty.

The measurement setup and sensitivity of the mass spectrometer used in this study does not allow ²⁰⁴Pb to be determined accurately, because we do not pre-clean the LA-ICP-MS gases by mercury traps and Hg signals are too low for accurately determining the isotopic composition of the mercury in our system. Hence we are limited to the ²⁰⁷Pb/²⁰⁶Pb- and the ²⁰⁸Pb/²⁰⁷Pb-based correction methods. In view of the drawbacks mentioned above for each of the methods, the common lead correction based on ²⁰⁷Pb is clearly favored as suggested by Gregory *et al.*¹³

Common lead correction requires knowledge of the initial Pb isotope signatures. A commonly used approach is based on a common lead evolution model;³⁹ previous studies of the magmatic allanite reference materials used model initial Pb isotope ratios as well. In order to maintain comparability between the different age data sets, the same strategy was followed here.

Cases exist where common lead correction based on model Pb isotope evolution fails to produce accurate age data. This situation is likely to be common for metamorphic allanite growth, but a discussion of such samples is beyond the scope of this study. Details on how to improve the common lead correction strategy for such cases will be presented elsewhere.

5. Results

5.1 TARA

TARA allanite (Fig. 8 and Table ESI1[†]) is suitable as a secondary standard material, returning a ²⁰⁷Pb-corrected weighted mean ²³²Th/²⁰⁸Pb age of 411.3 ± 1.4 Ma, MSWD = 0.82 (2s; Fig. 8d) and a probability of fit of 0.78. The simple 2 standard deviation of the data set (n = 41) is 8.3 Ma, the S_{sys} on ²³²Th/²⁰⁸Pb being 1.02%. The thorogenic isochron age is 411.4 ± 1.5 Ma (Fig. 8b). The common-Pb-corrected (based on ²⁰⁷Pb) weighted mean ²³⁸U/²⁰⁶Pb-age is 421.0 ± 3.5 Ma (2s), MSWD of 2.1 (Fig. 8e) and a probability of fit of zero. The simple 2 standard deviation of



Fig. 8 Results of TARA allanite age dating. (a) Tera–Wasserburg, (b) Th–Pb isochron, (c) $^{238}U-^{232}Th$ concordia, (d) and (e) weighted average diagrams. Uncertainties are 2σ .

the data set is 37.0 Ma, the $S_{\rm sys}$ on 238 U/ 206 Pb being 4.56%. A Tera–Wasserburg diagram returns 421.1 \pm 3.5 Ma (Fig. 8a).

Uncertainties (2s) in single spot 232 Th/ 208 Pb ages are 1.2– 4.2% (32 µm beam size), and 2.4–4.2% (24 µm beam size). The weighted average of all analytical data reduces the uncertainty in the mean 232 Th/ 208 Pb age to 0.34% (2s). 238 U/ 206 Pb-ages again have higher relative uncertainties: 3.5–6% (for 32 µm, single spot), 6–13% (for 24 µm, single spot), and 0.8% in the mean age (2s). Common lead fractions vary from 0.6–1.1% for f_{208} and from 12-21% for f_{206} .

5.2 CAP^b

CAP^b is a suitable secondary standard material (Fig. 9 and Table ESI2[†]), despite five age outliers in the presented data set of 42 spot analyses (Fig. 9d and e), which had to be rejected. The ²⁰⁷Pb-corrected weighted mean ²³²Th/²⁰⁸Pb age (after outlier rejection) is 274.4 \pm 1.1 Ma, MSWD = 0.83 (2s, Fig. 9d) and a probability of fit of 0.76. The simple 2 standard deviation of the data set (n = 37/42) is 3.7 Ma, the S_{sys} on ²³²Th/²⁰⁸Pb being 1.34%. The thorogenic isochron age is 274.5 \pm 1.1 Ma (Fig. 9b). The common-Pb-corrected (based on ²⁰⁷Pb) weighted mean ²³⁸U/²⁰⁶Pb age is 283.8 \pm 2.8 Ma (2s), MSWD of 2.5 and

a probability of fit of zero (Fig. 9e). The simple 2 standard deviation of the $^{238}\text{U}/^{206}\text{Pb}$ age is 16 Ma (after outlier rejection), the $S_{\rm sys}$ on $^{238}\text{U}/^{206}\text{Pb}$ being 5.79%. The data returns 284.9 \pm 2.8 Ma in a Tera–Wasserburg diagram (Fig. 9a).

