

An acetic-acid-based extraction protocol for the recovery of U, Th and Pb from calcium-carbonates for U-(Th)-Pb geochronology

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Keywords: U-Pb, speleothem, ion-exchange chromatography, geochronology, ICP-MS

Abstract

A new method for the simultaneous recovery of U, Th and Pb from c. 0.5 g calcium carbonate samples for the purpose of U-(Th)-Pb geochronometry is presented. The protocol employs ion-exchange chromatography. Standard anion-exchange resin (AG 1-X8 100-200 mesh) is used as the static phase and 90% acetic acid is used as the mobile phase to elute the unwanted matrix components; dilute nitric acid is used to elute the U, Th, and Pb. Blanks of 1.8 pg Th, 6.4 pg Pb and 8.4 pg U have been obtained.

The protocol has been evaluated by analysing the isotopic composition of U-Th-Pb separates obtained from an in-house standard (prepared from a natural speleothem) by MC-ICP-MS. An independently dated speleothem has also been reanalysed. Based on these tests, the

extraction protocol has an acceptable blank and produces a Pb-separate sufficiently free of matrix-induced instrumental biases to be appropriate for U-Th-Pb chronology.

1.0 Introduction

U-Th chronology has been widely used in the study of past climate records contained in natural calcium carbonates such as speleothems (e.g. Cheng *et al.* 2006, Hu *et al.* 2008, Vaks *et al.* 2007) and corals (e.g. Edwards *et al.* 2003, Stirling *et al.* 1995, Thomas *et al.*, 2009).

While U-Th chronology has proven extremely useful, its application is inherently limited to samples less than ≈ 0.5 million years (Ma) in age by the half-life of ^{230}Th . U-Pb chronology does not suffer this limitation and, while its application to carbonate chronology has been more limited, it has nevertheless been used to date speleothems (e.g. Richards *et al.* 1998, Polyak *et al.* 2008, Woodhead *et al.* 2006) and other carbonates (e.g. Rasbury *et al.* 1997, Getty *et al.* 2001). Both U-Th and U-Pb methods typically require the addition and equilibration of a tracer solution containing enriched isotopes of the elements of interest, followed by the chemical separation of the major matrix components, allowing U, Th, and Pb concentrations to be measured by the isotope dilution method using multi-collector (MC-) ICP-MS or TIMS analysis.

The purpose of this contribution is to document and test a new U-(Th)-Pb analytical procedure based around a novel separation protocol capable of simultaneously recovering U, Th and Pb from ≈ 0.5 g calcium carbonate samples for the purposes of geochronometry.

The primary requirement of the separation protocol is to separate U and Pb, ideally in the same procedure, from Ca and the other group II elements in the ≈ 0.5 g of carbonate required to obtain sufficient Pb for analysis. This protocol must produce U-Pb separates that are sufficiently clean of matrix to allow isotopic analysis at a useful level of accuracy and precision. In addition, it is desirable for the same procedure to recover Th so that ^{232}Th can be

used as a proxy for initial ^{230}Th in the ^{238}U decay chain, thus yielding information about the initial disequilibrium state. This is important for young samples where initial disequilibrium in the U decay chain can significantly bias the calculated age (e.g. Ludwig 1977, Richards *et al.* 1998).

Natural carbonates commonly have low concentrations of ^{232}Th . This means that, unlike in many other sample types, the daughter product, ^{208}Pb , is virtually non-radiogenic and thus provides a useful alternative to the lower-abundance ^{204}Pb as the basis of initial Pb correction. Measurement of ^{232}Th therefore also allows verification of the assumption that ^{208}Pb is non-radiogenic or correction for the small proportion of ingrown ^{208}Pb .

Protocols exist for the recovery of U, Th and Pb (e.g. Krogh 1973, Strelow and Toerien 1966, Edwards *et al.* 1986) but are generally either not intended for calcium carbonate matrices, or designed for U-Th chronology. Those procedures that have been used previously for U-Pb chronology of carbonates (e.g. Richards *et al.* 1998, Woodhead *et al.* 2006) typically do not recover Th, and also require separate purification of U and Pb. To this end, we have developed an anion separation procedure employing Biorad AG 1-X8 anion resin as the static phase and acetic acid as the mobile phase. Acetic acid was chosen for the extraction medium based on examination of available partition coefficient curves for anion resins (Saito 1984), on the basis that U, Th, and Pb should all be strongly retained in concentrated solutions of the acid, but group I and group II elements should be eluted, and thus in principle allow the simultaneous recovery of U, Th, and Pb.

In this study, three distinct groups of experiments/tests were carried out. The first involved the set-up and calibration of anion-exchange protocols for separation of U, Th and Pb from

the unwanted matrix components. The second examined whether the separation procedure provided U, Th and Pb solutions of sufficient cleanliness to control instrumental biases during MC-ICP-MS isotopic measurements, and assessed the precision that may be reasonably expected. The final test was to re-date a speleothem sample previously dated using an established technique, as a practical test of the whole procedure.

2.0 Anion exchange chromatography

2.1 Reagents and preparation

All preparation work has been carried out under clean laboratory conditions using 18 Mohm water and high-purity sub-boiling distilled acids (HNO_3 , CH_3COOH , HCl) either prepared in-house or obtained from Romil (UK) or ThermoFisher (UK). All consumable equipment coming in to contact with samples, reagents, reference materials etc. was thoroughly acid-leached with 1-2 mol l^{-1} distilled HNO_3 for several days and rinsed with 18 Mohm water before use. Savillex Teflon vials used in sample preparation were cleaned initially by immersion in hot concentrated reagent grade HNO_3 , then twice refluxed with distilled concentrated HCl , and then refluxed with distilled concentrated HNO_3 ; the vials were rinsed repeatedly with 18-Mohm water between each stage. Each cleaning stage was overnight or longer.

2.2 Equipment

Small polypropylene bottles (or similar sealable containers)

7 ml and 30 ml PFA Teflon vials with screw-cap Teflon lids (Savillex, USA)

2 ml Polyprep columns (Biorad, UK)

AG 1-X8 100-200-mesh resin, chloride form (Biorad, UK)

Custom-made polypropylene column stands (acrylic should be avoided due to its solubility in acetic acid)

Ultrasonic bath

Hotplate

Balance

Standard liquid-handling equipment (pipettes, measuring cylinders etc.)

2.3 Tracer solution

A mixed tracer solution for isotope dilution was prepared from ^{204}Pb metal (CK Gas Products Ltd, UK), ^{230}Th (NIST SRM060), ^{236}U (Oak Ridge National Laboratory, USA) for the main work. The tracer was calibrated against a gravimetric solution prepared from CRM145 uranium (New Brunswick Laboratory, USA), SRM981 Pb metal (NIST), and High Purity Standards Th solution (lot 0724812) by isotope-dilution using MC-ICP-MS (as below). The tracer has a $^{236}\text{U}/^{204}\text{Pb}$ ratio of 14.019 ± 0.014 (95%), including uncertainty on the gravimetric solution, and the isotopic reference materials used in the calibration. Further compositional information for the tracer solution is provided in Table 1. The spike calibration has been further verified using an EARTHTIME reference solution (Parrish_RFSOLN_1, made from NBS 982 Pb and CRM 112a U; www.earth-time.org).

2.4 Sample preparation

For the analysis of speleothem material, pieces of sample were cleaned firstly in small acid-leached polypropylene bottles with water in an ultrasonic bath, changing the water repeatedly until no suspended debris was visible. The pieces were then leached twice in 2% HNO_3 to remove the outermost layer along with any residual dirt. Each leach was for a few minutes; the leachate was decanted before the reaction between the acid and calcite ceased, to prevent adsorption of dissolved components back on to the surface of the sample. The samples were then rinsed repeatedly in H_2O to remove the acid residue, transferred to clean Teflon beakers, and allowed to dry.

