Ancient TL

Semi non-destructive, single aliquot ESR dating

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Introduction

In ESR dating of tooth enamel, the specimen is usually partly destroyed: enamel is separated from dentine, ground and about ten aliquots are produced for the establishment of the dose response curve (DRC). Furthermore, some enamel and dentine material is used for uranium analysis. This partial destruction of samples is not feasible if ESR dating is to be applied on valuable specimens, such as fossil hominids.

In principle, it is possible to measure ESR signals of large samples that have not been pretreated by:
1) inserting the whole specimen into an ESR spectrometer (cavity with an aperture; see Ikeya 1993, p.480),
2) placing a small ESR spectrometer close to or around the sample (Ikeya & Ishii 1989, Ishii & Ikeya 1990), or
3) ESR imaging of surfaces (Furusawa et al. 1991).

If a complete tooth is measured in the cavity, it will not be possible to separate the enamel and dentine components of a composite ESR spectrum (this may be overcome by applying a magnetic field gradient which allows the recording of spatially resolved ESR spectra). Therefore, subsequent ESR age estimates are most likely erroneous because ESR dating of dentine is fraught with severe age underestimations due to continuing crystallisation of the hydroxyapatite constituents (Grün & Schwarcz 1987). Imaging has a considerably lower ESR sensitivity (10^{-10}) compared to measuring the same sample in the cavity, and therefore only very high spin concentrations can be detected by imaging. If a tooth of a larger sample (e.g. a tooth sitting in a mandible) is to be measured, the whole specimen will have to be irradiated which in turn may impede subsequent investigations.

In most cases, fossil teeth have cracks and it easy for an experienced curator to remove small pieces of enamel from a tooth and later re-insert these fragments into place without any visual damage. Three bovid teeth excavated at the Florisbad archaeological site, South Africa, were selected for testing the validity of using single enamel pieces for the establishment of dose response curves. A relatively large enamel piece was separated from each of these three teeth and a smaller segment was cut from the centre of each sample, the outer portion was used to establish DRCs by the conventional multi-aliquot powder method (see e.g. Grün 1989).

Two main problems that had to be addressed were:
1) The sample had to be mounted into the cavity in a reproducible position. Unlike powders, single pieces show a very strong angular dependence of the ESR signals (the dating signal in tooth enamel is an axial species, therefore anisotropic). Gamma irradiation will generate free radicals in most materials used for fixing the sample. These signals are usually in the range of g=2 and will interfere with the dating signal. Therefore, the sample has to be removed from a holder for gamma irradiation and then reproducibly positioned into the cavity.
2) As it is not possible to remove any surface layers, the external alpha dose rate has to be considered.

Experimental and Results

For the insertion of the sample into the cavity a sample holder was designed as shown in Figure 1. It was made of silica tubing which contained small E' signals. These signals disappeared after annealing to 1100 °C for 10 h. Constant insertion depth is ensured by the glass O-ring which sits on top of the cavity. Vertical alignment is achieved as the holder is long enough to protrude from the lower ends of the cavity and can be held in place by the teflon clamps at the top and bottom end of the cavity. The tube fixed at the top is used for angular alignment of the sample holder with marks on the magnet pole shoes.
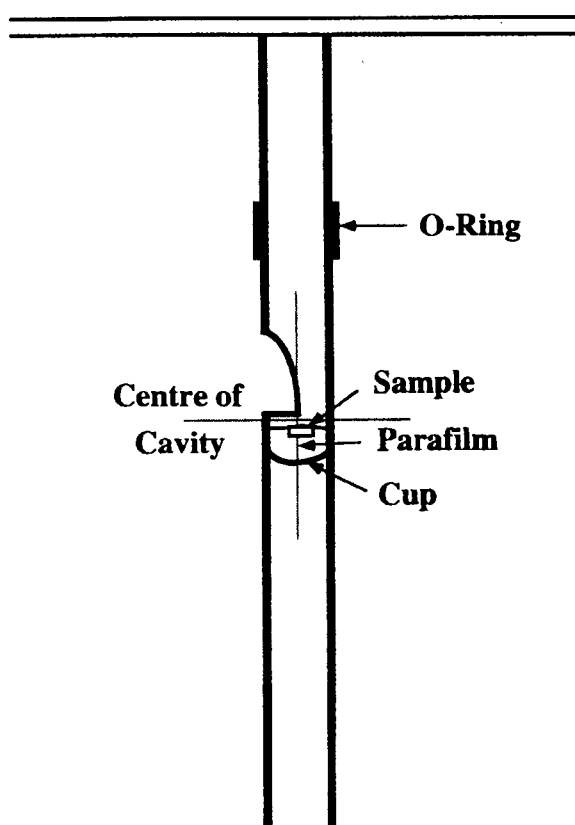
Figure 1

