

# 1 **Recent advances and future prospects of the U-Th and U-** 2 **Pb chronometers applicable to archaeology**

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18 *Keywords:*

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

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21 *Highlights:*

22 • We review recent use of the uranium series (U-Th and U-Pb) chronometer applicable to  
23 archaeology

24 • We provide an overview of the method itself, as well as how samples are prepared and  
25 analysed

26 • We have compiled a detailed table listing materials suitable for both U-Th and U-Pb  
27 dating

28 • We review published examples of successful U-Th and U-Pb dating applied to  
29 archaeology

30 • We provide our opinion of where the future of this field lies and where likely  
31 developments will take place

32

## 1 **Abstract**

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

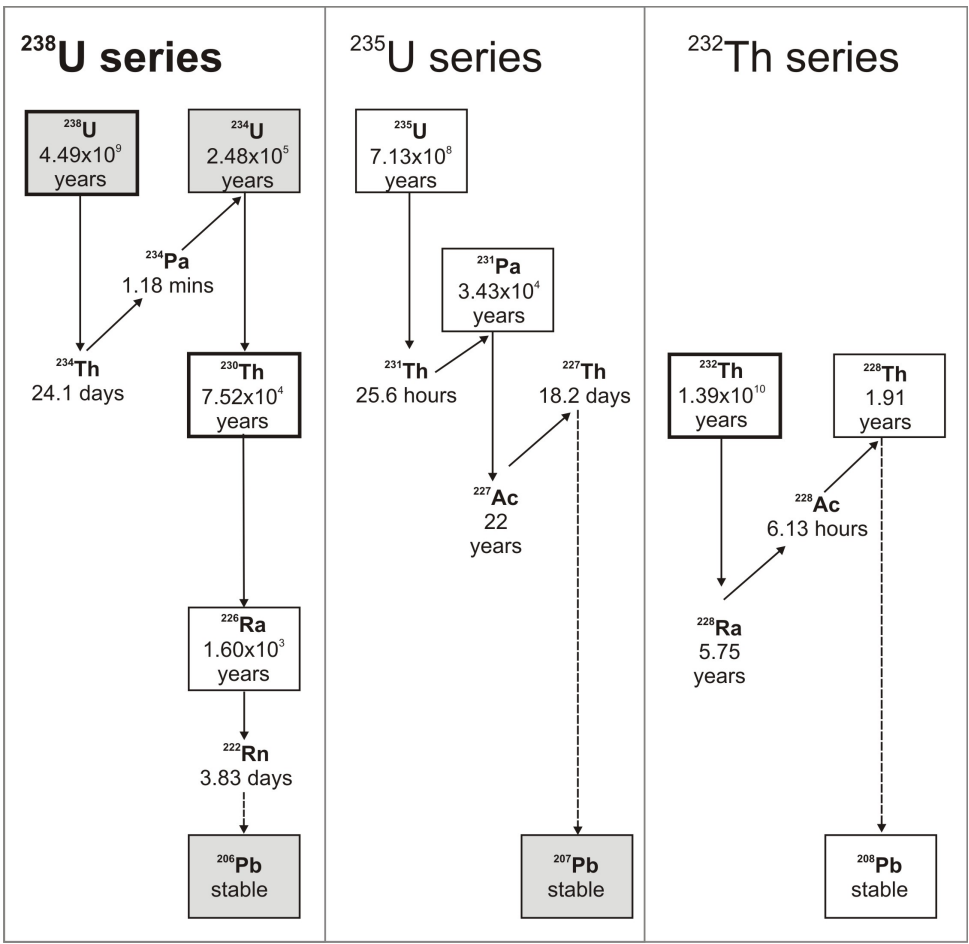
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## 24 **1. Introduction**

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

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

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



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

1

2 Here we will focus on the two techniques with the greatest utility,  $^{238}\text{U}$ – $^{234}\text{U}$ – $^{230}\text{Th}$  (U–Th)  
3 and  $^{238}\text{U}$ – $^{234}\text{U}$ – $^{230}\text{Th}$ – $^{206}\text{Pb}$ / $^{235}\text{U}$ – $^{231}\text{Pa}$ – $^{207}\text{Pb}$  (U–Pb). In terms of age range, U–Th dating is  
4 limited by the half life of  $^{230}\text{Th}$  which is 75,584 years (Cheng et al, 2013), so instead of  
5 accumulating indefinitely (as is the case for the U–Pb system) it approaches secular  
6 equilibrium with its parent isotope  $^{234}\text{U}$ , whereby it decays as fast as it is produced and gives  
7 the U–Th dating system an effective upper age limit of somewhat over 500,000 years.  
8 Advances in mass spectrometry mean that material as old as 600–650 ka can now be dated  
9 (Andersen, et al., 2008, Cheng, et al., 2013), with the other end of the datable age spectrum as  
10 recent as a few decades (Zhao, et al., 2009). The U-series decay chain continues on beyond  
11  $^{230}\text{Th}$  and ends in stable  $^{206}\text{Pb}$  where it accumulates indefinitely meaning that U–Pb dating is  
12 suitable for materials belonging to long geological time scales, including the age of the Earth  
13 itself (Patterson, 1956).