Approximately 0.5 g of cleaned sample was weighed in to a clean 30 ml Savillex beaker and covered in a small quantity of H_2O . Concentrated HNO_3 was then added in small aliquots to dissolve the samples. This slow addition of acid enables controlled dissolution of carbonate without excessive rates of CO_2 production. After complete dissolution, further concentrated HNO_3 was added to bring the solution to approximately $2 \text{ mol l}^{-1} \text{ HNO}_3$. The sample was then refluxed overnight to ensure the solution was homogenised. If required, the solution was then gravimetrically aliquoted, with $\approx 50\%$ separated into a separate beaker for addition of isotopic tracer solution (in which case $\sim 1 \text{ g}$ of sample was initially dissolved). In these cases, the solution was again refluxed overnight following tracer addition to allow equilibration.

The dissolved sample was then dried to incipient dryness at $80\text{--}120^\circ\text{C}$, followed by heating to c. 220°C overnight to complete dryness. The samples were then redissolved in 3.5 ml 88% (v/v in H_2O) acetic acid ready for loading on columns; the samples were heated gently and periodically agitated to assist dissolution.

2.5 Column calibration procedure

The final optimised anion separation procedure described below was developed and tested as follows. Around 20 g of natural calcite was dissolved with concentrated HNO_3 and H_2O and doped with natural U, Th, and Pb to mimic a natural carbonate sample while also containing adequate U, Th and Pb that blank contribution during the calibration was negligible. The solution was heated until dry and the salts were redissolved in 92.5% (v/v in H_2O) CH_3OOH , such that 1 ml of the final solution contains ~ 0.2 g of dissolved calcite and approximately $0.2 \mu\text{g ml}^{-1}$ each of U, Th, and Pb.

Aliquots of the calibration solution equivalent to c. 0.5 g of dissolved calcite (i.e. ≈ 2.5 ml aliquots) were loaded in a CH_3OOH -rich solution on Biorad Polyprep columns with a 2 ml resin bed of cleaned AG 1-X8 100-200-mesh anion resin. The basic premise, based on available partition coefficient curves (Saito 1984), is that U, Th, and Pb (but not the Group II matrix components) will be retained on the resin in concentrated CH_3COOH , and can be eluted in H_2O , dilute HNO_3 , or concentrated HCl . The main parameters varied, in an attempt to optimise the procedure, were the volume and CH_3OOH concentration of the load solution, the volume and CH_3OOH concentration of the elute solution, and the resin cleaning and preconditioning. All the solution passed through the column in each calibration was collected in increments for analysis to determine the position of the elution peaks relative to the total volume of solution added to the column. In the case of the final optimised procedure, the aliquots were also dried down and the salts converted to nitrate form, and the weight distribution of the salts determined.

A Thermo Element 2 single collector ICP-MS running in low resolution mode, and operating under standard ‘wet plasma’ running conditions was used to analyse the column calibrations.

The incremental elutions from the column were diluted in 2% HNO₃ and introduced using a self-aspirating PFA nebulizer and cyclonic spray chamber. For each calibration, the intensity of each element of interest was measured in all elutions relative to one another, allowing the proportional distribution of that element to be estimated relative to the total of that element collected. This semi-quantitative approach was chosen rather than full quantification because of its expediency, given that multiple iterations were required in optimising the separation procedure.

Preliminary Pb blanks were determined with reference to an aliquot of tracer containing ~10 pg of ²⁰⁴Pb taken through the anion exchange procedure. Approximate ²⁰⁸Pb/²⁰⁴Pb ratios of the mixtures were estimated on the Element 2, and the blanks determined by isotope dilution.

2.6 Column calibration results

The separation is strongly influenced by the CH₃COOH concentration used to elute the matrix. A concentration of 87.5% yields a cleaner separation from Ca, but slightly poorer U recovery and markedly poorer Th recovery. A concentration of 92.5% yields slightly better U and Th recoveries, but the separation from Ca is much poorer. Consequently, care must be taken if variable amounts of water are present in the nominal 100% CH₃COOH used to prepare the reagents so that the optimal CH₃COOH concentration is achieved.

Residual nitrate on the columns after cleaning the resin, and the incomplete evaporation of HNO₃ after sample dissolution, were identified as possible causes for poor U and Th recovery in early tests and should be avoided.

Calibration results for the optimised procedure are summarised in Figure 1. The geometry of the elution curves for U and Pb suggest little or none of these elements was retained on the column at the end of the calibration. Conversely, there is some tailing of the Th suggesting some Th was retained at the end of the calibration. The 2% HNO₃ elutions collectively contain >98% of the recovered Pb, suggesting near-quantitative recovery of Pb, and around 90% of the recovered U and 85% of the recovered Th. This is probably a reasonable estimate of the true U and Pb recovery, but is an overestimate of the absolute Th recovery because of the probable retention of some Th on the column at the end of the calibration. The 2% HNO₃ elutions cumulatively contain ~0.007% of the total Ca, indicating an enrichment of Pb relative to calcium of ~14,000 times. Na, Mg, Ba, Sr, and Fe were also largely removed. Tl was also largely stripped from the column prior to collection of the U-Th-Pb cut; important to minimise the ²⁰⁵Tl interference if a ²⁰⁵Pb tracer is used, or if Tl-doping is to be used to monitor mass fractionation during the Pb isotope measurements (e.g. White *et al.* 2000).

A similar calibration was carried out using a second column ('Mop' column; described below) stacked above the first column (the 'Sample' column'). This Mop column served to act as an in-line trap for reagent blank. Rather similar recoveries were achieved as without the Mop column (Table 2; >97% for Pb, ~87% for U, ~93% for Th, and ~0.024% for Ca were present in the 2% HNO₃ elution stage). The slightly poorer separation using the Mop column is attributed to sample adhering to the column reservoir. Without the Mop column, the wash acetic acid is loaded directly on to the 'sample' column, and hence any adherent sample droplets are washed on to the resin early in the procedure. With the Mop column the wash acetic acid is only added drop-wise so the reservoir of the Sample column is not so thoroughly washed of sample residue prior to the elution of U, Th, and Pb.

A sweep of the mass spectrum using the Element 2 in low resolution mode indicated that Ca and Zn were the main cationic impurities in the U-Th-Pb separate.

Pb blanks were determined from identical Mop and Sample columns. The Pb blank eluted from the Sample column was ~16 pg, and from the Mop column was ~50 pg. This suggests that the Mop column prevented around 75% of the Pb blank from entering the sample.

2.7 Final anion exchange procedure

2 ml of AG 1-X8 100-200-mesh, chloride-form resin was loaded in a 2 ml Biorad Polyprep columns. The resin had been repeatedly (10-15 times) batch cleaned, alternately with MilliQ H₂O and dilute distilled HCl. In the column the resin was further cleaned and preconditioned as follows:

- 5 column volumes 2% HNO₃ (w/w in H₂O)
- 5 column volumes 10 mol l⁻¹ HCl
- 5 column volumes 10 mol l⁻¹ HCl
- 5 column volumes H₂O
- 5 column volumes 10 mol l⁻¹ HCl
- 5 column volumes 10 mol l⁻¹ HCl
- 5 column volumes H₂O
- 5 column volumes H₂O
- Precondition with ~4 ml 90% acetic acid (v/v in H₂O)

The sample was then loaded and the matrix was eluted with ~15 column volumes (~30 ml) of 90% acetic acid (v/v in H₂O). U, Th and Pb were eluted together with 4-5 column volumes (8-10 ml) of 2% HNO₃ (w/w in H₂O).

