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SOME REMARKS ON "ESR DATING OF BONES"

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Bones and teeth constitute an important component of archaeological and Pleistocene geological deposits. They not only allow the determination of the palaeoenvironment from the known ecological ranges of the organisms, but they may allow us to determine both the relative (paleontological) and absolute ages of these deposits. The latter possibility has been, until recently, largely limited to the use of ^{14}C in the dating of either the collagen fraction of bone, or the carbonate fraction of the bone mineral. Many attempts have been made, however, to use other techniques to date bones ranging in age well beyond the 50 ka time limit normally accepted for radiocarbon. In particular, uranium series dating has been used on both bones and teeth, with varying degrees of success (see for example, discussion on the U-series dates of the bones from Del Mar and Sunnyvale: Bischoff & Rosenbauer, 1981; 1982; Bada & Finkel, 1982). In addition some relative dating methods seem to give promising results on bones, such as amino acid racemization (Bada & Protsch, 1973; DeLumley et al., 1977; Hille et al., 1981) or the determination of elemental concentrations of uranium (Oakley, 1980) or nitrogen and fluorine (Eisenbarth & Hille, 1977; Hille et al., 1981; Molleson, 1981).

More recently, it has been shown that tooth enamel can be dated by electron spin resonance (ESR) (Grun & Invernati, 1985; Grun, 1985; Grun et al., 1987). Having demonstrated that ESR is applicable to tooth enamel when appropriate methods are used for determining both the accumulated dose and the time-dependent dose-rate of radiation (Grun et al., 1987), we should now inquire whether it is indeed possible to apply these methods to bone, and in general what are the prospects for the ESR dating of this ubiquitous material. In fact, the method has already been used by other workers on whole bone (Ikeya, 1982; Ikeya & Miki, 1980; 1981a&b; Mascarenhas et al., 1982, Yokoyama et al., 1981; 1982), and this paper is also a critique of these previous attempts. It should also be apparent that many of the problems in ESR dating of bone will also constitute problems for U-series dating, which will not be specifically discussed here.

COMPARISON OF BONE AND ENAMEL

It is first important to note the anatomical, physical, and mineralogical differences between these two types of tissues, both in their living state, and as fossilized material.

Living bone is a composite material, constructed of a mineral phase intergrown with a complex of tissues consisting principally of proteins, and dominantly of one protein: collagen. In living bone, the inorganic phase is very poorly crystallized. Table 1 shows the proportions of these components in bone and dentine, and contrasts them with enamel which contains very little organic (non-mineral) matter and initially contains larger crystals than does bone. Furthermore, enamel contains no amorphous phase.

Table 1:

Composition of enamel, dentine and bone (after Driessens, 1980)

		Enamel	Dentine	Bone
organic compounds	(%)	0.4-0.8	≈20	≈25
water	(%)	3.2-3.6	≈10	≈25
mineral phase	(%)	96-97	≈70	≈50
MINERAL PHASE:				
hydroxyapatite	(%)	100	≈50	≈50
crystal size	(Å)	260x300x680	30x500x500	50x400x400 & 40x40xNx660
amorphous phase	(%)	0	≈50	≈50

Approximate sign indicates large variations in analyses.

As seen in Table 1, about 40% of the inorganic portion of bone and dentine consists of spherical aggregates of amorphous Ca phosphate with an approximate formula of $Ca_9(PO_4)_6$ (Brown & Chow, 1976). It is noteworthy that during the inorganic precipitation of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], these amorphous phosphates occur as precursors of the final mineral phase (Eanes et al., 1976). It has been shown by Williams & Sallis (1982) that these amorphous calcium phosphates can be transformed directly into hydroxyapatite. Other minerals in bone are fluorapatite $Ca_{10}(PO_4)_6F_2$ and octacalcium phosphate $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (Brown & Chow, 1976); the latter is also not found in enamel.