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

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

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

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

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

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

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

28 The most relevant process liable to fractionate isotopes in the U-series decay chain is the  
29 significant difference in solubility between U and Th, as U is highly soluble in natural waters  
30 and Th is not. As such cave drip waters contain U but are essentially devoid of Th, meaning  
31 that speleothems (typically stalagmites and flowstones) forming from these waters will inherit  
32 up to several parts per million of U and negligible amounts of Th. The subsequent *in situ*  
33 decay of  $^{238}\text{U}$  to  $^{234}\text{U}$  (with a half-life of 245,620 years; Cheng et al, 2013) and from  $^{234}\text{U}$  to  
34  $^{230}\text{Th}$  (75,584 years) can be used to date the material by measuring the present levels of all

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

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

17 In the U-Pb dating scheme, radiogenic (produced *in situ*)  $^{206}\text{Pb}$  can be completely obscured  
18 by common (initial)  $^{206}\text{Pb}$ , meaning that age determinations are usually undertaken by  
19 multiple sample analysis and isochron construction (Richards, et al., 1998, Woodhead, et al.,  
20 2006). As with U–Th, an important consideration in U-Pb dating of speleothem material is the  
21 initial  $^{234}\text{U}/^{238}\text{U}$  ratio, which is measured directly where possible but must usually be  
22 estimated for samples of more than about 2 Ma (Richards, et al., 1998, Woodhead, et al.,  
23 2006, Pickering, et al., 2010, Bajo, et al., 2012). Without taking the initial excess of  $^{234}\text{U}$  into  
24 account, ages can be greatly over-estimated, and where initial  $^{234}\text{U}/^{238}\text{U}$  cannot be directly  
25 determined it can lead to additional uncertainties of hundreds of thousands of years.

26

## 27 2.1. Age calculations

28 Calculation of a U–Th age requires accurate measurement of the ratios  $^{230}\text{Th}/^{238}\text{U}$  and  
29  $^{234}\text{U}/^{238}\text{U}$ , usually expressed as activity ratios, that is where secular equilibrium would be a  
30 ratio of 1 (Figure 2).

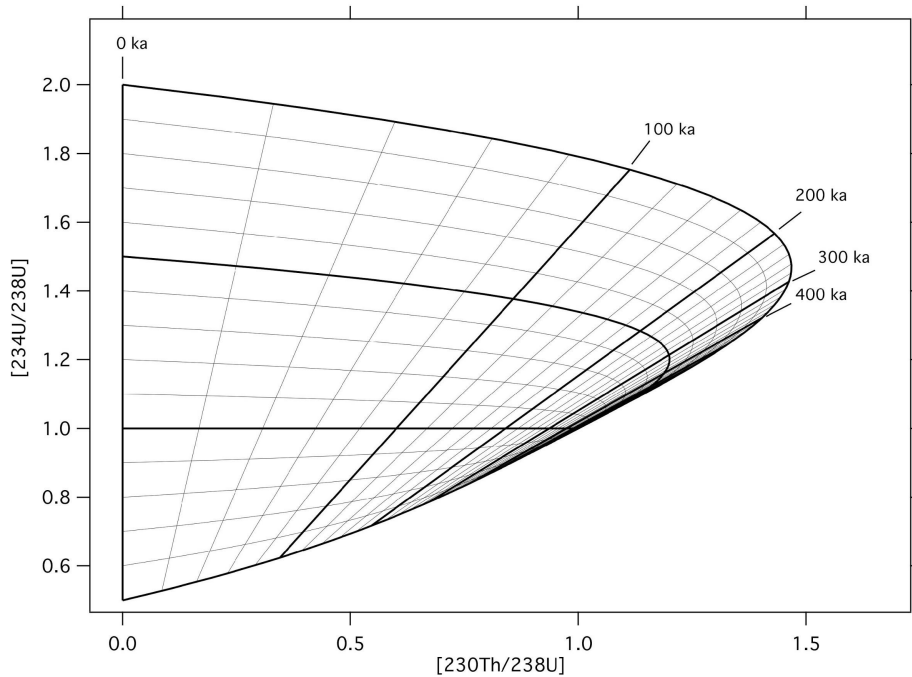
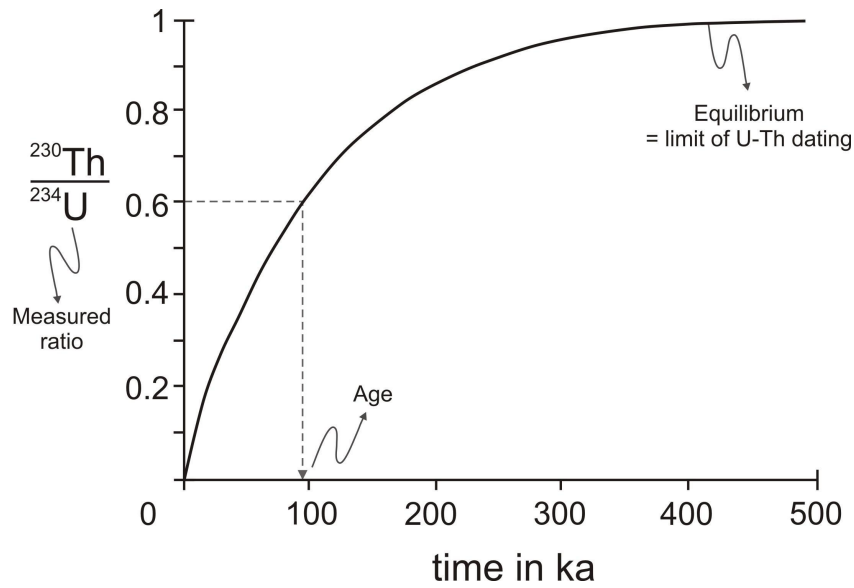


