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Uranium-series dating and the origin of modern man

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SUMMARY

Uranium-series dating is based on measurement of the radioactivity of short-lived daughter isotopes of uranium formed in samples which initially contained only the parent uranium. Materials suitable for U-series dating are found in many prehistoric archaeological sites, and include stalagmitic layers (flowstones), and spring-deposited travertines. Some marls and calcretes are also datable using isochron methods, whereas dates on molluscan shells, bones and teeth are less reliable. Ages obtained using alpha counting to determine isotope ratios have errors greater than 5%, and can range from 1 to 350 ka. Mass spectrometric methods slightly increase the range (0.1–500 ka) but greatly decrease the error to less than 1%, making this the optimal method for high-precision dating of the origin of modern man.

1. REQUIREMENTS OF A DATING METHOD

Modern humans of the species *Homo sapiens sapiens* are now believed to have evolved from an ancestral species over the past few hundred thousands of years. Our ability to define this transition is critically dependent on the availability of chronometers with which to date the stages in this evolutionary process. Any such 'timepiece' must satisfy the following three requirements.

1. Range. All dating methods have a specific time range over which they are applicable; the upper and lower limits of this range must be appropriate to the interval of interest.
2. Applicability (datable materials). The method must be applicable to materials likely to be found at hominid sites. These must be materials which were either formed at the time of occupation of the site (e.g. faunal remains, stalagmitic deposits); or which were altered in some way at that time (e.g. burnt flint).
3. Precision and accuracy. The dating method must be precise enough to resolve discrete evolutionary stages; although a low-precision method such as electron spin resonance (ESR) or thermoluminescence (TL) may be sufficient to define broad intervals, it is also desirable to have methods of high precision and accuracy with which to seriate hominids and artefact sequences from diverse loci.

Considering the time interval in which we are interested here, greater than 40 ka before present (BP), these criteria are satisfied by a variety of dating methods, including TL, optically stimulated luminescence (OSL), ESR, and uranium-series dating. Potassium–argon (K/Ar or $^{40}Ar/^{39}Ar$) dating is applicable to the rare sites in volcanic areas such as Italy where *Homo sapiens* is found. However, of these various methods only one, uranium-series dating of calcite, can provide high precision dates on materials found at a wide variety of hominid sites. The precision of dates obtainable by the other methods listed is significantly less, even when the most advanced techniques are used for each method. The additional advantage of uranium-series dating is that it does not rely on knowledge of the environmental conditions at a site through the time elapsed since its formation. By contrast, environmental radiation dose rates are needed for OSL, TL and ESR dating while for methods which are based on the rate of chemical reactions such as amino acid racemization (AAR), it is necessary to know the thermal history at the site.

2. URANIUM-SERIES DATING

Uranium (U) is present as a trace element in all natural materials. The two primordial isotopes of this element, ^{238}U and ^{235}U, each undergo radioactive decay to form a series of short-lived daughter radioisotopes (figure 1). In any U-bearing material which has lain undisturbed for millions of years, the activities of the isotopes within one decay series will all be equal to one another and to their respective parent (^{238}U or ^{235}U). Here we speak of activities as measured in numbers of disintegrations per minute per gram of the material. This state of 'secular equilibrium' can be disturbed by chemical or physical processes; then the activity of some of these isotopes can be greater or less than the equilibrium level. Uranium-series dating refers to methods in which the time of this disturbance is estimated from the degree of departure from equilibrium. U-series dating is possible as long as the time elapsed is comparable to the half-life of the isotope being measured. Daughter isotopes of U have half-lives ranging from a fraction of second to 250 ka. Of these, three in particular have promise for dating of