Uncertainties (2s) in the single spot 232 Th/ 208 Pb ages are 1.25–4.5% (32 µm beam size), and 2.6–4.4% (24 µm beam size). Averaging all analytical data reduces the uncertainty in the mean age to 0.4% (2s). 238 U/ 206 Pb ages again have higher relative uncertainties: 2.8–7% (32 µm, single spot), 6.4–13% (24 µm, single spot), and 1.0% in the mean age (2s). Common lead fractions vary from 0.6–2.1% for f_{208} and from 3.5–28% for f_{206} .

5.3 BONA^b

BONA is the secondary standard material of the lowest quality assessed in this study (Fig. 10 and Table ESI3†); nevertheless it returns consistent common-Pb-corrected (based on ²⁰⁷Pb) single spot ²³²Th/²⁰⁸Pb age data with a weighted mean of 29.99 \pm 0.18 Ma (2s), MSWD = 1.1 and a probability of fit 0.38 (Fig. 10d). The simple 2 standard deviation is 0.7 Ma (n = 44), the $S_{\rm sys}$ on ²³²Th/²⁰⁸Pb being 2.38%. The thorogenic ²⁰⁶Pb_c-isochron age is 29.94 \pm 0.19 Ma (Fig. 10b). The common-Pb-corrected (based on ²⁰⁷Pb) weighted mean of the single spot



Fig. 9 Results of CAP^b allanite age dating. (a) Tera–Wasserburg, (b) Th–Pb isochron, (c) $^{238}U-^{232}Th$ concordia, (d) and (e) weighted average diagrams. Uncertainties are 2σ .

 238 U/²⁰⁶Pb ages is 39.4 ± 1.9 Ma (2s Fig. 10e), MSWD of 1.6 and a probability of fit of zero. Its simple 2 standard deviation is 10 Ma, the $S_{\rm sys}$ on 238 U/²⁰⁶Pb being 25.0%. The Tera–Wasserburg diagram returns 40.0 ± 1.9 Ma (Fig. 10a).

Single spot uncertainties (2s) in 232 Th/ 208 Pb-ages are 3–6% for 32 µm spots, and 4.5–11% for 24 µm spots, averaging reduces the uncertainty to 0.6% (2s). 238 U/ 206 Pb ages have 15–66% (32 µm beam size) and 26 to >100% (for 24 µm beam size) uncertainties on the single spot; averaging reduces the uncertainty to 4.8% (2s). The range in f_{208} is between 15–33% and in f_{206} between 67–91%.

6. Discussion

For the novel LA-ICP-MS dating protocol employing non-matrixmatched external standardisation, two issues need special attention: (i) suitability of the standard materials (here: allanite), and (ii) evaluation of the dating procedure presented here. Allanite standard materials were primarily employed to develop the analytical routine and data reduction procedure; however, this revealed some limitations in the quality of the different allanite standard materials available. Different dating techniques do not always return compatible results (*e.g.* Fig. 11 and 12), and heterogeneities in age and common lead fractions incorporated in the different allanite reference materials complicate direct comparison of dates. Therefore, the quality of allanite reference materials and comparability of methods are addressed first, followed by a discussion of specific aspects of the novel dating approach presented here.

6.1 Comparison of allanite reference materials

The three materials BONA^b, CAP^b and TARA were not primarily investigated to determine the absolute ages of these allanite materials. However, the extensive data sets acquired for establishing the novel dating protocol can be usefully compared and discussed, notably because the data sets from several analytical sessions, using different reference materials and three isotopic systems, are internally consistent (Fig. ESI1†). BONA^b, CAP^b and TARA were separated from sample materials closely similar to the original standard reference materials; hence our data can be compared with the (widely dispersed and partially incomplete) data published for these. A first round of comparison is focused on age data, because these are the most complete data available in literature from a wide range of dating techniques. Note that



Fig. 10 Results of BONA^b allanite age dating. (a) Tera–Wasserburg, (b) Th–Pb isochron, (c) $^{238}U^{-232}$ Th concordia, (d) and (e) weighted average diagrams. Uncertainties are 2σ .

the comparison of 238 U/ 206 Pb-ages is based on ages not corrected for 206 Pb_{excess}, because its correction requires assumptions for the fractionation factor melt/allanite, which adds additional uncertainty to the comparison of the 238 U/ 206 Pb-age data (compare McFarlane⁸).

