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Progress in ESR dating of Pleistocene corals — a new approach for D_E determination☆

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Abstract

ESR dating has been widely applied for dating of corals of the age up to 500,000 to 600,000 years ago. Many studies have yielded promising results but the accurate determination of the equivalent dose (D_E) remains a major limitation. Inflexion points in the dose–response curve are shown to hinder correct fitting and limit the reliability of D_E values. Here, we present a new approach to obtain more reliable D_E values.

1. Introduction

Since the first application of ESR dating on corals by Ikeya and Ohmura (1983) and the first systematic studies by Radtke and Grün (1988) some further studies have been made to improve the ESR dating technique. Many studies have yielded promising results and helped to resolve problems, for example, in palaeo-sea-level changes and neotectonic movements. Exceptionally well preserved sequences of raised coral reef terraces have been dated with the ESR technique of up to ca 500,000–600,000 years ago e.g. on Sumba island (Pirazzoli et al., 1991) and on Barbados (Radtke and Grün, 1988; Radtke et al., 1988). Nevertheless, the method is still limited by the uncertainties in the determination of the equivalent dose (D_E) as well as by estimations of the present and past natural radiation dose rate (D'). Here, we concentrate on the problem of a more objective determination of the D_E value using the additive dose method.

2. Measurement conditions

The coral samples analysed in this study consist exclusively of the species *Acropora palmata*, collected from Barbados. The inner parts of the coral samples were ground to a particle diameter between 125 and 250 μm and 20–46 aliquots were γ-irradiated with a ^{60}Co source with dose rates between 1 and 2.5 Gy min^{-1}. D_E values were determined using the program 'fit-sim' by Grün (version 1993) and age calculations were carried out with the program 'Data VI' by Grün (version 1999). ESR intensity was measured using a Bruker ESP 300E spectrometer. Typical measurement parameters were: 25 mW microwave power, 0.5 G modulation amplitude, 20.972 s sweep time, 40 G scan width, and an accumulation of 5–10 scans.

3. Problems in the determination of D_E

Details of ESR dating of corals are described elsewhere (e.g. Radtke and Grün, 1988; Grün, 1989; Rink, 1997), and a review of recent development in ESR dating concepts and methods is given by Jonas (1997). Fig. 1 shows a typical ESR spectrum of a Last Interglacial coral from Barbados with three dominant peaks (g-values: 2.0057, 2.0032, and 2.0006). The peak at $g = 2.0006$ is the most suitable one for dating. It is γ-sensitive and it saturates much later than the less stable and rapid dose saturated signal at $g = 2.0032$ (Grün, 1989; Walther et al., 1992). But, as already reported by Walther et al. (1992), only the lower part of its growth curve can described sufficiently by a single exponential saturation function. Similar to its behaviour in other carbonates (Katzenberger and Willems, 1988; Grün and MacDonald, 1989; Schellmann and Radtke, 1997, 1999) the growth curve of the dating signal at $g = 2.0006$ in corals also contains clear inflexion points and some minor oscillations (Figs. 2 and 5), which complicates the D_E determination. The inflexion points

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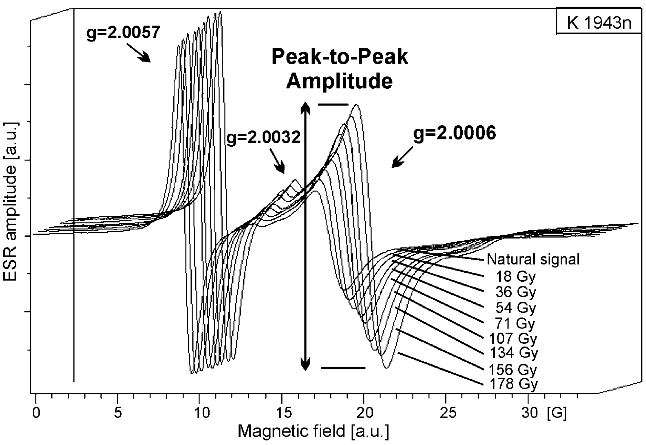

Fig. 1. ESR signals and signal growth of a γ-irradiated (^{60}Co) Last Interglacial coral (*Acropora palmata*, K1943n) from Barbados.