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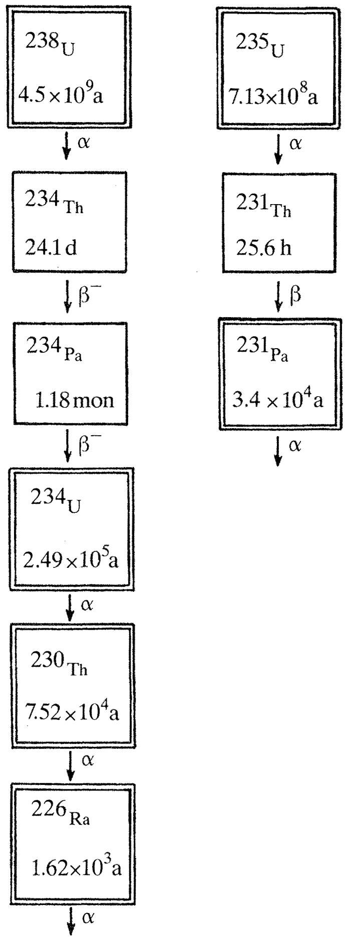

Figure 1. The beginning parts of the radioactive decay series that are produced by each of the primordial isotopes of uranium: ^{238}U and ^{235}U. The heavy boxes outline those longer-lived isotopes that are of use in dating prehistoric sites.

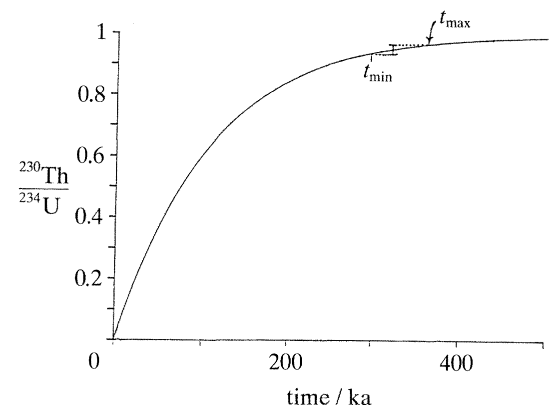

Figure 2. Graph of the ratio of the radioactivity of ^{230}Th to that of its parent isotope ^{234}U as a function of time. In a sample whose initial $^{230}Th/^{234}U$ ratio was zero (such as an uncontaminated stalagmite), the age can be determined by reading off on the horizontal axis the age corresponding to the sample's present-day $^{230}Th/^{234}U$ ratio. The error in age is determined by the error in measurement of the isotope ratio. For older samples, these errors are highly asymmetric as shown. The error bars shown are typical for alpha spectrometry; corresponding errors in thermal ionization mass spectrometry (TIMS) are about a tenth as large.

hominid evolution: ^{234}U, ^{230}Th, and ^{231}Pa. The last is a daughter of ^{235}U, which is an isotope of very low natural abundance (less than 1% of natural uranium), and is therefore less useful except where the U concentration is very high in the sample to be dated.

Most geological materials at hominid sites (sand, silt, rock fragments, etc.) are 'recycled' ancient materials and therefore are close to secular equilibrium. However, some materials are found which were formed *de novo*, such as stalagmites, travertines, bones, teeth or shells. Typically, all these materials are formed totally out of secular equilibrium. A typical example is a stalagmitic layer in a cave, formed by precipitation of calcite from lime-rich waters dripping from the roof of the cave. U is quite soluble in water, whereas thorium (including the daughter isotope ^{230}Th) is not. Therefore, at the time of its formation the calcite contains some ^{234}U and ^{238}U but virtually no ^{230}Th. The latter isotope begins to grow by decay of its parent ^{234}U, and the ratio of the activities of these two isotopes rises as shown in figure 2. The age of the stalagmite can then be estimated from this ratio; for example, if this ratio of activities is today observed to be equal to 0.50, we infer that the stalagmite is 75 ka old. This inference requires that two assumptions be true, one of which can be easily tested: (i) at the time of deposition, the $^{230}Th/^{234}U$ ratio of the stalagmite was zero; (ii) the only changes in this ratio through time have been due to radioactive decay. To test the first assumption, we look for the presence of primary, 'common' thorium, which is recognizable because it consists partly of the long-lived isotope ^{232}Th. The presence of this isotope in the sample tells us that there was probably also present, at the time of deposition, a matching amount of ^{230}Th, in a known proportion that can be roughly corrected for. It is much more difficult to test the second assumption, that is, to prove or disprove that the sample has been disturbed by recrystallization or diagenesis.

