Author/s:
Hellstrom, J;Pickering, R

Title:
Recent advances and future prospects of the U-Th and U-Pb chronometers applicable to archaeology

Date:
2015-04-01

Citation:
Hellstrom, J. & Pickering, R. (2015). Recent advances and future prospects of the U-Th and U-Pb chronometers applicable to archaeology. Journal of Archaeological Science, 56, pp.32-40. https://doi.org/10.1016/j.jas.2015.02.032.

Persistent Link:
https://hdl.handle.net/11343/233662

Recent advances and future prospects of the U-Th and U-Pb chronometers applicable to archaeology

John Hellstrom[1] & Robyn Pickering[1,2*]

[1]School of Earth Sciences, University of Melbourne, Parkville, 3010, Victoria, Australia
[2]Department of Geological Sciences, University of Cape Town, Rondebosch, 7701, South Africa

*Corresponding author
Robyn Pickering, rpi@unimelb.edu.au
School of Earth Sciences, McCoy Building, Cnr Swanston and Elgin streets
University of Melbourne, Parkville, 3010, Victoria, Australia
Telephone: +61 (0)3 8344 6531
Fax: +61 (0)3 8344 7761

Keywords:
U-Th dating; U-Pb dating; Archaeometry; Speleothem; Cave deposits; Human evolution

Highlights:

- We review recent use of the uranium series (U-Th and U-Pb) chronometer applicable to archaeology
- We provide an overview of the method itself, as well as how samples are prepared and analysed
- We have compiled a detailed table listing materials suitable for both U-Th and U-Pb dating
- We review published examples of successful U-Th and U-Pb dating applied to archaeology
- We provide our opinion of where the future of this field lies and where likely developments will take place

Abstract

The U–Th chronometer has revolutionized Quaternary science in the last few decades and can now be considered a well-established, mature technique with growing application in archaeology as an alternative to ^{14}C dating and OSL, reaching well beyond the cutoff for both these methods. Applying the U–Pb technique to material within a time frame of interest to archaeology is a challenge only recently overcome, with enormous potential for future development and use. In terms of range, U–Th can generally date material of between a few years and as much as 600 ka, while U–Pb is best suited to material of 1 million years and older. U–Th dating is typically precise, with error margins of better than 1 % routinely achievable for material of the last interglacial age or younger. Such precision is possible with U–Pb dating in the mid-Quaternary but most ages have uncertainties in the 5-10 % range. Carbonates are the most desirable U-series target material, with closed system behaviour being particularly important for U–Th dating; making inorganic deposits such as speleothems (secondary cave carbonates), tufa and calcrete ideal. Some biogenic carbonates such as coral and eggshell are often amenable to U-series dating, but less ideal material such as fossil teeth, bone and mollusc shell usually continue to gain uranium after deposition meaning accurate ages cannot be calculated. In all cases, the importance of a thorough understanding of the context of dated material cannot be overstated. In this contribution we review U-Th and U-Pb dating through an archaeological lens, focusing on the methods themselves; how to best interpret published data and how best to avoid common pitfalls. We highlight the major successes through a number of case studies and provide an overview of what we believe to be the future directions of this field.

1. Introduction

The study of our own human past, either through cultural remains encompassing archaeology or via human and other fossils involving palaeoanthropology and palaeontology, is fundamentally underlain by the need for widely applicable dating techniques which can provide precise ages to form the chronological backbone of such work. The U–Pb dating technique has had a profound impact on Earth Sciences in delivering an age for the Earth itself and underpinning all measurement of deep time. Both the U-Th and U-Pb (carbonate) dating techniques use one or more intermediate daughter products of the uranium to lead decay chain. The techniques have a growing application in Quaternary science and archaeology where they are now widely used because of the reliability of their status as absolute radiometric chronometers with no required calibrations. The evolution of the

technique began in the early 1900s with the seminal work of Marie Curie, leading to the discovery of natural radioactivity and the ^{238}U decay chain. The 1950s saw significant development, applied primarily to the dating of deep-ocean sediments, with the 1960s bringing the expansion to both marine and terrestrial carbonates, which remain the focus today. The modern era of U-series dating dawned with Edwards, et al. (1987) showing that U–Th dating could be conducted by mass spectrometric analysis, which, together with subsequent advances have resulted in an increase in efficiency of measurements by more than four orders of magnitude and has allowed U–Th dating to underpin much of the chronology of the late Quaternary.

Uranium (U) is present as a trace element in all natural materials and U-series dating techniques are based on the natural decay of ^{238}U to lead-206 (^{206}Pb), with a half-life of 4.47 billion years, and of ^{235}U to lead-207 (^{207}Pb) with a half-life of 704 million years (Grenthe, et al., 2011), via their intermediate daughter products (Figure 1).

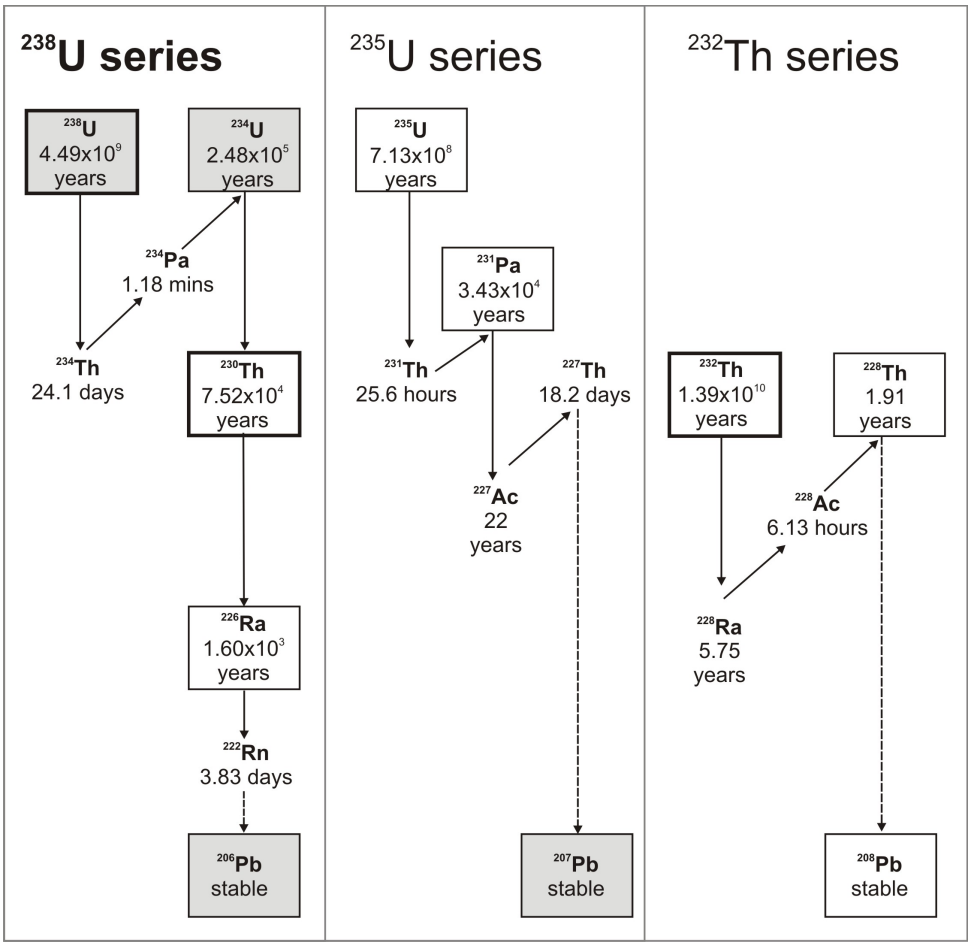

Figure 1. A schematic diagram of the U-series decay chains of ^{238}U, ^{235}U and ^{232}Th. Isotopes involved in U-Th dating are shown in bolded boxes, while isotopes used in U-Pb dating in grey shaded boxes (Image re-drawn and modified from Walker, 2005).