6.1.1 TARA. TARA allanite is (chemically and Th–U–Pb isotopically) the most homogeneous allanite reference material assessed in this study, as documented by various spot analysis techniques and by ID-TIMS (Fig. 11a). Whereas the TIMS data for TARA are heterogeneous, showing a trend to younger 232 Th/ 208 Pb ages (Fig. 11a; Smye *et al.*, 2014), all of the data sets obtained by *in situ* techniques are quite uniform. Only two out of six single grains analysed by ID-TIMS show concordance in the 232 Th/ 208 Pb and 238 U/ 206 Pb systems. Smye *et al.*²⁰ reported BSE-images showing thorite inclusions along fractures in TARA allanite. Alteration of allanite along fractures and associated exsolution of thorite suggests loss of 208 Pb, which evidently caused apparent ages to be variably too young.

What is the accurate reference age of TARA allanite? We proposed that the three oldest, mutually consistent ID-TIMS 232 Th/ 208 Pb-ages should be favored, returning a weighted mean thorogenic age of 412.0 \pm 2.3 Ma. This age is consistent

with uniform *in situ* ²³²Th/²⁰⁸Pb SHRIMP ages (414.9 \pm 3.3 Ma, 2σ ;¹³), LA-ICP-MS spot ages (411.3 \pm 1.4 Ma; 2s; this study), and LA-ICP-MS rastering ages (416.3 \pm 1.9 Ma, 2s;¹²).

Available ²⁰⁶Pb/²³⁸U ages are more difficult to evaluate (Fig. 12a and b). Spot data from SHRIMP are lacking, but all spot analysis techniques and ID-TIMS data show substantial variability of this chronometer and slightly older ages for data not corrected for ²⁰⁶Pb_{excess} (ID-TIMS: 407–430 \pm 1–5 Ma;²⁰ SHRIMP: 419.3 \pm 7.7 Ma;¹³ this study: 421.0 \pm 3.4, and rastering LA-ICP-QMS: 428 \pm 9 Ma (ref. 12)). For data from spot analyses, the larger variations in ²⁰⁶Pb/²³⁸U-ages in part result from lower signal intensities, but the data generally indicate that the uranogenic chronometer is disturbed. For these reasons, no precise and accurate ²³⁸U/²⁰⁶Pb age can be proposed for TARA allanite.

6.1.2 CAP. CAP is a promising standard reference material (Fig. 11b), given the very consistent ID-TIMS ²³²Th/²⁰⁸Pb-data (²³²Th/²⁰⁸Pb age = 275.0 ± 1.5 Ma, 2σ ;²⁴) with no significant outliers, despite a clearly recognized hydrothermal alteration and some chemical heterogeneity. The ²³⁸U/²⁰⁶Pb system, however, does show some variation in ages from 264.3–280.0 (±1 Ma, 2σ). This leaves only two of the four analyses concordant in the Th–U system. The first results of CAP SIMS-dating²⁵ produced widely



Fig. 11 Comparison of ²³²Th–²⁰⁸Pb ages from different analytical methods (ID-TIMS: squares; SIMS/SHRIMP: triangles; LA-ICP-MS: circles). Weighted averages (without outlier rejection) and their 2σ uncertainties are shown as black lines with colored envelopes for each data set. Data shown with open symbols are regarded as outliers and rejected in the final dataset for age comparison. Note that El Korh (2014) used three different reference materials (Plesovice, TARA, AVC) for external standardization.