Although the ratio $^{230}Th/^{234}U$ is the most widely used in dating, two other ratios, $^{231}Pa/^{235}U$, and $^{234}U/^{238}U$ are also employed. The ranges of applicability of each ratio are shown in figure 3, together with estimates of the precision of each method. The first two, $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$, require only the two assumptions cited above; $^{234}U/^{238}U$ ratios can be used for dating only where we also know the initial ratio at the time of deposition of the material. This is rarely true in archaeological sites except where the material (e.g. travertine) has been deposited from a source of water whose U isotope ratio has been stable for hundreds of millenia, such as seawater or spring water emerging from a large aquifer.

The measurement of the isotopes of U, Th and Pa can be done by two means. The more traditional approach is to prepare very thin layers of these isotopes (one atom thick) and to count their radioactivity. This can be done using an alpha-particle spectrometer (for U and Th) or a beta detector for Pa (which can also be determined indirectly by alpha counting). Alpha particles emitted from each isotope have characteristic energies which can be sorted electroni-

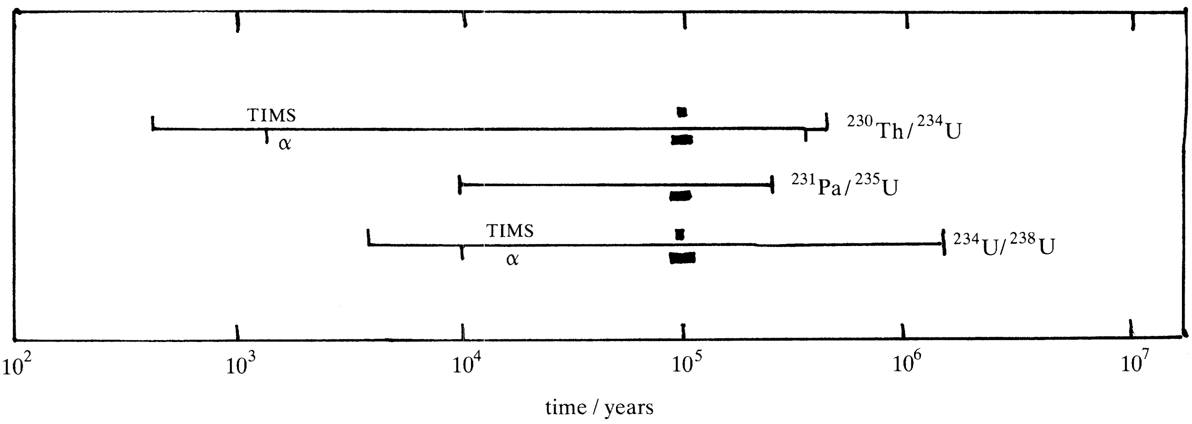

Figure 3. Range (lines) and precision (bars) of the U-series methods of dating. As explained in the text, the $^{234}U/^{238}U$ method is applicable only under special circumstances.

cally, permitting us to determine the ratio of the activities directly; it is the approach of these ratios to equilibrium that is our measure of age. The telltale ^{232}Th isotope, indicative of contamination, is also detectible by alpha spectrometry.

Recently we have begun to use thermal ionization mass spectrometry (TIMS) which is a more complex but also more sensitive technique, similar in concept to the accelerator mass spectrometry (AMS) method now used in ^{14}C dating in that we count atoms of the isotopes rather than wait for them to decay. The precision of TIMS is as much as ten times better that alpha counting, although the accuracy may not be improved by this factor, due to the limitations of the materials analysed.

3. DATABLE MATERIALS

Materials datable by U-series are widely available at archaeological sites, but the quality of these materials varies greatly. The best materials, from the standpoint of satisfying the criteria (i) and (ii) above, are deposits of calcite (calcium carbonate, $CaCO_3$) formed from dripping or running water: stalagmites, flowstones (*planchers stalagmitique*), and spring-deposited travertines. The first two of these materials are generally formed of densely packed crystals of calcite which can be quite pure (i.e. free of common thorium). Travertine, however, can be quite porous and subject to changes after deposition, as the pores gradually fill in with newly deposited calcite. The best travertine layers, however, resemble stalagmites and are usable for dating. Some sites are found enclosed in or associated with layers of freshwater limestone (marl) that may also be datable, as long as they are not too contaminated or altered.