Here we will focus on the two techniques with the greatest utility, $^{238}U–^{234}U–^{230}Th$ (U–Th) and $^{238}U–^{234}U–^{230}Th$-$^{206}Pb/^{235}U–^{231}Pa–^{207}Pb$ (U–Pb). In terms of age range, U–Th dating is limited by the half life of ^{230}Th which is 75,584 years (Cheng et al, 2013), so instead of accumulating indefinitely (as is the case for the U–Pb system) it approaches secular equilibrium with its parent isotope ^{234}U, whereby it decays as fast as it is produced and gives the U-Th dating system an effective upper age limit of somewhat over 500,000 years. Advances in mass spectrometry mean that material as old as 600–650 ka can now be dated (Andersen, et al., 2008, Cheng, et al., 2013), with the other end of the datable age spectrum as recent as a few decades (Zhao, et al., 2009). The U-series decay chain continues on beyond ^{230}Th and ends in stable ^{206}Pb where it accumulates indefinitely meaning that U-Pb dating is suitable for materials belonging to long geological time scales, including the age of the Earth itself (Patterson, 1956).

In archaeological applications the primary limitation of the utility of U-series dating methods is having suitable material in the right context to provide meaningful ages. The critical pre-requisite for successful dating is that the target material acts as a 'closed system', with no loss or gain of U isotopes since its time of formation (Walker, 2005), although it is also important that samples are 'clean' of Th- and Pb-bearing detritus. U-Th and U-Pb dating is best suited to inorganic carbonate materials, such as speleothems (cave dripstones), which typically form with very large U/Th and U/Pb ratios and bind U and its daughter products within large calcite crystals. Some biogenic carbonates such as coral or eggshell (Miller, et al., 1999) are often also suitable although these can suffer from post-depositional U mobility as they weather over time. In most archaeological settings, these materials may be rare or absent, while other biogenic carbonates and phosphates such as bones, teeth and shell, may be abundant. These latter materials rarely behave as 'closed systems' which means that, post-burial, U series isotopes move in and out of them making U-series dating challenging. Given the abundance of this type of material at arcaheological sites, considerable effort has gone into modeling this open system type of behavior for dating fossil bone (Pike, et al., 2002, Hedges and Millard, 1995), which has met with limited success but as yet cannot be considered an absolute dating technique.

We are not the first to review U–Th dating for an archaeological audience, Henry Schwarcz compiled numerous, well cited reviews (Schwarcz, 1989, Schwarcz, 1992a, Schwarcz, 2002, Schwarcz and Rink, 2001, Schwarcz, 1992b, Schwarcz, 1997), as have Smart (1991), Latham (2001), Pike and Pettitt (2003), and Walker (2005). More detailed,

technical reviews of the U-series method and its broad applications can be found in the edited volumes by Ivanovich and Harmon (1992) and Bourdon et al. (2003). The rapidly advancing field of U–Pb dating of carbonates is reviewed by Rasbury and Cole (2009), with a review of U–Pb dating speleothems in particular by Woodhead and Pickering (2012).

In this contribution we outline the U-Th and U-Pb dating methods, we discuss which materials are best suited to this type of dating and give a number of examples of successes of in archaeology. Finally we present our views on the future challenges and the innovations we would like to see over the coming years.

2. Principles of U-Th and U-Pb dating methods

U–Th and U–Pb dating are both based on the natural radioactive decay of ^{238}U through a series of short-lived daughter isotopes, ending in stable ^{206}Pb (Figure 1). U-Th is known as a 'U-series' technique as it utilizes intermediate isotopes in the U-series decay chain. By convention U-Pb is not a U-series technique, however when applied to young carbonates a number of the intermediate daughter isotopes must also be considered (most notably 234U) and in this context U-Pb can arguably be seen as a U-series technique .

The term 'secular equilibrium' is used to describe the state of the U-series decay chain when, in a closed system, the ratios of U to each of its daughter isotopes are such that each unstable daughter isotope decays at the same rate at which it is produced. The separation or fractionation of one or more of the elements in the decay chain through various natural processes will disturb this equilibrium. The gradual return of the system back to secular equilibrium allows for a quantification of the time elapsed since the fractionation event and is the basis of U-series methods other than U–Pb. In other words, the event that disturbed the equilibrium state of the isotopes, such as formation of a speleothem, can be dated by determining the extent to which the isotopes have re-established equilibrium. Once they have reached equilibrium (with respect to the limits of our ability to measure it) the age range of the disequilibrium technique has been exceeded.

The most relevant process liable to fractionate isotopes in the U-series decay chain is the significant difference in solubility between U and Th, as U is highly soluble in natural waters and Th is not. As such cave drip waters contain U but are essentially devoid of Th, meaning that speleothems (typically stalagmites and flowstones) forming from these waters will inherit up to several parts per million of U and negligible amounts of Th. The subsequent *in situ* decay of 238U to ^{234}U (with a half-life of 245,620 years; Cheng et al, 2013) and from 234U to ^{230}Th (75,584 years) can be used to date the material by measuring the present levels of all

three isotopes (Bourdon, et al., 2003). Many other inorganic and biogenic carbonates fractionate U and Th in the same way on formation. A complication is that processes operating during the dissolution of uranium from its host materials usually lead to disequilbrium between the dissolved 234U and 238U, usually in the form of excess 234U. U–Th dating thus requires measurement of both 234U/238U and 230Th/238U (fig. 2; Richards and Dorale, 2003).

Inorganic carbonates such as speleothems and similar materials can be contaminated by thorium-bearing detrital material (usually clays, silts) as they grow, which breaches the fundamental assumption of zero 230Th at time of formation and makes calculated ages appear too old. To monitor this, 232Th/238U is also measured as 232Th is not produced by decay of U and can only be present as contamination. There are various possible means of correction for this contamination, the simplest of which is to estimate an initial 230Th/232Th ratio (and its uncertainty) and calculate the proportion of contaminating 230Th (Hellstrom, 2006). In extreme cases the intial 230/232 ratio might need to be calculated using an isochron technique in which multiple measurements are taken (Luo and Ku, 1991; Schwarcz and Latham, 1989).

In the U-Pb dating scheme, radiogenic (produced *in situ*) ^{206}Pb can be completely obscured by common (initial) ^{206}Pb, meaning that age determinations are usually undertaken by multiple sample analysis and isochron construction (Richards, et al., 1998, Woodhead, et al., 2006). As with U–Th, an important consideration in U-Pb dating of speleothem material is the initial ^{234}U/^{238}U ratio, which is measured directly where possible but must usually be estimated for samples of more than about 2 Ma (Richards, et al., 1998, Woodhead, et al., 2006, Pickering, et al., 2010, Bajo, et al., 2012). Without taking the initial excess of ^{234}U into account, ages can be greatly over-estimated, and where initial ^{234}U/^{238}U cannot be directly determined it can lead to additional uncertainties of hundreds of thousands of years.

2.1. Age calculations

Calculation of a U–Th age requires accurate measurement of the ratios ^{230}Th/^{238}U and ^{234}U/^{238}U, usually expressed as activity ratios, that is where secular equilibrium would be a ratio of 1 (Figure 2).

