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QSR VIEWPOINT

In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology

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Abstract

The capabilities and potential applications of in situ dating of Quaternary materials using laser ablation-MC-ICPMS are explored. $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ can be measured with precision sufficient for dating at a spatial resolution of 100 μm or better in samples that contain as a little as 1 ppm uranium. Moreover, U and Th concentrations and U-series isotope ratios can be continuously profiled to determine changes in age that occur with sample growth (e.g. in speleothems). These capabilities additionally permit the dating of bones, teeth and possibly molluscs, which are subject to post-mortem open-system behaviour of U-series isotopes, and can be employed to elucidate processes of U-series migration during weathering and diagenesis. A drawback of laser ablation-MC-ICPMS is that it cannot in general provide U-series age estimates with the high precision and accuracy of conventional TIMS or solution MC-ICPMS methods. However, sample preparation is straightforward, the amount of sample consumed negligible, and it can be used to rapidly characterise or screen and select samples from which more precise and accurate dates can be obtained using conventional methods. Given further instrumental developments and the establishment of suitable matrix-matched standards for carbonates and other materials, we foresee that laser ablation-MC-ICPMS will play an increasingly important role in Quaternary dating research.

1. Introduction

U-series dating is a cornerstone of Quaternary research. It provides accurate chronologies for events from as young as a few years up to about 500,000 years and well beyond the radiocarbon barrier at ca 50,000 years. In addition to dating, U-series analysis is employed more widely to constrain rates of magma evolution, for the reconstruction of ocean circulation, and in ground water and weathering rate studies (for a comprehensive overview see Bourdon et al., 2003). Thus far, the application of U-series analysis has been restricted by the need for expensive clean-room facilities and time-consuming sample preparation, which involves dissolution, spiking, extraction and concentration of isotopes. In this paper, we report results of in situ U-series dating using laser ablation MC-ICPMS (multi-collector-inductively coupled plasma mass spectrometry), a new approach to U-series analysis that offers several advantages over conventional methods by: (i) providing spatially resolved (10–100 μm scale) distributions of the isotopes used for U-series dating (i.e., ^{238}U, ^{234}U and ^{230}Th); (ii) requiring only minor mechanical preparation of samples and avoiding chemical sample preparation; and (iii) allowing rapid measurement.

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These advantages trade-off against reduced sensitivity and precision compared to conventional thermal ionisation mass spectrometry (TIMS) and solution MC-ICPMS (see e.g. Goldstein and Stirling, 2003).

Until now, only a handful of studies have applied laser ablation-ICPMS with the intention of developing methods for in situ U-series dating of Quaternary materials. The first of these, by Stirling et al. (2000), reported high precision U-series analyses of natural opal and synthetic glass samples that contained tens to hundreds of ppm uranium using a quadrupled ($\lambda = 266$ nm) Nd-YAG laser coupled to a first generation (VG P54) MC-ICPMS. Eggins et al. (2003) subsequently demonstrated the feasibility of profiling U-series isotopes in compositionally zoned materials (teeth and bone) with similar U concentrations using an ArF ($\lambda = 193$ nm) excimer laser system linked to an Agilent 7500s quadrupole (Q)-ICPMS. In the current study, we explore the potential application of in situ U-series dating to a wide variety of Quaternary materials using a state-of-the-art laser ablation and MC-ICPMS system. We demonstrate the ability to measure U-series isotopes precisely and accurately in a wide range of materials containing low ppm levels of uranium, and highlight new opportunities for dating materials that are subject to open-system U-series behaviour. Potter et al. (2005) have concurrently developed a LA-MC-ICPMS method for analysis of coral samples containing only a few ppm uranium.

2. Instrumentation

U-series isotopes have been analysed using a HelEx ArF excimer laser ablation system that is interfaced to a Finnigan MAT Neptune MC-ICPMS (see Fig. 1). The HelEx ablation system employs simple, aperture-imaging optics to project and demagnify the image of a laser-illuminated mask onto the sample. This set-up facilitates sampling of circular pits from 10–400 μm in diameter, or other shapes with dimensions within the limits 400×1000 μm. Laser pulse rates can be varied between 1 and 100 Hz, and the laser fluence from <1 to >100 J/cm^2. In this study, laser pulse rates of 10 or 20 Hz were employed with a fluence of 10 J/cm^2, the latter resulting in removal of a uniformly thick layer ($\sim$0.2 μm) from the targeted sample site with each laser pulse. He rather than Ar is used as the ablation medium to reduce deposition of surface condensate around the ablation site and to produce a complementary increase in sample yield to the ICP (Eggins et al., 1998a). The HelEx system has been optimised for high resolution depth and surface compositional profiling (see Eggins et al., 1998a, b, 2003) by using a unique cell design (Fig. 2a) that incorporates a small effective ablation volume ($\sim$2.5 cm^3), in which laser ablated particulates have a very short residence time ($\sim$0.5 s). Samples are mounted in a much larger primary volume that can accommodate two $100 \times 25 \times 10$ mm samples (e.g. two 10 cm coral core slices or four 50 mm thin sections) or four 25.4 mm round mounts, in addition to three 25.4 mm and two 10 mm standard round mount positions (Fig. 2b). The sample block is moved within the laser focal plane by X–Y stepper motors under computer control, which allows for sequenced analysis of points, chained lines, or the rastering of areas. Sample preparation is simple and requires only the presentation of a cut or natural flat surface within the focal plane of the laser. Ideally, samples should be cleaned prior to analysis, but can also be 'laser cleaned' to remove

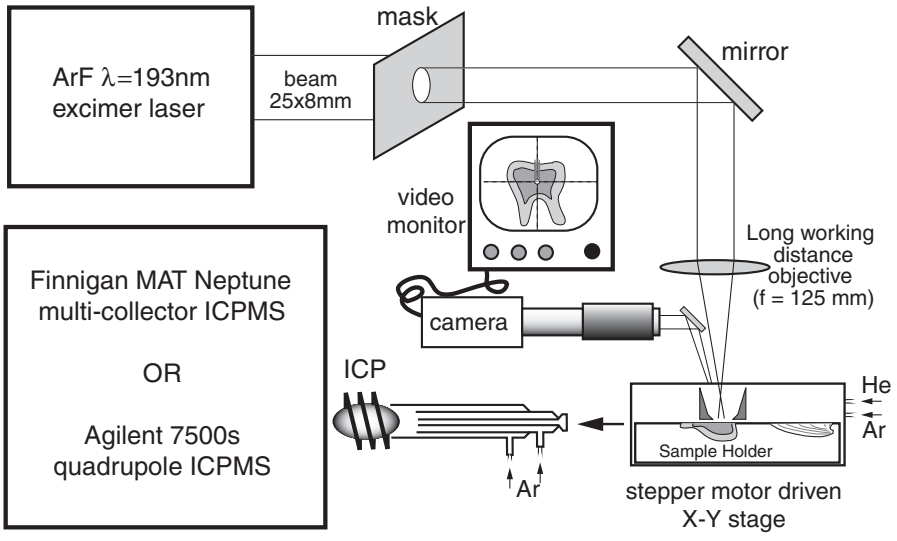

Fig. 1. Schematic diagram of the ArF ($\lambda = 193$ nm) excimer, laser ablation multi-collector ICPMS system used at the Australian National University.

residual surface contaminants by performing a laser ablation pre-scan.

The Finnigan Neptune MC-ICPMS is equipped with a moveable array of nine Faraday cups, four on either side of a fixed position, central cup. A secondary electron multiplier (SEM) is co-located in the central channel position and is deployed by steering the ion beam from the central Faraday cup. Measurement of the low abundance U-series isotopes ^{230}Th and ^{234}U requires either dynamic analysis (repeat switching of the central channel mass between ^{230}Th and ^{234}U) or consecutive static analysis measurements with the central channel mass set initially to ^{230}Th and subsequently to ^{234}U. Both ^{238}U and ^{235}U are monitored when ^{230}Th or ^{234}U is placed in the central ion counter, but ^{232}Th is only measured when ^{234}U is in the central position (see Table 1 for cup configuration details). In this study, we have implemented a static analysis approach by repeating each laser scan along the same pre-programmed track, with ^{230}Th being measured in the central channel during the first pass and ^{234}U during the second pass. This strategy minimises any bias on measured ^{230}Th/^{238}U ratios due to the significant Th/U elemental fractionation that can be encountered when ablating deeper (larger aspect ratio) trenches and when re-sampling surface condensates that are deposited by preceding laser ablation scans (Eggins et al., 1998a). It should be noted that the measurement of ^{235}U/^{238}U and ^{234}U/^{238}U ratios is not subject to these effects and can be carried out without compromise in the second laser pass. A potential drawback with this static analysis approach occurs where a sample is heterogeneous with depth, which would result in incorrectly matched ^{230}Th/^{234}U and ^{234}U/^{238}U measurements. However, the difference in laser sampling depth between consecutive laser scans is only of order 10–40 μm, subject to scan speed and laser repetition rate, which compares to the typical horizontal spatial resolution of 84 or 103 μm used in this study.