Figure 2. The ratio of the activity of  $^{230}\text{Th}$  to that of its parent isotope  $^{234}\text{U}$  as a function of time (top). If the initial  $^{230}\text{Th}/^{234}\text{U}$  ratio was zero, then age could be read from this chart using the present, measured  $^{230}\text{Th}/^{234}\text{U}$  ratio. As the  $^{230}\text{Th}/^{234}\text{U}$  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 initial  $^{234}\text{U}/^{238}\text{U}$ . Samples form at the left of the diagram with zero  $^{230}\text{Th}/^{238}\text{U}$  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  $^{232}\text{Th}/^{238}\text{U}$  to monitor and correct for the extent of any detrital contamination. These ratios were once calculated by direct measurement of radioactivity

1 using alpha spectrometry (Ivanovich, M., Harmon, R. S., 1992) but for the last 20 years have  
2 generally been measured using a mass spectrometer – at first by thermal ionization mass  
3 spectrometry (TIMS; Li et al, 1989). This has now been replaced by the faster and more  
4 efficient (multi-collector) inductively-coupled plasma mass spectrometry, (MC)-ICP-MS  
5 (Goldstein and Stirling, 2003). This technique allows measurement of the necessary ratios  
6 from as little as one billionth of a gram of U, which typically corresponds to between a  
7 fraction of a milligram and a few hundred milligrams of the material being dated (Hellstrom,  
8 2003; Pike et al 2012). U–Pb dating of archaeological materials requires accurate  
9 measurement of the ratios  $^{206}\text{Pb}/^{238}\text{U}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{234}\text{U}/^{238}\text{U}$  and is analytically more  
10 difficult than U–Th. Some laboratories still use TIMS for the Pb measurements although MC-  
11 ICP-MS allows much greater sample throughput – in either case, sample size requirements are  
12 up to 100 times greater than for U-Th .

13

## 14 2.2. Accuracy and precision of U-Th and U-Pb ages

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

32

## 33 2.3. Material suitable to U-Th and U-Pb dating

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

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

8 [insert Table 1]

9 Table 1. A summary table of the most common types of material dated with U-Th and U-Pb,  
10 including typical U concentrations, detrital Th contents and the relevant key references.  
11 Closed system behavior is absolutely essential for U-Th and U-Pb dating and where open  
12 system behavior is a possibility it should be checked by conducting multiple analyses (or by  
13 isochron dating as for U-Pb). High detrital Th content or common Pb content is undesirable –  
14 it can be corrected for but degrades age precision.  
15

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

27 Materials of greater interest to archaeologists, such as fossil bones, teeth, and shell, are  
28 usually inherently unsuitable for U-series dating because these organic materials are subject to  
29 post-mortem open-system behavior. Uranium and to a lesser extent thorium isotopes are  
30 mobile, and their uptake and loss needs to be modeled (Pike, et al., 2002, Hedges and Millard,  
31 1995, Pike and Pettitt, 2003). One possibility is to use *in situ* laser ablation, whereby, in some  
32 cases, U and Th isotopes can be measured directly from a sample surface to create profiles  
33 along sections through material such as bones, teeth, and possibly molluscs to map out the  
34 patterns of U migration (Eggins, et al., 2005, Grün, et al., 2014). This approach has also been  
35 attempted using the U-Pb system on fossil tooth enamel from the early human (hominin)  
36 bearing cave site of Swartkrans in South Africa (Balter, et al., 2008). Again, the problem is

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

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

#### 11 2.4. Analytical techniques and dating method

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

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

1 isotope ratios can be continuously profiled along a sample, which is especially useful when  
2 trying to date bones, teeth or shell (Duval, et al., 2011). Laser-ablation dating has an  
3 advantage of speed and of being generally less invasive, but is considerably less accurate than  
4 microsampling by drilling or milling where for similar uranium content samples of less than  
5 100 µg can often be used (Drysdale, et al., 2012, Spötl and Matthey, 2012).

6

## 7 2.5. Reporting U-Th and U-Pb ages

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

14

## 15 **3. Major achievements of U-Th and U-Pb dating**

### 16 3.1. U-Th dating examples

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

25

#### 26 *Dating early modern human occupation sites in South Africa*

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

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*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  $^{230}\text{Th}/^{232}\text{Th}$  activity ( $0.82 \pm 0.20$ ), which was used to produce a final corrected absolute age of  $7.8 \pm 0.5$  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

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

13

#### 14 *Dating coral associated with Polynesian settlements*

15 An elegant example of the utility of high precision U-Th ages is the work by Sharp, et al.  
16 (2010) who investigated that development and timing of building elaborate Polynesian  
17 temples (marae) on the island of Mo’orea in the Society Islands, near Tahiti, by U-Th dating  
18 of corals used as architectural elements (facing veneers, cut-and-dressed blocks, and  
19 offerings). While the coral from some of the wetter inland sites was shown to suffer from  
20 diagenesis, coral from 19 inland and 15 coastal marae produced reproducible ages for each  
21 site with a mean  $2\sigma$  uncertainty of an incredibly precise 9 years. The ages indicate that the  
22 temple architecture on Mo’orea Island developed rapidly over approximately 140 years from  
23 ca. AD1620-1769, with the largest coastal temples built prior to initial European contact in  
24 AD 1767. Sharp et al (2010) argue that this example demonstrates that the elaboration of  
25 ritual architecture in complex societies may be surprisingly rapid. A similar approach was  
26 used by Burley, et al. (2012) who used high precision U-Th ages on fossil coral to identify the  
27 founding event of the Kingdom of Tonga to  $2838 \pm 8$  years ago.