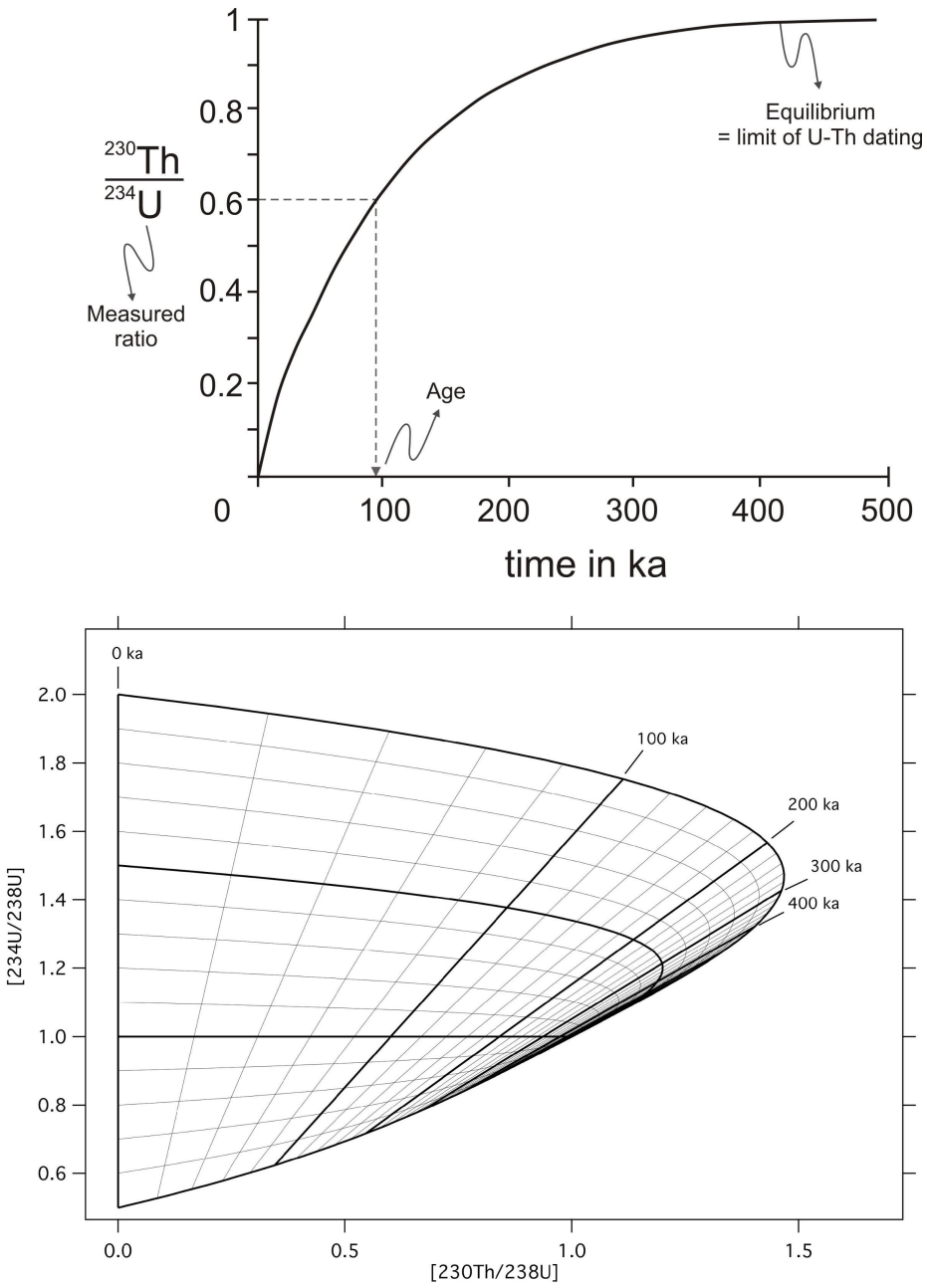

Figure 2. The ratio of the activity of ^{230}Th to that of its parent isotope ^{234}U as a function of time (top). If the initial ^{230}Th/^{234}U ratio was zero, then age could be read from this chart using the present, measured ^{230}Th/^{234}U ratio. As the ^{230}Th/^{234}U ratio approaches 1 the curve flattens out, giving an upper limit of ca. 500 ka (redrawn and modified from Schwarcz, 1992a). A U–Th isochron diagram (bottom) shows the effect of variable intial 234U/238U. Samples form at the left of the diagram with zero 230Th/238U and follow a curved path towards the right as shown. The straight isochron lines become more closely spaced with time leading to larger uncertainties until the limit of the method is reached at ca. 500 to 600 ka.

Also required is ^{232}Th/^{238}U to monitor and correct for the extent of any detrital contamination. These ratios were once calculated by direct measurement of radioactivity

using alpha spectrometry (Ivanovich, M., Harmon, R. S., 1992) but for the last 20 years have generally been measured using a mass spectrometer – at first by thermal ionization mass spectrometry (TIMS; Li et al, 1989). This has now been replaced by the faster and more efficient (multi-collector) inductively-coupled plasma mass spectrometry, (MC)-ICP-MS (Goldstein and Stirling, 2003). This technique allows measurement of the necessary ratios from as little as one billionth of a gram of U, which typically corresponds to between a fraction of a milligram and a few hundred milligrams of the material being dated (Hellstrom, 2003; Pike et al 2012). U–Pb dating of archaeological materials requires accurate measurement of the ratios $^{206}Pb/^{238}U$, $^{207}Pb/^{206}Pb$ and $^{234}U/^{238}U$ and is analytically more difficult than U–Th. Some laboratories still use TIMS for the Pb measurements although MC-ICP-MS allows much greater sample throughput – in either case, sample size requirements are up to 100 times greater than for U-Th .

2.2. Accuracy and precision of U-Th and U-Pb ages

U–Th and U–Pb are both absolute radiometric chronometers, meaning that in good material their accuracy is limited only by our ability to measure the necessary isotope ratios and no additional corrections or calibrations are required. Both techniques can be degraded by the presence of significant levels of the measured daughter isotope (^{230}Th or ^{206}Pb) at the time of sample formation, and both can solve this in the same way using "isochrons" whereby multiple measurements are made on sub-samples of the same age but of different initial isotopic composition. In practice, isochrons are almost always used for U–Pb and are rarely used for U–Th as initial contamination is a lesser problem for the latter technique. The precision of U–Th is generally better than 1% for material formed during or after the last interglacial (i.e. the last ca. 130,000 years), and then slowly degrades back to ca. 500 ka where it becomes rapidly worse. Where U–Th-dated material does contain high levels of detrital contamination the effect of correcting it can cause calculated ages to have large uncertainties of up to tens of percent. Carbonate U–Pb precision is at its best in the mid-Quaternary where it can be as low as one percent. Younger material gives less precise ages as the small amount of ^{206}Pb that has accumulated becomes difficult to measure, and older material is more difficult to correct for the effect of its initial $^{234}U/^{238}U$ ratio. For material older than about 2 Ma this limits uncertainty to several hundred thousand years.

2.3. Material suitable to U-Th and U-Pb dating

Carbonate material is inherently suitable to U-series dating, and has been the main focus of

the dating method since the 1960s. The primary controlling factor over the suitability of such material for U-series dating, is whether the carbonate material in question behaves as a 'closed' or 'open' system, that is, do the parent and daughter isotopes involved in the U-series decay chain all remain locked into the carbonate, or do some, almost always uranium, move in or out. Inorganic carbonates almost always adhere to 'closed system' behavior, making materials such as speleothems, calcrete and sometimes tufa ideal targets and indeed the most commonly U-series dated material (Table 1).

[insert Table 1]

Table 1. A summary table of the most common types of material dated with U-Th and U-Pb, including typical U concentrations, detrital Th contents and the relevant key references. Closed system behavior is absolutely essential for U-Th and U-Pb dating and where open system behavior is a possibility it should be checked by conducting multiple analyses (or by isochron dating as for U-Pb). High detrital Th content or common Pb content is undesirable – it can be corrected for but degrades age precision.

In archaeological applications the biggest pitfall in dating speleothems, flowstone and coral, is the context, how these materials relate to the archaeological deposits of interest. If a flowstone layer underlies an archaeological deposit, it provides a maximum age (*terminus post quem*) for the deposits. Similarly, if a flowstone overlies a deposit, it provides a minimum age (*terminus ante quem*). However, many thousands to tens of thousands of years may be left unrecorded between the formation of the flowstone and deposition of the archaeological sediments. Ideally, if flowstone layers occur both above and below the deposits, then U-series ages for these layers can be used to infer the age of the deposits sandwiched between them. These circumstances, however, are rare, so the importance of understanding the local geology, site formation processes, the stratigraphy of a deposit, and relationships between the dated layers and archaeological deposits, cannot be overstated.

Materials of greater interest to archaeologists, such as fossil bones, teeth, and shell, are usually inherently unsuitable for U-series dating because these organic materials are subject to post-mortem open-system behavior. Uranium and to a lesser extent thorium isotopes are mobile, and their uptake and loss needs to be modeled (Pike, et al., 2002, Hedges and Millard, 1995, Pike and Pettitt, 2003). One possibility is to use *in situ* laser ablation, whereby, in some cases, U and Th isotopes can be measured directly from a sample surface to create profiles along sections through material such as bones, teeth, and possibly molluscs to map out the patterns of U migration (Eggins, et al., 2005, Grün, et al., 2014). This approach has also been attempted using the U-Pb system on fossil tooth enamel from the early human (hominin) bearing cave site of Swartkrans in South Africa (Balter, et al., 2008). Again, the problem is

that the post-deposition U loss has to be modeled, leading to ages with large uncertainties and a reliance on the sample having behaved according to the model used. An encouraging new development to watch is the possibility of U-Th dating of extracted bone collagen which might not suffer from post-depositional U mobility (Hercman, 2014).