The Finnigan Neptune's gas flow and electrostatic lens settings have been optimised for maximum sensitivity, subject to maintaining low molecular species production ($ThO^+/Th^+ < 0.5\%$) and minimal elemental fractionation of Th and U. The latter is achieved by adjusting plasma sample conditions to produce relative ^{232}Th and ^{238}U yields near unity (specifically >0.85) when ablating SRM NIST610 glass. The typical signal intensity obtained for ^{238}U when ablating SRM NIST610 ($U = 461.5$ ppm; Reed, 1992) at 5 laser pulses/second with a 62 μm spot and laser fluence of 10 J/cm^2 is 0.7–0.8 V (i.e. ~1.6 mV ppm^{-1}). This corresponds to a sensitivity of ~100,000 cps ppm^{-1} and an overall ion transmission efficiency of almost 1%. Higher or lower sensitivities are obtained by adjusting the laser

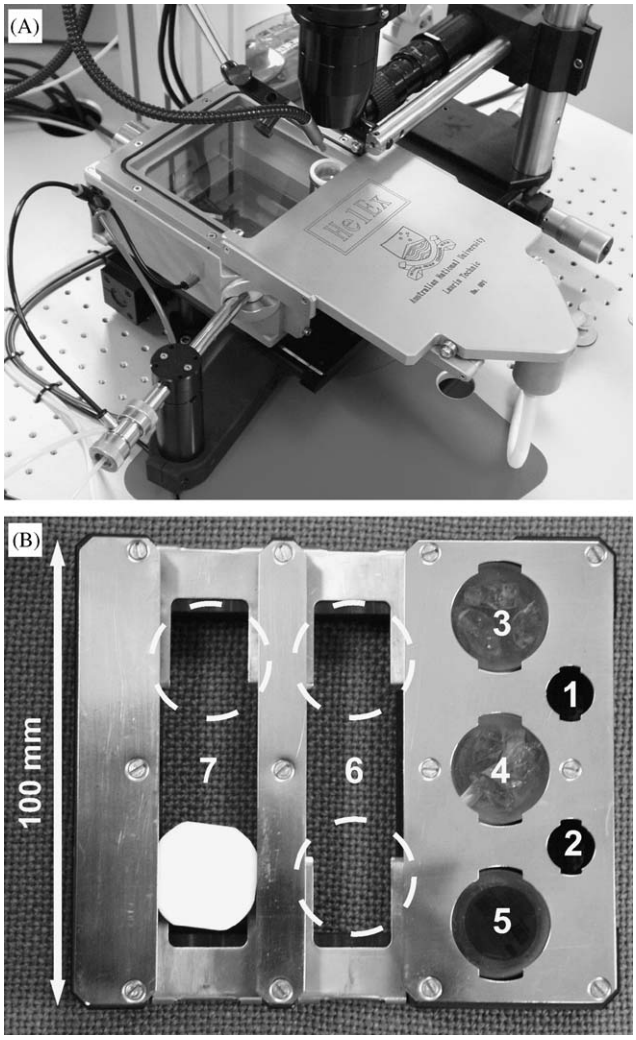

Fig. 2. (A) View of HelEx laser ablation cell that shows the large volume cell design, parts of the illumination and viewing system, and the objective lens assembly. (B) Top view of HelEx sample holder. Note the two 10 mm round mount 'standard' positions labelled 1 and 2 on the far right side, the three 25.4 mm round mount positions (labelled 3,4, and 5), and the two large sample positions on the left-hand side of the holder. The latter fit either two 100 mm long by 25 mm wide samples, four 50 mm thin sections, or four additional 25.4 mm round mounts.

Table 1
Finnigan Neptune Collector configuration

	L4 Faraday	L3 Faraday	L2 Faraday	L1 Faraday	C SEM	H1 Faraday	H2 Faraday	H3 Faraday	H4 Faraday
Line 1	–	–	–	^{232}Th	^{234}U	^{235}U	^{238}U	–	–
Line 2	–	–	–	–	^{230}Th	–	^{234}U	^{235}U	^{238}U

pulse rate (up to 100 Hz) and/or the ablation spot size (according to the spatial resolution requirements of the analysis). In this study, most analyses were performed using 84 or 103 μm diameter spots at pulse rates of 10 or 20 Hz, resulting in sensitivities between 250,000 and 1,000,000 cps ppm^{-1} for the U-series isotopes. SEM background count rates are typically between 0.4 and 1.5 cps with laser-off. It should be noted that the Finnigan Neptune employs a 'Pt-guard electrode' to reduce the spread of ion energies produced within the ICP and thereby increase the ion transmission efficiency through the mass spectrometer. This can produce ion density maxima for different elements at differing heights above the load coil in the Ar plasma (Appelblad et al., 2000) and make the simultaneous optimisation of Th and U difficult. However, it has been possible to counteract this effect by combining a small amount of N_2 (typically 2–4 ml/min) into the carrier gas flow, which compacts Th and U sensitivity maxima to a similar position within the plasma and facilitates Th and U isotope analysis with greatly reduced elemental fractionation.

3. Data acquisition

All data reported in this study were obtained using 1.024 s integrations, for periods ranging between 3 and 50 minutes while scanning the laser at constant speed (typically 0.48 or 0.6 mm/minute). Dynamic mode analyses, performed on some bone samples, have been conducted by repeated switching between ^{230}Th and ^{234}U following ten integrations on each mass. Instrumental mass fractionation has been corrected for using an exponential law based on the measured $^{238}U/^{235}U$ ratio, and applying a canonical $^{238}U/^{235}U$ ratio value of 137.88 (or 418.98 in the case of the NIST610 glass; Stirling et al., 2000). Baselines were measured 'on-peak' prior to each analysis or batch of analyses. SEM/Faraday cup yields were measured by repeated switching of a stable $^{235}U^+$ beam of up to 500,000 cps between the SEM and the central Faraday cup. The reproducibility of SEM/Faraday yields measured in this way is typically better than a few tenths of a per cent, and the accuracy is cross-checked for each analytical session by comparison of the $^{234}U/^{238}U$ ratio measured on the NIST610 glass (corrected for yield and mass fractionation) with the previously reported activity ratio for this reference material (i.e. $[^{234}U/^{238}U] = 0.17095$, Stirling et al., 2000; *n.b.* square brackets indicate isotope activity ratios). Peak tailing contributions to ^{234}U and ^{230}Th from both ^{238}U and ^{232}Th have been corrected based on interpolation of measured tailing at +1.5, +2.5, −1.5, −2.5, −3.5, −4.5, −7.5 and −8.5 mass units while introducing large (1–10 V) ^{232}Th and ^{238}U beams into the mass spectrometer. Typically observed tailing contributions at +2, −2, −4, and −8 amu are 0.36 ± 0.03, 0.77 ± 0.09, 0.30 ± 0.03, and 0.20 ± 0.01 ppm respectively. If uncorrected, these contributions can bias measured $^{234}U/^{238}U$ ratios significantly in the case of (atypical) low $^{234}U/^{238}U$ ratio values, and bias $^{230}Th/^{238}U$ ratios in the presence of large ^{232}Th signals or in very young samples. The Finnigan MAT Neptune also permits peak tailing contributions to be reduced by a further order of magnitude through implementation of an RPQ (retardation potential quadrupole) filter prior to the SEM. However, this approach results in reduction of the SEM yield, and no clear advantage over the application of peak tailing corrections given the limited precision and accuracy of LA-MC-ICPMS when analysing most environmental samples.

4. Correction of Th/U elemental fractionation

The yields of Th^+ and U^+ are dependent on the sample matrix and tend to drift monotonically in the course of an analytical session (~12 h). In particular, significant differences in relative Th^+ and U^+ yield occur between apatite matrixes and the NIST610 glass, and to a lesser extent between Ca-carbonate and the NIST610 reference glass. Accordingly, accurate U-series analysis of bone and teeth demands calibration against matrix-matched standards with known Th/U ratios. For this purpose we have investigated a range of materials of known U-series composition (determined by TIMS) including rhinoceros tooth dentine, pelletised phosphate rock NBS120b (following re-crushing in an agate ring mill to reduce its overly coarse grain size), and a suite of fossil bone 'standards' which span a range of different but homogeneous U distributions and U-series ratios. In the case of the bone standards, which have been previously measured by TIMS, we have consistently obtained linear calibration curves using LA-MC-ICPMS, to within 1–3% for $^{230}Th/^{238}U$ and better than 1% for $^{234}U/^{238}U$ at the 95% confidence level. For calcite matrixes, we have yet to find a natural reference material with suitably high and uniformly distributed U concentrations and U-series isotope ratios. The search for a suitable synthetic or natural reference material for this matrix type remains a high priority goal for the development of an accurate method for in situ U-series analysis of Ca-carbonate materials. In the mean time, we have used the NIST610 glass to constrain and correct for Th/U elemental fractionation during analysis of speleothems, corals, molluscs, etc. Comparison of results obtained with TIMS and solution MC-ICPMS measurements on the same samples (see below) indicates that calibration using the NIST610 glass typically produces a small but significant (~5–10%) overestimation of Th/U values, and therefore of $^{230}Th/^{238}U$ and $^{230}Th/^{234}U$ isotope ratios and sample age.