28

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

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

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

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

9

### 10 3.2. U-Pb dating examples

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

14

#### 15 *Dating the South African hominin cave sites*

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

1 Ma (Walker et al., 2006) and  $2.35 \pm 0.10$  Ma Pickering et al., 2010; Pickering and Kramers,  
2 2010) leading these authors to ascribe a coeval age for the fossil. Bruxelles, et al. (2014)  
3 present a detailed stratigraphic and geochemical study arguing that the flowstones in fact  
4 post-date the sediments surround the StW 573 and that fossil is considerably older. It is  
5 difficult to quantify the length of time between the deposition of the fossil and subsequent  
6 formation of the flowstones, but Bruxelles, et al. (2014) suggest several hundred thousand  
7 years. The error on the U-Pb ages of between 90 and 100 ka may well accommodate this.  
8 Ideally detailed stratigraphic work such as the Bruxelles, et al. (2014) study should be  
9 undertaken prior to any dating.

10

#### 11 *Dating buried speleothems in archaeological cave sites*

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

20

#### 21 *Dating past sea level high stands*

22 The caves sites at Pinnacle Point, mentioned earlier, are well known for their  
23 archaeological deposits but were thought to not preserve any material older than  $\sim 120$  ka.  
24 However, recent U-Pb dating of flowstone layers from two remnant cave deposits yielded  
25 ages of  $1.099 \pm 0.012$  to  $1.047 \pm 0.011$  Ma (Pickering, et al., 2013). The presence of these  
26 1.1-1.0 Ma deposits implies that older material in these coastal caves can be preserved and  
27 has survived multiple sea level highstands. This opens up the possibility for more deposits,  
28 from this region, some possibly archaeological, reaching back into the early to mid  
29 Pleistocene.

30

#### 31 *The frontiers of U-Pb dating*

32 Two exciting areas of development involving U-Pb dated speleothem samples are the  
33 extraction of pollen from speleothems as a palaeoenvironmental proxy (Sniderman, et al.,  
34 2014) and the progress in constructing U-Pb growth models for stalagmites (such as in Bajo,

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

#### 4 **4. Challenges, innovations and future gazing**

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

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

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

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

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

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

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

29

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3

1

Material	Open/Closed system	Typical U content ( $\mu\text{g/g}$ )*	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 $\mu\text{g/g}$	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 et 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

2

3

4 Table 1. A summary table of the most common types of material dated with U-Th and U-Pb,  
5 including typical U concentrations, detrital Th contents and the relevant key references.

6 Closed system behavior is absolutely essential for both U-Th and U-Pb dating and where  
7 open system behavior is a possibility it should be checked by conducting multiple analyses  
8 (or by isochron dating as for U-Pb). High detrital Th content or common Pb content is  
9 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  $\mu\text{g}$  of U, i.e. 0.01 g of material if it contains 1  $\mu\text{g/g}$  U.  
3