U-Th dating of molluscs has been attempted and reported many times in the past, but the repeated conclusion has been that this technique is not reliable due to ongoing, differential post-mortem uptake of U (Kaufman, et al., 1971, McLaren and Rowe, 1996). Nonetheless there have been indications that in some settings, mollusc shells can behave as closed systems and allow the determination of accurate U-Th ages (Arslanov, et al., 2002).

2.4. Analytical techniques and dating method

We do not go into great detail of the analytical methods of preparing and measuring samples for U-series dating here; these are described in detail in the edited volumes by Ivanovich and Harmon (1992) and Bourdon et al. (2003), and in most cases in technique papers specific to each U-series laboratory. Before any measurements can be undertaken, sufficient amounts of the required nuclides need to be separated from the material in which they occur, usually with each element of interest being collected as a separate fraction. This is achieved by through isotope dilution (Faure, 1977) by dissolving sample material in acid and adding a synthetic isotope tracer solution before using ion-exchange chromatography to separate and concentrate U, Th and Pb. The activities or concentrations and ratios of the isotopes are then measured, originally using alpha spectrometry, then by Thermal Ionization Mass Spectrometry (TIMS) and most recently and with the best results, by Multi Collector Inductively-Coupled Mass Spectrometry (MC-ICP-MS; see Goldstein and Stirling, 2003 for a full review). The upper limit of the alpha spectrometry method was around 350 ka and the perception that U-Th cannot date material older than this is still widely held in archaeology. With modern MC-ICP-MS measurement regimes it is possible to produce reliable U-Th ages as old as 600 ka (Andersen, et al., 2008). Alpha spectrometric U–Th ages required very large sample sizes of ca. 10,000 times more material than are now required for MC-ICP-MS analysis, meaning that optimum material could not always be selected and these results should be interpreted with care. Where important sites or findings still rely on alpha spectrometric dates consideration should be given to repeating them with modern techniques.

An alternative U–Th technique is to use a laser-ablation microprobe coupled to MC-ICP-MS and perform in situ measurements and age determinations on samples as small as 0.1 mm where U content is at least 1 ppm (μg/g; Eggins, et al., 2005). Using this approach U-series

isotope ratios can be continuously profiled along a sample, which is especially useful when trying to date bones, teeth or shell (Duval, et al., 2011). Laser-ablation dating has an advantage of speed and of being generally less invasive, but is considerably less accurate than microsampling by drilling or milling where for similar uranium content samples of less than 100 μg can often be used (Drysdale, et al., 2012, Spötl and Mattey, 2012).

2.5. Reporting U-Th and U-Pb ages

When reading and reporting U-series ages it should be remembered that mass spectrometric U-Th and U-Pb ages are always reported with errors given at 2σ, unlike many other dating techniques. We urge our archaeological colleagues to be aware of this and to take this into account when comparing ages from different methods. In terms of the actual ages, we stress that ‘‘before present’’ (BP) is a radiocarbon specific definition and should not be used to describe ages for U-series, or any other method.

3. Major achievements of U-Th and U-Pb dating

3.1. U-Th dating examples

In archaeological contexts, U-series dating is best applied to speleothems and their utility for providing ages for such sites has long been recognized (Schwarcz, et al., 1979). An early example of U-Th dating flowstones to provide ages for interstratified artefacts and fossils is the alpha-spectrometry dating of the cave site La Chaise-de-Vouthon in France by Blackwell, et al. (1983). The U-Th ages of 245 +45/-28 ka to 97 ± 6 ka form the chronology for the sequence of deposits and constrain the age of the Lower to Middle Palaeolithic artefacts and several Neanderthal fossils. The fossils themselves consist mainly of isolated teeth and were recovered from layers older than 101 ka (Blackwell, et al., 1983).

Dating early modern human occupation sites in South Africa

A more recent example of the same type of approach, using interstratified flowstone to provide ages for archaeological cave sediments is the dating of the Pinnacle Point sites along the southern Cape coast of South Africa. Here, U-Th ages for flowstone layers were combined with OSL dating of archaeological sediments to provide a more complete and indeed a very detailed picture of the development of the cave sites and their occupation by early modern humans (Marean, et al., 2007). The detailed and well dated archaeological record from Pinnacle Point is further enhanced by a high resolution, continuous speleothem record from the same set of caves which covers the period of 90 to 53 ka (Bar-Matthews, et al., 2010).

Dating buried soda straws

Flowstone layers may not always be present in association with deposits and/or artefacts of interest to archaeologists. An alternative is to date buried soda straws or tubular stalactites, which was suggested as a potential future advance by Schwarcz (1992a) and recently successfully undertaken by St Pierre, et al. (2009), who argue that straws are so fragile that they cannot survive re-working, so that their presence suggests rapid burial, and thus they can provide ages close to the time of sedimentation. This approach has been effectively used at Blanche Cave in South Australia (St Pierre, et al., 2012) and recently at the *Homo Floresiensis* site of Liang Bua cave in Indonesia (St Pierre, et al., 2013).

Dating flowstone remnants attached to fossils: the Red Deer people in China

Not all sites preserve intact, laterally persistent flowstone layers and often cultural remains and fossils have been fully excavated out, with the surrounding material thus lost. It can be possible, however, to date small, remnant fragments of speleothem material adhering to fossil bones. Curnoe, et al. (2012) employed just such an approach to dating the partial skull found in the late 1970s in the Longlin Cave in the Guangxi Zhaung region of China. This fossil, together with other material excavated from the Maludong (Red Deer) Cave in Yunnan Province, was dated by radiocarbon to between 14.5 and 11.5 ka. The small remnant of flowstone attached to LL1 vault contained significant contamination from detrital Th, but samples which proved unsuitable for age determinations were used instead to provide a robust estimate of the initial $^{230}Th/^{232}Th$ activity (0.82 ± 0.20), which was used to produce a final corrected absolute age of 7.8 ± 0.5 ka. As the flowstone covering the fossil must have formed post depositionally, this U-Th age confirms the Pleistocene-Holocene transition age determined by the radiocarbon ages (Curnoe, et al., 2012).

Dating cave art

The possibility of indirectly dating cave art by determination of ages for overlying and/or underlying thin films of speleothem material has recently become a reality as the required sample size for U–Th analysis has fallen. Pike, et al. (2012) recently demonstrated that by dating a large enough population of such overlying films it is possible to approach the oldest age of the underlying artwork, and finding cave art of at least 40.8 ka in Spain indicated that this was a practice of either the earliest anatomically modern humans or of Neandertals. A similar study undertaken in Indonesia found cave art as early as 39.9 ka by dating corraline

speleothem overgrowths (Aubert, et al., 2014). This later finding should be treated with caution until age replication has been established within individual layers as coralline speleothem has been shown previously to act as an open system (Prideaux, et al., 2007), which can have the effect of making samples appear considerably older than their true age. Pons-Branchu, et al. (2014) provide the most up to date review of U-Th dating rock art, and also urge caution in the interpretation of the ages. Taçon, et al. (2012) obtained younger ages of between 5738 and 2050 for flowstone underlying paintings in Jinsha River area of northwest Yunnan Province (southwest China), which they argue shows that the art likely extends back to at least the transition from the Palaeolithic to Neolithic in this part of China. Calcite overgrowth dating is likely to continue to expand in scope as U–Th sample size demands fall, and where overgrowths form on bones or artefacts they too can be similarly dated.