Age estimates have been calculated using mass fractionation, SEM yield, and Th/U elemental fractionation corrected $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ ratios, and the half-lives reported by Cheng et al. (2000a). At present, the uncertainty in most age estimates is dominated by uncertainties in Th/U elemental fractionation, except where samples have very low U concentrations or are very young and have low $[^{230}Th/^{238}U]$.

5. Applications

In the following sections, the capabilities of laser ablation-MC-ICPMS for U-series dating are illustrated by application to a variety of sample types which are of interest to Quaternary researchers. The examples range from closed-system U-seres dating of corals (e.g. Edwards et al., 1987a,b, Bard et al., 1990, 1998) and speleothems (e.g. Beck et al., 2001), to the much more novel application of open-system U-series dating of bones and teeth, and demonstration of a similar open-system dating potential for mollusc shells. Indeed, we foresee open-system U-series dating being an area of particular promise for laser ablation MC-ICPMS, because the technique can rapidly profile the distribution of uranium and U-series isotope ratios within samples, which is essential to constrain U-uptake histories and to establish robust open-system dates. This compares to the significantly greater time required for and cost of acquiring equivalent data sets using conventional micro-sampling in combination with U-series analysis by TIMS or solution–MC-ICPMS (e.g. Pike, 2000). We also foresee a significant role for laser ablation-ICPMS, through its ability to rapidly determine U and Th concentrations and U-series isotopic compositions, to screen and select samples of the greatest chronological importance and/or suitability for obtaining more accurate and precise dating by conventional analytical methods. We will also show how spatially resolved U-series analysis can shed light on problems encountered with conventional U-series dating, such as the selective migration of U-series parent and daughter isotopes, which are suspected to compromise the accuracy of high precision dating of corals by TIMS or solution MC-ICPMS.

5.1. Corals

U-series dating of coral reef terraces is arguably the most celebrated success of U-series dating, as it provides the foundation for constraining the timing of Quaternary climate and sea-level change as well as the calibration of radiocarbon and other chronologies (e.g. Bard et al., 1998). The aragonite skeletons precipitated by corals typically contain between 3 and 4 ppm U and virtually no Th, making them ideally suited to closed-system dating, provided no subsequent loss or gain of either parent or daughter isotopes takes place. In addition to changes in mineralogy (i.e. aragonite replacement by calcite) and trace element character, deviation of a coral's measured $^{234}U/^{238}U$ ratio outside a range (e.g. $[^{234}U/^{238}U] = 1.145–1.155$, McCulloch and Esat, 2000) that is considered to differ by an unacceptable amount from modern hermatypic corals ($[^{234}U/^{238}U] = 1.149 \pm 0.001$; Stirling et al., 1995) or modern seawater (i.e. $[^{234}U/^{238}U] = 1.144 \pm 0.007$; Chen et al., 1986) is the most commonly used means of establishing whether derived age estimates are reliable. To evaluate our ability to make in situ U-series isotope measurements on corals, we have analysed a selection of corals of known age from Marine Isotope Stage (MIS) 5e, and a modern *Porites* coral from Davies Reef, that is used as a reference material for trace element analysis of corals in our laboratory (Fallon et al., 1998). The profiles obtained for these samples are shown in Fig. 3 and the results are tabulated in Table 2. In each case the derived age estimates, although comparatively imprecise, are broadly consistent with conventional TIMS or solution MC-ICPMS data, albeit slightly older due to Th/U calibration against the NIST610 glass (see above). The precision of the measured $^{234}U/^{238}U$ ratios in the presence of 3 ppm U is 8–14 ‰, and is sufficient for the purpose of identifying those coral samples from which the best conventional age estimates are most likely to be obtained. In a concurrent study, Potter et al. (2005) have drawn the same conclusion and indicated the ability to measure with acceptable accuracy, by calibration against a reference coral, the U-series composition of up to 40–50 coral samples in a single day.

5.1.1. U and Th isotope migration in corals

A vexing question that has surrounded the reliability of U-series coral dating, particularly following the advent of high precision TIMS U-series dating (Edwards et al., 1987a), has been the cause of open-system behaviour of U-series isotopes. This has been the focus of recent studies by Thompson et al. (2003), Villemant and Feuillet, (2003) and Scholz et al. (2004), however, a clear consensus is yet to emerge that explains observed correlations between $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios, and measured $[^{234}U/^{238}U]$ and $[^{230}Th/^{238}U]$ values that are inconsistent with closed-system evolution from accepted seawater values (e.g., Bard, 1991; Gallup et al., 1994). Laser ablation MC-ICPMS presents a new tool for investigating and testing proposed models of open-system behaviour through its ability to characterise the distribution of U-series isotopes at μm-scale spatial resolution. This potential is illustrated by U-series profiles across an aragonite to calcite diagenesis front within a Last Interglacial coral from Huon Peninsula, Papua New Guinea. The variations in U concentration, $[^{234}U/^{238}U]$, and $[^{230}Th/^{238}U]$ along the

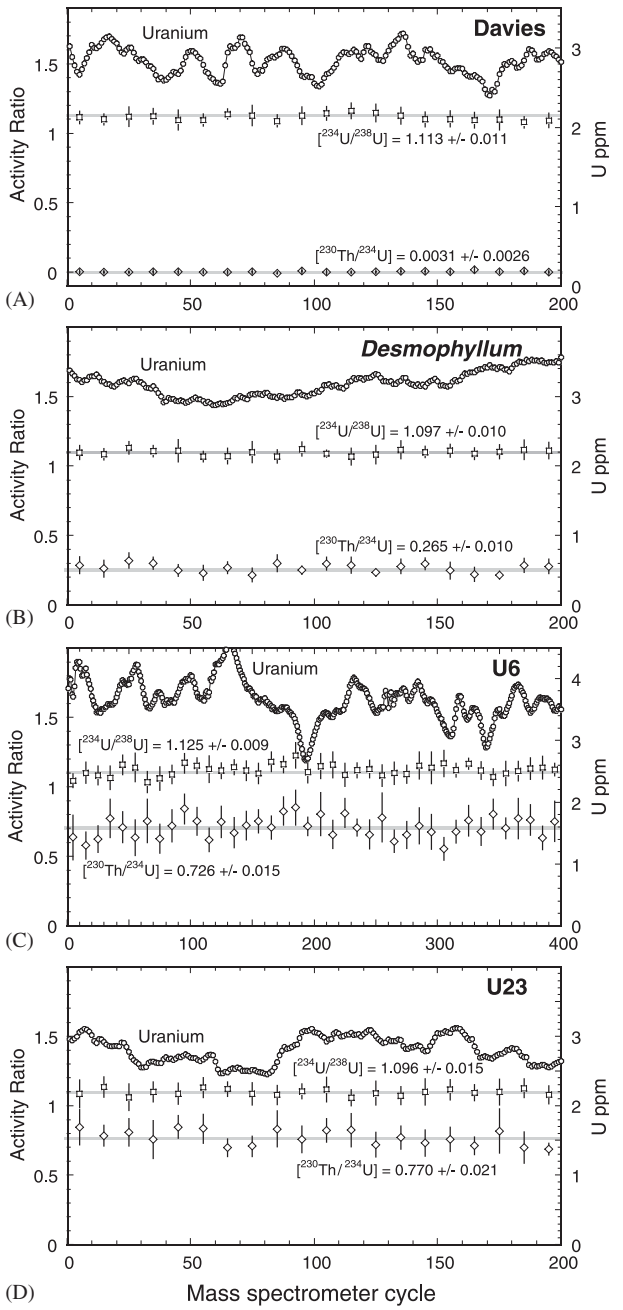

Fig. 3. Uranium concentration, and $[^{234}U/^{238}U]$ and $[^{230}Th/^{234}U]$ profiles measured along septa in fossil and modern corals by laser ablation MC-ICPMS, using a 100 mm diameter spot, 10 Hz laser pulse rate, and 0.6 mm/min scan speed. (A) Modern *Porites* coral from Davies Reef, Great Barrier Reef. (B) *Desmophyllum dianthus* deep sea coral obtained from the Great Australian Bight. (C) U6, coral from Stage 5e reef Barbados. (D) Sample U23, coral from Stage 5e reef Barbados. The ordinate value indicates the mass spectrometer cycle number, which equates to time in seconds x 1.024 and distance in μm × 10. Reported $[^{234}U/^{238}U]$ and $[^{230}Th/^{234}U]$ values are averages for 10 successive mass spectrometer cycles, and associated errors are reported at the 95% confidence level. The uranium concentrations are semi-quantitative estimates only, based on measured ^{238}U beam intensities referenced directly to those obtained on NIST 610 glass (cf. quantitative, yield-normalised, concentrations that are measured by Ca internal standardisation using laser ablation Quadrupole-ICPMS).

