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THE POTENTIAL OF ESR DATING OF TOOTH ENAMEL

by

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ABSTRACT

A problem often occurring in the attempt to date archaeological sites is a lack of material suited for the various dating methods, especially, when the site is assumed to be beyond the radiocarbon dating range.

Recent progress in ESR dating of tooth enamel opens the possibility to evaluate age assignments for many sites. The dating range of this new technique is between a few thousand to at least 1-2 million years, which covers approximately the entire Pleistocene epoch. However, this method, which is still under research, contains some problems, especially the still unknown process of uranium accumulation in teeth. Nevertheless, comparative studies with other dating methods, e.g., at Bilzingsleben gave very promising results.

INTRODUCTION

Electron spin resonance (ESR) spectroscopy allows the detection of free electrons or free radicals. After the discovery of the basic principles in 1945 by ZAVOISKY this method has been widely applied in mineraolgy, solid state physics, and biochemistry (see e.g. MARFUNIN, 1979; LOW, 1968; SYMONS, 1978).

ZELLER *et al.* (1967) were the first who suggested to use this technique for dating purposes, but it took until 1975 that Ikeya applied ESR for the dating of speleothems. From that time on, ESR dating was applied in many fields in geology and archaeology and review papers were published by IKEYA (1978), HENNIG and GRÜN (1983), and NAMBI (1985). Figure 1 summarizes the materials and minerals on which ESR dating has been applied so far (the brackets indicate that those materials still face some unsolved problems).

ESR DATING

In a mineral which is an insulator electrons can occur at two different energy states, the valence band and the conduction band (see Figure 2). Normally, all electrons are in the ground state, but they can be excited to the conduction band by interaction with radioactive particles (α-, β-, γ- , and cosmic rays). After a short time of diffusion these

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electrons recombine with the holes which were left behind near the conduction band. However, a few electrons are captured in the energy zone between those two bands by charge deficit sites (traps, which might be lattice defects or e.g., Y^{3+} substituting Ca^{2+}) and there they can be detected by ESR-spectroscopy. The number of trapped electrons is proportional to strength of the radioactivity and the irradiation time since these traps were emptied (zeroed) for the last time. Such a zeroing process can be the precipitation of the mineral (e.g., speleothems or, in this case, the growth of a tooth), heat (e.g., firing or contact-metamorphism), or stress (in fault zones).

Each of those defects shows a characteristic ESR-signal (see e.g., Figure 3) and the signal height is proportional to the number of trapped electrons and, hence, to the age of the sample. An ESR age is derived from the formula:

$$\text{AGE [a]} = \text{accumulated dose (AD) [Gy]} / \text{dose rate (D) [Gy/a]}$$

where the accumulated dose is the radioactive dose the sample has received since the time of its last zeroing and the dose rate is principally derived from the radioactive elements in the sample and its surroundings. In the attempt to date tooth enamel, several peculiarities have to be considered (a detailed description of this special application was given by GRÜN *et al.*, 1987).

DETERMINATION OF ACCUMULATED DOSE (AD)

The AD of the sample is determined by ESR spectroscopy. Several aliquots of the sample are irradiated with successively increasing artificial γ-doses and the extrapolation against zero-ESR intensity allows the determination of AD (Figure 4). However, several problems have to be considered: enamel (hydroxyapatite) shows an ESR signal at $g = 2.0018$ (see Figure 3, top) which is due to the CO^{3-}-radical. This peak is often interfered with organic radicals (see Figure 3, lower spectrum) which make it difficult to determine the height of the apatite signals. GRÜN *et al.* (1987) show that this effect can be eliminated by measuring the signal with a large modulation amplitude (5 G_{pp}), which actually "smears out" these interfering signals.

