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# Ancient TL

www.ancienttl.org · ISSN: 2693-0935

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Grün, R. and Robertson, S., 2001. *Dose evaluation on a fossil tooth using multiple and single powder aliquots as well as a fragment*. Ancient TL 19(1): 5-11.

<https://doi.org/10.26034/la.atl.2001.327>

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# Dose evaluation on a fossil tooth using multiple and single powder aliquots as well as a fragment

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(Received 12 February 2001 ; in final form 28 February 2001)

## Introduction

The use of single aliquots for ESR dating of tooth enamel has the advantage that small samples can be analysed (5 to 30 mg), requiring less sample preparation time, and that sample inhomogeneity becomes insignificant. Single aliquots dose measurements can be carried out on powders as well as fragments. The analysis of the latter is necessary when working on valuable samples, such as fossil human teeth. Thus far, no experiments have been carried out to validate single aliquot measurements on powders nor fragments.

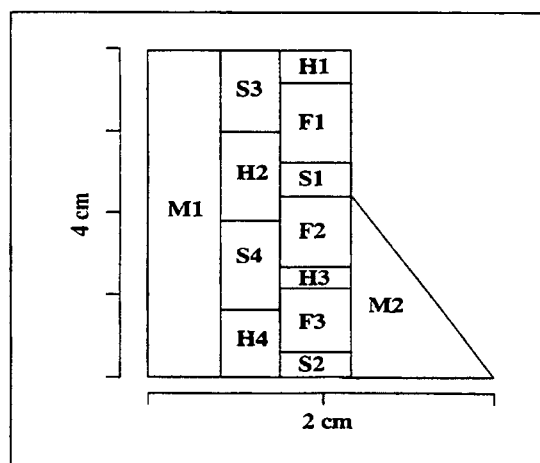
## Experimental

We have selected sample 698, a relatively large bovid molar for the archaeological site of La Quina, which allowed the preparation of a series of sub-samples. The following procedures for dose estimation were tested (for the relative location of the sub-samples see Figure 1):

- 1) conventional multiple aliquots, one set (M2) heated for 2h at 90 °C after irradiation, then stored for at least 1 day at ambient temperatures and humidity following the recommendations of Hayes et al. (2000), the other set (M1) not heat treated;
- 2) single powder aliquots, not heated treated (S1 to S4);
- 3) single powder aliquots, heated for 2h at 90 °C and equilibrated after each irradiation step (H1 to H4);
- 4) a fragment, not heat treated (F2 was measured only).

The enamel of the fragments and single aliquots had an average thickness of about 1200 µm, whilst the