Dating coral associated with Polynesian settlements

An elegant example of the utility of high precision U-Th ages is the work by Sharp, et al. (2010) who investigated that development and timing of building elaborate Polynesian temples (marae) on the island of Mo'orea in the Society Islands, near Tahiti, by U-Th dating of corals used as architectural elements (facing veneers, cut-and-dressed blocks, and offerings). While the coral from some of the wetter inland sites was shown to suffer from diagenesis, coral from 19 inland and 15 coastal marae produced reproducible ages for each site with a mean 2σ uncertainty of an incredibly precise 9 years. The ages indicate that the temple architecture on Mo'orea Island developed rapidly over approximately 140 years from ca. AD1620-1769, with the largest coastal temples built prior to initial European contact in AD 1767. Sharp et al (2010) argue that this example demonstrates that the elaboration of ritual architecture in complex societies may be surprisingly rapid. A similar approach was used by Burley, et al. (2012) who used high precision U-Th ages on fossil coral to identify the founding event of the Kingdom of Tonga to 2838 ± 8 years ago.

The fringe of U-Th: fossil wood, calcrete and other material

An exciting possible alternative to dating bone or teeth is dating buried wood. A method for this has been successfully applied to buried wood of pre-Holocene age from sediment sequences along the Hudson Bay lowlands in Canada (Allard, et al., 2012) and could have many applications in archaeological settings.

Calcrete is a ubiquitous feature of many open-air fossil and archaeological sites in southern

Africa and elsewhere in the world, and as a form of carbonate is potentially datable via U-series dating. Apart from the obvious and ever present caveat of the context of the dated material to the archaeology, calcretes forming from ground water and/or upwelling/springs may long post date the deposits of interest, so any ages obtained must be interpreted with caution. The site of Elandsfontein on the west coast of South Africa is under new investigation, with recent work indicating a mid Pleistocene occupation by hominins (Braun, et al., 2013). Part of this ongoing work is investigating the U-Th dating of the abundant calcrete, today found both at the surface and buried within the archaeological sediments.

3.2. U-Pb dating examples

The application of U-Pb dating to speleothem material has only recently reached a level of maturity where material can be dated routinely (Woodhead and Pickering, 2012, Woodhead, et al., 2006, Woodhead, et al., 2012).

Dating the South African hominin cave sites

While this innovation has wide implications for fields such as landscape evolution and palaeoclimate studies, its biggest contribution so far has been to the dating of the hominin bearing caves in South Africa. This collection of dolomite hosted cave sites in the region known as the 'Cradle of Humankind' is the richest source of early hominin fossils outside East Africa, with at least four species of hominin, as well as abundant fossil fauna and sparse stone tools present. The fossil bearing deposits are complex and often poorly exposed but interstratified flowstone layers are a ubiquitous feature. Pre-screening for layers rich in uranium has proved to be essential for successful U-Pb dating (Pickering, et al., 2010). U-Pb ages for flowstone layers from above and below fossil-bearing layers from the sites of Sterkfontein, Swartkrans, Coopers and Malapa provide the first set of direct, albeit broad, age ranges for these deposits between ~2.8 and ~1.4 Ma (de Ruiter, et al., 2009, Pickering and Kramers, 2010, Pickering, et al., 2011a, Pickering, et al., 2011b). These broad age ranges can be narrowed down by using the U-Pb ages to 'pin' accompanying palaeomagentic sequences of normal and reversed events to the known geomagnetic polarity time scale. This was done with great effect at Malapa, providing an age of 1.977±0.003 Ma for the partial skeletons of *Australopithecus sediba* (Pickering, et al., 2011b). An obvious caveat to this approach is, once again, the context and the relationship between the dated flowstones and the fossils of interest. Fossil StW 573 ("Little Foot") preserved in the Silberberg Grotto at Sterkfontein caves is a clear example. The flowstones surrounding the fossil are U-Pb dated to 2.25 ± 0.09

Ma (Walker et al., 2006) and 2.35 ± 0.10 Ma Pickering et al., 2010; Pickering and Kramers, 2010) leading these authors to ascribe a coeval age for the fossil. Bruxelles, et al. (2014) present a detailed stratigraphic and geochemical study arguing that the flowstones in fact post-date the sediments surround the StW 573 and that fossil is considerably older. It is difficult to quantify the length of time between the deposition of the fossil and subsequent formation of the flowtones, but Bruxelles, et al. (2014) suggest several hundred thousand years. The error on the U-Pb ages of between 90 and 100 ka may well accommodate this. Ideally detailed stratigraphic work such as the Bruxelles, et al. (2014) study should be undertaken prior to any dating.

Dating buried speleothems in archaeological cave sites

The site of Wonderwerk Cave in the Northern Cape of South Africa preserved important Earlier Stone Age (ESA) deposits, which include small buried stalagmites. Once again, laser ablation scans proved invaluable in identifying layers within the samples suitable for U-Pb dating trace element profiles excluded the possibility of any U mobility in or out of the samples, confirming the integrity of the U-Pb ages. Two samples from Stratum 10 gave U-Pb ages of 0.734 ± 0.069 Ma and 0.839 ± 0.026 Ma which suggest that the palaeomagnetic sequences hint at a younger age of ~780 ka to 1.07 Ma for the older deposits, but a much larger data set is needed before this can be done with confidence (Pickering, in press).

Dating past sea level high stands

The caves sites at Pinnacle Point, mentioned earlier, are well known for their archaeological deposits but were thought to not preserve any material older than ~120 ka. However, recent U-Pb dating of flowstone layers from two remnant cave deposits yielded ages of 1.099 ± 0.012 to 1.047 ± 0.011 Ma (Pickering, et al., 2013). The presence of these 1.1-1.0 Ma deposits implies that older material in these coastal caves can be preserved and has survived multiple sea level highstands. This opens up the possibility for more deposits, from this region, some possibly archaeological, reaching back into the early to mid Pleistocene.

The frontiers of U-Pb dating

Two exciting areas of development involving U-Pb dated speleothem samples are the extraction of pollen from speleothems as a palaeoenvironmental proxy (Sniderman, et al., 2014) and the progress in constructing U-Pb growth models for stalagmites (such as in Bajo,

et al., 2012) with a view to investigating palaeoclimate records beyond 500 ka where such archives, especially terrestrial ones, are rare.

4. Challenges, innovations and future gazing

Over the last 40 years the big breakthroughs and improvements in both U-th and U-Pb dating have been linked to big jumps forward in mass spectrometry technology, namely the advent of TIMS and then multi-collector ICPMS machines. No additional leaps in technology are visible on the horizon, as yet. One area of potential improvement is in mass spectrometer sampling efficiency – this is currently only about 2% at best, leaving considerably further room for improvement and thus a reduction of sample size requirement.

A significant recent advance in U-Th dating has been the increase of throughput using automated measurement of large sample batches, meaning that more material can be dated which increases the chances of success with marginal, higher risk material. This improvement will eventually also be applicable to U-Pb dating. As well as allowing more material to be dated, this also allows for the routine replication of measurements where open-system behavior is a suspected possibility, thereby enabling a more a widespread investigation of systems known to behave often as open systems, for example, shell, corraline speleothem overgrowths and coral.

U-Th dating of suitable carbonates, such as clean speleothems, has reached a level of maturity where it can be routinely applied and with great precision. Age errors on clean material should generally be less than 1% over the last glacial-interglacial cycle even at the 2-sigma level. Research into improving analytical precision as a means of pushing the age limit of the technique further back in time is ongoing. However, these gains are likely to be limited to high-quality speleothem material, as limitations of the samples themselves affect achievable accuracy in most other cases. The ability to effectively U-Th date progressively smaller samples will increase the chances of success with 'dirty' samples, as milligram-scale or smaller samples allow sub-millimeter domains of clean dateable calcite to be analysed. As sample size demands continue to fall, the possibility of phase-specific U–Th dating is further opening up, as recently demonstrated for bone collagen (Hercman, 2014).

U-Pb dating of young carbonates (under 2.5 million years), on the other hand, is a relatively new application and there is plenty of opportunity for improvement, e.g. working with material with lower (under ~1ug/g) U concentrations, gaining a better understanding of the common Pb distributions within samples, and handling samples with poorer U-Pb ratios. Improvements in measuring uranium isotopes, specifically the $^{234}U/^{238}U$ ratio will lead to

more precise U-Pb ages in the early- to mid-Quaternary. Modelling initial common Pb components to reduce the number of aliquots necessary for isochron ages and developing internal chronologies for U-Pb dated stalagmites, by imaging and counting annual layers themselves or a geochemical proxy of these, will open up the potential of this material as a palaeoclimate archive. One of the major aspirational goals for U-Pb is to develop the method to deal with smaller, less ideal samples where the age of this material is of great interest. This is good news for archaeology and such development needs to take place with the close collaboration of archaeologists.