scattering spot ages, but the averages looks fine (Fig. 11b). Results from 232 Th $/^{208}$ Pb SHRIMP spot dating (average = 276.9 \pm 2.2 Ma, 2σ ;¹³) and ²³²Th/²⁰⁸Pb LA-ICP-MS dating (average = 274.4 \pm 1.1 Ma, 2s; this study) are in agreement with the ID-TIMS data. The two spot analysis approaches found outliers in the ²³²Th/²⁰⁸Pb-system: single spots and some whole grains yielded older apparent ²³²Th/²⁰⁸Pb ages. Note that these studies did not analyze allanite from the same sample, and field evidence indicates that three small intrusions are present at the sample location indicated by Barth et al.24 However, the good agreement of ²³²Th/²⁰⁸Pb ages suggests that no age-difference among the samples dated can be resolved, hence the reference ²³²Th/²⁰⁸Pb age of 275.0 \pm 1.5 Ma determined by Barth *et al.*²⁴ is deemed appropriate for all of the samples compared here. We thus conclude that CAP and CAP^b are suitable reference materials for spot analysis techniques in the ²³²Th/²⁰⁸Pb-system. Care has to be taken to identify and avoid altered zones (often visible in SEM maps of grain mounts) and to test the data for outliers. With these precautions, the ²³²Th/²⁰⁸Pb age of CAP appears to be comparably uniform to that of TARA.



Fig. 12 ID-TIMS isotope data (blue) of the U/Pb decay system in allanite are related to our LA-ICP-MS spot analysis data (red; without outlier filtering) in Concordia ((a): TARA; (c): CAP; (e): BONA) and Tera–Wasserburg ((b): TARA; (d): CAP; (f): BONA) diagrams. ID-TIMS data for TARA and BONA are from Smye *et al.* (2014), for CAP from Barth *et al.* (1994). Data from our spot analyses lie on well constrained trends of the ID-TIMS data, indicating that our analyses are accurate. Intercept values of the trends have no geological significance because the causes for variation in the ID-TIMS data are *a priori* unknown. Symbols for BONA are larger than the uncertainty in the ID-TIMS data; for CAP the uncertainties could not be deduced from the original publications (hence, data shown as \times).

 238 U/²⁰⁶Pb age systematics are more complicated (Fig. 12c and d), as indicated by the early ID-TIMS work by Barth *et al.*²⁴ From the data of Gregory *et al.*¹³ it appears that spot analyses give one consistent age within their analytical uncertainty (MSWD: 0.9). However, single spot 238 U/²⁰⁶Pb uncertainties seem to be large, possibly due to counting statistics in standardisation and allanite unknowns. Individual spot ages were not reported, hence a more detailed interpretation of these data is not possible. Data for CAP^b in our study show a single spot variability exceeding measurement precision (see Section 6.4.) and yield a slightly older 238 U/²⁰⁶Pb age (283.8 ± 2.8 Ma, 2s) than the ID-TIMS and SHRIMP data. This implies that CAP^b is likely to be affected by 206 Pb_{excess}, as was shown for TARA.²⁰ Consequently, no 238 U/²⁰⁶Pb reference age can be defined for CAP^b based on the available data.

6.1.3 BONA. BONA allanite, from shallow parts of the granodiorite of the Oligocene Bergell pluton, is the youngest allanite reference material, and therefore time differences in magmatic growth zones can be most easily resolved. Several studies in the Bergell pluton show that zircon and allanite formation was a protracted process involving pulses of alteration and recrystallization.19,40 In tonalite from the deepest parts of the Bergell intrusive suite Oberli et al.⁴⁰ showed that allanite crystallized during a time period of 4 Ma (between 32 and 28 Ma). These deep parts of the Bergell pluton were the slowest to cool, and the time span for allanite formation estimated from deep samples sets an upper limit for shallower parts of the pluton. A large spread in zircon ages for Bergell granodiorite from a shallower part of the pluton was interpreted to reflect lead loss due to metamictization.¹⁹ However, this spread in the zircon data from the original BONA sample may also reflect an extended time span of crystallization or partial recrystallization.

Our spot analysis data for BONA^b show uniform allanite ages within uncertainty of the single spots (\sim 2 Ma). To compare Thages from all of the BONA data sets, Fig. 11c shows the weighted mean (and its uncertainty) for each of them. Clearly, some of the data sets are discrepant. All data sets by El Korh⁴¹ are for the same material (BONA^b), but rely on various reference materials as calibration standards; hence the inconsistencies presented, especially using Plesovice zircon, reflect problems in the analytical protocol used.37 The excellent agreement of our data for BONA^b with the TIMS data for BONA of von Blanckenburg,¹⁹ together with the chemical similarity of the samples, indicates that they may be regarded as equivalent. Comparing our spot analytical data with those of Gregory et al.13 and Darling et al.12 shows average ages slightly outside their respective 2σ -uncertainties; these minor discrepancies may indicate some small Th-age heterogeneity in this reference material. Therefore, BONA allanite qualifies as a low-quality secondary standard. The early ID-TIMS 232 Th/ 208 Pb age (30.1 \pm 0.25 Ma, 2s) is considered to represent the most reliable ²³²Th/²⁰⁸Pb reference age. Complexities in the U-Pb age system (Fig. 12e and f) are again caused at least in part by ²⁰⁶Pb_{excess}, hence no accurate ²³⁸U/²⁰⁶Pb age can be obtained here.