Besides calcite deposits, other less satisfactory materials which are found in archaeological contexts include mammalian teeth and bones, ostrich egg shells, and the shells of molluscs. All of these biogenic materials contain very little U when they are formed. When they are analysed many thousands of years later, we observe them to contain substantial amounts of U which has been absorbed sometime during the period of burial in the site. If we can assume a history of U uptake for these materials then we can use this information together with the ratios of their radioisotopes to determine their ages. For ostrich shells (Wendorf *et al.* 1991) and the outermost layers of some bones (Rae & Ivanovich 1986) and teeth (McKinney 1991), it appears that the U is taken up very early, and we can treat them like stalagmites or travertines. Most bone material and mollusc shells do not behave as simply and have not proven to be satisfactory for U-series dating. Mollusc shells, in particular, tend to give anomalously low ages (Kaufmann *et al.* 1977).

In summary, the best materials for U-series dating appear to be calcitic flowstones and stalagmites which entrapped their present-day complement of uranium at the time they were formed. Although many such deposits are quite pure, some are found to contain substantial amounts of common thorium as a result of transport of detritus into the deposits by wind water, or on the feet of the occupants of the site. This imparts to the samples an anomalously high ^{230}Th content and hence an anomalously high $^{230}Th/^{234}U$ ratio. We have learned how to correct for this contamination, however, by analysing several portions of the sample with varying amounts of contaminant and observing how the isotope ratios change as a function of the amount of contaminant (Schwarcz & Latham 1990). Alternately, we can analyse the sample in two parts: the calcite component which is soluble in dilute acid; and the acid-insoluble residue (particles of sand and dust) which must be dissolved in stronger acids and which contains a purer fraction of the contaminant (Luo & Ku 1991; Bischoff & Fitzpatrick 1991). Using either method, we obtain the $^{230}Th/^{234}U$ ratio of the pure calcite component from the slope of a line called an isochron, on a graph of isotope ratios (figure 4). To be datable by the isochron method, the samples must consist of mixtures of a pure calcite and a single, homogeneous 'dirt' component (Ku & Liang 1987; Schwarcz & Latham 1990).

4. RANGE, PRECISION AND ACCURACY

The third requirement for a chronometer to be useful in calibrating the emergence of modern man is that the method should be able to produce dates of

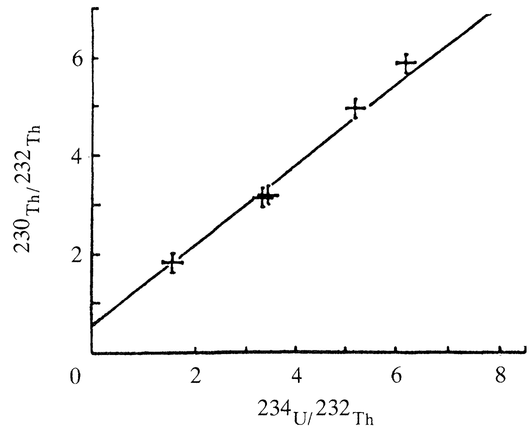

Figure 4. Isochron diagram: a plot of $^{230}Th/^{232}Th$ versus $^{234}U/^{232}Th$, for contaminated carbonate samples: if a series of cogenetic samples forms a linear array, the slope of the line gives the $^{230}Th/^{234}U$ ratio of the chemically precipitated carbonate component, and thus the age of the deposit.

adequate precision and accuracy over the range of interest. Figure 2 demonstrates the range of the $^{230}Th/^{234}U$ method. After that isotope ratio has reached its limiting value of 1.00, corresponding to secular equilibrium, no further changes occur, and the age of a sample with this ratio is indeterminate. This limit is reached at approximately 350 ka when using alpha spectrometry or about 500 ka with TIMS. The method of $^{231}Pa/^{235}U$ dating has a slightly shorter range (about 250 ka). In principle, the $^{234}U/^{238}U$ method has the largest range, greater than 1 million years. In practice, however, it is questionable whether any springs or other water sources had the same $^{234}U/^{238}U$ ratio when the sample formed as is observed in the spring water today.