Sample holder for measuring single pieces (not to scale). The holder is made of a round bottom silica tube, extended by a further silica tube. Above the cup, a triangular slot provides access. The sample is pressed into warm parafilm, which will turn into a flexible melt with negligible ESR signals (see Figure 2). The O-ring is a piece of a silica tube fused to the sample holder. The top cross tube can be aligned with markings on the pole shoes of the magnet.

Some parafilm was melted at 120 °C over night in the cup of the silica tube and the samples were then pressed into the hot melt. This created an imprint into the parafilm that is very stable at low temperatures and enables the easy removal and re-insertion of the sample. Apart from its high viscosity at room temperature, parafilm was chosen because it shows only minor ESR signals (see Figure 2). The holder assembly ensures that the sample sits very close to the centre of the cavity.

Preparation and ESR measurement of the powder samples were carried out without any special treatment. Because there was relatively little material available, only 9 and 7 aliquots (with the minimum acceptable routine weight of 15 mg) were prepared for samples 1159 and 1160, respectively, instead of the 10 aliquots that are usually measured (as for

1164A with 25 mg). The weights of the single pieces were 16.54, 23.07 and 17.10 mg for samples 1159, 1160 and 1164A, respectively. The irradiation doses of the powders were: 0, 10.2, 18.5, 34.4, 86.9, 127.6, 196.8, 338.0, 465.0 and 669.5 Gy. The cumulative doses for the single pieces were: 0, 9.3, 27.8, 55.1, 97.1, 187.3, 277.6, 367.8, 468.1, and 558.3 Gy. The powders were measured about 3 weeks after irradiation, single pieces were measured twice, within a few hours after irradiation and after heating at 60 °C for about 13h.

All measurements were carried out on a Bruker ECS 106 spectrometer with a 15 kG magnet and a rectangular 4102 ST cavity. The powder samples were recorded with the measurement parameters routinely applied in this laboratory: accumulation of 8 scans with 1.015 Gpp modulation amplitude, 10.24 ms conversion factor, 20.48 ms time constant, 2048 bit spectrum resolution (resulting in a total sweep time of 20.972 s), 120 G sweep width and 2 mW microwave power. The single pieces were recorded with the same measurement conditions except that the spectra resulted from 128 accumulated scans.

The main differences between the multi-aliquot powder and single sample approach are:
- different ESR spectra (see Figure 2),
- the powder samples are all irradiated at the same time, whereas the single samples are successively irradiated and measured.