Another problem is the saturation behaviour of the signal upon radiation. It was shown (GRÜN *et al.*, 1987) that geological samples with AD's of $\geq$ 10 Grays do not show a linear growth of the ESR signal. Therefore, a logarithmic evaluation of AD as suggested by APERS *et al.* (1981) has to be performed. Figure 5 shows the effect of the logarithmic AD-extrapolation compared to a linear evaluation: although the linear curve-fitting shows a correlation coefficient of $r = .9993$, the logarithmic AD is about 20 % lower with $r = .9999$.

DETERMINATION OF DOSE RATE (D)

An enamel layer can principally be found in three different environments (see Figure 6) and the trapped electrons are possibly generated from four different radioactive sources:

(i) cosmic rays
(ii) the radioactive elements of the surrounding matrix
(iii) uranium and its daughter products in the dentine or cement attached to the enamel layer
(iv) uranium and daughters in the enamel layer itself.

Alpha-, beta-, and gamma-particles have very different ranges; in a material with a density of 2.95 g cm^{-3} (hydroxyapatite) they are about 20 µm, 2 mm, and 30 cm, respectively.

Cosmic rays can be determined with a calibrated, portable gamma-spectrometer at the site where the tooth was found or from attenuation curves as published by PRESCOTT and STEPHAN (1982).

The effect of α-rays from the surroundings can be eliminated by removing at least the outer 20 μm from enamel sample. The concentrations of the radioactive elements of the surrounding matrix can be determined by a portable gamma-spectrometer in the field or by chemical analysis (neutron activation analysis, fission track, atomic absorption-, mass-, or γ-spectroscopy) in the lab.

Since the attached dentine or cement layers are relative thin, only beta irradiation from this source has to considered. Generally, Th and K concentrations in these layers are negligible.

Enamel irradiates itself with α- and ß- rays from the U-decay chains (internal dose rate). Since alpha-particles do not produce as much ESR-intensity as an equivalent ß- or γ-dose, the so called "α-efficiency" has to be determined. Since this evaluation is relative expensive (see GRÜN, 1985), a value of .15 (determined independently by ^{210}Po-doping (DeCANNIERE *et al.*, 1986) and external alpha-irradiation of fine grain samples (GRÜN, 1985)) is normally assumed.

After determining the concentrations of the radioactive elements in the various sources, the dose rate can then be calculated by using published tables (e.g., BELL, 1979 or NAMBI and AITKEN, 1986).

These dose rate calculations are complicated by the following factors:

- water content in the sediment and dentine/cement;
- a complex history of the water content in sediment;
- a complex history of the sedimentation-rate (influencing the cosmic- and gamma dose rate);
- beta-ray attenuation in thin layers (see GRÜN, 1986);
- radioactive disequilibria in the U-series decay chains (between ^{234}U and ^{238}U; ^{230}Th and ^{234}U; ^{231}Pa and ^{235}U);
- ^{226}Ra and ^{222}Rn escape from the tooth or the sediment.

A detailed discussion and mathematical treatment of these processes are given by GRÜN *et al.* (1987).

However, the still unsolved problem of uranium uptake by teeth introduces the largest uncertainty in this particular application of ESR-dating. Recent teeth contain uranium in the range of a few 100 ppb. Fossil teeth, however, display U-concentrations up to about 1000 ppm.

Two different U-uptake models for teeth are discussed in the litarature (see e.g., IKEYA, 1982):

- **early U-uptake**: concordant Th/U and Pa/U ratios within U-series dating of bones (see e.g., BISCHOFF and ROSENBAUER, 1981a and b) imply an uranium uptake of the bone within a few thousand years after the bone was buried.

- **continuous, linear U-uptake**: even very old bones from Pliocene (TUREKIAN *et al.*, 1970) show disequilibria in the U-decay chains. Investigations by BADONE and FARQUHAR (1982) and GRÜN and INVERNATI (1985) show, that uranium is accumulated by bones and teeth up to a saturation level (which may be in the range of 500

to 1000 ppm) and that a saturation front migrated into the bone or tooth.