The precision of $^{230}Th/^{234}U$ dates obtained by alpha counting is generally no better than $\pm 5\%$ of the date, and is limited by the number of counts obtained. This, in turn, requires that the samples be either rich in uranium (greater than 1 part per million) or that relatively large samples must be analysed. The TIMS method, on the other hand, requires smaller samples, and also provides higher precision. The best samples give dates with a reproducibility of better than 1% (e.g. less than 1000 years for a 100000-year-old sample). This is comparable to the precision of ^{14}C or $^{40}Ar/^{39}Ar$ dating. If the isochron method is used, then the precision of the dates is constrained by the scatter of points around the isochron, which is mainly determined by how well the samples obey the assumptions of the isochron method.

The accuracy of $^{230}Th/^{234}U$ dates is believed to be comparable to the precision, as the only parameters affecting the accuracy are the half-lives of the relevant isotopes. No systematic intercomparisons of U-series and other dating methods have been made for samples of more than 50 ka. On the other hand, such is the confidence in the accuracy of U-series dates on corals, that they have been used to calibrate the ^{14}C Chronometer in the period 10 to 30 ka (Bard *et al.* 1990). Coral is one of the best materials for U-series dating but it is seldom found in an archaeological context.

5. APPLICATIONS OF U-SERIES DATING TO HOMINID EVOLUTION

This method is, in principle, the ideal method with which to obtain highly precise dates beyond the range of ^{14}C, and also by which to obtain highly accurate dates beyond the range of dendrochronological calibration of ^{14}C. For the study of early modern hominids, it would be especially useful to have datable samples from the sites where critical skeletal material has been recovered. Unfortunately, we are somewhat in the position of the drunken man who lost his keys on a dark stretch of road but who is searching for them a few yards away, under a lamp-post, because the light is better there! Thus, we must sometimes content ourselves with dating sites or strata in sites which are far removed from critical hominid loci, but which are better suited for dating and can, hopefully, be correlated with the hominid sites. At the present time only a single site has been dated using TIMS; all other U-series dates on hominid sites have been by the less precise method of alpha spectrometry, in some cases coupled with isochron analyses of the data.

During the past 200 ka, hominids have occupied two habitats which are particularly amenable to U-series dating: caves and warm springs (where travertine mounds have been deposited). Speleothems (stalagmites, flowstones, etc.) are found in many of the caves which have also yielded hominids or Palaeolithic artefacts. It is not always possible to relate the timing of speleothem growth to the occupation of the site, however. Dates obtained on speleothems which are entirely out of a stratigraphic context are of no use to anthropologists. Unfortunately, the growth rate of speleothems is controlled by climate, and slows or ceases altogether during glacial stages (Gascoyne *et al.* 1983; Gordon *et al.* 1989). As a result it is more difficult (but not impossible) to find speleothems for U-series dating of those periods (e.g. 70 to 12 ka) in regions which experienced periglacial climate.

6. EUROPE

The last comprehensive summary of U-series dates from hominid sites was that of Cook *et al.* (1982), which surveyed and compared results from various other dating methods, as well, for hominid sites in Europe. Since then, U-series dates have been obtained on other Neanderthal sites in Europe including Grotte du Prince (Shen, 1986), Monte Circeo (Schwarcz *et al.* 1990), and Banyolas (Julia & Bischoff 1991). In addition, refinements of dates presented in Cook *et al.* (1982) have been published for some of these sites including Bilzingsleben (Schwarcz *et al.* 1988), La Chaise de Vouthon (Blackwell *et al.* 1983) and Petralona (Latham & Schwarcz 1992).

Examples from two of these sites should suffice to indicate the nature of the evidence that U-series dates provide. At the site of La Chaise-de-Vouthon, in the Charente district of France, two adjacent caves contain detrital sedimentary sequences which have yielded numerous hominid remains. Several layers of calcitic flowstone are interstratified with the sediments. Blackwell *et al.* (1983) obtained alpha-spectrometric dates on these flowstones, which serve as convenient datable horizons within the sequence. The calcite is relatively free of detrital contamination as was shown by the small activity of ^{232}Th in the alpha spectra. The ages of the flowstones range from $245 \pm ^{45}_{28}$ ka to 97 ± 6 ka; the ages agree with the stratigraphic order of the flowstones. Hominid remains, consisting principally of teeth, are found in layers older than 101 ka.