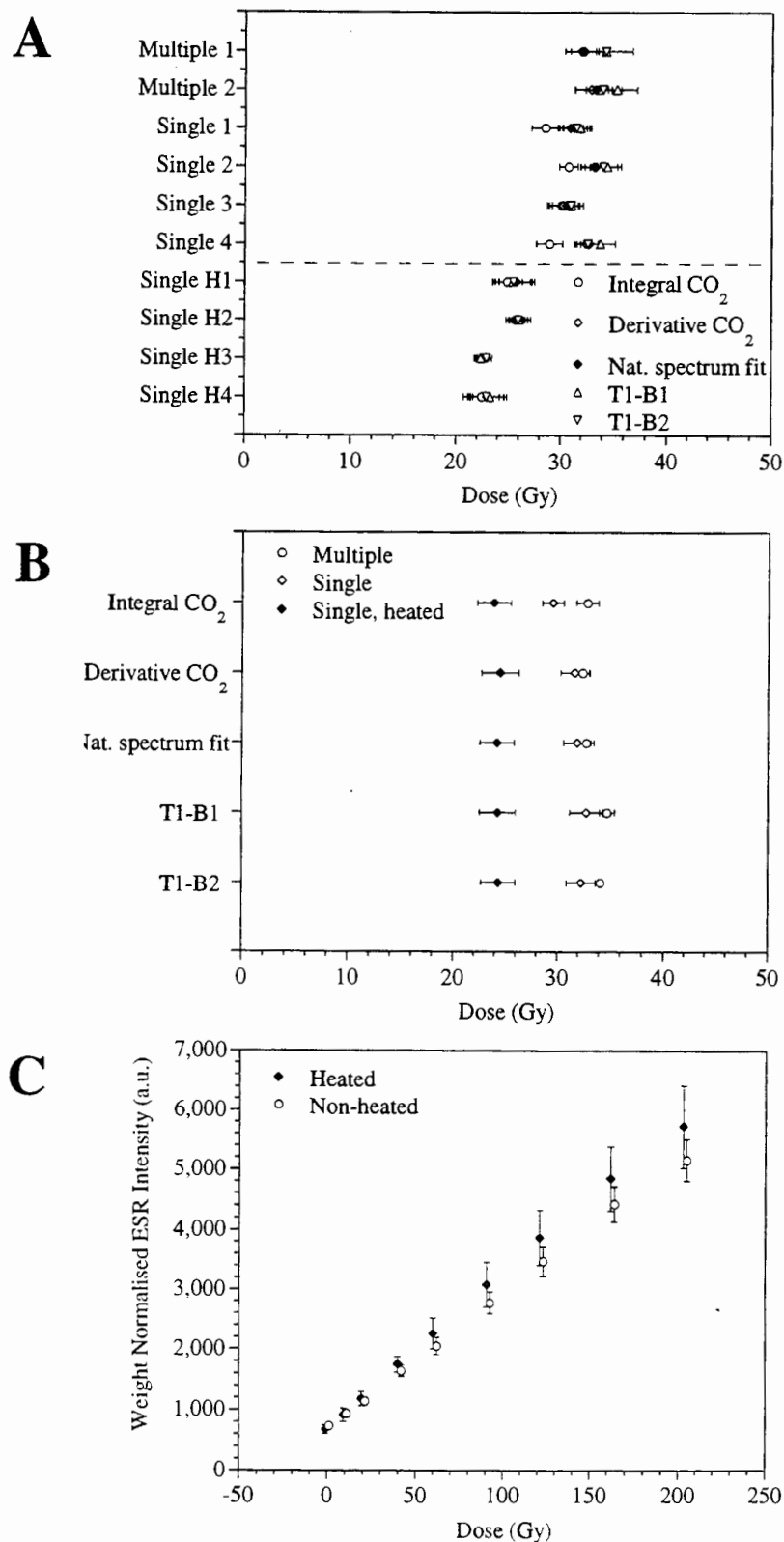
enamel of the multiple aliquots was thinner (800 to 1000 µm).



**Figure 1.**

*Schematic drawing of the positions of the samples. M: multiple aliquots, S: single aliquots, not preheated; H: single aliquots, preheated. The enamel in the area of M2 was thinner than for the other samples.*

Samples were irradiated with 0, 10.2, 20.4, 40.8, 81.6, 132.6, 163.2 and 204 Gy using a <sup>137</sup>Cs source and measured using routine measurement conditions. The fragment was mounted in a quartz holder such that the outer and inner surfaces of F2 were perpendicular to the rotational axis. The sample was measured in 10° intervals with a programmable goniometer. For spectrum evaluation of the powders, we used a series of well described procedures (Grün 2000), plus natural spectrum fitting (scaling the



**Figure 2.**

(A) Dose values for each sample using a variety of evaluation methods

(B) Averaged dose values for the sample groups for a variety of evaluation methods

(C) Average, weight normalised ESR intensities of the single aliquots, non-heated and heated. The data points are slightly offset for clarity

natural spectrum into the irradiated spectra, for more details see Grün, submitted). The latter study concluded that natural spectrum fitting ought to be the most reliable method for spectrum evaluation because it was least dependent on interferences. For the fragment, spectrum deconvolution (using four Gaussian peaks: see Robertson and Grün 2000) as well as natural spectrum fitting was applied. The dose values were obtained by linearisation of the single saturating exponential dose response function and Monte Carlo error calculation (Grün and Brumby 1994).

### Results and Discussion

Figure 2 presents the results on the powder samples. The dose results for each sub-sample are not dependent on the method of spectrum evaluation (Figure 2A): the dose values of a given sub-sample agree within error (there may be some tendency for lower dose estimation when using integral deconvolution for samples S1, S2 and S4). The dose values within each group of samples (i.e. multiple aliquots, single aliquots: non heated, single aliquots: heated) also agree within error. There is also no quantifiable difference between M1 (not heated) and M2 where each aliquot was heated after irradiation.