Figure 7 shows the effect of U-accumulation on the resulting age: as long as the U-concentration in dentine is low (< 5 ppm) the resulting age is mainly controlled by the radioactivity of the surrounding matrix. With increasing U-content the beta-dose rate from the dentine as well as the internal alpha- and beta- dose from the enamel gets more and more dominant and with it the discrepancy between the age calculated according an early and a continuous U-uptake (see Figure 7 below). The mathematical formulas for these models are given by GRÜN *et al.* (1987).

There are two possibilities to minimize the effect of U-uptake to some extent:

(i) samples are cut out of the center of a large tooth (e.g., mammoth), here, the outside accumulates nearly all the uranium and acts as a buffer for the center (see e.g., GRÜN and INVERNATI, 1985). Many such samples still show U-concentrations typical of recent teeth (see example from Saskatchewan).

(ii) small enamel pieces with no organic matter attached are collected, since the migration rate into enamel is much slower than into dentine or cement (by at least an order of magnitude) (see example from Bilzingsleben).

Although most of our results show a good agreement with other independent dating methods, when the model of linear U-uptake was applied, sometimes the early uptake model seems to give the "right" age (see e.g. ZYMELA, 1986). Therefore, it can only be stated, that the true age is normally somewhere between the "early" and the "linear" age.

LIMITS OF THE METHOD

The method is principally limited by two factors:

1. the sample is saturated, i.e. all traps available are filled with electrons and no signal increase can be induced by additional radiation. However, even after an artificial irradiation of 20 kGy no enamel sample which we have studied has been saturated. Considering dose rates in the range of 5000 mGy/ka complete saturation should not occur before 4 Ma.

2. thermal instability of the trapped electrons. All electrons have only a limited probability of being trapped. After the so-called mean life has passed about 69 % of the trapped electrons have left the trap (by recombination). This value can only roughly be determined (see DEBENHAM, 1983) and for tooth enamel, is supposed to be in the range of 10^7 to 10^8a (at 25°C). An age determination in the range of 20 % of this value (at least 2 Ma) would cause an underestimate of age of about 10 %.

APPLICATION

1. A mammoth tooth from the Saskatchewan Sands near Edmonton

The first example presented here is a mammoth tooth found in the Villeneuve Pit in Saskatchewan (see GRÜN *et al.*, 1987). Geological evidence shows only that the sediments are preglacial. Although the thirteen dates determined for this tooth scatter to such an extent (see Figure 8), that a very accurate age determination is not possible, the results combined with the geological setting (preglacial) allows a reliable assignment of these sediments into oxygen isotope stage 5.

2. Single enamel layers from Bilzingsleben archaeological site

The Bilzingsleben (E-Germany) archaeological site is famous for its *Homo erectus* remains. The remains from the so called "Steinrinne" are embedded in a spring deposited travertine, which today forms the top of a hill. Subsequent to the deposition of this travertine a valley lowering took place and at least three river terraces with gravel deposition were developed (for a profile see MANIA, 1983). Two previous U-series investigations on the travertine by HARMON *et al.* (1980) and BRUNNACKER *et al.* (1983) suggested an assignment of this deposit into stage 7 (about 190 to 250 ka, see Figure 9). This is in contradiction to the geological setting (at least stage 9) and the anthropological findings. Later, this profile was remeasured by the McMaster dating group headed by H.P. SCHWARCZ (for details and analytical data see SCHWARCZ *et al.*, 1988). All U-series results gave infinite ages. ESR-investigations on the travertine samples were complicated by interferences caused by organics (see GRÜN and DeCANNIERE, 1984); however, two samples yielded ages in the range of stage 11 to 13.

ESR studies on 4 enamel pieces (with dentine attached on one side) show, that even the age results determined according the early U-uptake are older than the previous U-series data by HARMON *et al.* (1980) and BRUNNACKER *et al.* (1983). The ages of the continuous linear U-accumulation suggest an assignment into stage 13. However, when we consider all results (U-series and ESR on the travertine and ESR on the teeth) this site can be correlated to stage 11 or 13; the resolution of the method is not good enough to distinguish between these two stages.