## 1   **References**

- 2
- 3   Richards, D., Dorale, J., 2003. Uranium-series chronology and environmental  
4   applications of speleothems. *Reviews in Mineralogy and Geochemistry* 52.
- 5
- 6   Li, W.-X., Lundberg, J., Dickin, A., Ford, D., Schwarcz, H.P., McNutt, R., Williams, D., 1989.  
7   High-precision mass-spectrometric uranium-series dating of cave deposits and  
8   implications for palaeoclimate studies. *Nature* 339, 534–536.
- 9
- 10
- 11
- 12   Edwards, L.R., Chen, J.H., Wasserburg, G.J., 1987.  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$ - $^{232}\text{Th}$  systematics and  
13   the precise measurement of time over the past 500,000 years, *Earth and Planetary Science*  
14   *Letters* 81, 175-192.
- 15   Grenthe, I., Drożdżyński, J., Fujino, T., Buck, E.C., Albrecht-Schmitt, T.E., Wolf, S.F., 2011.  
16   *The Chemistry of the Actinide and Transactinide Elements* 4th ed., Springer.
- 17   Walker, M., 2005. *Quaternary Dating Methods*, John Wiley, Chichester & New York.
- 18   Andersen, M.B., Stirling, C.H., Potter, E.-K., Halliday, A.N., Blake, S.G., McCulloch, M.T.,  
19   Ayling, B.F., O'Leary, M., 2008. High-precision U-series measurements of more than  
20   500,000 year old fossil corals, *Earth and Planetary Science Letters* 265, 229-245.
- 21   Cheng, H., Lawrence Edwards, R., Shen, C.C., Polyak, V.J., Asmerom, Y., Woodhead, J.,  
22   Hellstrom, J., Wang, Y., Kong, X., Spötl, C., Wang, X., Calvin Alexander, E., 2013.  
23   Improvements in  $^{230}\text{Th}$  dating,  $^{230}\text{Th}$  and  $^{234}\text{U}$  half-life values, and U-Th isotopic  
24   measurements by multi-collector inductively coupled plasma mass spectrometry, *Earth and*  
25   *Planetary Science Letters* 371-372, 82-91.
- 26   Zhao, J.-x., Yu, K.-f., Feng, Y.-x., 2009. High-precision  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  disequilibrium  
27   dating of the recent past: a review, *Quaternary Geochronology* 4, 423-433.
- 28   Patterson, C., 1956. Age of meteorites and the earth, *Geochimica et Cosmochimica Acta* 10,  
29   230-237.
- 30   Miller, G.H., Magee, J.W., Johnson, B.J., Fogel, M.L., Spooner, N.A., McCulloch, M.T.,  
31   Ayliffe, L.K., 1999. Pleistocene extinction of *Genyornis newtoni*: Human impact on  
32   Australian megafauna, *Science* 283, 205-208.
- 33   Pike, A.W.G., Hedges, R.E.M., Van Calsteren, P., 2002. U- series dating of bone using the  
34   diffusion- adsorption model, *Geochimica et Cosmochimica Acta* 66, 4273-4286.
- 35   Hedges, R.E.M., Millard, A.R., 1995. Bones and Groundwater: Towards the Modelling of  
36   Diagenetic Processes, *Journal of Archaeological Science* 22, 155-164.
- 37   Schwarcz, H.P., 1989. Uranium series dating of Quaternary deposits, *Quaternary International*  
38   1, 7-17.
- 39   Schwarcz, H.P., 1992a. Uranium-Series Dating and the Origin of Modern Man, *Philosophical*  
40   *Transactions: Biological Sciences* 337, 131-137.
- 41   Schwarcz, H.P., 2002. Chronometric dating in archaeology: A review, *Accounts of Chemical*  
42   *Research* 35, 637-643.
- 43   Schwarcz, H.P., Rink, W.J., 2001. Dating Methods for Sediments of Caves and Rockshelters,  
44   *Geoarchaeology - An International Journal* 16, 355-371.

- 1 Schwarcz, H.P., 1992b. Uranium series dating in paleoanthropology, *Evolutionary*  
2 *Anthropology* 1, 56-62.
- 3 Schwarcz, H.P., 1997. Uranium series dating, in: Taylor, R.E., Aitken, M.J. (Eds.),  
4 *Chronometric Dating in Archaeology*, Plenum Press, New York, pp. 159-182.
- 5 Smart, P.L., 1991. Uranium series dating, *Quaternary dating methods - a user's guide*, 45-83.
- 6 Latham, A.G., 2001. Uranium-Series Dating in: Brothwell, D.R., Pollard A.M. (Ed.), *Handbook*  
7 *of Archaeological Sciences.*, Wiley Interscience, Chichester and New York, pp. 63-72.
- 8 Pike, A.W.G., Pettitt, P.B., 2003. U-series dating and Human Evolution, in: Bourdon, B.,  
9 Turner, S., Henderson, G.M., Lundstrom, C.C. (Ed.), *U-series geochemistry: Reviews in*  
10 *Mineralogy and Geochemistry* pp. 607-630.
- 11 Ivanovich, M., Harmon, R. S., 1992. Uranium-series disequilibrium: applications to earth,  
12 marine and environmental science., Clarendon Press, Oxford, p. 910.
- 13 Bourdon, B., Henderson, G.M., Lundstrom, C.C., Turner, S., 2003. Introduction of U-series  
14 geochemistry., in: Rosso, J.J., Ribbe, P.H. (Ed.), *Reviews in Mineralogy and Geochemistry*,  
15 *Mineralogical Society of America*, Washington.
- 16 Rasbury, E.T., Cole, J.M., 2009. Directly dating geologic events: U-Pb dating of carbonates,  
17 *Reviews of Geophysics* 47.
- 18 Woodhead, J., Pickering, R., 2012. Beyond 500ka: Progress and prospects in the U-Pb  
19 chronology of speleothems, and their application to studies in palaeoclimate, human  
20 evolution, biodiversity and tectonics, *Chemical Geology* 322-323, 290-299.
- 21 Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., Asmerom, Y., 2000. The  
22 half-lives of uranium-234 and thorium-230, *Chemical Geology* 169, 17-33.
- 23 Simpson, J.J., Grün, R., 1998. Non-destructive gamma spectrometric U-series dating,  
24 *Quaternary Science Reviews* 17, 1009-1022.
- 25 Eggins, S.M., Grün, R., McCulloch, M.T., Pike, A.W.G., Chappell, J., Kinsley, L., Mortimer,  
26 G., Shelley, M., Murray-Wallace, C.V., Spötl, C., Taylor, L., 2005. In situ U-series dating by  
27 laser-ablation multi-collector ICPMS: New prospects for Quaternary geochronology,  
28 *Quaternary Science Reviews* 24, 2523-2538.
- 29 Grün, R., Eggins, S., Kinsley, L., Moseley, H., Sambridge, M., 2014. Laser ablation U-series  
30 analysis of fossil bones and teeth, *Palaeogeography, Palaeoclimatology, Palaeoecology* 416,  
31 150-167.
- 32 Balter, V., Blichert-Toft, J., Braga, J., Telouk, P., Thackeray, F., Albarede, F., 2008. U-Pb  
33 dating of fossil enamel from the Swartkrans Pleistocene hominid site, South Africa, *Earth and*  
34 *Planetary Science Letters* 267, 236-246.
- 35 Hercman, H., 2014. U-series dating of collagen - A step toward direct U-series dating of fossil  
36 bone?, *Quaternary International* 339-340, 4-10.
- 37 Kaufman, A., Broecker, W.S., Ku, T.L., Thurber, D.L., 1971. The status of U-series methods of  
38 mollusk dating, *Geochimica et Cosmochimica Acta* 35, 1155-1183.
- 39 McLaren, S.J., Rowe, P.J., 1996. The reliability of uranium-series mollusc dates from the  
40 western Mediterranean basin, *Quaternary Science Reviews* 15, 709-717.
- 41 Arslanov, K.A., Tertychny, N.I., Kuznetsov, V.Y., Chernov, S.B., Lokshin, N.Y., Gerasimova,  
42 S.A., Maksimov, F.E., Dodonov, A.E., 2002.  $^{230}\text{Th}/\text{U}$  and  $^{14}\text{C}$  dating of mollusc shells from  
43 the coasts of the Caspian, Barents, White and Black Seas, *Geochronometria: Journal on*  
44 *Methods & Applications of Absolute Chronology* 21, 49-56.
- 45 Faure, G., 1977. *Principles of isotope geology*, J. Wiley and Sons, New York.
- 46 Goldstein, S.J., Stirling, C.H., 2003. Techniques for measuring uranium-series nuclides: 1992-  
47 2002, in: Bourdon, B., Turner, S., Henderson, G.M., Lundstrom, C.C. (Ed.), *Uranium-series*  
48 *geochemistry: Reviews in Mineralogy and Geochemistry*, *Geochemical Society*, pp. 23-57.