The eluted U-Th-Pb solution was dried down and converted to nitrate form by adding a few drops of concentrated HNO₃ and again evaporating to dryness. The sample was then re-dissolved in 2% HNO₃ for analysis.

As a means of controlling blank (around 90 % of which initially originates from the CH₃OOH) the above procedure was modified to use two identical columns (as mentioned above) that were stacked. The upper Mop column was used as an in-line trap to capture blank from the CH₃OOH before it dripped onto the lower Sample column. The Mop column took no part in the actual separation, which occurred on the lower Sample column. This approach successfully decreased blank levels and was used routinely in subsequent analysis, although it might be replaced by a batch purification of the CH₃OOH prior to column chemistry.

3.0 Isotope ratio measurements

3.1 Mass spectrometry

Pb and U-Th isotope measurements (including tracer calibration) were carried out on a Nu Plasma multi-collector ICP-MS. The design of the Nu Plasma has been described in detail elsewhere (e.g. Belshaw *et al.* 1998), and will only be summarised here. The Nu Plasma is a variable-dispersion double-focusing instrument equipped with a fixed array of twelve Faraday collectors and three discrete-dynode ETP ion counters, and operating with an

accelerating voltage of ~4 kV. Two quadrupole lenses, which together form a ‘zoom’ lens, are used to change the dispersion of the instrument, allowing the isotope beams of interest to be aligned with the collector array. Of the three ion counters, one is mounted behind an energy filter designed to reduce peak tailing, and thereby improving abundance sensitivity. Sample was introduced using a self-aspirating PFA nebuliser and a DSN-100 desolvator. Typical running conditions were: RF power: 1300 watt; coolant gas: 11.7 L min⁻¹; auxiliary gas 0.8-1.2 L min⁻¹; membrane sweep gas 2.5-3.3 L min⁻¹; nebuliser pressure ~28 psi.

Gas lines to, and within the instrument, including the internal gas lines within the DSN-100, and the sample line between the DSN-100 and torch were replaced with acid cleaned PFA tubing in an attempt to control the Hg background (to minimise the ²⁰⁴Hg interference on ²⁰⁴Pb) during Pb analyses. The use of gold traps to remove Hg from the instrument Ar supply was assessed, but made no improvement, and the Hg contribution from the Ar appears to be negligible. The residual Hg background appears, instead, to originate from atmospheric exposure of the instrument interface – the Hg intensity decaying with a half-life of ~24 hours after start-up of the plasma, and worsening markedly with even brief shutdowns of the plasma.

U-Th measurements were carried out with ²³⁸U, ²³⁶U and ²³⁵U measured on Faraday collectors and ²³⁴U, ²³²Th, and ²³⁰Th on ion-counters (Table 3). All isotopes were measured simultaneously in a single static step. Additionally, half mass measurements were made dynamically at 236.5, 235.5, 234.5 and 233.5 using the high-mass ion counter to monitor and correct for abundance sensitivity. For optimally spiked samples the abundance sensitivity correction is typically <0.1‰ of the measured ²³⁶U and ²³⁵U beams, and ≤5 ‰ of the ²³⁴U beam. Mass fractionation and ion-counter gain was assessed using U-isotope ratios measured

on bracketing U standards (CRM145). The $^{232}\text{Th}/^{230}\text{Th}$ ratio was corrected by standard bracketing with an in-house Th standard (ThIS-1; Mason and Henderson 2010).

Spiked Pb measurements were carried out in two steps. Both steps measure ^{208}Pb , ^{207}Pb , ^{206}Pb , ^{204}Pb -Hg, ^{205}Tl , ^{203}Tl , ^{202}Hg and ^{200}Hg statically on Faraday collectors in the same configuration (Table 3). The first step measured these masses while aspirating clean 2% HNO_3 to determine the instrument background and the apparent $^{204}\text{Hg}/^{202}\text{Hg}$ and $^{202}\text{Hg}/^{200}\text{Hg}$ ratios of the instrumental Hg background. In the second step, the sample was introduced and measured. The $^{202}\text{Hg}/^{200}\text{Hg}$ was again measured and used to monitor and correct for any changes in the Hg composition. Mass fractionation is corrected by reference to an in-house Pb standard (SEAL-1) prepared from SRM982 (NIST) and enriched ^{204}Pb to resemble spiked, moderately radiogenic samples of natural carbonate. For spiked samples and bracketing SEAL-1 standards the ^{204}Hg accounts for <1 % of the total ^{204}Pb beam.

Unspiked Pb measurements have been made in an analogous way, except that the lower abundance of ^{204}Pb necessitates measurement on an ion counter (Table 3), which in turn (because of the collector configuration) requires ^{202}Hg and ^{200}Hg also to be measured in ion counters. Because the apparent $^{204}\text{Hg}/^{202}\text{Hg}$ and $^{202}\text{Hg}/^{200}\text{Hg}$ ratios are measured in the memory step, it is not necessary to determine the gains of the ion counters to apply the Hg interference correction. Mass fractionation and ion counter gain on ratios involving ^{204}Pb are corrected using bracketing SRM982 standards measured in an identical way. The Hg correction for unspiked samples and SRM982 bracketing standards is on the order of 3-10%; Hg corrections of up to 50-60% (measured on the ion-counters) are tolerated at the c. 2% level of accuracy and precision, which is adequate for the unspiked measurements.

In both Pb measurements ^{205}Tl and ^{203}Tl were also measured on Faraday collectors and corrected for instrumental memory but are only relevant to some of the initial tests using Tl-doping.

4.0 ASH-15 speleothem standard

To test the methodology (and, in the future, to assess long-term reproducibility) we use a natural speleothem ‘standard’ that can be repeatedly analysed. Around 0.7 kg of coarsely crystalline translucent calcite flowstone, free of detrital silicate material, from Ashalim cave in the Negev desert, Israel (30° 56' 36.2"N, 34° 44' 22.5"E) was cleaned, weighed, and dissolved in HNO_3 . The result was a solution containing 0.37 g/g of calcite in $\approx 1.5 \text{ mol l}^{-1}$ HNO_3 . After dissolution, this solution was heated to $\approx 80^\circ\text{C}$ for around 2 weeks, and periodically shaken, to ensure homogeneity.

5.0 Testing of the separation protocol

The primary concern when developing chemical pre-concentration for isotope analysis is that the resulting solution, when analysed, can be measured accurately, without inducing matrix-related mass fractionation or interferences.

5.1 U mass fractionation and interferences

To test that the new acetic-acid protocol enables accurate U isotope analysis, the ASH-15 standard was processed with three different chemical purification protocols:

- 1) The new acetic-acid chemistry.
- 2) The new acetic-acid chemistry, but with secondary purification of the recovered U to further remove Ca and Zn from the U-Th-Pb separates (see Table 4). This column removed the bulk of the Zn and $\approx 60\text{-}80\%$ of the residual Ca (Table 5)
- 3) Standard HNO_3/HCl U-Th chemistry (e.g. Robinson *et al.* 2002) without the use of the new acetic-acid chemistry (see Table 4). This chemistry provided a more variable separation of U and Ca (see Table 5)

This comparison of chemical approaches checks that further clean-up of the U solution does not change the measured U-isotope values, and compares the chemistry with a more commonly used U-Th chemical approach.