Table 2
U-series results obtained on coral samples

Sample	^{232}Th ppb ±2 se[a] LA-ICPMS	^{238}U ppm ±2σ[b] LA-ICPMS	$[^{234}U/^{238}U]$±2 se LA-ICPMS	$[^{230}Th/^{234}U]$±2 se LA-ICPMS	Age ka ±2σ	$[^{234}U/^{238}U]$±2 se TIMS/MC-ICPMS	$[^{230}Th/^{234}U]$±2 se TIMS/MC-ICPMS	Age ka ±2σ
U6	1.2±0.4	3.76±0.73	1.125±0.009	0.726±0.015	136.0±7.0			
U23	1.0±0.8	2.80±0.39	1.096±0.015	0.770±0.021	154.6±10.3	1.1176±0.0018	0.7221±0.0027	134.9±2.1
Modern	2.6±0.8	2.83±0.33	1.113±0.011	0.0031±0.0026	0.34±0.26	(1.144)	(0)	0.01[c]
Des	1.2±0.4	3.18±0.36	1.097±0.011	0.265±0.010	33.5±2.0	1.1323±0.0032	0.2370±0.0024	29.3+0.3/

U6, undated coral from Stage 5e terrace, Barbados (sampled provided by M. McCulloch and T. Esat); U23, Stage 5e coral from Barbados (unpublished MC-ICPMS results, M. McCulloch, T. Esat and G. Mortimer).
Des, *Desmophyllum dianthus* deep sea coral from the Great Australian Bight (unpublished MC-ICPMS results, M. McCulloch, P. Montagna and G. Mortimer).
[a]se = standard error.
[b]σ = standard deviation—used to indicate variability of U concentration in coral, square brackets denote activity ratios calculated using half lives reported by Cheng et al. (2000a).
[c]Modern, modern coral collected in 1995 from Davies Reef, Great Barrier Reef (Fallon et al., 1998).

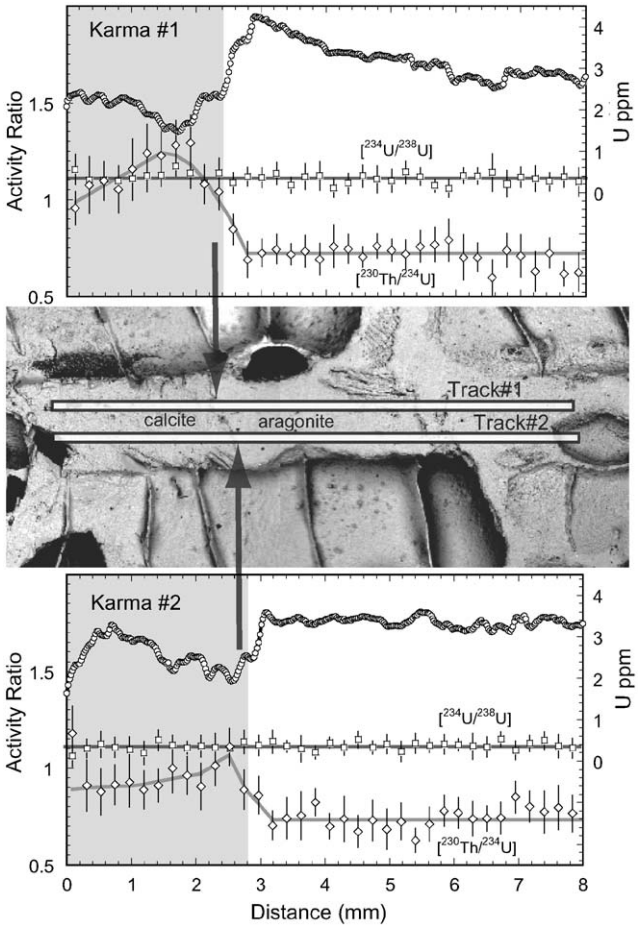

Fig. 4. Uranium concentration, [^{234}U/^{238}U] (□) and [^{230}Th/^{234}U] (◇) profiles (top and bottom) measured in situ by two separate laser ablation-MC-ICPMS scans along a sectioned fossil coral from the MIS Stage 5e reef tract at Karma, Huon Peninular. The SEM image (middle) shows the position of the two laser ablation scans, and the position of an aragonite to calcite diagenesis front in relation to distance along the two scans. Trend lines for the mean [^{234}U/^{238}U] and [^{230}Th/^{234}U] values obtained in the aragonitic part of the coral are continued using a smooth fit curve through the diagenetically altered (calcitic) part of the coral. The variability of measured [^{234}U/^{238}U] and [^{230}Th/^{234}U] values, averaged over 10 successive mass spectrometer cycles, reflects the very low count rates obtained on the ^{230}Th and ^{234}U isotopes due to the low, ppm level abundance of ^{238}U in the sample. The scale of the SEM image is the same as the compositional profiles. Both scans were undertaken at 0.6 mm/min using a 100 μm diameter laser spot and 20 Hz laser pulse rate.

laser scan paths are illustrated with reference to a backscattered electron image that shows the location of the profiles and the position of the diagenesis front (Fig. 4). The region that has been transformed to calcite is characterised by up to 50% reduction in U concentration and significantly higher [^{230}Th/^{234}U], but otherwise indistinguishable [^{234}U/^{238}U] from the region of aragonite mineralogy. Average ^{230}Th count rates remain constant along the traverse (35.9 ± 1.2 cps (2 se, standard error of the mean) in calcite versus 36.0 ± 1.5 cps (2 se) in aragonite), providing further evidence to support the conclusion that ^{238}U and ^{234}U have been preferentially and recently lost from the sample where it has been transformed to calcite. During this process, ^{230}Th either remained fixed or was transported only a very short distance.

5.1.2. Deep sea corals

The isotopic and trace element compositions of deep-sea corals are emerging as valuable new proxies for reconstructing past changes in ventilation and water mass chemistry of the deep ocean (e.g. Adkins et al., 1998, Cheng et al., 2000b). Obtaining accurate age estimates for individual deep-sea corals and constraining their life-spans is crucial for the interpretation of these proxy records. Because of the nature of the deep-sea environment and complications arising from the geometry of some coral species, U-series dating is challenged by the presence of detrital material and contributions from Mn and Fe oxide/hydroxide coatings, which can adsorb substantial amounts of Th and U from seawater. The high spatial resolution afforded by laser ablation presents an opportunity to sample along the fine septa of some coral species, and thereby avoid the need to remove such contaminating material using rigorous physical and chemical cleaning steps (Lomitschka and Mangini, 1999). A U-series profile that was obtained by scanning the laser along the thin septa of a *Desmophyllum* sp. coral is shown in Fig. 3b. The in situ age estimate obtained for this sample is 33.4 ± 2.0 ka (2σ) and, although less precise, is similar to the age (29.3 ± 0.3 ka, Table 2) obtained by conventional solution MC-ICPMS analysis following rigorous cleaning. Both this example and the analysis of reef-building corals indicate that laser ablation MC-ICPMS is presently unable to attain age estimates with the precision ultimately demanded by deep-sea and reef coral research, but does provide a useful means of rapidly determining approximate ages and thereby screening and selecting coral samples that lie within the age range of interest.

5.2. Speleothems

Speleothems are important chronometers for dating faunal and human remains preserved in cave deposits and are increasingly being employed to extract long, high resolution climatic records based on their oxygen isotope composition (e.g. Hellstrom and McCulloch, 2000; Beck et al., 2001; Wang et al., 2001, Spötl and Mangini, 2002). Individual speleothems can grow over a few tens to hundreds of thousands of years, but extension rates often vary and hiatuses can occur due to changes in climate or local hydrology. This demands a high sampling density for U-series dating to constrain the timing and to verify the continuity of any record, and it is often necessary to extend or fill-in gaps by

splicing together records from different speleothems. Unfortunately, speleothems are generally not well suited for laser ablation U-series analysis because their U-concentrations are typically <200 ppb. Nonetheless, in cases where U-concentrations exceed $\sim$1 ppm, it is feasible to employ laser ablation-MC-ICPMS to characterise the distribution of U and Th isotopes for age estimation, and to identify hiatuses or changes in growth rate.