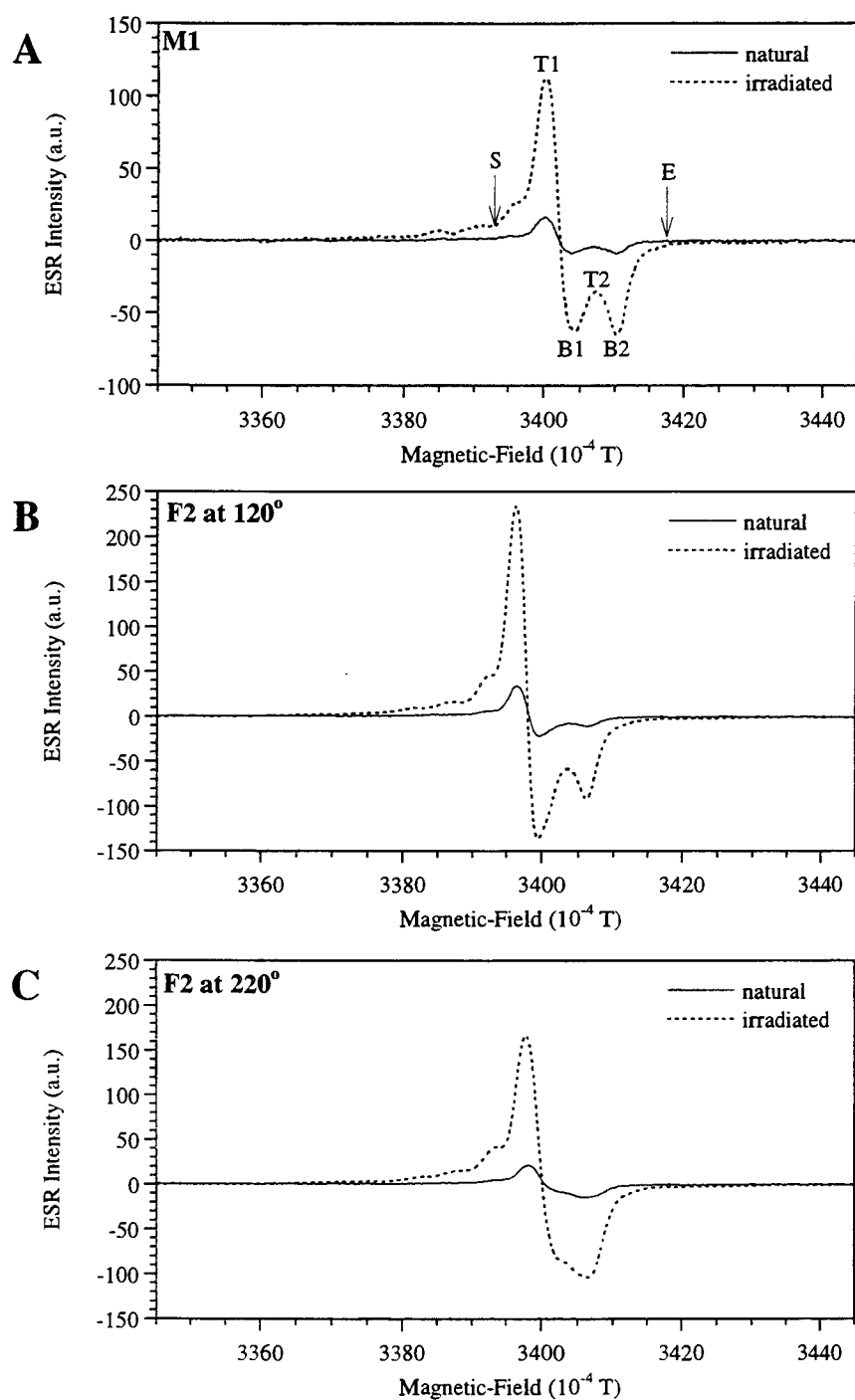
Figure 2B shows the average dose values for each sample group. Again, the dose values show little dependence on the method of spectrum evaluation. The dose results of the multiple aliquots and the single, non-heated aliquots agree within error. The small systematic offset between the means of the multiple aliquots and the non-heated single aliquots can be attributed to the difference in enamel thickness. However, it seems clear that repeated preheating leads to significant smaller doses when using single aliquots (Figure 2B). The reason for the dose differences lie in changes in the natural, as well as the dosed samples. The heating decreases the natural intensity by about 9% whereas the intensity of the highest dose point increases by about 11% (Figure 2C). The effect could be explained by the presence of a less stable component (or indeed part of the stable component, depending on the kinetics) which is removed from the natural sample and that some other charges (not present in the natural sample) are re-distributed after irradiation (see also Brik et al. 2000, Hayes and Haskell 2000). Heating experiments by Scherbina and Brik (2000) indicate some charge transfer between the  $\text{CO}_2^-$  radicals with other "unobservable" centres at temperatures above 80°C. Alternatively, the heating could lead to the generation of additional precursors similar to those observed in speleothems (Yokoyama et al. 1985),

mollusc shells (Brumby and Yoshida 1994) and corals (Yoshida and Brumby 1999)