6.1.4 Assessment of allanite isotopic and age data and recommendation for the use as standard reference materials. Comparison of our age data with those from the literature reveals two main problems: (i) data from different dating methods sometimes render inconsistent results, and (ii) U-Pb ages are too variable between different analytical methods to be directly compared. Th-Pb ages, however, are sufficiently close to permit a comparison of allanite reference materials (Fig. 11). It is clear that some major differences are related to the methodology of dating. For instance, Smye et al.20 found outliers in their ID-TIMS data for TARA allanite reference material (Fig. 11a) which they interpreted to represent specific single crystals that experienced partial alteration along fractures, with exsolution of thorite. In situ analytical techniques allow such alteration features to be avoided, and the resulting age data for TARA are then very uniform. For CAP, Barth et al.24 concluded

that their Th–Pb TIMS ages were not affected by the postmagmatic alteration of allanite, whereas the U–Pb system was. Spot analyses for CAP^b by both SIMS and LA-ICP-MS show effects attributable to alteration for both systems, but careful selection of analytical spots and removal of (the few) outlier data yield uniform Th–Pb age data.

This evaluation of the Th-Pb ages documents that all allanite materials presented here are suitable for matrix-matched allanite ²³²Th/²⁰⁸Pb dating, either as primary or as secondary standard. For BONA slight heterogeneity in ²³²Th/²⁰⁸Pb system complicates the definition of a precise reference age. The reference ²³²Th/²⁰⁸Pb ratios are derived from the respective Thages for each reference material (as discussed above). Since matrix matched calibration is not required for ID-TIMS measurements, such data should serve as the benchmark to which in situ age data are compared, except where postcrystallization overprinting affected the grains used for ID-TIMS. Conversely, the superior precision of ID-TIMS data for any reference material cannot be immediately used to define the reference age for *in situ* dating, if spot analyses of comparable material indicate more variability than the compounded analytical scatter. As shown above, TIMS datasets for some reference materials gave disparate results, substantiating heterogeneity, and this is expressed in the U-Pb system.

The variability in U–Pb age data observed between different methods hampers a definition of U–Pb reference ages for the evaluated standard reference materials. Consequently, evaluation of our U–Pb age data and the definition of U–Pb reference values for the standard reference materials investigated here are not straightforward. These two issues are addressed in the following.

Our LA-ICP-MS in situ data are now evaluated relative to ID-TIMS data employing uranogenic Concordia and complementary Tera-Wasserburg diagrams (Fig. 12). These allow us to identify problems related to the amount of initial common lead, ²⁰⁶Pb_{excess}, and possible lead loss due to alteration, as illustrated in Fig. 12a and b. The ID-TIMS data define well constrained trends in U-Concordia and Tera-Wasserburg diagrams, suggesting that there may be one dominant cause for the variation in U/Pb isotopic data. Spot analyses, for which only pristine parts of allanite were selected, generally define a less variable group of points that plot on the more radiogenic side along the same trend as the ID-TIMS data (Fig. 12). This suggests that ID-TIMS single grain analyses include either material with a higher Pbc fraction (e.g. the epidote rim in BONA), or altered allanite affected by a late magmatic lead gain. The fact that our spot analyses data lie in the trend outlined by the ID-TIMS data indicates that our U-Pb measurements are accurate.