The results of continuous in situ U-series profiling along $\sim$16.5 cm of an Alpine speleothem (SPA52) are shown in Fig. 5a. Corresponding in situ age estimates are shown in Fig. 5b along with conventional TIMS U-series age estimates (Spötl et al., 2002). Measured ^{238}U and ^{232}Th concentrations and [^{234}U/^{238}U] ratios are in close agreement with values determined on this speleothem by TIMS (Spötl et al., 2002), with the reproducibility of measured [^{234}U/^{238}U] values improving with higher U concentration levels. A small but distinct jump in [^{234}U/^{238}U] values measured by TIMS at 85–90 mm, also occurs in the laser ablation data although the offset is larger and the laser [^{234}U/^{238}U] values are slightly higher than the TIMS results. Age estimates calculated for data bins of 10 measurement cycles are generally consistent with those obtained by conventional TIMS analysis (see Fig. 5c). However, in two zones, between 55 and 65 mm and between 85 and 110 mm, anomalously old age estimates have been obtained, the reasons for which are the subject of ongoing investigation.

5.3. Bones and teeth

The restricted range of radiocarbon dating and the lack of suitable material for dating at archaeological and paleoanthropological sites has prompted concerted attempts to apply U-series dating to faunal material (for a review see Pike and Pettit, 2003). However, bones and teeth are well-known to be open systems for uranium. Modern bones and teeth invariably have very low concentrations of U ($<$1–50 ppb) whereas archaeological specimens often contain tens or even hundreds of ppm U, which has been taken up from the surrounding environment. To calculate a date from measured [^{230}Th/^{234}U] and [^{234}U/^{238}U] values the temporal uptake of U needs to be considered. If U-uptake has taken place continuously following burial, an apparent (closed system) U-series age would underestimate the correct age of the bone. On the other hand, if U has been leached from the bone following earlier U-uptake, a closed-system U-series age might overestimate the true age.

Uranium uptake in bones and teeth has been shown to occur by diffusion of uranyl (UO_2^{2+}), with adsorption onto the large surface area that is presented by the bone mineral hydroxyapatite (Millard and Hedges, 1996, Pike et al., 2002). The diffusion–adsorption (D–A) model developed by these authors predicts the development of a spatial distribution of U and U-series isotopes across a bone. Under constant conditions with uranium diffusing from the outer surface toward the interior, U-shaped (concave up) U-profiles that fill-in and flatten with time are predicted as the bone equilibrates with the U in groundwater (Fig. 6a). The distribution of apparent closed-system U-series ages follows a similar pattern, with apparent ages decreasing towards the centre of the bone (Fig. 6b). The D–A model can also predict the development of characteristic profiles in cases where U is leached from the bone, or there has been increased U uptake later in its burial history (Pike et al., 2002). Application of the D-A model to dating requires identifying and rejecting bones with profiles that indicate leaching or a recent increase in U-uptake (although these scenarios may still yield minimum or maximum ages), and selecting those most suitable for open-system dating.

The D–A model has been verified and reliable dates produced for bones and also teeth using TIMS (Pike and Hedges, 2001, Pike et al., 2002). However, measurement of U-series isotope profiles using this method is extremely time-consuming, suffers from limited spatial resolution, and may cause the destruction of often irreplaceable and highly-valued fossils. TIMS analysis requires a cross-section of a thick ($>$5 mm) long bone, which effectively precludes the application of TIMS U-series dating to the few diagnostic fossil hominids that are available. This contrasts with laser ablation-ICPMS, which has the ability to measure U-series dates rapidly, with high spatial resolution, and with virtually no visible evidence of sample destruction.

Examples of the application of LA-ICPMS and the D-A model to the dating of two bones from Steetly Wood Cave are given in Fig. 7, which shows U concentration profiles and the closed system age profile that is predicted by the D–A model for different values of the diffusion parameter, D/R (e.g. see Pike et al., 2002). As bones approach equilibrium with time, the gradient of the U concentration profile decreases, and the rate of diffusive uptake slows. Both SWC2 and SWC3 are near equilibrium, and their U concentration profiles are almost uniform. Date profiles have been fitted to the measured profile to give the D–A date using the procedures outlined in Pike et al. (2002). In this case, we calculate a maximum likelihood date of 67 ± 8 ka (at 95% confidence) for SWC2 and 65 ± 4 ka for SWC3.

In general, the D–A model has been applied with greater success to bones than teeth, partly because of the low U concentration in enamel and the difficulty in measuring profiles in thin enamel layers. Preliminary results suggest that in exceptional cases, U-series profiles and D–A modelling of tooth enamel is possible.

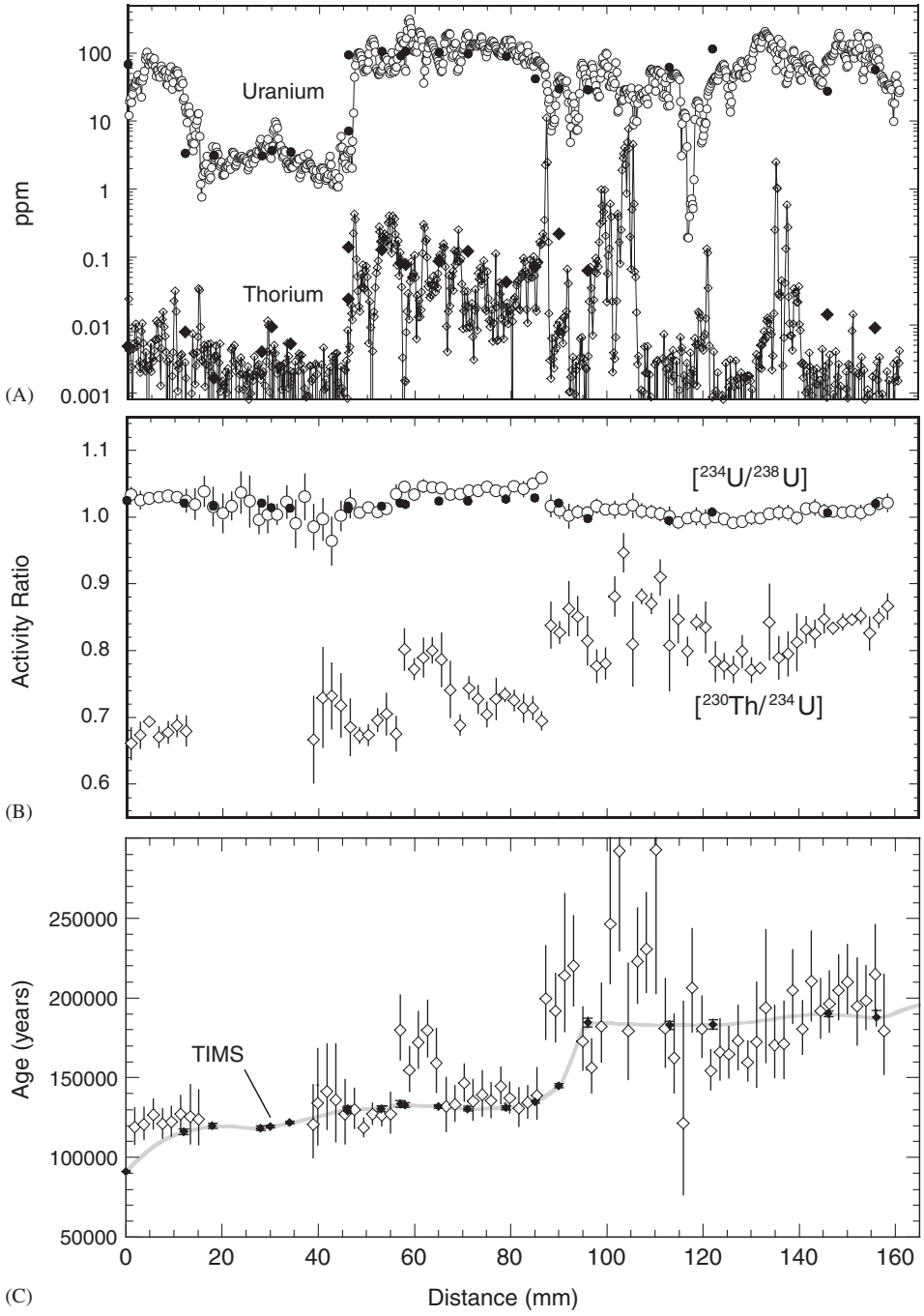

Fig. 5. (A) Uranium (○) and Thorium (◇) concentration profiles and (B) measured [^{234}U/^{238}U] (○) and [^{230}Th/^{234}U] (◇) value profiles determined in situ by laser ablation MC-ICPMS scans along a 16.5 cm length of the growth axis of Alpine Speleothem Spa52b. Results are compared to concentration data measured by isotope dilution for Uranium (●), and Thorium (◆), and to [^{234}U/^{238}U] ratios (●) reported by Spötl et al., (2002). ^{230}Th was not measured between, 15 and 38 mm across the low uranium section of the speleothem. (C) In situ U-series age estimates (◇) measured by laser ablation-MC-ICPMS are compared to TIMS ages (◆), and a smooth curve fit through the TIMS dates. The reported [^{234}U/^{238}U] and [^{230}Th/^{234}U] values, and U-series age estimates and their quoted uncertainties (95% confidence level) are based on the average of ten successive mass spectrometer cycle measurements (i.e. ~10 s of data collection).