CONCLUSION

In my opinion, ESR dating of tooth enamel is at the present time a method which can support or contradict independent age determinations of other methods. The problem of U-uptake causes an uncertainty which often does not allow us to determine particular stage-assignments. However, as the two examples show, it can be a useful tool to get better stratigraphic evidence. It is hoped that comaprative U-series and ESR studies will solve the problem of U-uptake (GRÜN *et al.*, 1988).

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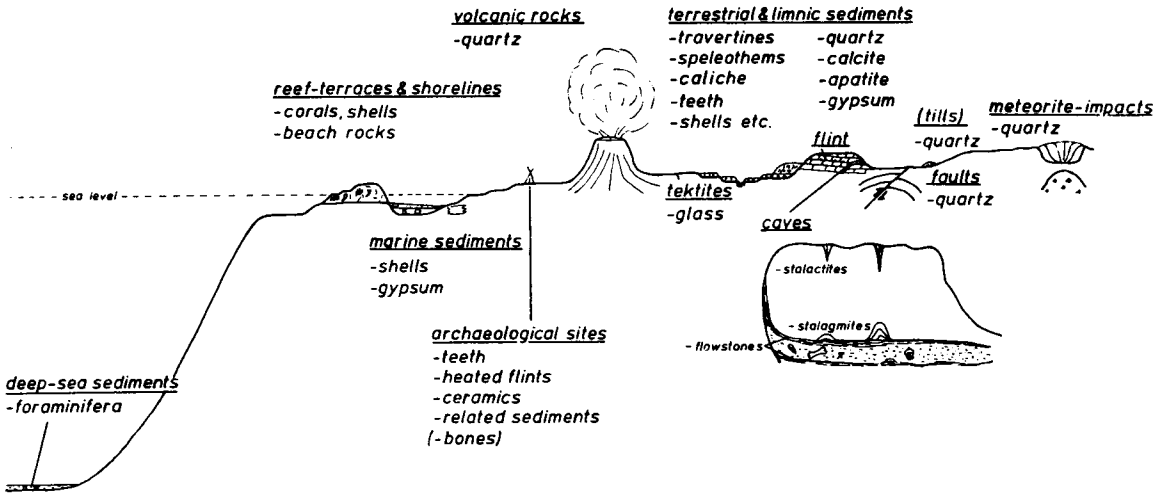

FIGURE 1

Fields and minerals on which ESR dating can be applied
(in brackets: many problems are not yet solved)

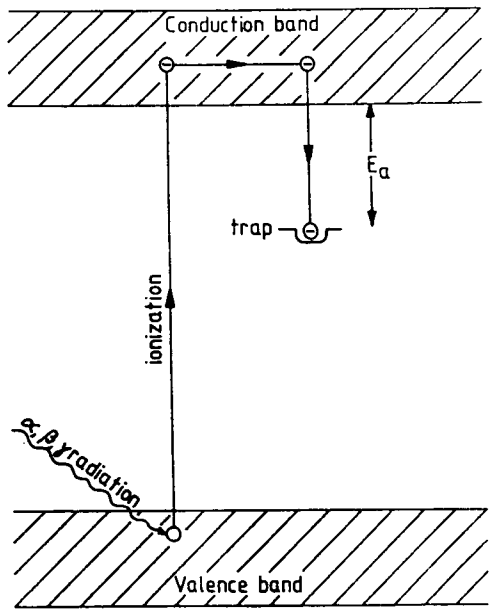

FIGURE 2

Trapping scheme of electrons in minerals

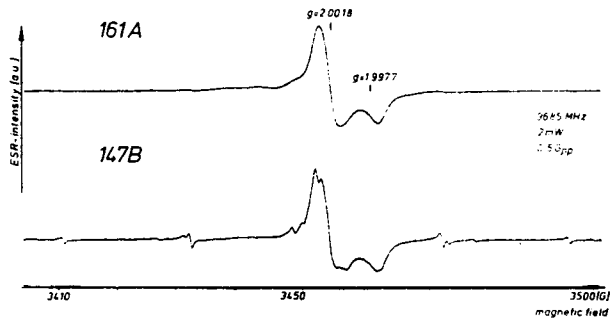

FIGURE 3

ESR spectra of tooth enamel
(hydroxyapatite)

