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Uranium and thorium in fossil bones: activity ratios and dating

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Abstract—We have analysed fossil bones by U-series disequilibrium from five different sites (Ngandong and Sonde, Indonesia; Gold Ox Hill, People's Republic of China; Pestera, Romania and Ksar Akil, Lebanon). Two samples were taken from all bones: one representing surface material, and one from the inner bone (bulk) material. In general, the U concentration at the surface was found to be lower than in the bulk, resulting in higher ages. This might be explained by leaching of U from the surface area of the bone, which means that the surface material of the bones cannot be considered to be a closed system. An exception is the Gold Ox Hill series, where we found that the U concentration is roughly constant throughout the bone. Also the ages are roughly the same for surface and bulk material in this case.

INTRODUCTION

SEVERAL dating methods have been applied to fossil bones: radiocarbon (MOOK and WATERBOLK, 1985), amino acid racemization or AAR (BADA and SCHROEDER, 1975), electron spin resonance or ESR (HENNIG and GRUHN, 1983) and U/Th dating (SCHWARCZ, 1982). The degree of success of such methods depends on parameters which cannot be controlled. For instance, AAR requires detailed knowledge of the environmental chemical conditions at the bone deposition site, not to mention calibration problems with the method. For the ESR method, the radiation dose to which the bone has been exposed has to be known. Thus far, the most widely applied method of bone dating is by radiometric analysis, such as radiocarbon dating. This method is limited to using hydroxyproline, the amino acid characteristic of bone collagen (POLACH, 1971). More seriously, the measurable age is limited to ≃45 ka. For bones older than this limit, the only possible absolute dating method is the U-series disequilibrium method. In principle, materials can be dated by this method to about 300 ka (IVANOVICH and HARMON, 1982).

Fossil bones contain high concentrations of U (1–1000 ppm), while in modern bones the U concentration usually does not exceed 0.1 ppm. This indicates that U is taken up by bones post mortem, presumably from ground water (SCHWARCZ, 1982). Previous work (SZABO, 1980) has shown that U is probably taken up by the bone over a short length of time (2–3 ka) relative to the age of the bone. This would imply that the bone can be regarded as a closed system afterwards; provided there is also no migration of U or daughter products, this is essential for the U-series disequilibrium method. Many studies have been dedicated to evaluating the validity of this assumption, yielding widely different conclusions. For example, HENNIG and GRUHN (1983) reviewed a great number of radiometric bone dates obtained from various sites, and argued that the closed system behaviour should be doubted. On the other hand, RAE and IVANOVICH (1986) observed that the outer layers of bones absorb U on a relatively short time scale (<2 ka) and subsequently behave as a closed system. They recommend analysis of this surface layer rather than whole-bone analysis.

Here, we present the first U-series disequilibrium dating results of bones from five different sites. In all cases, two samples of bone material were analysed, corresponding to surface material and inner-bone (bulk) material. We intend to discuss some general trends that have been observed so far. A more detailed evaluation of these and additional data will be published in a forthcoming paper.

U-SERIES DISEQUILIBRIUM DATING

The U-series disequilibrium dating method is based on the decay of ^{238}U and its radioactive daughter nuclei. One of the decay products of ^{238}U is ^{234}U, which in turn decays with a half life of 248 ka (by emitting an α-particle) into ^{230}Th. The ^{230}Th itself decays (also by emitting an α-particle) with a half life of 75 ka. This decay is the only source for ^{230}Th available in nature.

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Thus, as long as the production of ^{230}Th exceeds its radioactive decay, ^{230}Th accumulates and the ^{230}Th/^{234}U activity ratio is a measure of the age, provided the system is chemically closed. After approximately 300 ka radioactive equilibrium is reached where the decay of ^{230}Th balances its production. From this moment on the ^{230}Th/^{234}U activity ratio is approximately unity, independent of time. In addition, the presence of ^{232}Th in the sample is an indication of the amount of contamination with detrital inorganic material. For a detailed review of the physical background and the mathematical equations involved, we refer to IVANOVICH (1982).

EXPERIMENTAL METHOD

From each bone analysed, two samples were taken: one from the surface, and one from the bulk. Samples were removed by careful milling.

In order to extract U and Th from the bone material, the samples were dissolved in HCl (36%) overnight. The remaining solids (not more than a few weight percent) were removed by centrifugation. A known quantity of ^{232}U/^{228}Th spike activity was added for calibration purposes. From the solutions, U and Th were co-precipitated with $Fe(OH)_3$. Quite often, Th yields were low because of large amounts of phosphate. In those cases, yield was improved by selective precipitation at pH 3.5 (RAE and IVANOVICH, 1986). The precipitate was redissolved, and U, Th and Fe were separated and purified on an ion-exchange column. Thin α-sources were prepared by electroplating on a stainless steel planchette (per sample, one for U and one for Th). The activity of the sources was measured by means of silicon semiconductor detectors, mounted in an α-spectrometer as described by VAN DER WIJK (1987).