As a consequence it is recommended here that none of the allanite standard reference material evaluated here should be employed as an external standard for the U–Pb system. However, ion-probe analytical techniques require matrix-matched standardization, and a possible solution for this case is outlined here. As shown above, spot analyses techniques successfully avoid alteration domains for CAP and TARA standard reference materials and lead to well-characterized clusters

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in Tera-Wasserburg and U-Pb Concordia diagrams. The average values of these clusters can then be used as an approximation for reference values of pristine allanite standard reference material. In order to accommodate for the variability observed in the pristine allanite of CAP and TARA standard reference material, which is introduced mainly by variable amounts of ²⁰⁶Pb_{excess}, the respective uncertainties to this values are expressed as 2 standard deviations. This results in the following recommended values (Fig. ESI2[†]) for the ²⁰⁶Pb/²³⁸U ratio: 0.0802 ± 0.0063 (TARA) and 0.0525 ± 0.0079 (CAP); for the 207 Pb/ 206 Pb ratio: 0.179 \pm 0.031 (TARA) and 0.166 \pm 0.068 (CAP). In order to apply these reference values a sufficient number (at least 10 grains) of fresh allanite standard material needs to be analyzed, in order to recognize outliers in the standardization. Finally, uncertainties on these values need to be propagated into the final age.

6.2 Correction method for dating minerals by non-matrix matched standardisation

This study developed an approach to allow for non-matrixmatched standardization that is complementary to that presented by McFarlane⁸ for cases where no compromise in spatial resolution can be accepted. It involves correcting for both time-dependent and time-independent elemental fractionation via empirically determined fractionation factors. These require empirical calibration as no sound theoretical basis exists for the underlying phenomena in LA-ICP-MS. Empirical correction factors are strictly valid only for a given analytical setup and operating conditions, but we expect that the procedures presented here have general validity provided the calibration is properly done for each analytical setup employed. Our procedure represents an alternative step towards a uniform standard reference material for U-Th-Pb dating by LA-ICP-MS techniques, as one excellent standard could become sufficient for dating diverse minerals. A homogeneous and well-characterized silicate glass may even be a good candidate for this purpose (compare McFarlane,⁸); however, this proposition was not evaluated here. Even with the present approach, well characterized, matrix-matched reference minerals remain a prerequisite for continuous accuracy testing during analytical sessions (secondary standards or "known unknowns") and for further developing U-Th-Pb mineral dating procedures.

6.2.1 Accuracy and precision of the novel procedure. The discussion above on the allanite reference materials already indicates that the mean ²³²Th/²⁰⁸Pb-ages obtained by using our method reproduce the ages of reference materials within their uncertainty (2s, excluding S_{sys} as is available in the published data). It is thus concluded that the non-matrix-matched LA-ICP-MS dating procedure produces accurate ²³²Th/²⁰⁸Pb isotope data. Uranogenic age data do not agree with the thorogenic reference ages of the allanite standard materials investigated here. We emphasize that this discrepancy is not due to flaws in the non-matrix-matched LA-ICP-MS calibration procedures, since TIMS data²⁰ show similar discrepancies. These seem to be caused by problems related to ²⁰⁶Pb_{excess}.

In order to estimate the uncertainty of the single spot analyses, the statistical parameters of CAP and TARA are evaluated. Assuming perfect and comprehensive uncertainty estimations on homogenous standard reference material, the mean square weighted deviation (MSWD) and the probability of fit (the *p*value) should both be equal to one:

$$MSWD = 1; p-value = 1$$
(9)

The 232 Th/ 208 Pb age data for CAP^b and TARA show MSWD < 1, implying that uncertainties are slightly overestimated in general. However, a weighted MSWD, in which the deviations of ²³²Th/²⁰⁸Pb-ages with small uncertainties have a larger weight, yields MSWD > 1 (see Table ESI4[†] for a full set of statistical parameters). This implies that for ²³²Th/²⁰⁸Pb-ages with small uncertainties, these uncertainties are slightly underestimated. At this point it is important to appreciate how uncertainties from final isotope ratios affect age uncertainties after common lead correction. For CAP^b and TARA ²³²Th/²⁰⁸Pb, with a common lead fraction of $\leq 1\%$, age uncertainties depend solely on the uncertainties of the ²⁰⁸Pb/²³²Th final isotope ratio. For BONA^b, the common lead fraction is higher, and the age uncertainty increases because of the uncertainties inherent in model ²⁰⁶Pb/²⁰⁸Pb and in ²⁰⁶Pb/²⁰⁷Pb ratios employed for common lead correction. For TARA and CAP^b, however, the underestimated age uncertainties are likely due to an underestimation of the uncertainty in the final ²⁰⁸Pb/²³²Th isotope ratio. The uncertainty estimate for that ratio combines the uncertainties from the standardisation and from the variability of the analytical signal. As a matter of fact, the ²³²Th/²⁰⁸Pb-ages with particularly small uncertainties all belong to the same analytical block, for which the uncertainty due to the standardisation is less than half the uncertainty of the other cases (0.4% compared to 1-1.7%). In conclusion, uncertainties in ²³²Th/²⁰⁸Pb-ages are generally accurately estimated for cases where the uncertainty on the standardization is >1%. The S_{sys} on the ²³²Th/²⁰⁸Pb ratio of the allanite reference material is 1.02% for TARA, 1.34% for CAP^b and 2.38% for BONA.