Figure 2 shows the single piece and powder ESR spectra of the three samples. It can be seen that all powder spectra are basically identical apart from an occurrence of a radiation induced peak at lower magnetic fields (around 3410 G). The main differences in the single piece spectra occur at the lower end of the main peak (especially for the natural samples), and in the position of the lower dip of the main peak relative to the dip of the second peak. In the powder spectra, the second dip is always below the first one, whereas in the single piece spectra the second dip occurs above the first dip. This may be due to the fact that all enamel pieces were inserted into the parafilm melt in the same way (the outside of the tooth was always horizontal, facing down) and the relative position of the two lower dips is most probably the result of preferential growth of hydroxyapatite crystals within the enamel layer.
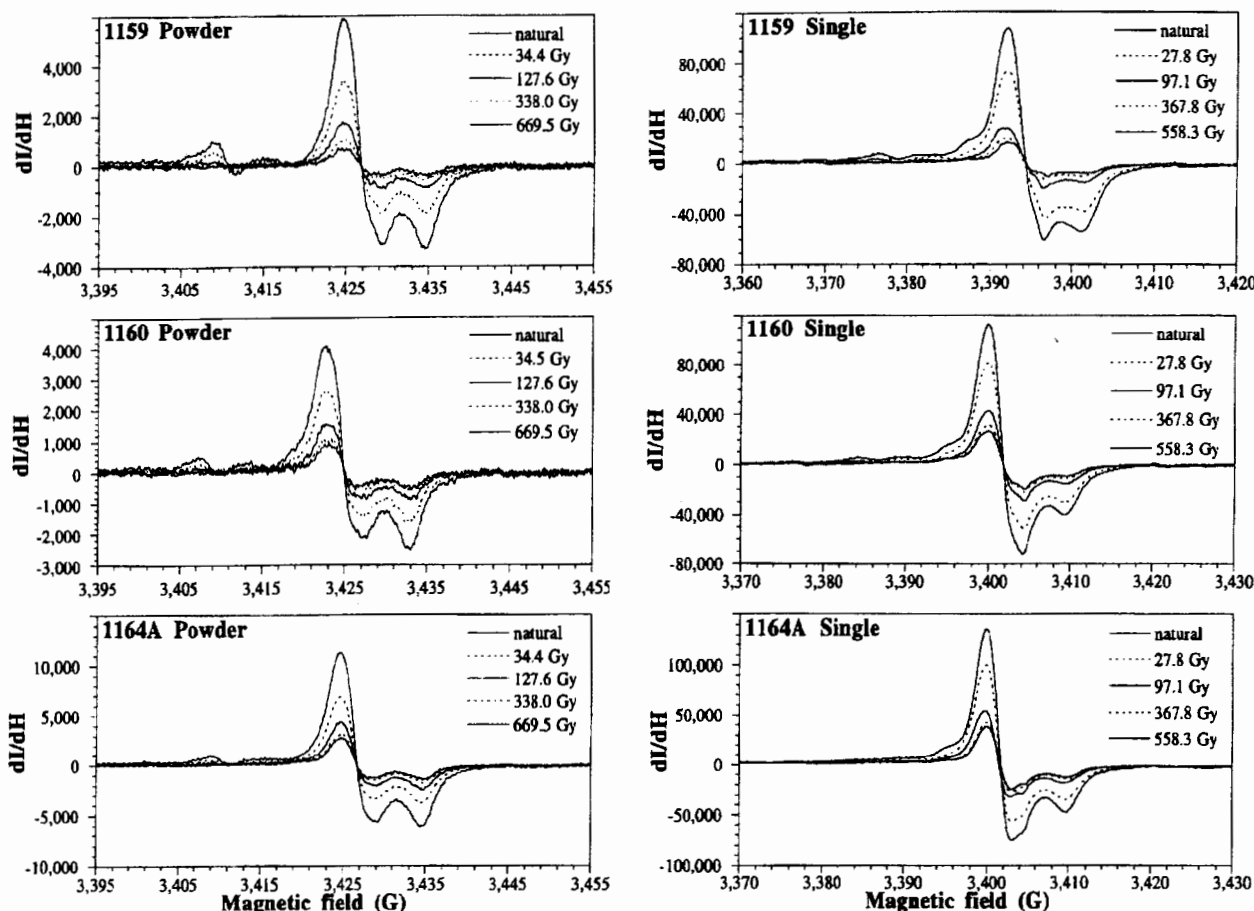
Figure 2
Powder and single piece spectra for three tooth enamel samples