5.4. Combined in situ U-series and ESR dating

As with U-series dating, the main obstacle for ESR dating of tooth enamel is constraining the U-uptake history. Grün et al. (1988) developed a combined U-series/ESR (US-ESR) approach to solve for U-uptake. The systematic application of combined US-ESR dating has shown that simplistic models, such as early or linear U-uptake (Ikeya, 1982) may yield erroneous results (e.g. Grün and Schwarcz, 2000). Laser ablation-MC-ICPMS

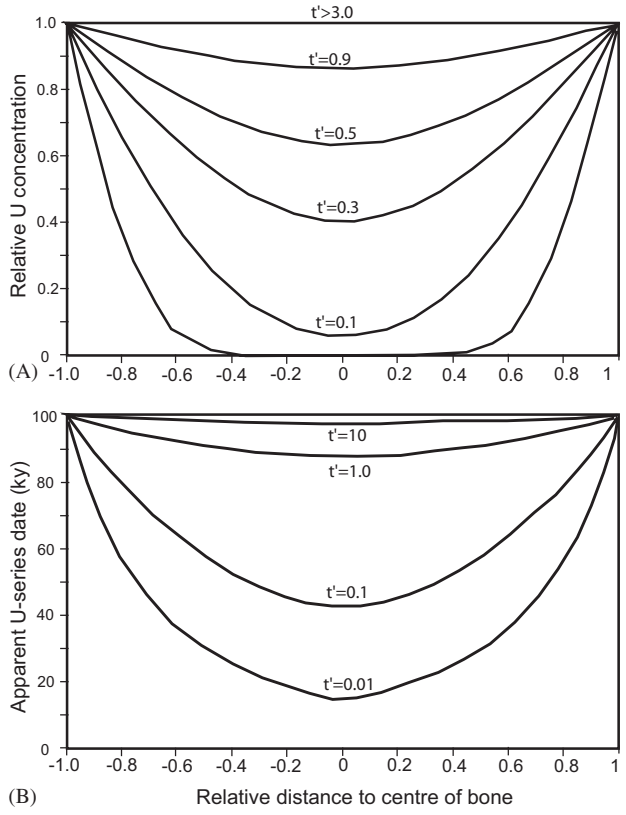

Fig. 6. (A) Uranium concentration profiles across a transverse bone section as predicted from the D-A model. The shape of the profile is characterised as a function of the model parameter t', see text and Pike et al. 2002 for details. (B) Apparent closed-system date profiles predicted by the D-A model for a 100 ka bone.

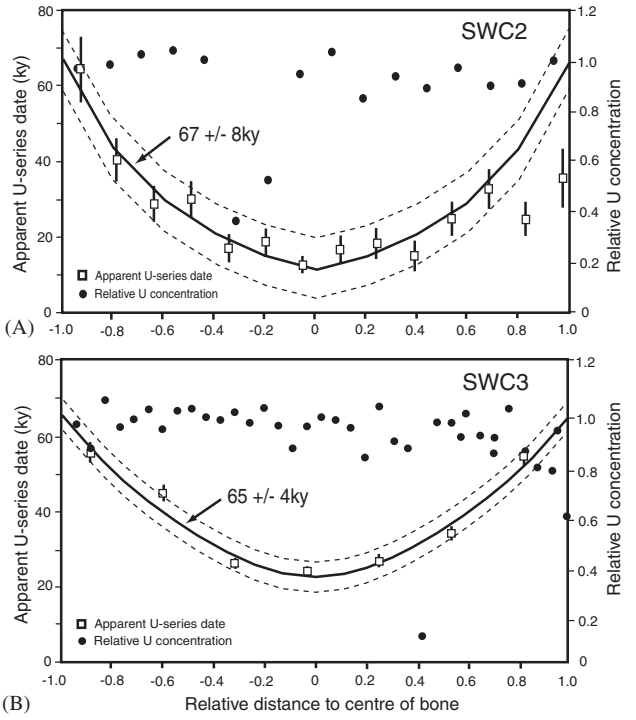

Fig. 7. U concentration and, measured and modelled maximum likelihood date profiles for samples SWC2 (A) and SWC3 (B) from Steetly Wood Cave, United Kingdom (Pike et al., 2005).

provides the opportunity to rapidly assess U-series isotope compositions for open-system modelling. Because low U-concentrations have negligible effects on ESR dating results, such analysis needs only to be performed if the samples have relatively high U-concentrations ($>$ 250 ppb in enamel and >1 ppm in dentine).

We have applied laser ablation MC-ICPMS to in situ U-series and ESR dating of a suite of teeth from Klasies River Mouth Cave, South Africa. Previous ESR dating (Grün et al., 1990) produced large differences between early and linear U-uptake age estimates, that made any chronological interpretation difficult. Fig. 8a shows the re-calculated early and linear U-uptake ESR results; recalculation has been necessary because of subsequent advances in ESR dating, particularly the revision of beta attenuations factors (Marsh, 1999) and the incorporation of the cosmic dose rate (for a more thorough discussion see Grün and Beaumont, 2001). The important Howiesons Poort layers, which contain sample 545 near their base, are bracketed by samples 546 and 544 from the bottom of the overlying Middle Stone Age layers (MSA3) and top of the underlying MSA2 sequence, respectively. Sample 543 was found at the base of the MSA 2 sequence. Conventional early and linear U-uptake, age determinations would permit ages between 46 and 70 ka for the Howiesons Poort and somewhere between 80 and 125 ka for the base of the MSA2. Using in situ U-series analysis and the approach of Grün et al. (1990) we obtain more tightly constrained US-ESR age estimates (Fig. 8b) of between 53 and 64 ka for the Howiesons Poort layer and 101 ± 12 ka (2σ) for the base of MSA2.

The Klasies River Mouth Cave site has been dated previously by a range of independent techniques. Vogel (2000) obtained U-series age estimates of 65.6 ± 5.3 (2σ) ka on a calcite crust from the Howiesons Poort layers, dates of between 77.4 ± 7.0 and 100.8 ± 7.5 ka for samples from the MSA2 sequence and 108.6 ± 3.4 ka for a speleothem intercalated between the MSA2 and underlying light brown sands (LBS) layers. Feathers (2002) obtained optically stimulated luminescence (OSL) dates of 46.7 ± 3.3 and 52.4 ± 4.0 ka from the Howiesons Poort layers, dates of between 68.4 ± 6.5 and 80.6 ± 17.6 ka for the MSA2 layers, and 106.8 ± 12.6 ka for the LBS. Thermoluminescence analysis of burnt quartzite stones yielded a weighted mean age of 56 ± 3 ka for the Howiesons Poort (Tribolo, 2003). In general, there is broad agreement between our new in situ US-ESR age estimates and the previous dating results, except for the Howiesons Poort layers.