1 Duval, M., Aubert, M., Hellstrom, J., Grün, R., 2011. High resolution LA-ICP-MS mapping of  
2 U and Th isotopes in an early Pleistocene equid tooth from Fuente Nueva-3 (Orce, Andalusia,  
3 Spain), *Quaternary Geochronology* 6, 458-467.

4 Drysdale, R.N., Paul, B.T., Hellstrom, J.C., Couchoud, I., Greig, A., Bajo, P., Zanchetta, G.,  
5 Isola, I., Spötl, C., Baneschi, I., Regattieri, E., Woodhead, J.D., 2012. Precise microsampling  
6 of poorly laminated speleothems for U-series dating, *Quaternary Geochronology* 14, 38-47.

7 Spötl, C., Mathey, D., 2012. Scientific drilling of speleothems - a technical note, *International*  
8 *Journal of Speleology* 41, 29-34.

9 Schwarcz, H.P., Blackwell, B., Goldberg, P., Marks, A.E., 1979. Uranium series dating of  
10 travertine from archaeological sites, Nahal Zin, Israel [10], *Nature* 277, 558-560.

11 Blackwell, B., Schwarcz, H.P., Debenath, A., 1983. Absolute dating of hominids and  
12 palaeolithic artifacts of the cave of La Chaise-de-Vouthon (Charente), France, *Journal of*  
13 *Archaeological Science* 10, 493-513.

14 Marean, C.W., Bar-Matthews, M., Bernatchez, J., Fisher, E., Goldberg, P., Herries, A.I.R.,  
15 Jacobs, Z., Jerardino, A., Karkanas, P., Minichillo, T., Nilssen, P.J., Thompson, E., Watts, I.,  
16 Williams, H.M., 2007. Early human use of marine resources and pigment in South Africa  
17 during the Middle Pleistocene, *Nature* 449, 905-911.

18 Bar-Matthews, M., Marean, C.W., Jacobs, Z., Karkanas, P., Fisher, E.C., Herries, A.I.R.,  
19 Brown, K., Williams, H.M., Bernatchez, J., Ayalon, A., Nilssen, P.J., 2010. A high resolution  
20 and continuous isotopic speleothem record of paleoclimate and paleoenvironment from 90 to  
21 53 ka from Pinnacle Point on the south coast of South Africa, *Quaternary Science Reviews*  
22 29, 2131-2145.

23 St Pierre, E., Zhao, J.x., Reed, E., 2009. Expanding the utility of Uranium-series dating of  
24 speleothems for archaeological and palaeontological applications, *Journal of Archaeological*  
25 *Science* 36, 1416-1423.

26 St Pierre, E., Zhao, J.-x., Feng, Y.-x., Reed, E., 2012. U-series dating of soda straw stalactites  
27 from excavated deposits: method development and application to Blanche Cave, Naracoorte,  
28 South Australia, *Journal of Archaeological Science* 39, 922-930.

29 St Pierre, E.J., Westaway, K.E., Zhao, J.X., Gagan, M.K., Lentfer, C., Due, R.A., Morwood,  
30 M.J., Hantoro, W.S., Djubiantono, T., Suwargadi, B.W., 2013. Preliminary U-series and  
31 Thermoluminescence dating of excavated deposits in Liang Bua sub-chamber, Flores,  
32 Indonesia, *Journal of Archaeological Science* 40, 148-155.