The site of Banyolas in Spain exemplifies the application of U-series dating to a hominid site associated with a travertine deposit. The mandible of a hominid was discovered in 1887 in a travertine quarry, which has been subsequently filled in. Julia & Bischoff (1991) have, however, succeeded in discovering the probable location of the site and associating it with exposures of travertine in other open quarries nearby; they were also able to analyse travertine that was still attached to the mandible. The travertines were significantly contaminated with detritus but they obtained isochron dates on both the travertine deposits as well as the travertine coating of the mandible. The latter gave an isochron age of 45 ± 4 ka, which was in agreement with the uppermost layers of one of the travertine deposits. This date is, however, surprising, in view of the previous assignment of this fossil to an early stage of hominid evolution, prior to appearance of the Neanderthals (Roth 1989). A similar conflict between the evidence of U-series dating and inferences from anatomical as well as other site characteristics was encountered by Schwarcz & Latham (1984, 1990) in their study of travertines at the site of Vértesszöllös.

7. ASIA AND AFRICA

In recent years, the focus of interest in the study of late hominid evolution has shifted to inlude western Asia and Africa. Thanks to the application of TL and ESR dates to sites in these areas (Grün & Stringer 1991), we now recognize that the transition to *Homo sapiens sapiens* must have occurred long before the arrival of this species in Europe. The TL and ESR dates from these sites, while clearly pushing back the timing of the appearance of *H.s.s.* have large uncertainties associated with them, and it would be desirable to refine these results using high-precision U-series dates. Unfortunately, materials datable by U-series are not commonly found at these sites, and we must resort to dates at nearby sites which can be related to the hominid sites through archaeological or faunal correlations.

One example of this is the region of Nahal Zin, in the northern Negev Desert of Israel, where several Middle and Upper Palaeolithic sites were studied by A. Marks and colleagues in the 1970s and 1980s (Marks 1976). The site of Nahal Avdat consists of a travertine deposit in which are found embedded lithic artefacts correlatable with the earliest phase of the Upper Palaeolithic. The transition was better preserved at the nearby site of Boqer Tachtit which, however, contained no U-series datable materials. Samples of travertine from Nahal Avdat gave a date 47 ± 3 ka. The site of Ein Aqev a few km away contains Middle Palaeolithic (Levalloiseo–Mousterian) artefacts that were dated to 80 ± 10 ka.

These results are especially interesting in the light of the TL and ESR dates that have now been obtained for *H.s.s.* at sites in Galilee and Mount Carmel, of approximately 100 ka. The lithic artefacts associated with the hominids at these sites are of Middle Palaeolithic character. Therefore the transition from Middle to Upper Palaeolithic that we have dated at Nahal Zin may not represent the transition from Neanderthal to Modern humans, as is commonly assumed for this transition in Europe. Neanderthals were, however, present in Israel later that 100 ka (Schwarcz *et al.* 1989), and sites such as Nahal Zin may be critical in sorting out the relation between the cultural and biological transitions that have occurred over the past 100 ka.

Elsewhere in Israel, we have attempted to apply U-series dating to cave-deposited carbonates, with varying degrees of success (Schwarcz *et al.* 1979). These speleothems tend to be highly contaminated with detritus including a component of windblown limestone dust, that is particularly difficult to correct for. Therefore, it will be important to restudy these sites using TIMS-based U-series dating on subsamples of higher purity. Caves containing archaeological deposits occur elsewhere in this region, especially in the coastal caves of Lebanon. At the site of Nahr Ibrahim, for example we have analysed a flowstone capping a Mousterian sequence, and obtained a date of 100 ka. Spring deposited travertines from the Syrian desert are also potentially able to yield U-series over the last glacial cycle (Hennig & Hours 1982) but these deposits are also heavily contaminated with limestone particles that tend to increase the apparent ages.