Five aliquots of the ASH-15 solution were passed through the acetic-acid chemistry, each corresponding to ~ 500 mg of carbonate. Approximately 20% of the U-Th-Pb separate from each of these was then further processed through the secondary U clean-up procedure. Five additional analyses, each corresponding to ~ 250 mg of dissolved carbonate, were processed using the standard U-Th chemistry. $^{238}\text{U}/^{235}\text{U}$, $^{238}\text{U}/^{234}\text{U}$ and $^{235}\text{U}/^{234}\text{U}$ ratios were measured by ICP-MS using the natural-uranium standard, CRM145, as a bracketing standard.

U-isotope data on ASH-15 samples processed using the new acetic acid procedure are indistinguishable between aliquots measured with or without the clean-up column (Figure 2). The lack of any change in the apparent isotope ratios in the additionally purified aliquots indicates that the acetic-acid separation adequately controls instrumental biases. In contrast, samples treated with the traditional U-Th chemistry show more variability (Figure 2), consistent with the non-uniform removal of Ca (Table 5). This variability defines a linear

trend compatible with mass fractionation, and passing through the cluster of data obtained using the acetic-acid separation. While this indicates some degree of failure of the traditional U-Th separation, it is reassuring that all data fall around a common mass fractionation trend and thus appears to exclude significant molecular interferences in all of the separation chemistries.

5.2 Pb mass fractionation and interferences

Assessing the success of the new chemistry for Pb isotope analysis cannot be performed using a secondary clean-up chemistry because the isotopic compositions of the small quantities (<1 ng) of Pb being measured are susceptible to change by blank addition during any second column. Instead, the possibility of any matrix effect on mass fractionation was testing using Tl-doping (e.g. Belshaw *et al.* 1998).

Identical Tl solution was added to the U-Th-Pb separate from the acetic-acid chemistry, and to pure SRM982 Pb standard. Side-by-side measurement of Tl isotopes in these two solutions checked for any matrix-induced variation in mass fractionation resulting from incomplete separation during chemistry. Resulting analyses show a maximum deviation in the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio between the two solutions of 0.08 ‰ per AMU. This result suggests that the Pb solution following the acetic-acid chemistry is sufficiently clean not to perturb instrumental mass fractionation in Tl and, by analogy, in Pb. Trace Tl present in the samples prior to doping was measured and would have biased the measured ratio by <40 ppm.

Molecular interferences greater than a few per cent of the beam intensity could not be seen at a resolution of ~10,000 on ^{206}Pb , ^{207}Pb and ^{208}Pb in the ASH-15 separates using an Element 2

in high-resolution mode; lower intensity interferences or those on the small ^{204}Pb beam would not, however, have been observable above detector noise. Simple oxide, argide etc. interferences are not anticipated based on a low-resolution sweep of the entire mass spectrum using the Element 2, which, with the exception of ^{138}Ba and $^{238}\text{U}^{++}$ contains no peaks larger than ^{206}Pb for >100 AMU below Pb.

5.3 Interference from scattered U ions

The Pb measurement may also be biased by scattering of ions from the much larger ^{238}U ion beam because the chemistry does not separate U from Pb. Normal tailing (i.e. abundance sensitivity) should be insignificant at a mass separation of 30 AMU, but scattering of ions from the flight tube or other internal components of the instrument is possible. To evaluate this, a ≈ 4.6 ppm natural U solution (comparable to the U concentration expected in a Pb analysis) was introduced to the mass spectrometry and the signal intensity at half masses either side of the Pb (and Hg) isotopes were measured to determine if signals were detectable above the collector baselines. The apparent $^{202}\text{Hg}/^{200}\text{Hg}$ ratio of the instrumental Hg background was also measured with and without U present, on the basis that scattered U ions in the vicinity of Pb would also be likely to perturb this ratio.

The tests for scattered U ions in the vicinity of Pb revealed no detectable signal on the half mass measurements. No detectable variation in the apparent composition of the instrumental Hg background was detected in the presence of U.

5.4 Impact of Pb blank variation

An additional concern with Pb measurements is the possible variability of blank between samples. Because of the small quantities of sample Pb, even low-blank chemistry can contribute a few per cent of the total Pb analysed. Consequently, variability in the blank will impact on the reproducibility of the measured ratios. To test the impact of variable blank contribution, five replicate aliquots of the ASH-15 standard (and a procedural blank) were processed using the acetic-acid procedure and analysed. This approach is preferred to direct determination of replicate blanks via isotope dilution because dissolved samples are more difficult to manipulate during the separation protocol than blanks, so that handling of real samples is a more realistic assessment of blank effects.

The measured $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of these repeat ASH-15 aliquots form a linear array with total spread of ~1% and 0.9% respectively (Figure 4). The array points towards the isotopic composition of the blank, suggestive of a mixing line. SRM982 standards analysed along with the samples have a much smaller spread of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (0.09% and 0.1% respectively) suggesting that most of the variation in the samples results from variable blank contribution. Based on the relative intensities of the measured ASH-15 standards and the associated procedural blank measurement, the blank contribution on ^{206}Pb , ^{207}Pb and ^{208}Pb is around 0.5%, 1.3% and 1.4% respectively. Compared to the uncertainty arising from the blank, the <0.08 ‰ per AMU variation in mass fractionation behaviour between samples and standards is insignificant, indicating that Pb analysis precision is limited by ability to control blank contamination during chemistry. Despite this limitation, the low level of blank Pb measured through the acetic-acid separation approach on real sample material indicates the success of the technique for future application in geochronology.

6.0 Dating of a speleothem

To fully test the chemical procedures described in this paper we have dated a speleothem sample previously dated using established techniques by another lab (Melbourne: Vaks *et al.* in review). The previous dating of this sample was conducted by MC-ICP-MS, as in this study, but using conventional anion exchange chemistry using HBr/HCl to purify Pb and EICHRON TRU-resin with HNO₃/HCl/HF media to purify U, and with a ²³³U-²⁰⁵Pb spike (Woodhead *et al.* 2006).

6.1 Sampling and Sample Preparation

The sample (ASH-15D) comprises part of the same flowstone used to prepare the ASH-15 standard. Seven subsamples were taken: two comprised ~350 mg for unspiked Pb analysis to measure the natural ²⁰⁸Pb/²⁰⁴Pb ratio; and the remaining five of ~1 g, intended to allow both spiked and unspiked analyses. The subsamples were collected as a small number of chips or cut pieces to minimise the surface area of the samples.

U, Th, and Pb were determined by isotope dilution using the procedures described above. Procedural blanks were also measured by isotope dilution, and have been corrected for.

6.2 A ²⁰⁸Pb-based initial Pb correction

It has been common to correct for initial Pb based on non-radiogenic ²⁰⁴Pb, using some form of crustal Pb-growth model or use a ²⁰⁴Pb-normalised isochron approach (e.g. Smith *et al.* 1991, Wang *et al.* 1998). An alternative approach is to construct a ²⁰⁷Pb/²⁰⁶Pb-²³⁸U/²⁰⁶Pb isochron on a Tera-Wasserberg-type concordia diagram, and use the intersection of the

isochron with concordia to obtain an age (e.g. Richards *et al.* 1998). This implicitly corrects for initial Pb, but for young samples, it has the limitation that the position of concordia is not fixed and varies according to the initial disequilibrium state of the U-Pb system.

Many speleothems contain virtually no ^{232}Th rendering its decay product, ^{208}Pb , effectively non-radiogenic, particularly for young samples given the long half-life of ^{232}Th . This provides a higher-abundance alternative to ^{204}Pb for normalisation and, thus potentially allows a sufficiently precise initial Pb correction that the radiogenic composition of the sample can be obtained and used to additionally constrain the intersection with concordia (and hence the position of concordia itself) on Tera-Wasserberg type plots. This requires ^{232}Th to be measured to confirm that its concentration is insignificant relative to ^{208}Pb .