In our experience, the best U-Th and U-Pb ages are achieved from samples where careful fieldwork was undertaken in close collaboration with the archaeologists or palaeoanthropologists, so that the best material within the context of that site was collected. Samples for dating should always be taken by a specialist but we acknowledge this is not always feasible or practical. We stress that all dating can be improved by creating a feedback loop where laboratory observations of samples which were successfully dated are transferred back into the field, so that further samples can be collected with 'new/informed eyes'.

As with all geochronological technologies applicable to archaeology, U-Th and U-Pb dating has seen remarkable improvements over the last decades, primarily from advances in mass spectrometry technology, meaning that today large volumes of precise ages can be routinely and quickly obtained from as little as a few milligrams of sample material. Further development of U-Th dating of less traditional material such as straw stalactites, calcrete, eggshell, bone collagen and fish otoliths will expand the ability to date sediments both within and outside the cave environment. New applications for both U–Th and U–Pb will continue to come to light in the coming years – for archaeologists a strong message should be that if a material or some sub phase within it seems likely to have behaved as a closed system then there is no harm in approaching a U-series specialist and asking if dating is possible. We see a major contribution of U-series dating in the future will be to close the gap between the reaches of the U-Th and U-Pb chronometers, so that any material from a few hundreds of years old to several million can be easily and precisely dated.

5. Acknowledgements

We would particularly like to thank our colleagues at the University of Melbourne: Jon Woodhead, Russell Drysdale, Roland Maas, Alan Grieg, Bence Paul, Petra Bajo, Helen Green and Warrick Joe, as well as the many other people who have provided us with samples, field and laboratory support, discussion and encouragement. We also thank the editors for the

invitation to contribute to this special issue, the two reviewers for their thorough and thoughtful comments and Avonne Pickering for her sharp editorial eye.

Material	Open/Closed system	Typical U content (µg/g)*	Detrital Th content	Key references
Stalagmite	Almost always closed but can suffer from U loss if aragonite present at time of formation	0.01 to 10	Usually low to very low but can be high in some settings	Bar-Matthews et al., 2010
Flowstone	Almost always closed unless obviously dissolved but can suffer from U loss if aragonite present	0.01 to 10	Highly variable. Often high in archaeological settings but good material can be found with care	Marean et al., 2007
>500 ka flowstone, stalagmite, coral, calcrete	Almost always closed if well preserved	1.0-1.5	n/a Pb content ideally very low, average 0.02 µg/g	Pickering & Kramers, 2010; Pickering et al., 2011a,b
Thin-coat speleothem overgrowths of rock art, artifacts bone etc	Likely to be closed but not reliably so	0.01 to 10	Variable but often low	Taçon et al., 2012 Pike et al., 2012 Aubert et al, 2014
Buried soda straw stalactites	Closed if well preserved	0.01 to 10	Moderate to low	St Pierre et al., 2009; 2012; 2013
Coral	Often closed system	2-5	Typically very low	Kirch & Sharp, 2005 Burley at al., 2012
Tufa	Often closed system	0.5-2	Moderate to high	Auler et al, 2004
Calcrete	Usually closed system where well indurated	0.1 to 2	Usually moderate to high but clean enough material can be often found with care	Candy & Black, 2009, R. Pickering, unpublished data
Eggshell	Often closed system	0.01 to 0.5	Moderate to high, but can be reduced with careful pre-cleaning	Miller et al., 1999
Mollusc	Usually open system but can sometimes be dated where U uptake has been extremely low	0.01 to 5	Usually low after removal of outer sections of shell	Arslanov et al., 2002
Lacustrine limestone	May behave as open system	~1	High	Carey et al, 2011
Bone/teeth	Always open-system, can sometimes be partially dated using diffusion modeling. Collagen dating is a possibility.		Locally high at outer edges, low otherwise	Grün et al, 2010; 2014 Hercman, 2014

Table 1. A summary table of the most common types of material dated with U-Th and U-Pb, including typical U concentrations, detrital Th contents and the relevant key references. Closed system behavior is absolutely essential for both U-Th and U-Pb dating and where open system behavior is a possibility it should be checked by conducting multiple analyses (or by isochron dating as for U-Pb). High detrital Th content or common Pb content is undesirable – it can be corrected for but degrades age precision.

1 *micrograms/gram equivalent to parts per million (ppm). Most U-Th research groups can
2 now date samples containing 0.01 μg of U, i.e. 0.01 g of material if it contains 1 μg/g U.
3

References

Richards, D., Dorale, J., 2003. Uranium-series chronology and environmental applications of speleothems. Reviews in Mineralogy and Geochemistry 52.

Li, W.-X., Lundberg, J., Dickin, A., Ford, D., Schwarcz, H.P., McNutt, R., Williams, D., 1989. High-precision mass-spectrometric uranium-series dating of cave deposits and implications for palaeoclimate studies. Nature 339, 534–536.

Edwards, L.R., Chen, J.H., Wasserburg, G.J., 1987. 238U-234U-230Th-232Th systematics and the precise measurement of time over the past 500,000 years, Earth and Planetary Science Letters 81, 175-192.

Grenthe, I., Drożdżyński, J., Fujino, T., Buck, E.C., Albrecht-Schmitt, T.E., Wolf, S.F., 2011. The Chemistry of the Actinide and Transactinide Elements 4th ed., Springer.

Walker, M., 2005. Quaternary Dating Methods, John Wiley, Chichester & New York.

Andersen, M.B., Stirling, C.H., Potter, E.-K., Halliday, A.N., Blake, S.G., McCulloch, M.T., Ayling, B.F., O'Leary, M., 2008. High-precision U-series measurements of more than 500,000 year old fossil corals, Earth and Planetary Science Letters 265, 229-245.

Cheng, H., Lawrence Edwards, R., Shen, C.C., Polyak, V.J., Asmerom, Y., Woodhead, J., Hellstrom, J., Wang, Y., Kong, X., Spötl, C., Wang, X., Calvin Alexander, E., 2013. Improvements in 230Th dating, 230Th and 234U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry, Earth and Planetary Science Letters 371-372, 82-91.

Zhao, J.-x., Yu, K.-f., Feng, Y.-x., 2009. High-precision 238U–234U–230Th disequilibrium dating of the recent past: a review, Quaternary Geochronology 4, 423-433.

Patterson, C., 1956. Age of meteorites and the earth, Geochimica et Cosmochimica Acta 10, 230-237.

Miller, G.H., Magee, J.W., Johnson, B.J., Fogel, M.L., Spooner, N.A., McCulloch, M.T., Ayliffe, L.K., 1999. Pleistocene extinction of Genyornis newtoni: Human impact on Australian megafauna, Science 283, 205-208.

Pike, A.W.G., Hedges, R.E.M., Van Calsteren, P., 2002. U- series dating of bone using the diffusion- adsorption model, Geochimica et Cosmochimica Acta 66, 4273-4286.

Hedges, R.E.M., Millard, A.R., 1995. Bones and Groundwater: Towards the Modelling of Diagenetic Processes, Journal of Archaeological Science 22, 155-164.

Schwarcz, H.P., 1989. Uranium series dating of Quaternary deposits, Quaternary International 1, 7-17.

Schwarcz, H.P., 1992a. Uranium-Series Dating and the Origin of Modern Man, Philosophical Transactions: Biological Sciences 337, 131-137.

Schwarcz, H.P., 2002. Chronometric dating in archaeology: A review, Accounts of Chemical Research 35, 637-643.

Schwarcz, H.P., Rink, W.J., 2001. Dating Methods for Sediments of Caves and Rockshelters, Geoarchaeology - An International Journal 16, 355-371.