Soon after death (within a few minutes) the ultrastructure of bone begins to change, a process which steadily continues long after death, and is still going on in buried fossil bone many millennia or hundreds of millennia after death. The major processes which characterize this postmortem transformation of bone appear to be:

1.) increase in crystal size
2.) crystallization of all amorphous Ca phosphate
3.) dehydration
4.) denaturation and biodecomposition of protein and other organic constituents.
5.) chemical change of the mineral phase, largely through uptake of ions from ground water, such as U, F. (see, for example, Henderson et al, 1983; Badone and Farquhar, 1982; Molleson, 1981)

Other more drastic changes that can take place include replacement of the bone mineral (apatite) by other phosphates or other non-phosphate minerals (eg calcite); dissolution of significant amounts of the bone mineral; and filling of the pore space in bone that survives in the ground for more than a few million years; such bone is referred to as "mineralized".

Unfortunately, at the present time we have only a very poor understanding of the details of these processes. A thorough review of the literature has revealed only a handful of papers written over the past 20 years that are devoted to mineralogical or chemical changes in buried bone.

On the other hand, much less change is expected during fossilization of enamel

due to its initially larger crystal size, absence of amorphous phase, and lack of organic matter. Thus, for example, Wyckoff et al. (1963) note no visible changes in 100 Ma old tooth enamel, but a little alteration of the associated dentine. However, Brophy & Hatch (1962) observe definite recrystallization of Pleistocene tooth enamel.

ESR SPECTRA OF BONE AND ENAMEL

The ESR-Spectra for bone and teeth are essentially the same. The radiation sensitive signals at g = 2.0018 and g =1.9976 are certainly due to the mineral phase of bone and teeth (Houben, 1970; Ostrowski et al., 1971; 1974) and have been attributed to a CO_3^{3-} radical (Cevc et al., 1972; Sato, 1979; Caddie et al., 1985); this was, however, doubted by other authors (Peckauskas & Pullman . 1978; Van Willigen et al., 1980; Bacquet et al., 1981; Geoffroy & Tochon-Danguy, 1982). Doi et al. (1979 a&b; 1980,1981) attributed the signals at g=2.0023 and 1.9976 to CO_3^{3-} and postulated a different but unknown center for the dominant g=2.0018 line. However, irradiation and annealing behaviour of the lines g=2.0018 and 1.9976 suggest strongly that these belong to the same center (Grun et al, 1987).

Ikeya (1985) suggested, that fluorine uptake might lead to a decrease of ESR-sensitivity (and underestimation of AD) since his laboratory tests showed a decrease of ESR intensity with increasing F concentration. F-ions replace the OH-group in the hydroxyapatite lattice. Assuming that the ESR signal in fossil teeth and bone represent a CO_3^{3-} center this uptake of fluorine should only affect, if at all, the signal from CO_3 ions at the OH sites (up to 11% of the total, Elliott et al., 1985). It is generally questionable, whether a continuous decrease of available traps would lead to an underestimation of AD, as long as this partial destruction of traps affects the "filled" and "unfilled" traps to the same extent. It is not likely, that fluorination leads to a recombination of trapped electrons followed by creation of new (and empty) traps with the same magnetic characteristics. It is more likely that fluorination will simply lead to a slight decrease in the sensitivity of the hydroxyapatite crystal.

The ESR signal of the amorphous phase seems to be identical to that of hydroxyapatite, but shows a low thermal stability (20% remaining after storage for 40h at room temperature: Houben 1970). Since the stable ESR signals of enamel, bone and synthetic hydroxyapatite are identical (Ostrowski, 1974), it is rather likely that the stable ESR-signals of bones originate within the hydroxyapatite crystals (unstable components might be generated by collagen, proteins or surface interactions of small sized hydroxyapatite crystals; Ostrowski et al, 1974).

Assuming that indeed the main ESR signal is due to CO_3^{3-}, we must note that $C0_3$ can occur in the hydroxyapatite lattice substituting for either a PO_4 or two OH ions (where it constitutes about 11% in human tooth enamel; Elliot et al., 1985). According to Doi et al. (1980) the resulting ESR signals are not measurably different.