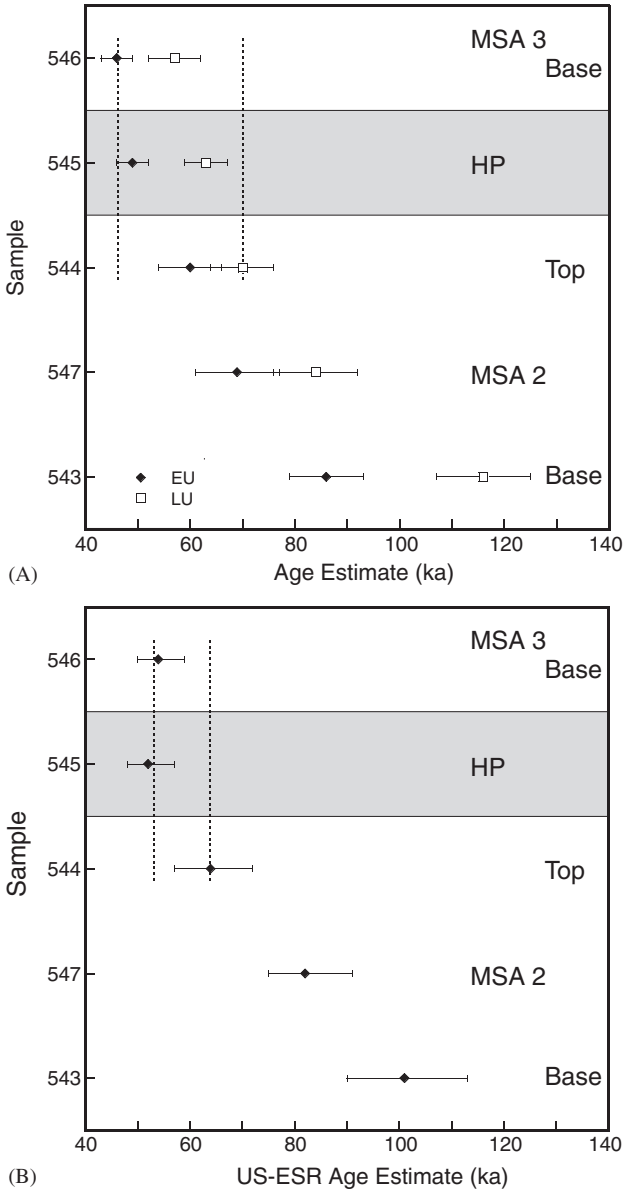

Fig. 8. (A) Comparison of ESR age estimates obtained assuming early uptake (EU) and linear uptake (LU) of uranium for a stratigraphic sequence of faunal teeth samples from the Middle Stone Age 2 (MSA2), Howiesons Poort (HP), and Middle Stone Age 3 (MSA3) units within the Klassies River Mouth Cave, South Africa. (B) Revised age estimates based on combined laser ablation-ICPMS U-series-ESR dating of the same samples.

Based on our new results we place the Howiesons Poort-MSA3 transition at 53–56 ka. This is slightly younger than the equivalent transition at Border Cave, which has been placed at about 58 ka (Grün et al., 2003). The age obtained for sample 543 is of particular significance because human remains found in the same layer and also in the underlying LBS layers, are considered to be of anatomically modern humans (Singer and Wymer, 1982, Rightmire and Deacon, 1991, 2001, Bräuer et al., 1992).

5.5. Mollusc shells

U-series dating of fossil mollusc shells has been considered to be notoriously unreliable since Kaufman et al. (1971) demonstrated that U-series age estimates were subject to open-system behaviour (both uptake and loss) of U. This has resulted in the application of alternative, intrinsically less precise dating methods (e.g. ESR and amino acid racemisation, AAR) to date fossil shells from marine terraces in the absence of corals.

The open-system behaviour of U in mollusc shells was revisited by Kaufman et al. (1996) and by Labonne and Hillaire–Marcel (2000), using mechanical coring techniques to make multiple (up to 6) serial analyses through the walls of modern and fossil shells. Both studies reported U-concentration and $^{234}U/^{238}U$ ratio profiles that indicated post mortem U-uptake. Kaufmann et al. (1996) found early U-uptake in the inner layer compared to greater and more protracted U-uptake in the outer layer of *Merceneria* sp. shells. In contrast, Labonne and Hillaire–Marcel (2000) found preferential U-uptake in the inner (aragonitic) versus outer (calcitic) wall layers of *Conchelepas* sp. shells. These studies indicate that U-uptake depends on both shell mineralogy and geometry, in keeping with observed differences in U concentration and closed-system U-series ages for different species at particular localities (e.g. Radtke et al., 1985, Causse et al., 1993). But rather than accounting for the open-system U behaviour, subsequent studies have continued to pursue closed-system U-series dating of specific shell parts. Specifically, the inner wall layer has been assumed to accumulate most of its U shortly after burial (early U-uptake), and accordingly has been targeted for closed-system age dating (e.g. Hillaire–Marcel et al., 1996). However, when inconsistent or a range of dates were encountered, they were attributed to unresolved open-system uranium behaviour or the reworking of shells from older units. This approach is clearly of limited value because it can neither be used to obtain independent age estimates nor routinely applied to many sites.

For U-series dating of mollusc shells to provide independent and reliable age estimates, it is necessary to constrain (rather than assume) the U uptake history in individual shells. Early open-system models employed deviations from concordia of combined Pa/U and Th/U alpha-spectrometric measurements (Rosholt, 1967, Szabo and Rosholt, 1969). The first of these studies was undertaken on shells from raised marine terraces in California and found U-leaching to be the cause of large age overestimations. However, subsequent studies have nearly always found U-uptake to be the dominant process, leading to age underestimations (see e.g. Kaufman et al., 1971, McLaren and Rowe, 1996). To shed further light on the nature of U-uptake in mollusc shells, we have investigated the distribution of U, Th and

U-series isotopes in modern, sub-fossil and fossil shells of *Anadara trapezia*, a robust bivalve mollusc of considerable palaeoenvironmental value that inhabits shallow tidal mud-flats and sea-grass beds within estuaries of temperate Australia (Murray–Wallace et al., 2000).

Profiles of U-concentration and U-series isotope ratios across a Last Interglacial (MIS 5e) *A. trapezia* shell are shown in Fig. 9a. It is evident that the fossil shells have experienced significant U-uptake based on comparison to lower U concentrations in sub-fossil and very low U concentrations in live-collected shells (our unpublished data show that the latter typically contain only about 1 ppb ^{238}U). The fluctuations present in the fossil shell U-profiles are replicated in successive scans and are also present in the ^{234}U and ^{230}Th scans (Fig. 9a). These fluctuations are most likely related to variations in shell microstructure across growth layering within the shell. As a consequence, U migration may need to be reconstructed parallel to growth layers before the D–A model can be tested for its suitability to shells. We further note that the inner layer of fossil *A. trapezia* shells typically show no obvious concentration gradients and have much lower U concentrations than the outer layer.

Measured [$^{234}U/^{238}U$] and [$^{230}Th/^{234}U$] ratios (averaged over 0.5 mm intervals) of the last interglacial *A. trapezia* are shown in Fig. 9b, along with [$^{234}U/^{238}U$] ratios of a sub-fossil shell. These U-series results illustrate the ability of laser ablation-MC-ICPMS to measure in situ U-concentration profiles, as well as reasonably precise and accurate [$^{234}U/^{238}U$] and [$^{230}Th/^{234}U$] values on samples where concentrations exceed about 0.5 ppm U (see Fig. 9b). The accuracy of the [$^{234}U/^{238}U$] values is demonstrated by the results obtained on the sub-fossil shell, which closely match the modern seawater value (i.e. $[^{234}U/^{238}U] = 1.144 \pm 0.002$, Chen et al., 1986). These first in situ U-series results provide new insight into the nature of uranium uptake and U-series systematics in mollusc shells. In particular, the MIS 5e shell appears to have experienced continuous uranium uptake, as evidenced by the steady decrease of [$^{230}Th/^{234}U$] values from the exterior to the interior of the shell. The accompanying decrease in [$^{234}U/^{238}U$] values further suggests that the main phase of uranium uptake took place after the shell was removed from seawater (with the lowering of sea-level following the last interglacial). This is similar to relationships between [$^{230}Th/^{234}U$] and [$^{234}U/^{238}U$] that have been observed in other studies on bulk and partly separated shells (e.g. Kaufman et al., 1971, 1996, McLaren and Rowe, 1996). The measured U-concentration and U-series profiles of the outer shell are consistent with qualitative predictions based on the D–A model. The oldest apparent ages are obtained at the exterior surface of the shell, where apparent U-series ages (Fig. 9c) agree within error with the age of MIS 5e (about 122–126 ka; Martinson et al., 1987). In comparison, the shell interior has accumulated smaller amounts of uranium and has significantly younger apparent ages by about 50,000 years (due to delayed U-migration). These results are notable for contradicting established wisdom, which assumes that the most reliable ages can be obtained from the inner layers of mollusc shells due to the arrest of U-uptake following a phase of early U-uptake (e.g. Hillaire-Marcel et al., 1996).

6. Future prospects

Technical advances stand to further enhance the potential of laser ablation-MC-ICPMS for in situ U-series analysis beyond the capabilities that have been demonstrated in this study. The deployment of multiple ion counters, already available in some MC-ICPMS instruments, permits the simultaneous analysis of ^{230}Th and ^{234}U, rather than consecutive or dynamic analyses as required when using the detector array employed here. This halves the required analysis time and improves the precision with which $^{230}Th/^{234}U$ isotope ratios can be measured and samples dated. It also avoids the potential problem with our sequential analysis strategy where material with differing U-series isotope composition are sampled from different depths.