33 Curnoe, D., Xueping, J., Herries, A.I.R., Kanning, B., Taçon, P.S.C., Zhende, B., Fink, D.,  
34 Yunsheng, Z., Hellstrom, J., Yun, L., Cassis, G., Bing, S., Wroe, S., Shi, H., Parr, W.C.H.,  
35 Shengmin, H., Rogers, N., 2012. Human remains from the pleistocene-holocene transition of  
36 Southwest China suggest a complex evolutionary history for East Asians, *PLoS ONE* 7.

37 Pike, A.W.G., Hoffmann, D.L., García-Diez, M., Pettitt, P.B., Alcolea, J., De Balbín, R.,  
38 González-Sainz, C., De Las Heras, C., Lasheras, J.A., Montes, R., Zilhão, J., 2012. U-series  
39 dating of paleolithic art in 11 caves in Spain, *Science* 336, 1409-1413.

40 Aubert, M., Brumm, A., Ramli, M., Sutikna, T., Saptomo, E.W., Hakim, B., Morwood, M.J.,  
41 van den Bergh, G.D., Kinsley, L., Dosseto, A., 2014. Pleistocene cave art from Sulawesi,  
42 Indonesia, *Nature* 514, 223-227.

43 Prideaux, G.J., Roberts, R.G., Megirian, D., Westaway, K.E., Hellstrom, J.C., Olley, J.M.,  
44 2007. Mammalian responses to Pleistocene climate change in southeastern Australia, *Geology*  
45 35, 33-36.

46 Pons-Branchu, E., Bourrillon, R., Conkey, M.W., Fontugne, M., Fritz, C., Gárate, D., Quiles,  
47 A., Rivero, O., Sauvet, G., Tosello, G., Valladas, H., White, R., 2014. Uranium-series dating  
48 of carbonate formations overlying Paleolithic art: Interest and limitations, *Bulletin de la*  
49 *Societe Prehistorique Francaise* 111, 211-224.

1 Taçon, P.S.C., Aubert, M., Gang, L., Decong, Y., Hong, L., May, S.K., Fallon, S., Xueping, J.,  
2 Curnoe, D., Herries, A.I.R., 2012. Uranium-series age estimates for rock art in southwest  
3 China, *Journal of Archaeological Science* 39, 492-499.

4 Sharp, W.D., Kahn, J.G., Polito, C.M., Kirch, P.V., 2010. Rapid evolution of ritual architecture  
5 in central Polynesia indicated by precise  $^{230}\text{Th}/\text{U}$  coral dating, *Proceedings of the National*  
6 *Academy of Sciences of the United States of America* 107, 13234-13239.

7 Burley, D., Weisler, M.I., Zhao, J.-x., 2012. High Precision U/Th Dating of First Polynesian  
8 Settlement, *PLoS ONE* 7, e48769.

9 Allard, G., Roy, M., Ghaleb, B., Richard, P.J.H., Larouche, A.C., Veillette, J.J., Parent, M.,  
10 2012. Constraining the age of the last interglacial-glacial transition in the Hudson Bay  
11 lowlands (Canada) using U-Th dating of buried wood, *Quaternary Geochronology* 7, 37-47.

12 Braun, D.R., Levin, N.E., Stynder, D., Herries, A.I.R., Archer, W., Forrest, F., Roberts, D.L.,  
13 Bishop, L.C., Matthews, T., Lehmann, S.B., Pickering, R., Fitzsimmons, K.E., 2013. Mid-  
14 Pleistocene Hominin occupation at Elandsfontein, Western Cape, South Africa, *Quaternary*  
15 *Science Reviews* 82, 145-166.

16 Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P., Taylor, E.,  
17 2006. U-Pb geochronology of speleothems by MC-ICPMS, *Quaternary Geochronology* 1,  
18 208-221.

19 Woodhead, J., Hellstrom, J., Pickering, R., Drysdale, R., Paul, B., Bajo, P., 2012. U and Pb  
20 variability in older speleothems and strategies for their chronology, *Quaternary*  
21 *Geochronology* 14, 105-113.

22 Pickering, R., Kramers, J.D., Partridge, T., Kodolanyi, J., Pettke, T., 2010. U-Pb dating of  
23 calcite-aragonite layers in speleothems from hominin sites in South Africa by MC-ICP-MS,  
24 *Quaternary Geochronology* 5, 544-558.

25 de Ruiter, D.J., Pickering, R., Steininger, C.M., Kramers, J.D., Hancox, P.J., Churchill, S.E.,  
26 Berger, L.R., Backwell, L., 2009. New *Australopithecus robustus* fossils and associated U-Pb  
27 dates from Cooper's Cave (Gauteng, South Africa), *Journal Of Human Evolution* 56, 497-513.

28 Pickering, R., Kramers, J.D., 2010. A re-appraisal of the stratigraphy and new U-Pb dates at the  
29 Sterkfontein hominin site, South Africa, *Journal Of Human Evolution* 59, 70-86.

30 Pickering, R., Kramers, J.D., Hancox, P.J., de Ruiter, D.J., Woodhead, J.D., 2011a.  
31 Contemporary flowstone development links early hominin bearing cave deposits in South  
32 Africa, *Earth and Planetary Science Letters* 306, 23-32.