The ESR spectra of bone are additionally complicated by the fact that they may display fairly intense signals from free-radicals of amino acids or other organic compounds. This problem is greater in bone than in teeth, due to the higher

organic content of the former. The g- value of the "alanine" free-radical is not very far removed (g=2.0036) from that of the 2.0018 signal for the bone/tooth mineral itself, and will interfere in determinations of AD by the additive dose method, due to the great sensitivity of the free-radical to irradiation.
TL-dating on bone and enamel has also been attempted (e.g., Cristodulides & Fremlin, 1971; Driver, 1979). The method seems to be promising but the TL-spectra seem to be strongly interfered by chemiluminescence effects. Another problem is that the second glow curve of tooth enamel and probably bone as well is affected by decomposition of the organic matter.

URANIUM UPTAKE

One serious problem occurring in the dating of both bones and enamel is the accumulation of uranium (Charalambous & Papastefanou, 1977; Molleson, 1981; Henderson et al., 1983). Two different U-accumulation models have been proposed (see Ikeya, 1982; Grun et al., 1987): early uranium uptake (henceforth EU) where the present-day content of uranium is assumed to have been accumulated soon after burial; and continuous, linear U-uptake (LU), in which the content of uranium is approximated by a linear function of time. Since there is generally no independent indication as to which model should be applied for a sample under investigation, two ages are generally calculated.

In considering U-uptake, it is important to appreciate the various mechanisms by which this may occur. In general, U is present in soil as an insoluble U^{4+} species, possible bound on or in some silicate or oxide mineral. Soluble uranyl ions are produced by oxidation, and can then travel through soil water to be taken up by bones or teeth. The uptake can occur either by:

a) reduction of the U^{6+} back to insoluble U^{4+}
b) adsorption of uranyl ions by humic matter formed during decomposition of collagen, etc.
c) uptake of either U^{4+} or U^{6+} by the apatite crystals
d) physical trapping of U-bearing minerals in the pore-spaces of the bone.

It can be seen that U-uptake is likely to be greater in bone than in teeth, as is shown also by the much higher concentrations of U in the former (see Szabo, 1982; Seitz & Taylor, 1974). Also, as the bone constantly recrystallizes and as its large initial content of organic matter decreases through time, the rate of uptake is likely to change markedly, making it very difficult to model this process. On the contrary, enamel does not recrystallize as much, due to its larger initial crystal size, and should experience much less uptake by organic matter. Nevertheless, both teeth and bones are seen to increase their U content through time. Furthermore, Badone & Farquhar (1982) found that the U concentration in bones can actually go through a maximum, possibly due to loss of organic-bound U.
Note, however, that the problem of U uptake by bone (as opposed to enamel) is a serious one in the dating of enamel as well. This is because a large part of the beta-ray dose accumulated by the enamel arises from U in the adjacent layers of dentine or cementum. Therefore, it is important to understand the U-uptake process in this case, as well.

AN EXPERIMENTAL TEST

In order to get a clearer idea of the difference in behaviour of enamel and bone, we have done ESR analyses of enamel and associated dentine from the Bilzingsleben archaeological site. The dentine/cement is taken to behave like bone, which it resembles histologically. Table 2 and Fig. 1 show the calculated ages for these samples. The details of sample preparation, signal processing and age calculation and measured values of the enamel samples are given in Grun et al. (1987) and Schwarcz et al. (1987).

Independent U-series and ESR results on the surrounding travertine and the geomorphological history of this site imply an age at least as old as that corresponding to oxygen isotope stage 9 (303-339 ka, Imbrie et al., 1984), but more likely attributable to stage 11 (362-423 ka). As can be seen from Fig. 1, the LU-enamel ages agree with stage 11 and the EU-enamel ages with stage 9. It is hoped that improvements in our modelling of the U-uptake history via studies of U-series disequilibria (Grun & Schwarcz, in preparation) will resolve the uncertainty in the age of the enamel samples.