Unfortunately, spectrum analysis does not show an unambiguously identifiable component that is apparently re-distributed in the spectra. However, the results clearly demonstrate that the prescribed heating procedure does not simulate geological aging, because the overall effect on the irradiated spectra ought to be qualitatively the same as for the natural spectra (i.e. an overall decrease in the ESR intensity should occur). It should be noted here that experiments by Skinner et al. (2000) showed an increase of the dose value of a non-heated sample over 6 months. They concluded that this process could be simulated by preheating the aliquots for 3 days at 90 °C. On the other hand, Rhodes and Grün (1991) did not detect any changes in the dose values of two non-heated samples 2 years after the initial measurement. Whilst it is at present not possible to state that preheating is generally to be avoided, the setting chosen in this study is clearly inappropriate for single aliquots of geological samples. The experience from a large number of studies implies that ESR results obtained on non-heated samples does not yield systematic age overestimations. Indeed, samples from La Quina have caused consternation because they seem to yield ages, which are systematically too young (see Grün et al. 1997).

Figure 3 shows the powder spectra of M1 (Figure 3A) and the spectra for the enamel fragment F2 at 120° (Figure 3B) and at 220° (Figure 3C). These two angles show the largest spectral differences. Because of the angular distortions caused by the anisotropic crystal magnetic field of the hydroxyapatite fragment, the resulting spectra cannot be fitted with an ideal

powder  $\text{CO}_2^-$  spectrum. The spectra of the fragment were analysed using spectrum deconvolution with four Gaussian lines (for more details see Robertson and Grün 2000), where Ax1 and Ax2 present the low and higher field component of the central, apparently axial signal. Peak-fitting with the natural spectrum was applied by optimising for the "whole peak" between S and E (see Figure 3A) as well as selected partial regions: T1 (between half height T1 and zero passing between T1 and B1), B1 (zero passing to half height between B1 and T2), B2 (half height between T2 and B2 and B2 to zero), the combinations of T1-B1, T1-B2 as well as T1-B2 width (S to T1 and B1 to E) and peak width (S to half height of T1 region and half height B2 to E). The latter two fitting methods are less dependent on interferences within the central peak region. Peak-to-peak methods were used for T1, B1, B2, T1-B1 and



**Figure 3.**

*ESR spectra of a powder (A) and the fragment measured at angles of 120° (B) and 220° (C). The positions S, T1, B1, T2, B2 and E denote positions used for peak-to-peak measurements and to define regions for natural spectrum fitting.*

T1-B2. The dose values of all spectrum evaluation methods show angular dependencies (Figure 4). At about 120°, the T1-B1 peak is largest and the dose values derived from Ax1, Ax1 + Ax2 as well as natural spectrum fitting are about the highest. At 220°, where B2 is largest, doses derived from Ax2 are highest, those of Ax1, Ax1 + Ax2 as well as natural spectrum fitting about lowest, respectively. Natural spectrum fitting yields average dose results that are close to the average dose of the single, non-heated aliquots, whereas all dose results from the deconvolution (Ax1+Ax2) lie below this value.

Figure 5 shows the average dose values for the various methods of spectrum evaluation for the fragment.. The errors bars represent the magnitude of the angular dose dependency. Spectrum deconvolution (Ax1 + Ax2) shows the least angular dependency, but also yields the smallest dose value as well as the largest deviation from the average dose value of the single aliquot powders (if sample selection and spectrum evaluation were ideal, the dose value of the fragment should be equal to the dose value of the single aliquot powder). All regions of interest of the natural fitting as well as all peak-to-peak dose evaluations, albeit associated with larger errors, agree with the average dose value of the single aliquot powders. The reason why spectrum deconvolution of the absorption spectrum yielded the largest deviation from the average dose value of the powders most likely lies in the correct placement of the "wide" line in the deconvolution process (for more details see Robertson and Grün 2000).

When the dose response curves are normalised on the natural intensity, it can be observed that the angular dose dependency is caused by an angular sensitivity change. Similar observations were made by Brik et al. (2000) who attributed these interferences to a chaotic CO<sub>2</sub> radical. Alternative explanations involve phase sensitive interferences or some anisotropic, non-radiation sensitive peaks. At the moment, however, we are not able to unambiguously identify these interferences or provide a plausible explanation for them.