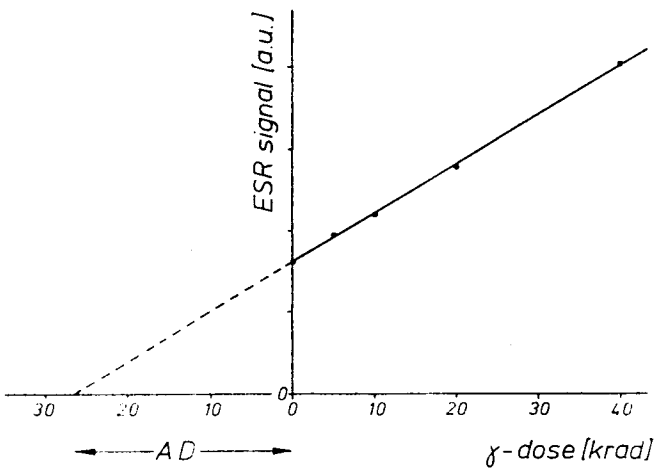

FIGURE 4

Determination of AD by artificial gamma-irradiation

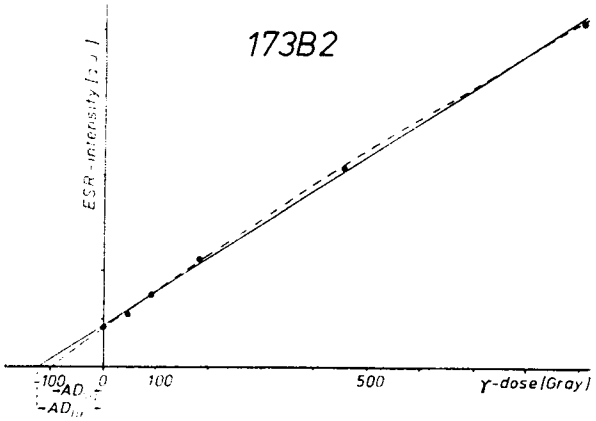

FIGURE 5

Determination of AD using linear extrapolation (ADlin: solid line) and logarithmic extrapolation (ADlog: dashed line)