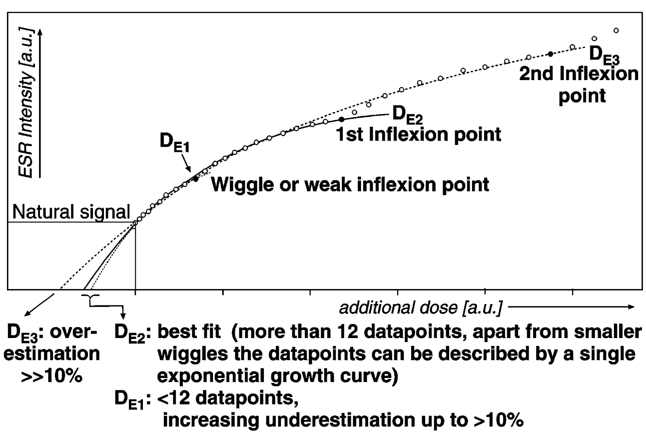

Fig. 2. Typical ESR signal growth curve ($g = 2.0006$) of a Pleistocene coral (arbitrary data points for illustrations) and the effects of inflexion points on D_E values if calculated with a single saturating exponential curve.

are characterised by a sudden increase in the radiation sensivity. The inflexion points could be explained either by competition processes or by different filling mechanisms for multiple traps with the same ESR characteristics. Finally, it cannot be ruled out that they is mainly a result of the strong artifical γ-irradiation. They cannot be resolved by using preheating procedures or by changing ESR measurement parameters (e.g. Jonas, 1997; Schellmann and Radtke, 1999). For the detection of inflexion points or weaker oscillations in the signal growth curve, it is necessary to use as many aliquots as possible and to narrow the distances between the data points.

The important consequence of D_E calculation by fitting all data points on such a 'disturbed' growth curve with a single exponential function is a significant overestimation of the calculated D_E values (Fig. 2). Only the lower part of the additive growth curve up to the first inflexion point can be described by a single exponential saturation function. Here, irradiation sensibility of the

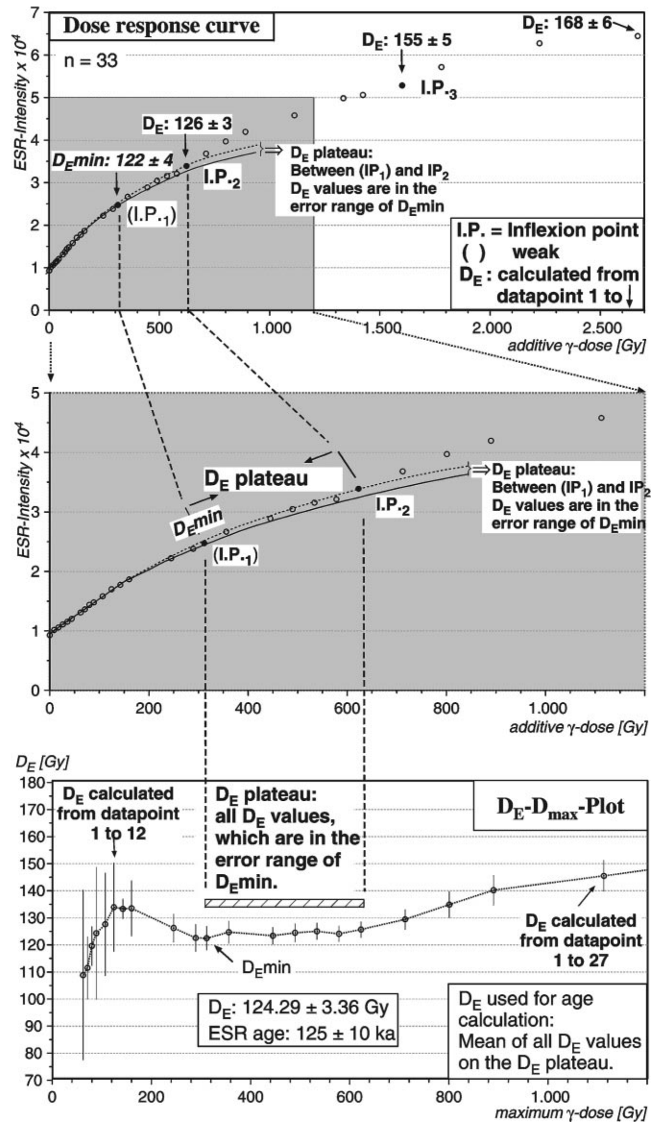

Fig. 3. Dose response curve and D_E–D_{max}- plot of a Last Interglacial (oxygen isotope stage 5e) coral sample (*Acropora palmata*, K245653) from Barbados.