All age-results on the dentine are, however, far too young compared with the expected age of the site even when calculated for a 100% Rn-loss (which was not assumed in the enamel calculations). U-series studies show, that the $^{230}Th/^{234}U$ ratios of enamel are lower than the ratios in the attached dentine or cement layers. This indicates that uranium concentration has risen faster in the dentine/cement than in the enamel. This finding would imply, that the dose rate for the enamel should be calculated according a mixed model, but it also suggests that the LU-uptake model is more appropriate for enamel and the EU-model (or some approximation to it) for dentine. This, however, increases the discrepancy in ESR ages between the enamel and dentine, and does not account for the low dentine ages compared to the independent U-series and geological estimates.

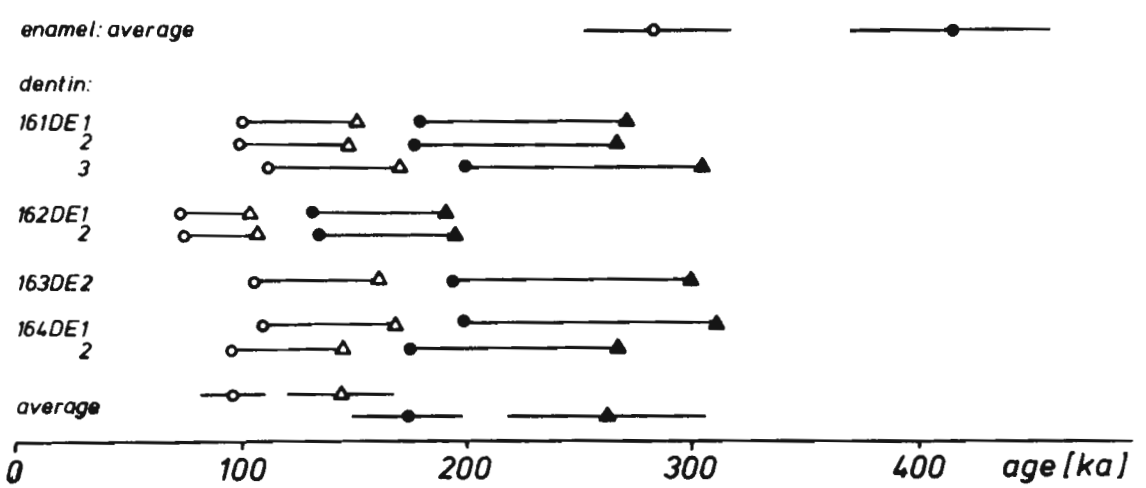

Figure 1. *ESR age results on tooth enamel and dentine from the Bilzingsleben archaeological site*
circles: no Rn-loss *open: ages according early U-uptake (EU)*
triangles: 100% Rn-loss *black: ages according linear U-uptake (LU)*

Table 2:
Results of the chemical and ESR analyses on dentine samples from Bilzingsleben archaeological site

No.	AD	U-cont	H_2O		Sediment			Dose-rates			EARLY U-ACCUM.		LINEAR U-ACCUM.	
		[ppm]	DENT	SED	U	Th	K	Cos.	Sed		int. D-r	AGE	int.D-r	AGE
161 DE1	865	26.9	5	15	1.92	4	0.60	75	552.8	a:	8182.8	99.4	4304.5	179
										b:	5292.7	149	2691.4	269
161 DE2	909	29.1	5	15	1.92	4	0.60	75	552.8	a:	8789.9	97.6	4625.0	176
										b:	5706.2	146	2904.9	265
161 DE3	982	26.5	5	15	1.92	4	0.60	75	552.8	a:	8374.0	110	4403.9	199
										b:	5321.2	169	2698.6	304
162 DE1	834	42.18	6	15	1.71	3	0.63	75	496.8	a:	11165.6	71.7	5906.5	130
										b:	7683.5	102	3939.8	189
162 DE2	860	42.32	6	15	1.71	3	0.63	75	496.8	a:	11290.2	73.2	5982.7	133
										b:	7750.2	105	3969.5	194
163 DE2	1373	40.82	5	15	1.71	3	0.59	75	488.6	a:	12691.3	105	6697.5	192
										b:	8133.5	161	4147.4	299
164 DE1	1553	43.49	4	15	2.08	3	0.67	75	541.4	a:	13846.6	108	7316.6	198
										b:	8843.9	167	4506.9	310
164 DE2	1335	44.40	4	15	2.08	3	0.67	75	541.4	a:	13497.2	95.5	7125.9	174
										b:	8816.7	144	4502.7	267
Units		[Gy]	[ppm]	[wt.%]		[ppm]	[%]		[mGy/ka]		[mGy/ka]	ka	[mGy/ka]	ka