THE SITES

Bone samples from five sites were analysed. The Ngandong and Sonde sites are located in Java, Indonesia. The Ngandong site contains remains of *Homo erectus* (BARTSTRA, 1982). All localities and sites lie near the Solo River, the largest river of central Java. Preliminary results of dating bones from the Solo High Terrace at the Ngandong site (taking total bone sample material) have been published by BARTSTRA *et al.* (1988). These authors argued that U uptake by the bones ceased after the water table close to the river sank below the terrace levels. The latter is a necessary condition for closed-system behaviour.

The Gold Ox Hill site is a cave deposit site in eastern China. Well preserved hominid remains have been found at this site, and it is debated whether the hominid is to be classified as *Homo erectus* or *Homo sapiens* (CHEN and YUAN, 1988).

Finally, limited data were obtained from bone material from two other sites: Pestera and Ksar Akil. Work started on these bones because they are dateable using ^{14}C and hence offer an independent radiometric control of the U-series disequilibrium method. The Pestera site is essentially a Middle Palaeolithic cave in southwestern Romania. The Ksar Akil site is located in Lebanon, and consists of sediments deposited since the last glaciation. Many bone samples from these two sites are presently being dated by U-series disequilibrium. The results of these analyses, with comparisons with ^{14}C dates where possible, will be published in a forthcoming paper.

RESULTS AND DISCUSSION

From the data shown in Table 1, a few general observations can be made. First, all samples show high ^{230}Th/^{232}Th activity ratios, indicating that there has been little or no contamination with environmental Th. The only exception is the Pestera sample. In addition, for GOH-B through GOH-J, the ^{230}Th/^{232}Th ratio tends to be higher in the bulk bone than at the surface bone, which indicates only surface contamination with detrital material. The same is true for Sonde-B, C and D. The other samples appear to be more contaminated in the bulk.

For the Ngandong and Sonde samples, the U concentrations of the bulk bone are generally higher than those of the surface bone. This is not consistent with results published in the literature, where the U concentration as a function of depth (going from outside to the marrow cavity) follows a parabolic (U-shaped) trend (see FARQUHAR *et al.*, 1978; SCHWARCZ, 1982). The Gold Ox Hill samples, however, do not show this trend; the surface bone and bulk bone concentrations are almost identical for all samples, within the uncertainty limits.

There appears to be a correlation between the U concentration and the deduced ages. The observed trend for the ages indicates that where the U concentration is higher (i.e. in the bulk samples), the ages are systematically lower. This is apparently caused by the fact that as a result of the increased U concentration towards the core of the bone the ^{230}Th/^{234}U activity ratio decreases. This is true for the Ngandong and Sonde series. For the Gold Ox Hill series, where the U concentration is roughly constant throughout the bone, the ^{230}Th/^{234}U ages are also roughly the same for bulk and surface material. It should be kept in mind, however, that these bones from China were washed and cleaned before they arrived in our laboratory, which possibly might have affected the U concentration at the surface.

For the Ngandong site, the ages for the bulk samples are in good agreement with previously published results (BARTSTRA *et al.*, 1988). Furthermore, they are in agreement with expectations based on geomorphological reasoning (BARTSTRA *et al.*, 1988). The Gold Ox Hill ages are in fair agreement with those determined by CHEN and YUAN (1988), who in several cases obtained dates by means of ^{231}Pa dating. The Pestera and Ksar Akil sites are of importance because of their overlap with the radiocarbon dating