33 Pickering, R., Dirks, P.H.G.M., Jinnah, Z., de Ruiter, D.J., Churchill, S.E., Herries, A.I.R.,  
34 Woodhead, J.D., Hellstrom, J.C., Berger, L.R., 2011b. *Australopithecus sediba* at 1.977 Ma  
35 and Implications for the Origins of the Genus *Homo*, *Science* 333, 1421-1423.

36 Walker, J., Cliff, R.A., Latham, A.G., 2006. U-Pb isotopic age of the StW 573 hominid from  
37 Sterkfontein, South Africa, *Science* 314, 1592-1594.

38 Pickering, R., in press. U-Pb dating small buried stalagmites from Wonderwerk Cave, South  
39 Africa: a new chronometer for Earlier Stone Age cave deposits, *African Archaeological*  
40 *Review* accepted May 2014.

41 Pickering, R., Jacobs, Z., Herries, A.I.R., Karkanias, P., Bar-Matthews, M., Woodhead, J.D.,  
42 Kappen, P., Fisher, E., Marean, C.W., 2013. Paleoanthropologically Significant South African  
43 Sea Caves dated to 1.0 Million Years using a combination of U-Pb, TT-OSL and  
44 palaeomagnetism, *Quaternary Science Reviews* 65, 39-52.

45 Sniderman, K., Woodhead, J., Hellstrom, J., Elith, J., Porch, N., 2014. Latest Miocene-Early  
46 Pliocene vegetation and climate of the Nullarbor Plain: New insights from fossil pollen  
47 records of U-Pb dated speleothems. , *Climate Change: The Karst Record*. 7th International  
48 Conference, Melbourne, Australia.

1 Bajo, P., Drysdale, R., Woodhead, J., Hellstrom, J., Zanchetta, G., 2012. High-resolution U-Pb  
2 dating of an Early Pleistocene stalagmite from Corchia Cave (central Italy), *Quaternary*  
3 *Geochronology* 14, 5-17.  
4  
5  
6 Walker, M., 2005. *Quaternary Dating Methods*, John Wiley, Chichester & New York.  
7 Schwarcz, H.P., Latham, A.G., 1989. Dirty calcites 1. Uranium-series dating of  
8 contaminated calcite using leachates alone, *Chemical Geology* 80, 35-43.  
9 Ku, T.-L., Liang, Z.-C., 1984. The dating of impure carbonates with decay-series isotopes,  
10 *Nuclear Instruments and Methods in Physics Research* 223, 563-571.  
11 Bischoff, J.L., Fitzpatrick, J.A., 1991. U-series dating of impure carbonates: An isochron  
12 technique using total-sample dissolution, *Geochimica et Cosmochimica Acta* 55, 543-  
13 554.  
14 Richards, D.A., Bottrell, S.H., Cliff, R.A., Strohle, K., Rowe, P.J., 1998. U-Pb dating of a  
15 speleothem of Quaternary age, *Geochimica Et Cosmochimica Acta* 62, 3683-3688.  
16 Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P., Taylor, E.,  
17 2006. U-Pb geochronology of speleothems by MC-ICPMS, *Quaternary Geochronology* 1,  
18 208-221.  
19 Pickering, R., Kramers, J.D., Partridge, T., Kodolanyi, J., Pettke, T., 2010. U-Pb dating of  
20 calcite–aragonite layers in speleothems from hominin sites in South Africa by MC-ICP-  
21 MS, *Quaternary Geochronology* 5, 544-558.  
22 Bajo, P., Drysdale, R., Woodhead, J., Hellstrom, J., Zanchetta, G., 2012. High-resolution U-  
23 Pb dating of an Early Pleistocene stalagmite from Corchia Cave (central Italy),  
24 *Quaternary Geochronology* 14, 5-17.  
25 Walker, J., Cliff, R.A., Latham, A.G., 2006. U-Pb isotopic age of the StW 573 hominid from  
26 Sterkfontein, South Africa, *Science* 314, 1592-1594.  
27 Bruxelles, L., Clarke, R.J., Maire, R., Ortega, R., Stratford, D., 2014. Stratigraphic analysis  
28 of the Sterkfontein StW 573 *Australopithecus* skeleton and implications for its age,  
29 *Journal of Human Evolution* 70, 36-48.  
30 Kirch, P.V., Sharp, W.D., 2005. Coral <sup>230</sup>Th Dating of the Imposition of a Ritual Control  
31 Hierarchy in Precontact Hawaii, *Science* 307, 102-104.  
32 Candy, I., Black, S., 2009. The timing of Quaternary calcrete development in semi-arid  
33 southeast Spain: Investigating the role of climate on calcrete genesis, *Sedimentary*  
34 *Geology* 218, 6-15.  
35 Carey, S.P., Camens, A.B., Cupper, M.L., Grün, R., Hellstrom, J.C., McKnight, S.W.,  
36 McLennan, I., Pickering, D.A., Trusler, P., Aubert, M., 2011. A diverse Pleistocene  
37 marsupial trackway assemblage from the Victorian Volcanic Plains, Australia,  
38 *Quaternary Science Reviews* 30, 591-610.  
39 Grün, R., Aubert, M., Hellstrom, J., Duval, M., 2010. The challenge of direct dating old  
40 human fossils, *Quaternary International* 223–224, 87-93.  
41