Notes.
a: 0% Radon loss b: 100% Radon loss.

Considering the various differences between enamel and bone as discussed above, we can propose various hypotheses to account for this difference. First, if bone continuously recrystallizes while it is buried, then the ESR signal stored in newly formed crystals will be much "younger" than the age of burial, as the crystals themselves will have formed continuously since that time. The creation of new traps leads to an increase of ESR sensitivity, which in turn causes an underestimation of AD when using the additive dose method. Secondly, as the bone is altered by decomposition of the organic matrix, it becomes more porous and two processes can occur: a) trapping of U-bearing colloidal particles from the soil water; b) increased exposure of the newly recrystallized apatite to U-bearing water. Both of these processes will tend to lead to sub-linear U-uptake (ie accelerating through time), and will produce ages that are anomalously young. One can equally well imagine other situations where the U content passes through a maximum (as observed by Seitz and Taylor, 1974; Badone & Farquhar, 1982), which would cause underestimates of the integrated dose rate. In general therefore, we expect to observe rather erratic results in ESR dating of bone.

The question arising is, why "good agreements" have been observed by other workers between ESR results and supposed geological or archaeological age. It appears that in most cases the ESR "ages" were not determined but the dose rate was assumed (Ikeya & Miki, 1980; 1981a&b; Mascarenhas et al., 1982): about 10 mGy/a for open sites and 1-2 mGy/a for caves. For a 100 ka sample, a mean dose rate of 10 mGy/a and of 1 mGy/a would be produced internally by about 4 and 40 ppm U respectively, assuming k=0.1 (or 8 and 80 ppm with linear U-accumulation). For a 500 ka sample, 2.5 ppm U is sufficient to produce a mean dose rate of 1 mGy/a due to the fact that its daughters have grown into equilibrium. But in any case we must assume that bones accumulate U over time (although the precise

mechanism is unknown) leading again to an increasing dose rate with time. Therefore, it is rather dangerous to assume a constant dose rate for a specific type of locality. Indeed, the U-concentration in bones within one site and even in one stratigraphic layer can vary greatly, even over one order of magnitude (Hennig & Grun 1983; Seitz and Taylor, 1974).
In those cases where the dose rate for bones was determined from the U-concentrations (e.g. Yokoyama et al., 1981; 1982) severe age underestimations were observed.

CONCLUSIONS

Given the complexity of the diagenetic processes affecting fossil bone (including the complexity of its U-uptake history), it is, in our opinion, impossible at this time to perform ESR dating on bones. If extensive basic studies of bone-fossilization and further laboratory experiments are first carried out, then it may be possible to find optimal conditions and types of bone for which ESR ages can be applied.Furthermore, careful comparisons between such ESR ages and other independent estimates of age as have been done here, must be carried out. In the meantime, the term "ESR-dating of bones " should be avoided.

REFERENCES

Bacquet, G., Truong, V.Q., Vignoles, M., Trombe, J, C. & Bonel, G (1981): ESR of C0\S\UP-,Do2 in X-irradiated tooth enamel and A-type carbonated apatite. *Calcified Tissue Int.* , **33**, 105-109.