The use of ^{204}Pb as a tracer, as pursued in this study, in principle requires the measurement of both spiked and unspiked aliquots of a sample to correct the isotope dilution calculation for natural (and blank) ^{204}Pb present in the sample. However, a partial workaround is provided by ^{208}Pb in systems where ^{208}Pb can be considered non-radiogenic. In such cases, provided the natural $^{208}\text{Pb}/^{204}\text{Pb}$ ratio is known or can be reasonably estimated, the ^{208}Pb can be used as a proxy for the natural ^{204}Pb in the spiked analyses.

6.3 Reduction of data

Analytical uncertainties, along with estimated uncertainties on the blanks and natural $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (and where appropriate the common Pb correction) were propagated through the isotope dilution maths using a Monte Carlo approach to provide 95% confidence

limits. Correlation coefficients were also determined empirically from the output of the simulation. The common Pb composition used for correction was obtained using $^{238}\text{U}/^{208}\text{Pb}$ - $^{206}\text{Pb}/^{208}\text{Pb}$ and $^{235}\text{U}/^{208}\text{Pb}$ - $^{207}\text{Pb}/^{208}\text{Pb}$ isochrons.

Concordia has been calculated by simplifying the ^{238}U decay chain to ^{238}U ($\lambda=1.55125 \times 10^{-10}$) \rightarrow ^{234}U ($\lambda=2.8263 \times 10^{-6}$) \rightarrow ^{230}Th ($\lambda=9.1577 \times 10^{-6}$) \rightarrow ^{226}Ra ($\lambda=4.33488 \times 10^{-4}$) \rightarrow ^{206}Pb ; and the ^{235}U decay chain to ^{235}U ($\lambda=9.8485 \times 10^{-10}$) \rightarrow ^{231}Pa ($\lambda=2.11583 \times 10^{-5}$) \rightarrow ^{207}Pb . Decay constants are from Cheng *et al.* (2000) and Steiger and Jaeger (1977). The decay equations used are those summarised in Faure and Mensing (2005, p.39-40)

Isochrons have been fitted using least squares regression (York 1969) and uncertainty envelopes calculated based on the equations of York *et al.* (2004).

6.4 Results

Procedural blanks obtained during the processing of ASH-15D were 1.8 pg Th, 6.4 pg Pb and 8.4 pg U. Blank accounts for: 30-100% of the total analysed Th; 0.9-2.4% of the ^{208}Pb ; 0.9-2.0% of the ^{207}Pb ; 0.33-0.40% of the ^{206}Pb ; and 0.0010-0.0012 % of the U. The high relative blank proportion of Th is a consequence of the samples containing very little ^{232}Th .

$^{232}\text{Th}/^{208}\text{Pb}$ ratios range between 0 and 0.0231 and based on the calculated age (see below)

^{232}Th decay will have contributed at most ~35 ppm of the total ^{208}Pb ; ^{208}Pb can thus be treated as non-radiogenic. Based on unspiked measurements of the first two subsamples a $^{208}\text{Pb}/^{204}\text{Pb}$ ratio of 39 ± 5 (1 sigma) was used to correct for non-spike ^{204}Pb in the spiked analyses. A large uncertainty on this value is assumed, to cover any foreseeable variation in

the natural ratio, and any contribution from blank $^{208}\text{Pb}/^{204}\text{Pb}$ variability. Greater than 95% of the ^{204}Pb in the spiked analyses originates from the spike, and consequently the correction for the sample ^{204}Pb is insensitive to the choice of sample $^{208}\text{Pb}/^{204}\text{Pb}$.

U and Pb isotope data form a coherent array (Table 6; Figure 5), but with some scatter in excess of analytical precision (MSWD 2.9). Data obtained on a different part of the same sample by J. Woodhead (Vaks *et al.*, in review) are shown for comparison on Figure 5a. The two data sets are indistinguishable in terms of their intercept with concordia, and indicate an age of ≈ 3 Ma with respect to the reference equilibrium concordia calculated here. The slope of the two isochrons is distinctly different suggesting some variation in the common Pb composition between the subsamples analysed here and by Woodhead.

The agreement of the two data sets increases confidence in the accuracy of both the method presented here and that used by Woodhead. One possible advantage of the method developed here is that it provides some constraint on the initial disequilibrium state of the U-Pb system and, hence the choice of concordia used in age calculation (Figure 5b).

7.0 Conclusions

We present a new acetic-acid-based separation protocol which recovers trace quantities of U, Th, and Pb from c. 0.5 g of calcium-carbonate speleothem. The resulting U-Th-Pb concentrate is sufficiently clean of residual matrix components that U and Pb isotopic compositions determined by MC-ICP-MS on such concentrates are free of matrix effects. Pb blank, although small, still represents the major limiting factor to the analytical precision. We

have demonstrated the success of this new chemical preconcentration technique by replicating the U-Pb age on a speleothem sample previously analysed using established approaches.

8.0 Acknowledgements

Dr. Jon Woodhead is thanked for useful discussion and for access to unpublished ASH-15D data. Dr. Dan Condon is thanked for providing the EARTHTIME NBS 982 Pb – CRM 112a U reference solution. Dr. M. Bar-Matthews (Geological Survey of Israel) is thanked for providing a large sample of ASH-15. Mr S. Wyatt is thanked for technical assistance. NERC Fellowship number NE/G013829/1 (Asian paleoclimate reconstruction from Siberian and Mongolian speleothems) is acknowledged for contributing to funding this work.

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Fig 1. Calibration column separation on 2 ml AG 1-X8. Ac=acetic acid. The acetic acid concentration is volume/volume per cent based on nominal 100% acetic acid diluted with water; the nitric acid is 2 weight % HNO_3 in water. The analyte proportion is estimated relative to the total of each element eluted and is semi-quantitative, but clearly demonstrates the matrix components are washed out prior to U, Th and Pb elution. Note that Ca is shown twice at different scales to demonstrate the success of removal of Ca from the U, Th and Pb elutant.

Fig 2. Plot of $^{238}\text{U}/^{235}\text{U}$ and $^{238}\text{U}/^{234}\text{U}$ ratios normalised to CRM145 for ASH-15 aliquots prepared using the acetic acid chemistry alone, the acetic acid chemistry with secondary purification of U, and U separated using only standard U-Th chemistry. The diagonal line has a slope of 4/3 and indicates the approximate trend that would be expected due to variation in mass fractionation. Errors are 2 sigma.

Fig 3. Permil deviation in the mean measured $^{205}\text{Tl}/^{203}\text{Tl}$ ratio between Tl-doped ASH-15 standards purified using the acetic acid column separation, and Tl-doped bracketing SRM982 Pb standards without any chemistry. The two left hand points in run 1 are analyses of the same solution.

Fig 4. Raw $^{208}\text{Pb}/^{206}\text{Pb}$ measurements of the ASH-15 standard. The measurements form an array pointing towards the procedural Pb blank composition at $^{208}\text{Pb}/^{206}\text{Pb} \sim 2.139$ and $^{207}\text{Pb}/^{206}\text{Pb} \sim 0.9013$. Bracketing SRM982 standard measurements (inset) obtained in the same run show a much smaller scatter indicating that the variation in ASH-15 is not due to instrumental instability. x and y increments are the same in the main plot and inset. Errors are 2 sigma internal.