Schwarcz, H.P., 1992b. Uranium series dating in paleoanthropology, Evolutionary Anthropology 1, 56-62.
Schwarcz, H.P., 1997. Uranium series dating, in: Taylor, R.E., Aitken, M.J. (Eds.), Chronometric Dating in Archaeology, Plenum Press, New York, pp. 159-182.
Smart, P.L., 1991. Uranium series dating, Quaternary dating methods - a user's guide, 45-83.
Latham, A.G., 2001. Uranium-Series Dating in: Brothwell, D.R., Pollard A.M. (Ed.), Handbook of Archaeological Sciences. , Wiley Interscience, Chichester and New York, pp. 63-72.
Pike, A.W.G., Pettitt, P.B., 2003. U-series dating and Human Evolution, in: Bourdon, B., Turner, S., Henderson, G.M., Lundstrom, C.C. (Ed.), U-series geochemistry: Reviews in Mineralogy and Geochemistry pp. 607-630.
Ivanovich, M., Harmon, R. S., 1992. Uranium-series disequilibrium: applications to earth, marine and environmental science. , Clarendon Press, Oxford, p. 910.
Bourdon, B., Henderson, G.M., Lundstrom, C.C., Turner, S., 2003. Introduction of U-series geochemistry., in: Rosso, J.J., Ribbe, P.H. (Ed.), Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington.
Rasbury, E.T., Cole, J.M., 2009. Directly dating geologic events: U-Pb dating of carbonates, Reviews of Geophysics 47.
Woodhead, J., Pickering, R., 2012. Beyond 500ka: Progress and prospects in the U-Pb chronology of speleothems, and their application to studies in palaeoclimate, human evolution, biodiversity and tectonics, Chemical Geology 322-323, 290-299.
Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., Asmerom, Y., 2000. The half-lives of uranium-234 and thorium-230, Chemical Geology 169, 17-33.
Simpson, J.J., Grün, R., 1998. Non-destructive gamma spectrometric U-series dating, Quaternary Science Reviews 17, 1009-1022.
Eggins, S.M., Grün, R., McCulloch, M.T., Pike, A.W.G., Chappell, J., Kinsley, L., Mortimer, G., Shelley, M., Murray-Wallace, C.V., Spötl, C., Taylor, L., 2005. In situ U-series dating by laser-ablation multi-collector ICPMS: New prospects for Quaternary geochronology, Quaternary Science Reviews 24, 2523-2538.
Grün, R., Eggins, S., Kinsley, L., Moseley, H., Sambridge, M., 2014. Laser ablation U-series analysis of fossil bones and teeth, Palaeogeography, Palaeoclimatology, Palaeoecology 416, 150-167.
Balter, V., Blichert-Toft, J., Braga, J., Telouk, P., Thackeray, F., Albarede, F., 2008. U-Pb dating of fossil enamel from the Swartkrans Pleistocene hominid site, South Africa, Earth and Planetary Science Letters 267, 236-246.
Hercman, H., 2014. U-series dating of collagen - A step toward direct U-series dating of fossil bone?, Quaternary International 339-340, 4-10.
Kaufman, A., Broecker, W.S., Ku, T.L., Thurber, D.L., 1971. The status of U-series methods of mollusk dating, Geochimica et Cosmochimica Acta 35, 1155-1183.
McLaren, S.J., Rowe, P.J., 1996. The reliability of uranium-series mollusc dates from the western Mediterranean basin, Quaternary Science Reviews 15, 709-717.
Arslanov, K.A., Tertychny, N.I., Kuznetsov, V.Y., Chernov, S.B., Lokshin, N.Y., Gerasimova, S.A., Maksimov, F.E., Dodonov, A.E., 2002. 230Th/U and 14C dating of mollusc shells from the coasts of the Caspian, Barents, White and Black Seas, Geochronometria: Journal on Methods & Applications of Absolute Chronology 21, 49-56.
Faure, G., 1977. Principles of isotope geology, J. Wiley and Sons, New York.
Goldstein, S.J., Stirling, C.H., 2003. Techniques for measuring uranium-series nuclides: 1992-2002, in: Bourdon, B., Turner, S., Henderson, G.M., Lundstrom, C.C. (Ed.), Uranium-series geochemsitry: Reviews in Mineralogy and Geochemistry, Geochemical Society, pp. 23-57.

Duval, M., Aubert, M., Hellstrom, J., Grün, R., 2011. High resolution LA-ICP-MS mapping of U and Th isotopes in an early Pleistocene equid tooth from Fuente Nueva-3 (Orce, Andalusia, Spain), Quaternary Geochronology 6, 458-467.
Drysdale, R.N., Paul, B.T., Hellstrom, J.C., Couchoud, I., Greig, A., Bajo, P., Zanchetta, G., Isola, I., Spötl, C., Baneschi, I., Regattieri, E., Woodhead, J.D., 2012. Precise microsampling of poorly laminated speleothems for U-series dating, Quaternary Geochronology 14, 38-47.
Spötl, C., Mattey, D., 2012. Scientific drilling of speleothems - a technical note, International Journal of Speleology 41, 29-34.
Schwarcz, H.P., Blackwell, B., Goldberg, P., Marks, A.E., 1979. Uranium series dating of travertine from archaeological sites, Nahal Zin, Israel [10], Nature 277, 558-560.
Blackwell, B., Schwarcz, H.P., Debenath, A., 1983. Absolute dating of hominids and palaeolithic artifacts of the cave of La Chaise-de-Vouthon (Charente), France, Journal of Archaeological Science 10, 493-513.
Marean, C.W., Bar-Matthews, M., Bernatchez, J., Fisher, E., Goldberg, P., Herries, A.I.R., Jacobs, Z., Jerardino, A., Karkanas, P., Minichillo, T., Nilssen, P.J., Thompson, E., Watts, I., Williams, H.M., 2007. Early human use of marine resources and pigment in South Africa during the Middle Pleistocene, Nature 449, 905-911.
Bar-Matthews, M., Marean, C.W., Jacobs, Z., Karkanas, P., Fisher, E.C., Herries, A.I.R., Brown, K., Williams, H.M., Bernatchez, J., Ayalon, A., Nilssen, P.J., 2010. A high resolution and continuous isotopic speleothem record of paleoclimate and paleoenvironment from 90 to 53 ka from Pinnacle Point on the south coast of South Africa, Quaternary Science Reviews 29, 2131-2145.
St Pierre, E., Zhao, J.x., Reed, E., 2009. Expanding the utility of Uranium-series dating of speleothems for archaeological and palaeontological applications, Journal of Archaeological Science 36, 1416-1423.
St Pierre, E., Zhao, J.-x., Feng, Y.-x., Reed, E., 2012. U-series dating of soda straw stalactites from excavated deposits: method development and application to Blanche Cave, Naracoorte, South Australia, Journal of Archaeological Science 39, 922-930.
St Pierre, E.J., Westaway, K.E., Zhao, J.X., Gagan, M.K., Lentfer, C., Due, R.A., Morwood, M.J., Hantoro, W.S., Djubiantono, T., Suwargadi, B.W., 2013. Preliminary U-series and Thermoluminescence dating of excavated deposits in Liang Bua sub-chamber, Flores, Indonesia, Journal of Archaeological Science 40, 148-155.
Curnoe, D., Xueping, J., Herries, A.I.R., Kanning, B., Taçon, P.S.C., Zhende, B., Fink, D., Yunsheng, Z., Hellstrom, J., Yun, L., Cassis, G., Bing, S., Wroe, S., Shi, H., Parr, W.C.H., Shengmin, H., Rogers, N., 2012. Human remains from the pleistocene-holocene transition of Southwest China suggest a complex evolutionary history for East Asians, PLoS ONE 7.
Pike, A.W.G., Hoffmann, D.L., García-Diez, M., Pettitt, P.B., Alcolea, J., De Balbín, R., González-Sainz, C., De Las Heras, C., Lasheras, J.A., Montes, R., Zilhão, J., 2012. U-series dating of paleolithic art in 11 caves in Spain, Science 336, 1409-1413.
Aubert, M., Brumm, A., Ramli, M., Sutikna, T., Saptomo, E.W., Hakim, B., Morwood, M.J., van den Bergh, G.D., Kinsley, L., Dosseto, A., 2014. Pleistocene cave art from Sulawesi, Indonesia, Nature 514, 223-227.
Prideaux, G.J., Roberts, R.G., Megirian, D., Westaway, K.E., Hellstrom, J.C., Olley, J.M., 2007. Mammalian responses to Pleistocene climate change in southeastern Australia, Geology 35, 33-36.
Pons-Branchu, E., Bourrillon, R., Conkey, M.W., Fontugne, M., Fritz, C., Gárate, D., Quiles, A., Rivero, O., Sauvet, G., Tosello, G., Valladas, H., White, R., 2014. Uranium-series dating of carbonate formations overlying Paleolithic art: Interest and limitations, Bulletin de la Societe Prehistorique Francaise 111, 211-224.