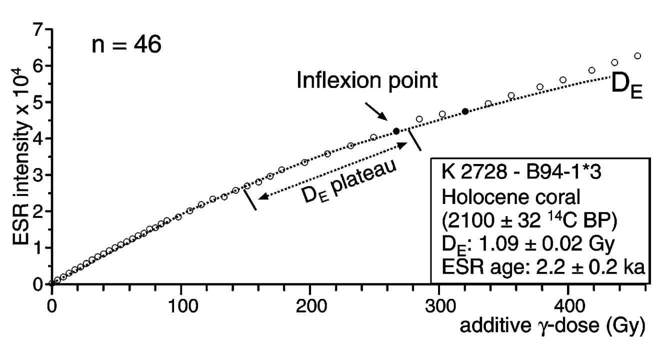

Fig. 4. Dose response curve of a Holocene coral (*Acropora palmata*) from Barbados (K 2728) irradiated with 46 irradiation steps between 4.4–20 Gy up to 454 Gy.

dating signal increases apart from smaller wiggles monotonically. This means, a D_E value has to be calculated only with the data points on the lower side of the additive

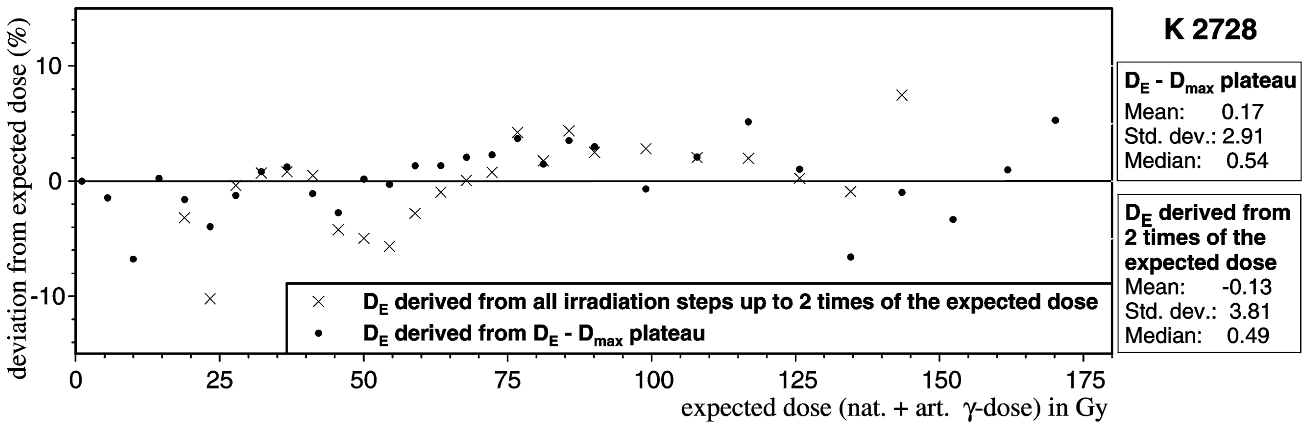

Fig. 5. Plot of deviation from expected dose in percent on Y-axis versus expected dose in Gy on X-axis. Comparison of D_E from D-DP procedure versus D_E shown using all irradiation steps up to 2 times the value of the expected dose (calculated from dose–response curve in Fig. 4).