Fig 5. Isochron diagram showing data from ASH-15D flowstone. A) Comparison of data produced in this study (Oxford data) with that produced by J. Woodhead for the same sample. The horizontal line is equilibrium concordia; B) Details of the Oxford data intersect with several possible concordias. Data corrected for non-radiogenic Pb are also shown. The non-radiogenic Pb composition used for the correction was obtained using $^{235}\text{U}/^{208}\text{Pb}$ - $^{207}\text{Pb}/^{208}\text{Pb}$ and $^{238}\text{U}/^{208}\text{Pb}$ - $^{206}\text{Pb}/^{208}\text{Pb}$ isochrons, and allows the radiogenic composition of the samples to be estimated with sufficient precision that certain concordias may be rejected, and thus provides additional chronological constraint. All concordia curves have initial activity ratios of $(^{230}\text{Th}/^{238}\text{U}) = 0$, $(^{226}\text{Ra}/^{238}\text{U}) = 1$ and $(^{231}\text{Pa}/^{235}\text{U}) = 0$, but differing $(^{234}\text{U}/^{238}\text{U})$. The sub-vertical shaded region is the regression fit through the measured $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ measurements and its 95% confidence envelope; the actual measured data plot off the scale and can be seen in A.

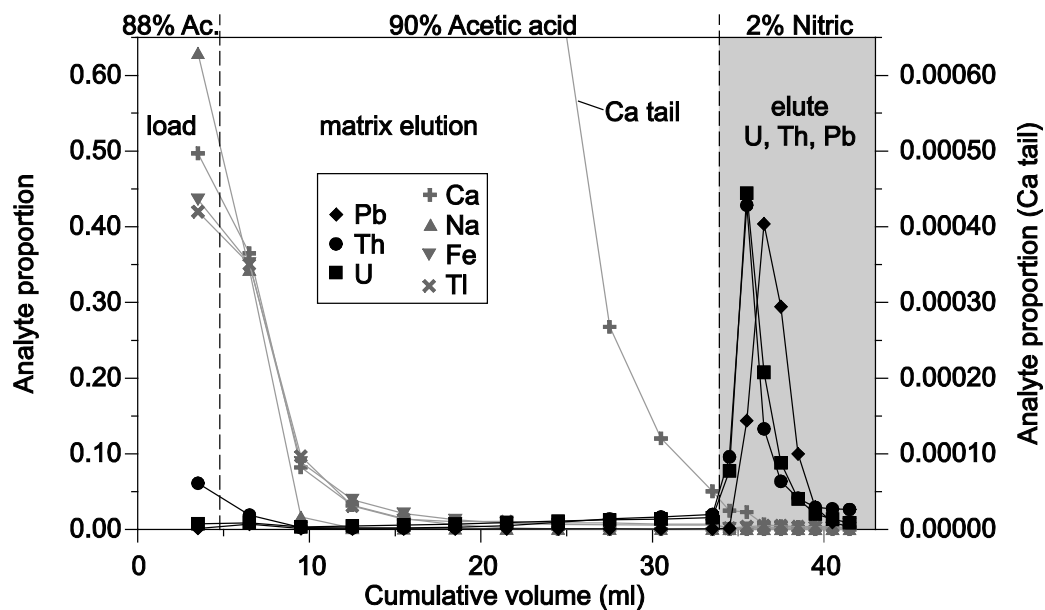


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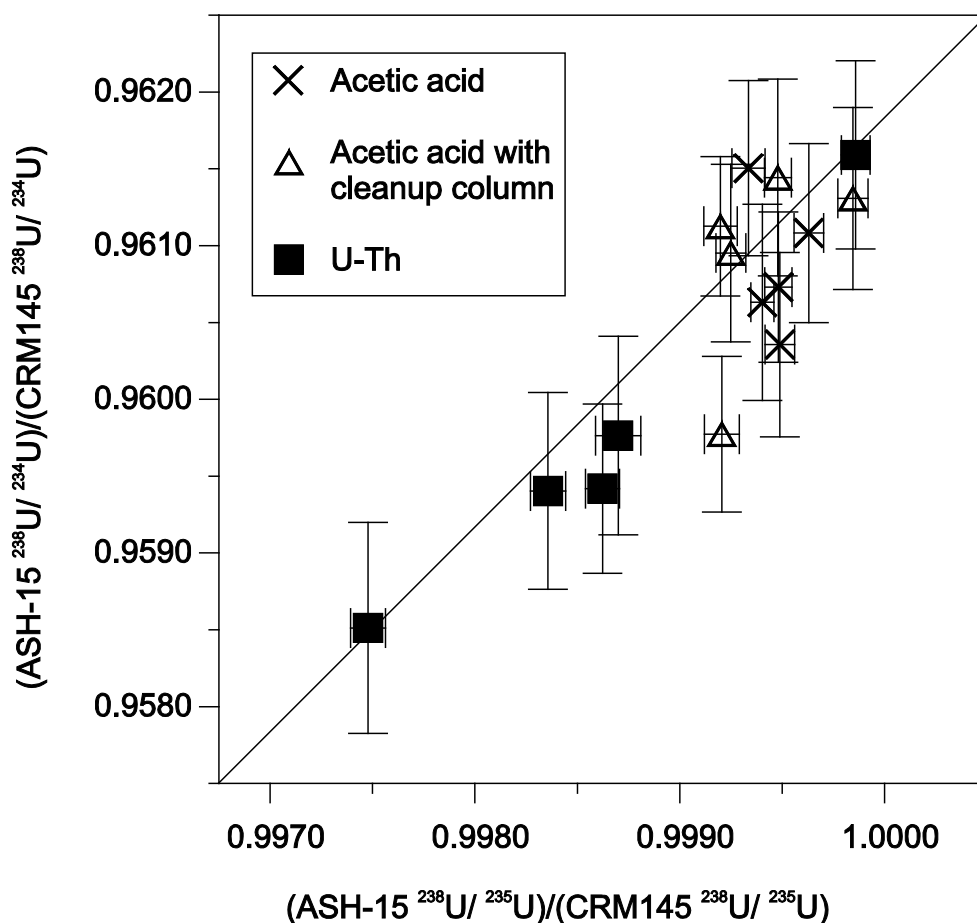


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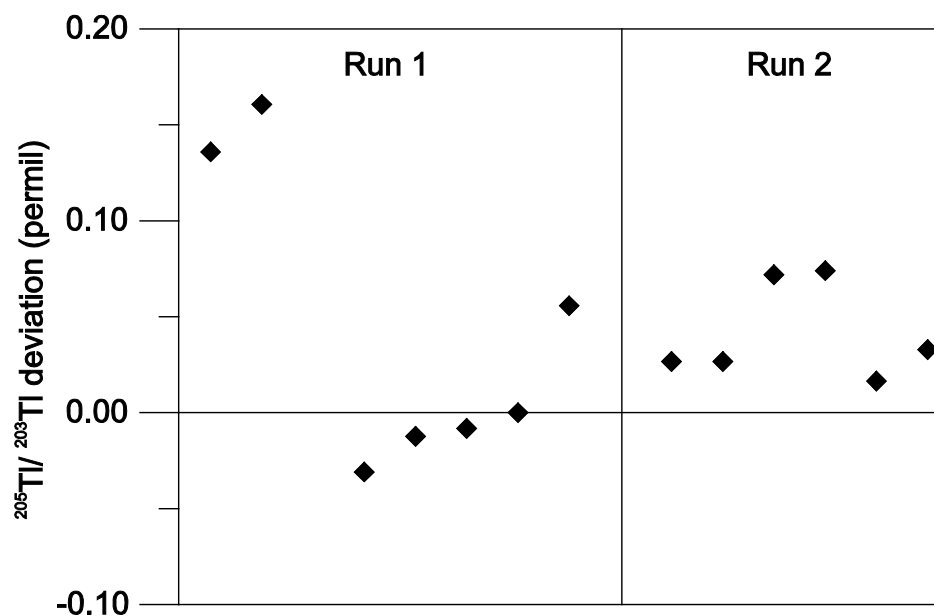