Bada, J. L. & Finkel, R. (1982): Comment on "Uranium series ages of the Del Mar Man and Sunnyvale skeletons".*Science* , 217, 755.

Bada, J. L. & Protsch, R. (1973): Racemization reaction of aspartic acid and its use in dating fossil bones.*Proc. of the Nat. Acad. of Sci. of the USA* , **70**, 1331 - 1334.

Badone, E., & Farquhar, R. M. (1982): Application of neutron activation analysis to the study of elemental concentration and exchange in fossil bones. *J. Radioanalytical Chem.* , **69**, 291-311.

Bischoff, J. L. & Rosenbauer, R. J. v(1981): Uranium series dating of human skeletal remains from the Del Mar and Sunnyvale sites. California, *Science* , **213**, 1003-1005.

Bischoff, J. & Rosenbauer, R. J. (1982): Reply.*Science* , **217**, 756.

Brophy, G. P. & Hatch, T. M. (1962): Recrystallization of fossil horse teeth. *American Mineralogist* , **47**, 1174-1180.

Brown, W. E. & Chow, L. C. (1976): Chemical properties of bone mineral. *Ann. Rev. of Mat. Sci.* , **6**, 213-236.

Caddie, D. A. , Hall, H. J., Hunter, D.S. & Pomery, P.J. (1985): ESR considerations in the dating of Holocene and Late Pleistocene bone material. In: Ikeya, M. & Miki, T. (eds), *ESR Dating and Dosimetry* , 353-362.

Cevc, P., Schara, M. & Ravnik, C. (1972): Electron paramagnetic resonance study of irradiated tooth enamel. *Rad. Research* , **51**, 581 - 589.

Charalambous, S. & Papastefanou, C. (1977): On the radioactivity of fossil bones. *Nucl. Inst. and Methods* , **142**, 581 -588.

Christodoulides, C. & Fremlin, J.H. (1971): Thermoluminescence of biological materials. *Nature* , **232**, 257 -258.

DeLumley, H., DeLumley, M.A., Bada, J.L. & Turekian, K.K. (1977): The dating of Pre-Neandertal remains at Caune de l'Arago, Tautavel, Pyrenees-Orientales, France. *J. Human Evolution* , **6**, 223 - 225.

Doi, Y., Aoba, T., Moriwaki, Y., Okazaki, M., & Takahashi (1980): Orientation of carbonate ions in human tooth enamel studied with use of the CO_3^{3-} radical ions as probes. *J. Dental Research* , **9**, 1473-1477.

Doi, Y., Aoba, T., Okazaki, M., Takahashi, J. & Moriwaki, Y. (1979): Analysis of paramagnetic centers in X-ray irradiated enamel, bone and carbonate-containing hydroxyapatite by electron spin resonance spectroscopy. *Calcified Tissue Int.* , **28**, 107 - 112.

Doi, Y., Aoba, T., Okazaki, M., Takahashi, J. & Moriwaki, Y. (1981): ^{13}C enriched carbonate apatites studied by ESR: comparison with human tooth enamel apatites. *Calcified Tissue Int.* , **33**, 81-82.

Driessens, F.C.M. (1980): The mineral in bone, dentine and tooth enamel. *Bull. Soc. Chimique de Belgique* , **89**, 663-689.

Driver, H.S.T. (1979): The preparation of thin slices of bone and shell for thermoluminescence. *PACT J.* , **3**, 290-297.

Eanes, E.D., Termine, J. D. & Nylen, M.U. (1973): An electron microscopic study of the formation of amorphous calcium phosphate and its transformation to crystalline apatite. *Calcified Tissue Research* , **12**, 143 - 158.

Eisenbarth, P. & Hille, P. (1977): A non destructive method for age determination of fossil bone - A critical review -, *J. Radioanalytical Chemistry* , **40**, 203-211.

Elliott, J.C., Holcomb, D. W. & Young, R.A. (1985): Infrared determination of the degree of substitution of hydroxyl by carbonate ions in human dental enamel. *Calcified Tissue Int.* , **37**, 372 - 375.