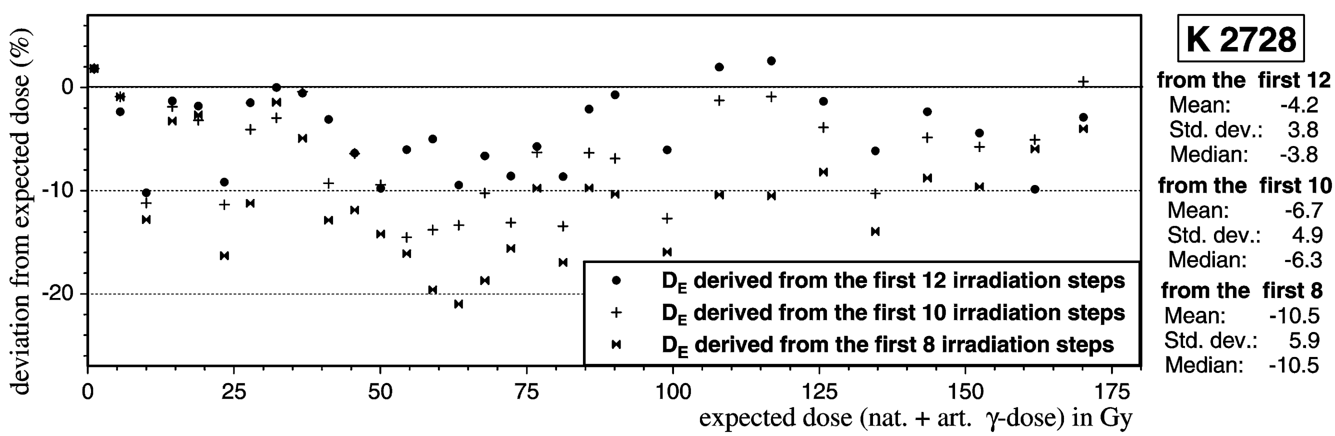

Fig. 6. Plot deviation from expected dose in percent on Y-axis versus expected dose in Gy on X-axis. Comparison of D_E shown using the first 12, the first 10 and the first 8 irradiation steps dose (calculated from dose–response curve in Fig. 4).

dose–response curve: from the natural non-irradiated first aliquot and all the following aliquots up to the first inflexion point (Fig. 2). The resulting D_E value is a local minimum, $D_E$min. D_E values get higher if further data points after the first inflexion point are included into the D_E calculations (Figs. 2, 3 and 5) as do the resulting ESR ages.

3.1. D_E determination by D_E–D_{max} plot procedure

The best way to illustrate these effects are D_E–D_{max}-plots (D–D_P) (Fig. 3) (Schellmann and Radtke, 1997, 1999). They are constructed as follows: the first D_E value is calculated by using all data points (see e.g. Fig. 3 below: with 27 data points). Subsequently, the data set is reduced by successively eliminating the highest dose point. The D_E values obtained in this manner are than plotted versus the maximum dose, D_{max}, used in the fitting procedure. If the dose–response curve is constructed with small dose steps there is a D_E plateau defined by the local $D_E$min. This D_E plateau includes all values that are within the range of uncertainty of the minimum value. The plateau D_E value results from the average of all D_E values within the plateau range and the error given has been calculated from the average of the individual errors. For age calculations the plateau D_E should be used, because it incorporates more data points and it has a lower uncertainty.

To test the validity of the D–DP procedure, we irradiated a Younger Holocene coral, K 2728, with 46 radiation steps between 4.4–20 Gy up to 454 Gy (Fig. 4). The D_E value of this sample was 1.09 ± 0.02 Gy and the resulting ESR age of 2.2 ± 0.2 ky BP agrees very well with the uncalibrated radiocarbon age of $2{,}100 \pm 32$ y ^{14}C BP.

The dose–response curve was used to create three data sets where the D_E values are known (Figs. 5 and 6): for all data sets the D_E value is considered to be 1.09 Gy (see above) plus the first radiation step (4.4 Gy). The subsequent radiation steps are then used to estimate the D_E value: for the first data set by applying the D–DP procedure, and for the second data set by using all irradiation steps up to 2 times the value of D_E (Fig. 5). In a third data set we tested the deviation of D_E when using only the first 12, 10, and 8 data points on the additive growth curve for D_E calculations (Fig. 6).

The resulting D_E values (Fig. 5) of both methods (a) derived from all irradiations steps or (b) from D_E–D_{max} plateau (D–DP procedure) show a lower scattering between the 10% deviation lines; most data points are close to the zero line and therefore demonstrate the high potential for ESR dating of corals. It should be mentioned that the first approach (using all irradiations steps for a D_E calculation up to 2 times of the D_E value) is a theoretical one because normally the D_E is unknown. But nevertheless, the modelling illustrates that a D_E determination using additional irradiation of up to 2 times of the natural D_E is justified.