The reproducibility of the ESR signals that were due to the positioning of the single piece samples in the cavity was within 2% (repeatedly inserting the whole holder assembly into the cavity). The reproducibility of mounting the sample into the parafilm and positioning the assembly into the cavity was statistically indistinguishable from the previous approach. Samples were first measured with a single piece standard in order to address the problem of equipment stability. However, the equipment stability was better than the reproducibility of the standard, hence, no normalisation was carried out.

There have been several papers reporting that unstable signals occur after irradiation of hydroxyapatite (e.g. Houben 1971, Ostrowski et al. 1974 and Caddie et al. 1985), decaying within about one week. However, no such effect could be seen in the ESR spectra recorded one hour after irradiation and those recorded 4 days after irradiation. Some heating was carried out after irradiation (at 60 °C

between 8 hours and 100 hours). No quantitative effect could be observed from this treatment either.

The dose response curves of the powders and the single pieces are shown in Figure 3. The DRCs are normalised on the natural ESR intensities (set to 100) of the sample pairs. The data were fitted with a single saturating function (see Grün & Brumby 1994). The visible differences between the respective dose response curves are mainly due to the normalisation process which causes maximum deviations at the highest dose points.

Discussion

The D_E values of the powders and single pieces of the three samples agree well within the calculated errors. It can also be seen that the DRCs of the powder/single piece pairs have similar characteristics: for example, the DRCs of sample 1159 are nearly linear $(I_{MAX} \gg I(D_{MAX})$; $D_0 \gg D_{MAX})$ whereas the DRCs of sample 1160
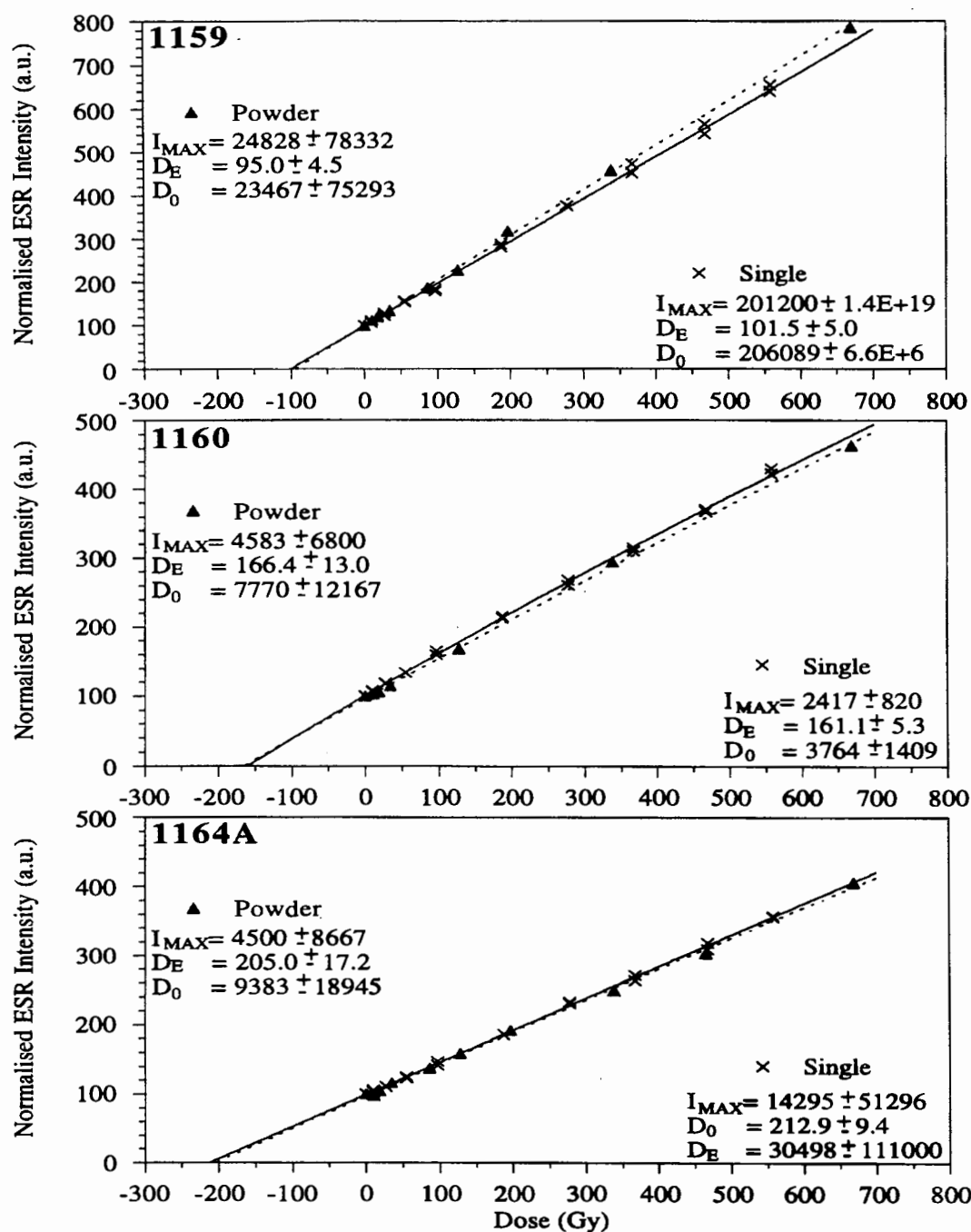
Figure 3
    Dose response curves for the multi-aliquot powder and single piece method. The dotted lines are the calculated best fits for the powder DRCs and the solid line is the best fit for the single piece DRCs