The evaluation of uncertainties in the ²³⁸U/²⁰⁶Pb system is hampered by the fact that none of the allanite reference materials is sufficiently homogenous in their apparent ²³⁸U/²⁰⁶Pb age (recall the ²⁰⁶Pb_{excess} problem). However, because Plesovice zircon is an excellent primary standard for the 238U/206Pb-ages, the analytical approach presented in this study should measure 206Pb/238U isotope ratios more precisely than approaches that rely on allanite as primary standard. Consequently, the uncertainty in ²⁰⁶Pb/²³⁸U isotope ratios is mainly controlled by the uncertainty in the analytical signal, not in the standardisation. All statistical parameters characterizing the quality of the estimated mean (weighted by the inverse variance) indicate a poor fit, suggesting underestimation of uncertainties in apparent ²³⁸U/²⁰⁶Pb-ages. Causes to be considered for this are (i) uncertainties in the analytical signals are underestimated, (ii) uncertainties in external standardisation are underestimated, and/or (iii) the pivot point for the DF correction changes from session to session. Addressing (i), we note that the way uncertainties in the signal are estimated for ²³⁸U/²⁰⁶Pb is analogous to the ²³²Th/²⁰⁸Pb-sytem, for which our

assessment of uncertainties proved justified; we see no reason why the same should not hold $^{238}U/^{206}Pb$ as well. (ii) Uncertainties in external standardisation are unlikely to be higher than used, as the Plesovice zircon is homogeneous in ²³⁸U/²⁰⁶Pb.²⁷ (iii) Uncertainties due to the downhole-fractionation correction should affect final isotope ratios of any one block of data in one direction only; i.e. a single block should have a systematic shift in final isotope ratios. However, this is not observed. All of the data blocks show the same variability in ²³⁸U/²⁰⁶Pb-ages, hence (iii) can be excluded. We thus conclude that the uncertainty estimation in the ²³⁸U/²⁰⁶Pb-system is accurate and that allanite reference materials show increased natural variability in the ²³⁸U/²⁰⁶Pb-system. This was noted also in previous studies¹² and is likely attributable to variable amounts of ²⁰⁶Pb_{excess} from ²³⁰Th decay in allanite. The $S_{\rm sys}$ on the ${}^{238}{\rm U}/{}^{206}{\rm Pb}$ ratio of the allanite reference material is 4.56% for TARA, 5.79% for CAP^b and 225.0% for BONA^b.

6.2.2 Our novel procedure compared to other approaches. TARA is used to evaluate the comparability of dating approaches because this allanite material is most uniform in chemical and Th-U-Pb isotopic composition, and it has been quantified with very diverse analytical techniques (Fig. 11a). Allanite from the same sample location was employed for studies by ID-TIMS,²⁰ SHRIMP,13 LA-ICP-QMS rastering approach,12 LA-ICP-QMS dating with allanite reference material,41 and LA-ICP-QMS with non-matrix-matched standardisation (this work). Chemical compositions reported in these studies are uniform. Consequently, the reported differences in age are most likely due to the dating procedures employed, and this is evaluated in the following. Uncertainties in the external reproducibility of spot ages reported are smallest for the LA-ICP-QMS rastering approach (1 SD = 0.84% (ref. 12)) and the approach used in this study ($S_{sys} = 1.02\%$). LA-ICP-QMS single spot dating with allanite as a primary standard⁴¹ resulted in larger scatter (1 SD = 1.92%) and a systematic offset of the mean age. The SHRIMP data set shows more scatter (1 SD = 2.96%) than any of the LA-ICP-MS data sets, and uncertainties for single spot SHRIMP analyses are also larger.13 Limiting factors for the precision of SHRIMP data include the much smaller volume sampled by the ion probe than by laser ablation, resulting in elevated uncertainty from counting statistics, and possibly the heterogeneity of allanite primary standards employed in SHRIMP dating. By contrast, minor heterogeneity in TARA allanite due to postcrystallisation overprint limits the usefulness of ID-TIMS data, despite their superior analytical precision. The reproducibility of ID-TIMS analyses (STD = 8.8%) is severely impaired by the heterogeneity of the TARA allanite reference material. In summary, this evaluation illustrates that in situ techniques are required for accurate age dating of heterogeneous materials. Among these techniques, our approach of LA-ICP-MS allanite dating is highly accurate, at a spatial analytical resolution only slightly below that of ion probes, thus offering a very valuable alternative to established techniques.