3.2. Aliquot and irradiaton steps

As discussed by Grün and Rhodes (1991, 1992) and Grün and Brumby (1994), using computer simulations the number of aliquots and the choice of adequate irradiation steps are important factors in obtaining a correct D_E value. Schellmann and Radtke (1999) showed in studies on the structure of the ESR dose–response curve of aragonitic mollusc shells that 20 aliquots seem to be sufficient for a reliable D_E estimation and a good compromise between reaching the first-D_E plateau and taking small irradiation steps. We obtained similar results in our recent investigations on corals. To determine D_{max} and the optimal size of irradiation steps, a so-called sample screening, as suggested by Radtke (1988), can be used to obtain an approximate age of the sample. The dose range used for fitting should be as high as two to three times the value of the extrapolated D_E value of the corals. The first segment of the dose response curve, which is very important for a mathematically correct description of the growth curve, should be built up using small irradiation steps with differential doses in the range of 10–20% of the expected D_E value. But, as shown in Fig. 6, at least the first 12 irradiation steps should be used for a reliable D_E calculation. The D_E values will be strongly underestimated if only the first 10 or 8 aliquots are used.

In Fig. 7 two examples are shown as how to use the proposed D_E determination method on corals. The two dose–response curves display two weak inflexion points and two minimum D_E values. The first $D_E$min is detected in the area where the low irradiation doses produce a slow increase of ESR signal intensities. As already stated above, the D_E should be calculated with at least the first 12 data points; therefore in both examples the first $D_E$min values should not be used for D_E determination, because they are obtained by fitting less than the first 12 datapoints (e.g. 8 and 11 data points in Fig. 6).

The effect on the ESR age by using the first or the second of such marginally different D_E plateaux is low (Fig. 6), but — as illustrated in Fig. 8 — not important.