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79x51mm (300 x 300 DPI)

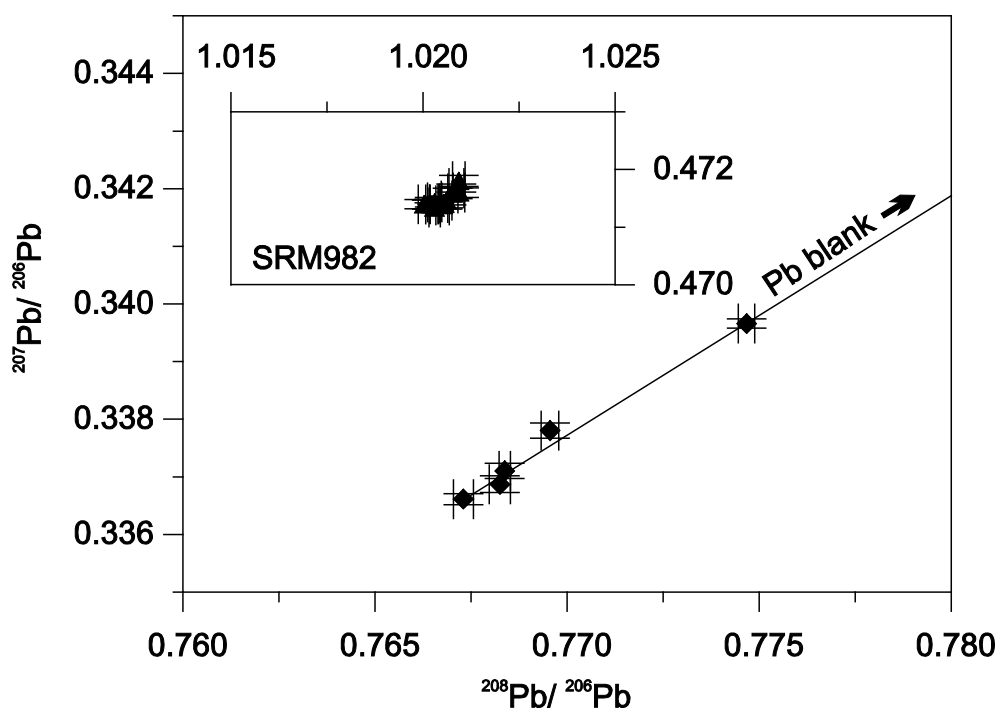


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92x65mm (300 x 300 DPI)

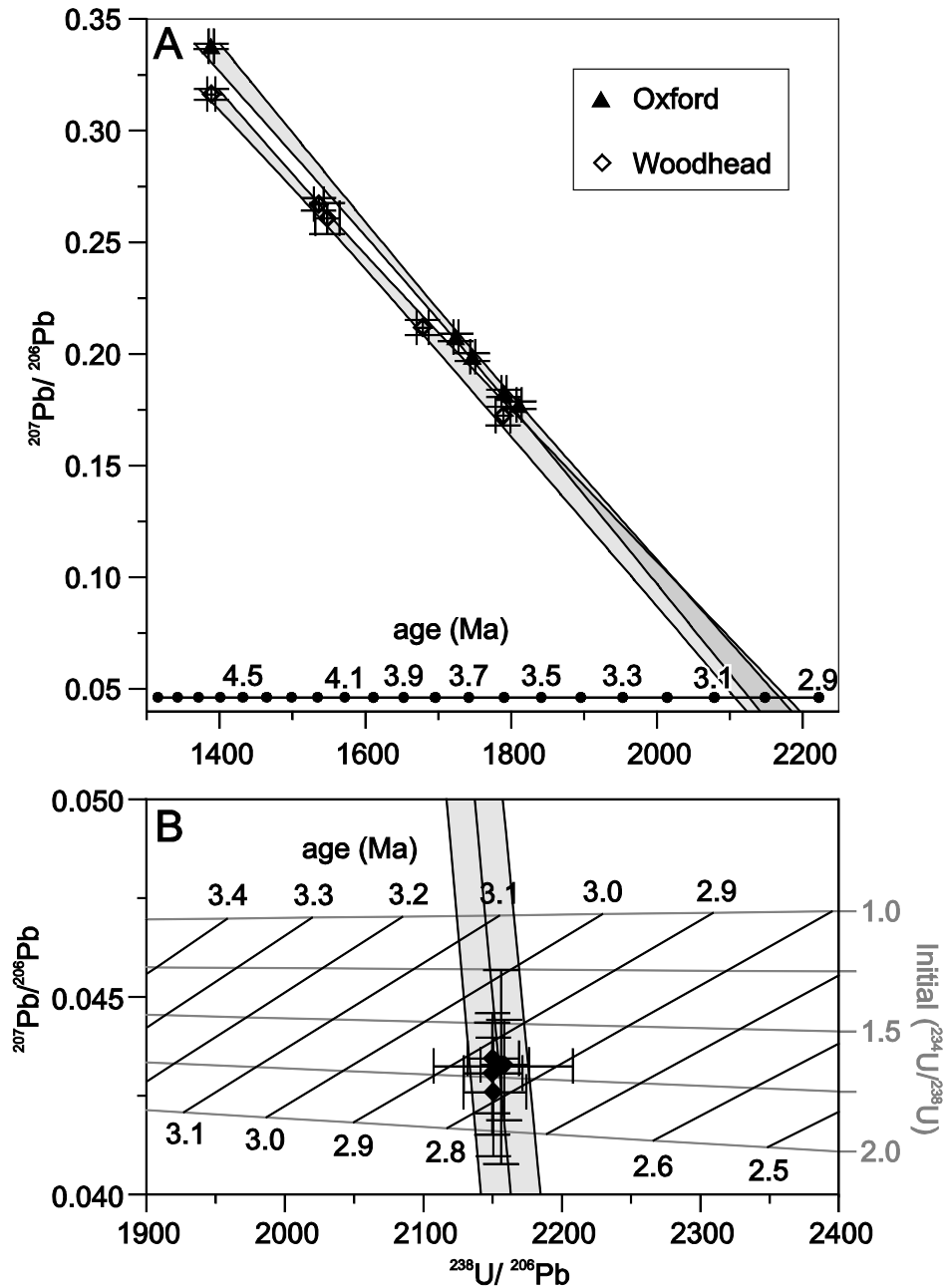


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187x257mm (300 x 300 DPI)

Table 1 Tracer solution composition

^{236}U concentration 15×10^{-9} g/g (approx.)

Critical ratios

$^{236}\text{U}/^{204}\text{Pb}$ 14.019 +/- 0.014 (95% conf.)

$^{236}\text{U}/^{230}\text{Th}$ 31.321 +/- 0.078 (95% conf.)