### Summary

Dose evaluations on multiple and single aliquots of powders yield consistent results. However, post irradiation heating causes severe dose underestimations. Although it is difficult to pinpoint the interferences which cause the intensity changes in the heated samples, it is clear that the prescribed heating does not simulate the geological ageing process, at least for this sample. We find that the average dose value of the single aliquot powders lie within the dose range provided from a variety of

spectrum methods on the spectra of the fragment. Spectrum deconvolution, though being by far the most time intensive method, yielded the largest deviation between the dose values of the fragment and the powders, respectively.

It is clear that more experiments are required to pinpoint (and eliminate) any interfering signals in the ESR spectra of powders and fragments and that systematic fading tests ought to be carried out. At this stage, that pre-heating procedures should be treated with suspicion.

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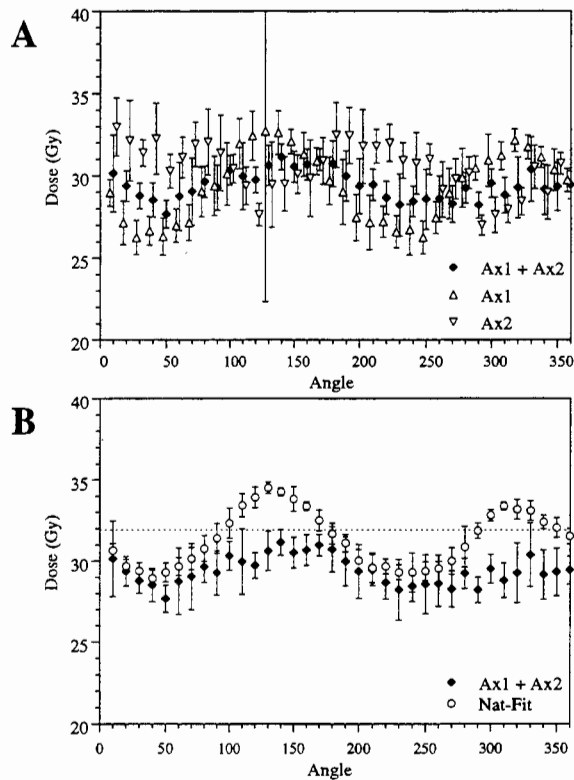


Figure 4.

(A) Dose values of the fragment F1 derived from spectrum deconvolution (for details see Robertson and Grün, 2000)

(B) Comparison of the dose values of the fragment obtained by spectrum deconvolution and natural spectrum fitting

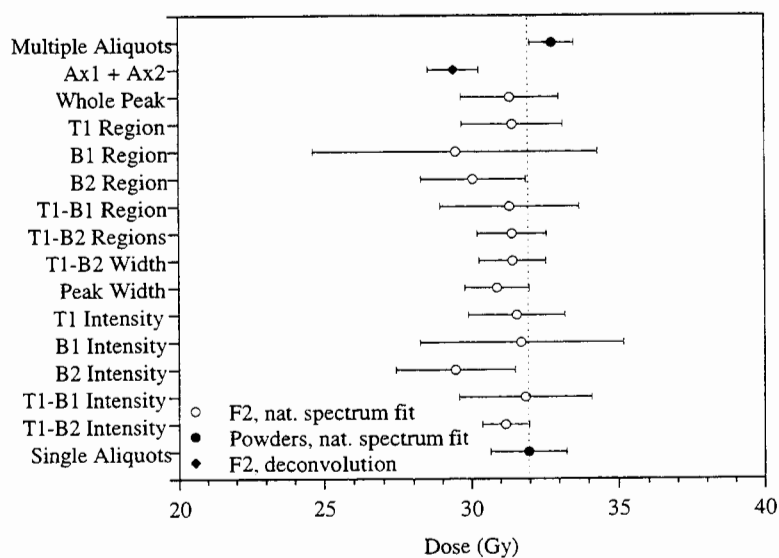


Figure 5.

Summary of dose results. If there were no interferences, the dose of the fragment ought be the same as of the non-heated, single aliquots (dotted line). All evaluation strategies on the fragment yield dose values that are statistically indistinguishable from the single aliquots. There seems a tendency towards smaller dose values in the B2 region (see values for B2 region and B2 intensity).

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**Reviewer**

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