Geoffroy, M. & Tochon-Danguy, H.J. (1982): ESR identification of radiation damage in synthetic apatites: a study of the 13C-hyperfine coupling, *Calcified Tissue Int.* , **34**, S99-S102.

Grun, R. (1985): Beitrage zur ESR-Datierrung, *Sonderveroffentlichungen des Geologischen Instituts der Universitat zu Koln* , **59**, 1-157.

Grun, R. & Invernati, C. (1985): Uranium accumulation in teeth and its effect on ESR dating - A detailed study of a mammoth tooth, *Nucl. Tracks* , **10**, 869-878.

Grun, R. & Schwarcz, H.P. (in preparation): U disequilibrium, U uptake, and ESR dating of teeth, Presentation to be held at : 5th Int. Specialist Seminar on TL and ESR Dating, 6-10 July, 1987, Cambridge.

Grun, R., Schwarcz, H.P. & Zymela, S. (1987): ESR dating of tooth enamel. *Can. J. Earth Sci.* , **24**, (in press).

Henderson, P., Marlow, C.A., Molleson, T.I. & Williams, C.T. (1983): Patterns of chemical change during bone fossilization, *Nature*, **306**, 358-360.

Hennig, G.J. & Grun, R. (1983): ESR dating in Quaternary Geology , *Quat.Sci. Rev.*, **2**, 157-238.

Hille, P., Mais, K., Rabeder, G., Vavra, N. & Wild, E. (1981): uber Aminosauren - und Stickstoff/Fluor-Datierung fossiler knochen in ostereichischen Hohlen. *Die Hohle* , **32**, 74-91.

Houben, J.L. (1971): Free radicals produced by ionizing radiation in bone and is constituents, *Int. J. of Radiation Biology* , **20**, 373-389.

Ikeya, M. (1982): A model of linear uranium accumulation for ESR age of Heidelberg (Mauer) and Tautavel bones. *Jap. J. Appl.Phys.* , **21**, L690-L692.

Ikeya, M. (1985): Dating methosds of Pleistocene deposits and their problems:: IX) Electron spin resonance, *Geoscience Canada* , Reprint Series, **2**, 73-87.

Ikeya, M. & Miki, T. (1981): Archaeological dose of Arago and Choukoutien Materials with electron spin resonance (ESR), In: DeLumley, H. & Labeyrie, J. (eds): *Absolute dating and isotope analysis in prehistory - methods and limits*, Proceedings, Pretirage, 493-505.

Ikeya, M. & Miki, T. (1981): Archaeological radiation dose of bones at archaeologically important sites with electron spin resonance, *Union Int. des Sciences Prehistorie et Protohistorie, X Congress, Mexico* , Proceedings, 39-53.

Imbrie, J., Hays, J.D., Martinson, D.G., McIntyre, A., Mix,, A.C., Morley, J.J., Pisias, N.G., Prell, W. L. & Shackleton, N.J. (1984): The orbital theory of Pleistocene climate: support from a revised chronology of the marine 180 record, In: Berger, A., Imbrie, J., Hays, J., Kukla, G. & Saltzman, B. (eds), *Milankovitch and Climate* , Part I, 251-264.

Mascarenhas, S., Baffa Filho, O. & Ikeya, M. (1982): Electron spin resonance dating of human bones from Brazilian shell mounds (Sambaquis), *Am. J. Physical Anthrop.* , **59**, 413-417.

Molleson, T.I. (1981): The application of the principles of bone fossilization to relative dating poroblems, with particular reference to the bones from the Caune de l'Arago at Tautavel, In: DeLumley, H. & Labeyrie, J. (eds): *Absolute dating and isotope analysis in prehistory - methods and limits*, Proceedings, Pretirage, 659-676.

Oakley, K.P. (1980): Relative dating of the fossil hominids of Europe, *Bull. of the Brit. Mus. of Nat. Hist. (Geology)* , **34**, 25-46.