Table 1. Analysis of surface (S) and bulk (B) material of fossil bone

Site	Code	[U] (ppm)	^{234}U/^{238}U	^{230}Th/^{234}U	^{230}Th/^{232}Th	Age (ka)
Ngandong						
A	G-87602 S	56 (2)	1.11 (0.02)	0.84 (0.04)	415 (70)	188 (+26, −21)
	G-88028 B	91 (2)	1.06 (0.02)	0.42 (0.02)	38 (10)	58 (+4, −4)
B	G-87603 S	34 (1)	1.15 (0.04)	0.65 (0.03)	80 (12)	109 (+10, −9)
	G-88029 B	24 (1)	1.14 (0.05)	0.40 (0.03)	16 (4)	55 (+5, −5)
C	G-87604 S	23 (1)	1.11 (0.06)	0.75 (0.05)	117 (37)	145 (+24, −19)
	G-88030 B	24 (1)	1.11 (0.04)	0.42 (0.02)	32 (9)	59 (+5, −5)
Sonde						
A	G-88032 S	377 (5)	1.07 (0.01)	0.57 (0.01)	170 (30)	90 (+3, −3)
	G-88036 B	369 (4)	1.03 (0.01)	0.17 (0.01)	61 (7)	21 (+1, −1)
B	G-88033 S	215 (3)	1.02 (0.02)	0.30 (0.01)	60 (14)	39 (+2, −2)
	G-88037 B	499 (6)	1.01 (0.01)	0.11 (0.01)	135 (30)	13 (+1, −1)
C	G-88034 S	52 (1)	1.03 (0.03)	0.22 (0.01)	12 (2)	27 (+2, −2)
	G-88038 B	111 (1)	1.04 (0.01)	0.14 (0.01)	118 (36)	17 (+1, −1)
D	G-88035 S	45 (1)	1.22 (0.04)	0.23 (0.01)	7 (1)	28 (+2, −2)
	G-88039 B	81 (1)	1.05 (0.01)	0.21 (0.01)	49 (6)	26 (+1, −1)
Gold Ox Hill						
A	G-88040 S	37 (1)	1.51 (0.05)	0.78 (0.03)	314 (141)	145 (+13, −12)
	G-88048 B	32 (1)	1.50 (0.04)	0.85 (0.03)	93 (23)	171 (+16, −14)
B	G-88041 S	37 (1)	1.61 (0.05)	0.98 (0.03)	63 (10)	240 (und, −31)
	G-88049 B	32 (1)	1.74 (0.05)	0.94 (0.03)	103 (26)	206 (+22, −19)
C	G-88042 S	49 (1)	1.49 (0.04)	0.75 (0.02)	71 (11)	136 (+9, −8)
	G-88050 B	58 (1)	1.57 (0.05)	0.75 (0.03)	136 (36)	134 (+9, −9)
D	G-88043 S	55 (1)	1.52 (0.04)	0.80 (0.02)	128 (18)	150 (+10, −9)
	G-88051 B	63 (1)	1.54 (0.03)	0.79 (0.03)	169 (39)	148 (+11, −10)
E	G-88044 S	51 (1)	1.60 (0.02)	0.84 (0.02)	46 (3)	164 (+8, −7)
	G-88052 B	54 (1)	1.59 (0.04)	0.79 (0.02)	130 (28)	147 (+10, −9)
F	G-87600 S	61 (2)	1.58 (0.06)	1.00 (0.04)	19 (2)	257 (+51, −35)
	G-88053 B	63 (1)	1.55 (0.04)	1.07 (0.03)	655 (218)	>350
G	G-87601 S	116 (2)	1.26 (0.02)	0.73 (0.03)	80 (16)	135 (+11, −10)
	G-88054 B	118 (2)	1.32 (0.02)	0.76 (0.02)	410 (103)	143 (+8, −7)
H	G-88045 S	51 (1)	1.30 (0.02)	0.88 (0.02)	122 (20)	195 (+15, −13)
	G-88055 B	55 (2)	1.32 (0.04)	0.96 (0.03)	210 (64)	249 (+40, −30)
J	G-88046 S	65 (1)	1.26 (0.02)	0.78 (0.02)	148 (24)	151 (+8, −7)
	G-88056 B	43 (1)	1.16 (0.02)	0.66 (0.02)	142 (25)	113 (+5, −5)
Pestera						
15	G-88061 S	2.3 (0.2)	1.05 (0.13)	0.33 (0.07)	1.5 (0.4)	44 (+12, −11)
	G-88062 B	0.6 (0.1)	1.40 (0.24)	0.20 (0.06)	0.5 (0.2)	24 (+8, −8)
Ksar Akil						
XXVI BE V	G-88174 S	7.9 (0.6)	1.05 (0.11)	0.35 (0.05)	12 (5)	47 (+9, −9)
	G-88173 B	6.1 (0.1)	1.20 (0.14)	0.16 (0.03)	2.2 (0.8)	19 (+5, −5)
XXXII F V	G-88177 S	28 (1)	1.04 (0.05)	0.38 (0.02)	33 (9)	51 (+4, −4)
	G-88178 B	23 (1)	1.24 (0.07)	0.37 (0.03)	15 (4)	49 (+5, −5)

method. Unfortunately, in both sites the bones contain considerably less U than we found for the other three sites. The Pestera sample is dated at 26 ka by ^{14}C (GrN-15051), which is in remarkably good agreement with the bulk ^{230}Th/^{234}U date. Of the whole Ksar Akil site, only three radiocarbon dates are known and these were measured many years ago (MC-411, GrN-2195 and GrN-2579). Based on these data, we expect an age of ≃40 ka (GrN-2579: 43.8 ± 1.5 ka) for the layers considered in this work. At this moment we are not able to come to a definite conclusion on these data.

CONCLUSIONS

We have analysed fossil bones from five sites by the U-series disequilibrium method. From each bone, two samples were taken: one representing surface material, and one representing the inner bone (bulk).

The main trend observed for the Ngandong and Sonde sites is that the U concentration at the surface is lower than in the middle of the bone. This is obviously in contradiction with what has been found previously and this also seems to be the case for the limited data we have so far for the Pestera and Ksar

Akil sites. This can possibly be explained by leaching of U from the surface area of the bone at some time after deposition and initial U uptake. It indicates that the outer area (surface material) of the bones is not necessarily a closed system under all circumstances, so that U-series disequilibrium dating of this material may yield erroneous results.

In the near future, more bones will be analysed from both the Pestera and Ksar Akil sites, because of their overlap with the radiocarbon dating method. This should give more information on the validity of dates obtained by U-series disequilibrium. Furthermore, it is intended to analyse—where possible—the fossil bones by ^{231}Pa/^{235}U dating as well. Using appropriate models, one might be able to date bones which can not be considered to be a closed system.

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