Minor/major isotope ratios (uncertainty approx. +/- 10%)

$^{234}\text{U}/^{236}\text{U}$ $<< 3.3 \times 10^{-7}$ (^{234}U not detectable)

$^{235}\text{U}/^{236}\text{U}$ 3.76×10^{-5}

$^{238}\text{U}/^{236}\text{U}$ 2.34×10^{-4}

$^{206}\text{Pb}/^{204}\text{Pb}$ 3.86×10^{-3}

$^{207}\text{Pb}/^{204}\text{Pb}$ 5.53×10^{-4}

$^{208}\text{Pb}/^{204}\text{Pb}$ 1.11×10^{-3}

$^{232}\text{Th}/^{230}\text{Th}$ 1.45×10^{-3}

Table 2 Acetic acid protocol with 'Mop' column - calibration summary

		Proportion in cut				
Cut	Cut vol. (ml)	²⁰⁸ Pb	²³² Th	²³⁸ U	⁴³ Ca	dried salts
load (88% acetic)	3.5	0.0020	0.0405	0.0044	0.4792	0.5129
wash 1 (90% acetic)	10	0.0175	0.0189	0.0404	0.4943	0.4637
wash 2 (90% acetic)	10	0.0020	0.0078	0.0330	0.0245	0.0214
wash 3 (90% acetic)	10	0.0026	0.0053	0.0505	0.0018	0.0018
elute (2% HNO ₃)	9	0.9759	0.9275	0.8718	0.0002	0.0002

Table 3. Collector configurations used and masses measured in U, Th, and Pb data acquisition.

High mass				Axial								Low mass				
DVM0	gap	DVM1	gap	DVM2	DVM3	DVM4	DVM5	DVM6	DVM7	DVM8	IC0	DVM9	IC1	DVM10	IC2	DVM11
Spiked U-Th																
							238		236	235	234		232		230	
											233.5					
											234.5					
											235.5					
											236.5					
Unspiked Pb																
							208	207	206	205	204	203	202		200	
Spiked Pb																
				208	207	206	205	204	203	202		200				

DVM' collectors are Farady collectors, 'IC' collectors are ion-counters. IC1 is mounted behind a retardation filter.

Table 4 U-Th and U clean-up protocols

Standard U-Th protocol		U clean-up protocol	
2ml Biorad AG 1-X8 100-200 mesh Polyprep columns		c. 80 microlitre AG 1-X8 100-200 mesh teflon columns	
10 ml H ₂ O	cleaning	1 ml 10 mol l ⁻¹ HCl	cleaning
10 ml 6 mol l ⁻¹ HCl	cleaning	1 ml H ₂ O	cleaning
10 ml H ₂ O	cleaning	1 ml 10 mol l ⁻¹ HCl	cleaning
5 ml 7.5 mol l ⁻¹ HNO ₃	condition resin	0.1 ml 7.5 mol l ⁻¹ HNO ₃	condition resin
5 ml 7.5 mol l ⁻¹ HNO ₃	condition resin	0.1 ml 7.5 mol l ⁻¹ HNO ₃	condition resin
Load nitrate-converted samples in 4ml 7.5M HNO ₃		0.1 ml 7.5 mol l ⁻¹ HNO ₃	condition resin
2 ml 7.5 mol l ⁻¹ HNO ₃	elute matrix	Load nitrate-converted samples in 0.04 ml 7.5 mol l ⁻¹ HNO ₃	
2 ml 7.5 mol l ⁻¹ HNO ₃	elute matrix	0.08 ml 7.5 mol l ⁻¹ HNO ₃	elute matrix
0.25 ml 6 mol l ⁻¹ HCl	chloride conversion	0.09 ml 10 mol l ⁻¹ HCl	elute matrix
0.25 ml 6 mol l ⁻¹ HCl	chloride conversion	0.09 ml 10 mol l ⁻¹ HCl	elute matrix
0.25 ml 6 mol l ⁻¹ HCl	chloride conversion	0.09 ml 10 mol l ⁻¹ HCl	elute matrix
0.25 ml 6 mol l ⁻¹ HCl	chloride conversion	0.09 ml 10 mol l ⁻¹ HCl	elute matrix
0.5 ml 6 mol l ⁻¹ HCl	chloride conversion	0.5 ml H ₂ O	elute U
0.5 ml 6 mol l ⁻¹ HCl	chloride conversion	0.5 ml H ₂ O	elute U
1 ml 6 mol l ⁻¹ HCl	elute Th		
1 ml 6 mol l ⁻¹ HCl	elute Th		
2 ml 6 mol l ⁻¹ HCl	elute Th		
2 ml 6 mol l ⁻¹ HCl	elute Th		
1 ml H ₂ O	elute U		
1 ml H ₂ O	elute U		
4 ml H ₂ O	elute U		

Standard U-Th procedure modified from Robinson *et al.* (2002) based on Edwards *et al.* (1986)
U clean-up procedure modified from the above protocol.

Table 5. Main impurities ratioed to ^{238}U . The ratios are in raw counts per second and not calibrated.

	$^{43}\text{Ca}/^{238}\text{U}$	$^{64}\text{Zn}/^{238}\text{U}$
Acetic acid protocol		
1	0.0045	0.3761
2	0.0048	0.3741
3	0.0049	0.3699
4	0.0111	0.4017
5	0.0082	0.3907
Acetic acid protocol with cleanup		
1	0.0017	0.0069
2	0.0017	0.0062
3	0.0018	0.0070
4	0.0018	0.0075
5	0.0020	0.0079
U-Th protocol		
1	0.0268	0.0021
2	0.1348	0.0026
3	0.0954	0.0024
4	0.0017	0.0016
5	0.1903	0.0029

Table 6 Isotopic data for ASH-15D. Ratios are not common Pb corrected

	$^{238}\text{U}/^{206}\text{Pb}$			$^{207}\text{Pb}/^{206}\text{Pb}$			Corr. coef.
	+	-		+	-		
ASH15-D_3	1810.6	5.8	8.0	0.1771	0.0027	0.0041	-0.867
ASH15-D_1	1790.0	5.8	8.2	0.1824	0.0027	0.0040	-0.842
ASH15-D_2	1723.7	5.9	8.1	0.2074	0.0028	0.0042	-0.865
ASH15-D_4	1746.7	6.0	8.0	0.1986	0.0028	0.0043	-0.894
ASH15-D_5	1388.1	5.4	8.7	0.3377	0.0018	0.0031	-0.543

	$^{238}\text{U}/^{206}\text{Pb}$			$^{208}\text{Pb}/^{206}\text{Pb}$			Corr. coef.
	+	-		+	-		
ASH15-D_3	1810.6	5.8	8.0	0.3416	0.0070	0.0074	-0.886
ASH15-D_1	1790.0	5.8	8.2	0.3549	0.0069	0.0072	-0.860
ASH15-D_2	1723.7	5.9	8.1	0.4208	0.0072	0.0075	-0.885
ASH15-D_4	1746.7	6.0	8.0	0.3971	0.0071	0.0075	-0.915
ASH15-D_5	1388.1	5.4	8.7	0.7536	0.0046	0.0052	-0.559

	$^{235}\text{U}/^{207}\text{Pb}$			$^{208}\text{Pb}/^{207}\text{Pb}$			Corr. coef.
	+	-		+	-		
ASH15-D_3	73.5	2.0	1.4	1.929	0.012	0.005	-0.375
ASH15-D_1	70.5	1.8	1.3	1.946	0.012	0.004	-0.310
ASH15-D_2	59.7	1.4	1.0	2.028	0.012	0.003	-0.108
ASH15-D_4	63.2	1.6	1.1	2.000	0.012	0.004	-0.181
ASH15-D_5	29.5	0.4	0.3	2.232	0.007	0.001	0.390

Calculated common Pb composition

$^{208}\text{Pb}/^{206}\text{Pb}$			$^{208}\text{Pb}/^{207}\text{Pb}$		
+	-		+	-	
2.114	0.090	0.090	2.435	0.010	0.010

All ratios are blank corrected. Errors are 95% confidence, absolute.