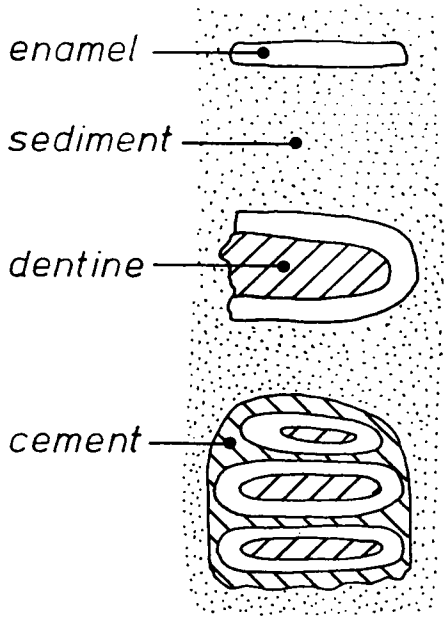

FIGURE 6

Possible environments of an enamel layer

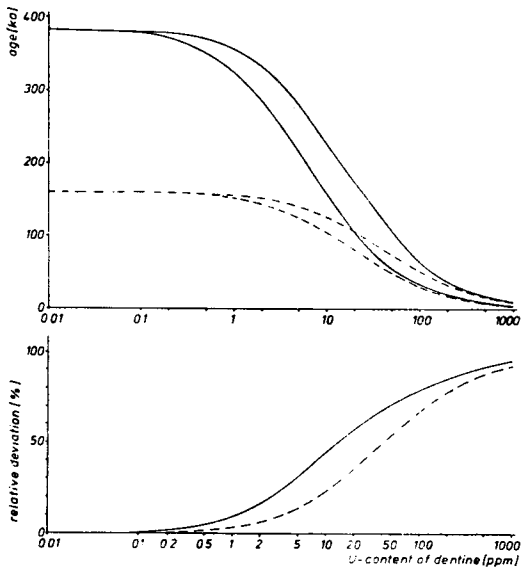

FIGURE 7

Dependence of the calculated age on the U-concentration in dentine (assuming U(enamel- = 1/10 U(dentine)). Solid line: average values for clay; dashed line: average values for sand. The line-splitting is cause by U-accumulation and each upper curve corresponds to continuous, linear U-uptake, the lower early U-accumulation. Below: relative deviation of the calculated ages due to the applied U-uptake models.

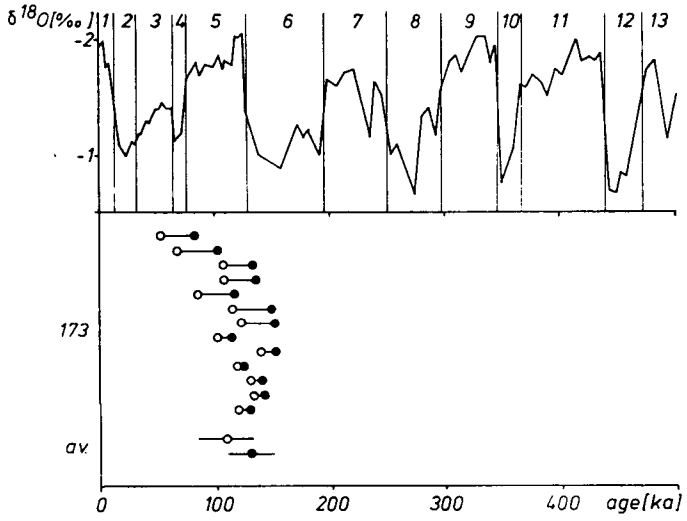

FIGURE 8

Repeated ESR ages of a single mammoth tooth from the Saskatchewan Sands near Edmonton. Open circles: ages according early U-uptake; black circles: ages according continuous U-accumulation. av: average ages with standard-deviation.

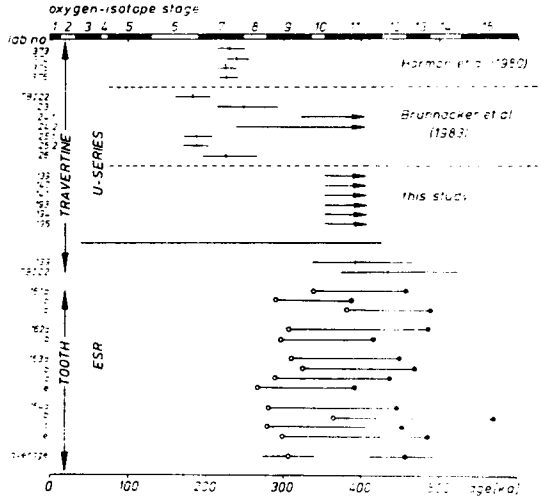

FIGURE 9

U-series and ESR results on travertines and tooth enamel from the archaeological site at Bilzingsleben. U-series results: meanvalues with 1-σ-uncertainty; arrows = infinite ages. ESR : travertine: mean values with estimated error; teeth: open circle = ages according early U-uptake; black circles = ages according continuous U-accumulation. Averages are given with standard-deviation.