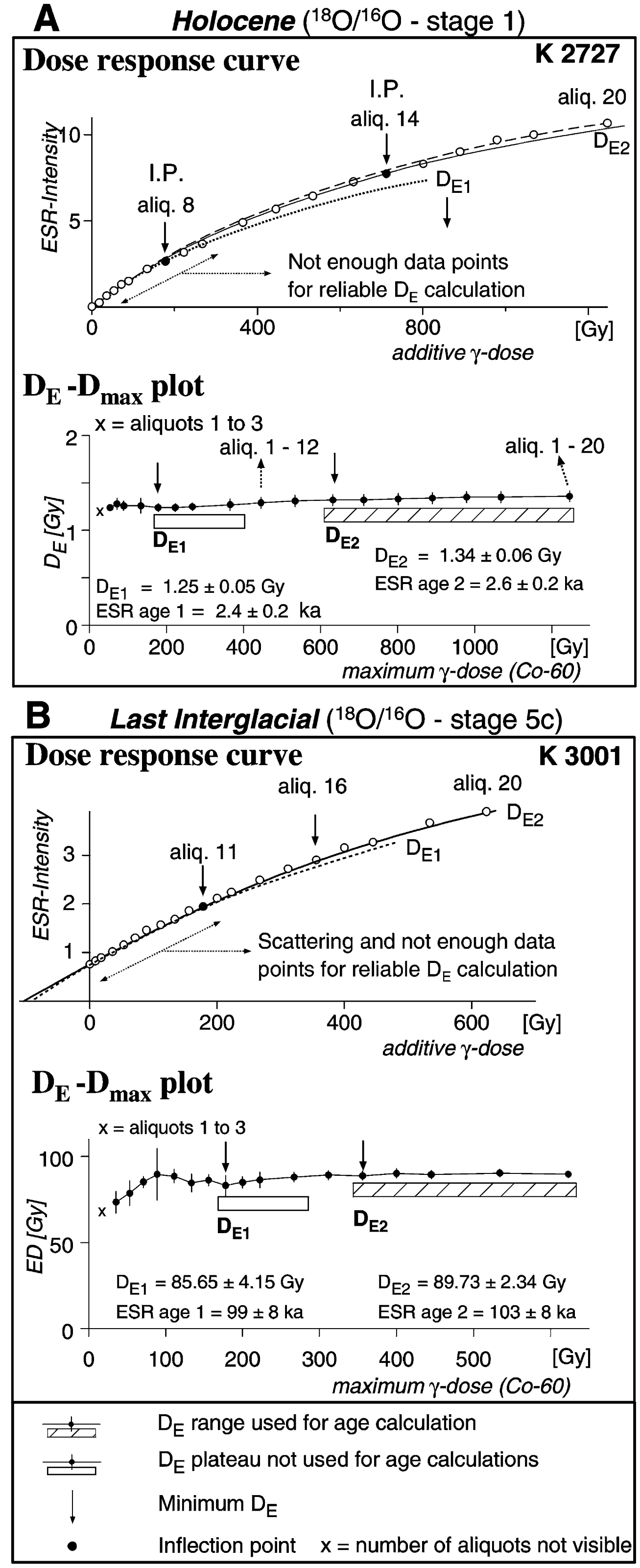

Fig. 7. Typical ESR dose response curves and D_E–D_{max} plots of fossil aragonitic corals (*Acropora palmata*) from the South coast of Barbados (WI) with two different D_E plateaux. The plots show that: (A) The first D_E should not be used for age determination, because it is calculated by < 12 data points. (B) The first D_E should not be used for age determination, because it is calculated by < 12 data points and there is a large scattering of the data points in the lower part of the dose–response curve.

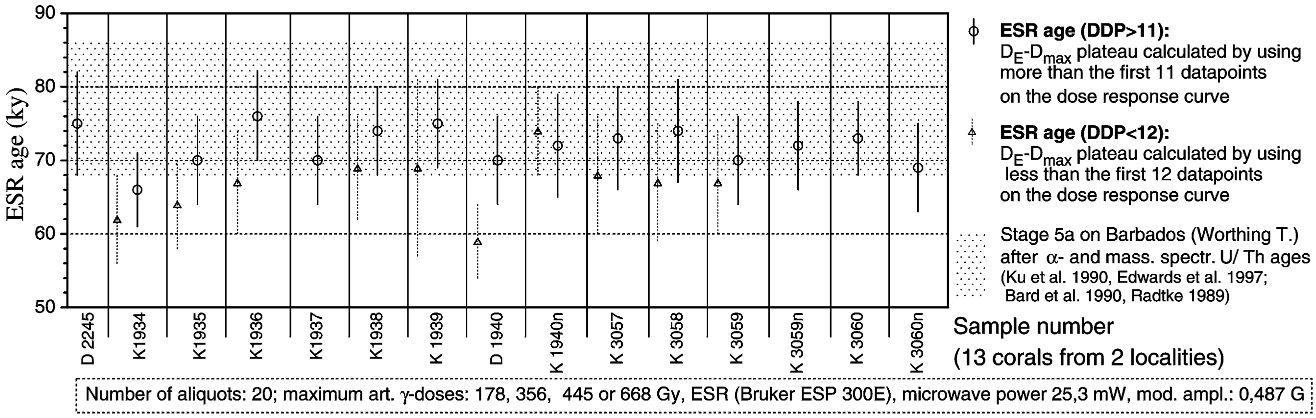

Fig. 8. Plot showing different ESR ages of Last Interglacial corals (Oxygen Isotope Stage 5a) from the south coast of Barbados (T1a coral reef terrace) as a result of different methods of D_E calculations.

Nine samples from a data set of 13 coral samples from a Barbados stage 5a coral reef have two slightly different D_E plateaux: a first one at the 12th data point and a second one on the upper part of the growth curve. The ESR ages resulting from D_E determination using more than the first 11 data points on the additive growth curve are consistent within the range of U-series data (68–86 ka), whereas the ESR ages resulting from using less than the first 12 datapoints on the dose–response curve display a clear trend to a severe age underestimation.

4. Conclusions

ESR age estimates on fossil aragonitic corals have been improved by introducing the D_E–D_{max} plot procedure (D–DP procedure). This procedure reduces the effect of the so-called infletion points in the dose–response growth curve and allows therefore a reliable determination of the accumulated dose (D_E).

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