An important but as yet unresolved question is whether the yield of U series isotope analysis by laser ablation MC-ICPMS can be improved beyond the current level of efficiency of ~1%. Large transmission losses occur in the interface region of the mass spectrometer, during sampling of the supersonic plasma expansion by the skimmer cone, and subsequently also during initial electrostatic acceleration and extraction of the ion beam. Improvements in ion transmission have been achieved by modifying the sample and skimmer cone geometries (orifice diameters, cone spacing and shape; e.g. Latkoczy and Gunther, 2002), however, a more substantive breakthrough will be required to advance significantly beyond current efficiency levels. One possibility lies in further reducing the interface pressure by employing a much higher pumping capacity (e.g using a Roots pump) in combination with a larger diameter (e.g. 2 mm) skimmer cone orifice. This has been shown to produce up to an order of magnitude improvement in ion transmission through the interface over conventional interface designs (Olney et al., 1999). This would extend the capabilities of in situ U-series analysis to a greater range of samples and materials that contain up to an order of magnitude lower U-concentration, well into the sub ppm range.

With regard to applications, we foresee the continuing development of open-system U-series dating of bones, teeth, and mollusc shells. This stands to provide new

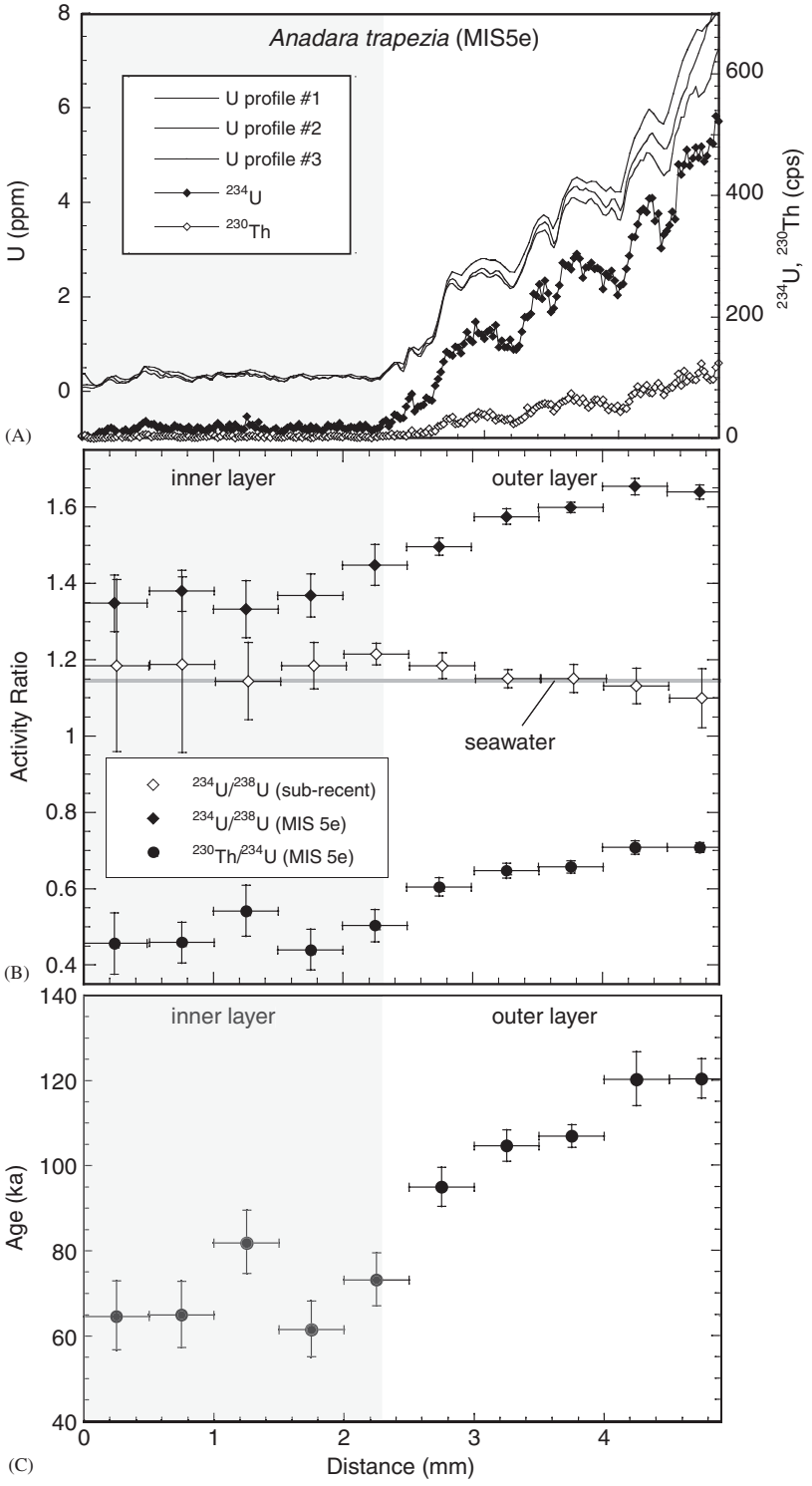

Fig. 9. (A) Uranium concentration, measured ^{234}U and ^{230}Th intensity profiles from the inner to the outer surface of a fossil *A. trapezia* shell from the last interglacial (MIS 5e) Glanville Formation at Tourville bay, Eyre Peninsula, South Australia. (B) Mean [$^{234}U/^{238}U$] (♦) and [$^{230}Th/^{234}U$] (●) activity ratio values calculated for 0.5 mm bins across the same shell section for which data are shown in (A), and mean [$^{234}U/^{238}U$] activity ratio values measured across a sub-fossil shell of similar thickness from Byron Bay, New South Wales. Note the good agreement obtained between the sub-fossil shell's [$^{234}U/^{238}U$] (◇) activity ratio and the value of modern seawater, particularly in the context of the very low U content of this shell, which averages 26 ppb U in the inner layer (0–1.6 mm), 190 ppb U in the outer layer, and reaches a maximum of 390 ppb in the outer layer. The grey and white shaded regions indicate the extent of the inner and outer layers in the MIS 5e shell. (C) Closed-system U-series age estimates (●) calculated from the binned [$^{234}U/^{238}U$] and [$^{230}Th/^{234}U$] activity ratio values across the last interglacial shell. Note the approach of these estimated ages to MIS 5e values toward the outer surface of the outer layer.

opportunities to address important questions in the archaeological and palaeoanthropological record, particularly beyond the radiocarbon barrier. The development of a reliable open-system method for dating mollusc shells would open up the possibility of dating marine terraces and other shoreline deposits that occur outside the tropics and in the absence of corals. We also anticipate extension of the technique to a wider variety of sample types than demonstrated here. Possible applications include the closed-system dating of pedogenic carbonates, particularly where high-spatial resolution U-series analysis may be advantageous (cf. Sharp et al., 2003), and tracing the migration of uranium through the regolith or dating the formation of weathering products, though analysis of U-rich phosphates and Fe-oxy-hydroxides (Bernal et al, in press).

7. Summary and conclusions

Laser ablation–MC-ICPMS provides a number of significant advantages compared to conventional mass spectrometric methods (TIMS or solution MC-ICP-MS), particularly in terms of the ease of sample preparation, the rapidity of analysis, and ability to obtain continuous, high spatial resolution, elemental and isotopic profiles in samples that contain sufficiently high U-concentrations (>0.5 ppm U). These capabilities present an opportunity to extend the application of U-series dating beyond conventional closed-system dating of corals, speleothems, etc., to include a broader range of materials, particularly those that behave as open-systems with respect to uranium. Specific applications identified by this study include:

(1) Rapid screening of samples for ages within the range of interest and/or suitability for more accurate and precise dating by conventional methods (see also Potter et al., 2005).
(2) High spatial resolution analysis of small samples, structures or layers in samples that would otherwise be contaminated with surrounding detrital/adsorbed U and Th (e.g. septa in deep-sea corals) and/or to resolve growth banding at scales in the range from 10 to 100 μm (e.g. in pedogenic carbonates, high uranium speleothems).
(3) Open system dating of bones, teeth and potentially also mollusc shells using appropriate diffusion-adsorption uranium-uptake models. This supercedes alternative conventional TIMS or solution MC-ICPMS analysis used in combination with micro-sampling techniques (e.g. Pike et al., 2002) which, because of the numbers of analyses required to generate a single date, can be time-consuming and expensive. Moreover, the microscopic scale of laser ablation MC-ICPMS analysis makes it an acceptable method for analysis of hominid and other valuable fossils.
(4) Understanding open-system behaviour/migration of U and Th isotopes during diagenesis and weathering processes.

The principle drawback associated with laser ablation-MC-ICPMS is that U-series isotope measurements cannot be determined with the same high precision as TIMS or solution MC-ICPMS, resulting in larger age uncertainties and a reduction in the age range over which dating can be performed. Furthermore, the accuracy to which Th/U ratios can presently be measured is compromised by the lack of suitable and widely available matrix-matched reference materials that have well characterised U-series isotope compositions. In the case of carbonate analysis, our results show that a small but significant bias upon measured $^{230}Th/^{234}U$ and $^{230}Th/^{238}U$ ratio values and corresponding age overestimation arises from calibration against NIST610 glass.

Acknowledgments

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