In North Africa, critical archaeological sites are seldom found associated with U-series datable materials, with the possible exception of spring deposits of marls of spring-fed lakes. The area of Bir Tarfawi and Bir Sahara in southwestern Egypt is now a hyperarid desert. Sometime around 140 ka this area was occupied by a flourishing swampy, spring-fed lake which was visited by hominids using a Middle Paleolithic industry similar to that found in southwest Asia (Wendorf *et al.* 1992). Alpha-spectrometric U-series analyses were done on marls deposited in those lakes. The individual deposits give stratigraphically discordant results (age inversions), but when plotted on isochron diagrams they yield consistent ages of between 140 and 105 ka.

This site has also yielded the first TIMS U-series dates on archaeological material, namely ostrich egg-shell fragments from within one of the sites associated with lake filling. Three samples gave dates of 136 ± 3, 137 ± 3 and 126 ± 8 ka. The dates are consistent with the isochron dates for the associated marls, and imply that ostrich shells take up uranium soon after deposition and remain closed systems thereafter. A fourth sample from the same layer gave a date of 179 ± 19 ka; this shell fragment was contaminated with detritus. These data show the potential of high precision U-series for the fine temporal resolution of past hominid activities.

South of the Sahara, the possibilities of applying U-series methods to dating of the transition to *H.s.s.* are limited by the scarcity of carbonate deposits, with the exception of those in South Africa, where the sites of Boomplaas and Klasies River Mouth contain stalagmites whose U-series dates are under study by J. Vogel.

8. CONCLUSIONS: POTENTIAL FOR FURTHER STUDIES

It should be clear that TIMS U-series dating can provide a high-resolution chronology for the later stages of hominid evolution, including the contentious transition from early modern *Homo sapiens sapiens* to the present species, and the disappearance of *Homo sapiens neandertalensis*. The application of this technique is, however, limited by the need to have suitable material for dating, preferably chemically precipitated calcite. Although this material is widely encountered in archaeological settings, it is necessary to use great care to select the correct material for analysis, especially so that the material satisfies two criteria: (i) purity; and (ii) chrono-stratigraphic relevance to the hominid remains or archaeological deposit. Both of these aspects have been discussed here and in earlier papers (e.g. Blackwell & Schwarcz 1992).

Potential areas where further advances may be made include the following.

1. Coatings on bone. Where fossil material, including hominid skeletal fragments, has been collected from sites in lime-rich terrains, a coating of calcium carbonate is commonly found adhering to the exterior of the bones, or as a partial filling of cavities in the bone. This is particularly true in sub-arid regions. By dating this material we obtain an *ante quem* date for the individual. The amounts of carbonate encountered are usually so small that TIMS would be required for their analysis.
2. Stalactite 'rain'. In some caves, calcite deposition is intermittently active and results in the formation of fine tubular stalactites on the roof of the cave, which can then fall to the floor and make up several percent of the coarse fraction of the sediment in the cave. The lifetime of these stalactites on the roof of the cave is quite short (much less than 1000 years), and their age can be used as an estimate of the date for the layer in which they are found.

In addition, the more typical examples of stalagmitic layers, travertine deposits, etc., continue to provide targets for higher-resolution dating in the time range up to 400 ka. Further resolution and improvement of precision is attainable by coupling the TIMS method to the isochron technique. However, there is a purely analytical problem that must be considerd here as well: samples contaminated with common thorium have high ^{232}Th abundances and low ^{230}Th/^{232}Th ratios. In TIMS, this means that the isotopic (not activity) ^{232}Th/^{230}Th ratio is high, typically greater than 100 000, which introduces the problem of the contribution of the 'tail' of the very high ^{232}Th peak under the very small ^{230}Th peak only two mass units away. The use of two-stage mass spectrometers can provide adequate abundance sensitivity to eliminate the tail contribution. Clearly, however, such equipment is too expensive to be widely available, and it is expected that future advances in this field will require collaborative efforts comparable to those that have been seen in ^{14}C dating by AMS.

Much of the research referred to here was carried out in collaboration with my colleagues including Bonnie Blackwell and Alf Latham. I also thank numerous archaeological and anthropological colleagues in Europe and Israel who, through the years, have presented me with challenging problems in dating. Valuable critical comments were made by Martin Aitken. This research was supported by grants from the Social Sciences and Humanities Research Council (Canada).

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