Ostrowski, K., Dziedzic-Goclawska, A., Stachowicz, W., Michalik, J., Tarsoly, E. & Komender, A. (1971): Application of the electron spin resonance technique for quantitative evaluation of the resorption rate of irradiated bone grafts, *Calcified Tissue Research* , **7**, 58-66.

Ostrowski, K., Dziedzic-Goclawska, A., Stachowicz, W., & Michalik, J. (1974): Accuracy, sensitivity, and specificity of electron spin resonance analysis of mineral constituents of irradiated tissues,

Annals New York Acad. of Sci. , **238**, 186-200.
Peckauskas, R.A. & Pullman, I. (1978): Radiogenic free radicals as molecular probes in bone, *Calcified Tissue Research* , **25**, 37-43.

Sato, K. (1979): Study of asymmetric ESR signal in X-irradiated human tooth enamel, *Calcified Tissue Int.* , **29**, 95-99.
Schwarcz, H.P., Grun, R., Latham, A.G., Mania, D. & Brunnacker, K. (1987): New evidence for the age of the Bilzingsleben archaeological site, *Archaeometry* , (submitted manuscrjipt).
Seitz, M.G. & Taylor, R.E. (1974): Uranium variations in a dated fossil bone series from Olduvai Gorge, Tanzania, *Archaeometry* , **16**, 129-135.
Szabo, B.J. (1982): Uranium-series disequilibrium data for tooth fragments from the fossil hominid site at Ternifine, Algeria, *S. African J. Sci.* , **78**, 205.
Van Willigen, H., Roufosse, A.H. & Glimcher, M.J. (1980): Proton and phosphorous ENDOR on paramagnetic centers in X-irradiated, oriented human tooth enamel, *Cacified Tissue Int.* , **31**, 70.
Williams, G. & Sallis, J.D. (1982): Structural factors influencing the ability of compounds to inhibit hydroxyapatite formation, *Calcified Tissue Int.* , **34**, 169-177.
Wyckoff, R.W.G., Hoffmann, V.J. & Matter III, P. (1963): Microradiography of fossilized teeth, *Science* , **140**, 78-80.
Yokoyama, Y., Nguyen, H.V., Quaegebeur, J. -P. & Poupeau, G. (1982): Some problems encountered in the evaluation of annual dose rate in the electron spin resonance dating of fossil bones, *PACT J.* , **6**, 103-115.
Yokoyama, Y., Quaegegeur, J.P., Bibron, R., Leger, C., Nguyen, H.V. & Poupeau, G. (1981): Electron spin resonance (ESR) dating of fossil bones of the Caune de l'Arago at Tautavel, In: DeLumley, H. & Labeyrie, J. (eds): *Absolute dating and isotope analysis in prehistory - methods and limits* Proceedings, Pretirage, 457-492.

PR Reviewers comments (Barnaby Smith)

This paper clearly shows the probelms which can arise when ESR (or TL) dating is attempted on a complex material such as bone. The samples were presumably crushed for measurement, which may have further complicated the picture. Rae and Ivanovich (Applied Geochemistry, **1**, pp 419 -426, 1986) have had success dating fossil bones by uranium series when only the outer 0.5 to 2 mm was used. This portion of the bone generally had the highest uranium content and gave ages in agreement with control dates whereas total cross-sections gave anomalously young ages. The surface layers therefore appear to better approximate a closed system. Choosing these for ESR analyses would allow more accurate alpha (and probably beta) dose calculations, but the problems of recrystallization may still remain. Another point which has not been raised in the paper is the possibility of systematic errors in the fitting of the ESR growth curve. Presumably the saturation level is high enough for the form of the curve fitting to make little difference and therefore not account for the massive discrepency.

Authors' Response

We did not mention the possibility of taking samples from the outside in order to investigate a closed system for U-uptake, since there are still some objections against it (work by Pavlish and Farquhar at the Univ. of Toronto).