Although the comparison between the powders and the single pieces is very good it seems advisable, if single aliquot measurements are carried out, to measure at least 10 dose points on several pieces of the same specimen. Unlike single aliquot measurements in luminescence dating (e.g. Duller 1991, 1994, Murray et al., 1995 instead of in press), the single aliquot ESR approach involves significantly more work than the routine multi-

aliquot method. This is due to the fact that the multi-aliquot ESR approach involves only one gamma irradiation session (we use a sample holder that allows the irradiation of ten aliquots of 16 samples simultaneously). Gamma sources are usually located in some distance away from the dating laboratory whereas beta dosing for luminescence dating is usually carried out by an automated irradiation facility in the dating laboratory.

Compared to the powder samples, it is not possible to remove the volume from the single pieces that has been irradiated by external alpha rays. If we assume that the sample has a minimum thickness of 500 μm, the average effective "α" -doses from the Th- and U-decay chains are 0.65% and 0.54% of the effective infinite matrix doses, respectively (Grün 1987). Assuming an "α" -efficiency of 0.227, which is the highest value so far measured for tooth enamel (Chen et al. 1994), the alpha dose contribution to the total external dose rate (alpha + attenuated beta + gamma) is 1.6% for both the Th- and U-decay chains. The alpha dose contribution of thicker samples will be proportionally smaller. The calculation shows that external alpha dosage seems to have a minor influence on the D_E -value.

For the internal dose rate it is necessary to assess the U concentrations in enamel and dentine. Presently, we envisage using ICP-MS on samples with a mass of about 5 mg. Although this means that ESR dating is still not entirely non-destructive (in the sense that no material is lost for analysis) we shall be able to come very close to it.

Conclusion

Dose determination of tooth enamel can be carried out semi non-destructively on a single piece of enamel. This piece can be separated from a larger specimen and can later be reinserted into its original place. For dose rate estimation, however, it is still necessary to destroy some, though small, amount of the specimen.

Acknowledgment

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