Taçon, P.S.C., Aubert, M., Gang, L., Decong, Y., Hong, L., May, S.K., Fallon, S., Xueping, J., Curnoe, D., Herries, A.I.R., 2012. Uranium-series age estimates for rock art in southwest China, Journal of Archaeological Science 39, 492-499.
Sharp, W.D., Kahn, J.G., Polito, C.M., Kirch, P.V., 2010. Rapid evolution of ritual architecture in central Polynesia indicated by precise 230Th/U coral dating, Proceedings of the National Academy of Sciences of the United States of America 107, 13234-13239.
Burley, D., Weisler, M.I., Zhao, J.-x., 2012. High Precision U/Th Dating of First Polynesian Settlement, PLoS ONE 7, e48769.
Allard, G., Roy, M., Ghaleb, B., Richard, P.J.H., Larouche, A.C., Veillette, J.J., Parent, M., 2012. Constraining the age of the last interglacial-glacial transition in the Hudson Bay lowlands (Canada) using U-Th dating of buried wood, Quaternary Geochronology 7, 37-47.
Braun, D.R., Levin, N.E., Stynder, D., Herries, A.I.R., Archer, W., Forrest, F., Roberts, D.L., Bishop, L.C., Matthews, T., Lehmann, S.B., Pickering, R., Fitzsimmons, K.E., 2013. Mid-Pleistocene Hominin occupation at Elandsfontein, Western Cape, South Africa, Quaternary Science Reviews 82, 145-166.
Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P., Taylor, E., 2006. U-Pb geochronology of speleothems by MC-ICPMS, Quaternary Geochronology 1, 208-221.
Woodhead, J., Hellstrom, J., Pickering, R., Drysdale, R., Paul, B., Bajo, P., 2012. U and Pb variability in older speleothems and strategies for their chronology, Quaternary Geochronology 14, 105-113.
Pickering, R., Kramers, J.D., Partridge, T., Kodolanyi, J., Pettke, T., 2010. U–Pb dating of calcite–aragonite layers in speleothems from hominin sites in South Africa by MC-ICP-MS, Quaternary Geochronology 5, 544-558.
de Ruiter, D.J., Pickering, R., Steininger, C.M., Kramers, J.D., Hancox, P.J., Churchill, S.E., Berger, L.R., Backwell, L., 2009. New Australopithecus robustus fossils and associated U-Pb dates from Cooper's Cave (Gauteng, South Africa), Journal Of Human Evolution 56, 497-513.
Pickering, R., Kramers, J.D., 2010. A re-appraisal of the stratigraphy and new U-Pb dates at the Sterkfontein hominin site, South Africa, Journal Of Human Evolution 59, 70-86.
Pickering, R., Kramers, J.D., Hancox, P.J., de Ruiter, D.J., Woodhead, J.D., 2011a. Contemporary flowstone development links early hominin bearing cave deposits in South Africa, Earth and Planetary Science Letters 306, 23-32.
Pickering, R., Dirks, P.H.G.M., Jinnah, Z., de Ruiter, D.J., Churchill, S.E., Herries, A.I.R., Woodhead, J.D., Hellstrom, J.C., Berger, L.R., 2011b. Australopithecus sediba at 1.977 Ma and Implications for the Origins of the Genus Homo, Science 333, 1421-1423.
Walker, J., Cliff, R.A., Latham, A.G., 2006. U-Pb isotopic age of the StW 573 hominid from Sterkfontein, South Africa, Science 314, 1592-1594.
Pickering, R., in press. U-Pb dating small buried stalagmites from Wonderwerk Cave, South Africa: a new chronometer for Earlier Stone Age cave deposits, African Archaeological Review accepted May 2014.
Pickering, R., Jacobs, Z., Herries, A.I.R., Karkanas, P., Bar-Matthews, M., Woodhead, J.D., Kappen, P., Fisher, E., Marean, C.W., 2013. Paleoanthropologically Significant South African Sea Caves dated to 1.0 Million Years using a combination of U-Pb, TT-OSL and palaeomagnetism, Quaternary Science Reviews 65, 39-52.
Sniderman, K., Woodhead, J., Hellstrom, J., Elith, J., Porch, N., 2014. Latest Miocene-Early Pliocene vegetation and climate of the Nullarbor Plain: New insights from fossil pollen records of U-Pb dated speleothems. , Climate Change: The Karst Record. 7th International Conference, Melbourne, Australia.

Bajo, P., Drysdale, R., Woodhead, J., Hellstrom, J., Zanchetta, G., 2012. High-resolution U-Pb dating of an Early Pleistocene stalagmite from Corchia Cave (central Italy), Quaternary Geochronology 14, 5-17.

Walker, M., 2005. Quaternary Dating Methods, John Wiley, Chichester & New York.
Schwarcz, H.P., Latham, A.G., 1989. Dirty calcites 1. Uranium-series dating of contaminated calcite using leachates alone, Chemical Geology 80, 35-43.
Ku, T.-L., Liang, Z.-C., 1984. The dating of impure carbonates with decay-series isotopes, Nuclear Instruments and Methods in Physics Research 223, 563-571.
Bischoff, J.L., Fitzpatrick, J.A., 1991. U-series dating of impure carbonates: An isochron technique using total-sample dissolution, Geochimica et Cosmochimica Acta 55, 543-554.
Richards, D.A., Bottrell, S.H., Cliff, R.A., Strohle, K., Rowe, P.J., 1998. U-Pb dating of a speleothem of Quaternary age, Geochimica Et Cosmochimica Acta 62, 3683-3688.
Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P., Taylor, E., 2006. U-Pb geochronology of speleothems by MC-ICPMS, Quaternary Geochronology 1, 208-221.
Pickering, R., Kramers, J.D., Partridge, T., Kodolanyi, J., Pettke, T., 2010. U–Pb dating of calcite–aragonite layers in speleothems from hominin sites in South Africa by MC-ICP-MS, Quaternary Geochronology 5, 544-558.
Bajo, P., Drysdale, R., Woodhead, J., Hellstrom, J., Zanchetta, G., 2012. High-resolution U-Pb dating of an Early Pleistocene stalagmite from Corchia Cave (central Italy), Quaternary Geochronology 14, 5-17.
Walker, J., Cliff, R.A., Latham, A.G., 2006. U-Pb isotopic age of the StW 573 hominid from Sterkfontein, South Africa, Science 314, 1592-1594.
Bruxelles, L., Clarke, R.J., Maire, R., Ortega, R., Stratford, D., 2014. Stratigraphic analysis of the Sterkfontein StW 573 Australopithecus skeleton and implications for its age, Journal of Human Evolution 70, 36-48.
Kirch, P.V., Sharp, W.D., 2005. Coral 230Th Dating of the Imposition of a Ritual Control Hierarchy in Precontact Hawaii, Science 307, 102-104.
Candy, I., Black, S., 2009. The timing of Quaternary calcrete development in semi-arid southeast Spain: Investigating the role of climate on calcrete genesis, Sedimentary Geology 218, 6-15.
Carey, S.P., Camens, A.B., Cupper, M.L., Grün, R., Hellstrom, J.C., McKnight, S.W., McLennan, I., Pickering, D.A., Trusler, P., Aubert, M., 2011. A diverse Pleistocene marsupial trackway assemblage from the Victorian Volcanic Plains, Australia, Quaternary Science Reviews 30, 591-610.
Grün, R., Aubert, M., Hellstrom, J., Duval, M., 2010. The challenge of direct dating old human fossils, Quaternary International 223–224, 87-93.