7. Conclusions

Natural allanite reference materials were newly sampled and dated by quadrupole LA-ICP-MS using a novel procedure of

measurement and data reduction employing non-matrixmatched external standardisation. This study shows that:

(1) Non-matrix-matched standardisation in high spatial resolution LA-ICP-MS Th–U–Pb dating techniques can be successfully applied, provided the matrix-dependent downhole fractionation evolution in LA-ICP-MS analysis is properly corrected for *via* empirical calibration of correction factors. As these depend on the analytical setup, they need to be specifically determined for every instrumental setup used, but they have proven robust over 30 months in our lab.

(2) For allanite dating, Plesovice zircon reference material is much preferred over all presently available allanite reference materials for external calibration of *in situ* analysis; this zircon is more homogeneous, and the isotopic ratios of interest have lower uncertainties. However, matrix matched secondary reference materials are inevitable to define the empirical correction factors and for constant quality control.

(3) BONA^b, CAP^b, TARA evaluated here are grain separates from newly sampled rocks which are comparable in quality with the original allanite reference materials. Our data for the newly collected material demonstrate that they can be related to published data sets.

(4) Our thorogenic age data for these allanite materials show excellent reproducibility and, when corrected for common lead, yield 232 Th/ 208 Pb ages as accurate as the best spot-dating techniques to date. 238 U/ 206 Pb data for the same allanite materials, however, yield apparent ages that confirm complexities including 206 Pb_{excess} as already identified before.

(5) We investigated differences between analytical results obtained by ID-TIMS and *in situ* dating techniques. The comparison illustrates the limited usefulness of bulk sample ID-TIMS data for cases where inhomogeneous crystals are dated. Even the best reference allanite materials available to date show some intracrystal heterogeneity.

(6) Allanite spot-dating techniques successfully detect intra- and inter-crystal heterogeneity, providing a tool to understand samples with complex growth zonation and/or postcrystallization overprint features.

(7) Our analytical procedure for non-matrix-matched external standardization is highly complementary to that presented by McFarlane⁸ which, however, offers lower spatial resolution but does not require the quantification of instrument-specific correction factors for downhole fractionation.

(8) Non-matrix-matched standardization should be considered for a wider variety of major and accessory minerals employing analytical protocols for non-matrix-matched external calibration based on widely available and precisely characterized external calibration materials. This way, valuable, matrix matched reference materials can be employed as a secondary standard to evaluate accuracy of analytical procedures.

(9) In order to report and discuss the significance of ages for unknowns, measurement uncertainties are to be combined with total systematic uncertainties (S_{sys} (ref. 27)), determined here for three potential allanite secondary standard materials. The best for ²³²Th/²⁰⁸Pb is TARA with 1.02%, corresponding to expected S_{sys} for LA-ICP-MS measurement on our setup.²⁷

Higher S_{sys} for CAP and BONA suggest sample heterogeneities resolved at our measurement conditions.

(10) Future improvements in ion transmission and duty cycles of mass spectrometers are expected to further increase spatial resolution of measurements of commonly complexly zoned accessory minerals such as allanite.

Acknowledgements

The authors kindly acknowledge fruitful discussions with Alfons Berger and Daniela Rubatto and the suggestions of two anonymous reviewers that greatly improved the clarity of this paper. This work was supported by the Swiss National Science Foundation (project 200020-146175).

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