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Dose response of the paramagnetic centre at g = 2.0007 in corals

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In ESR dating, the accumulated dose AD is usually determined via the additive dose method (Aitken, 1985). In order to get reliable estimates of this parameter, the dose response has to be mathematically described and the results are then applied to the extrapolation procedure. In the early days of TL/ESR dating, it was often assumed that the sample was in "the linear part" of the dose response curve and hence linear fitting was applied. Apers et al. (1981) suggested an exponential fitting procedure by plotting $- \ln(1 - I/I_{max})$ versus the artificial dose (where I is the measured ESR signal intensity and I_{max} is the maximum ESR signal intensity when all traps are filled). As pointed out by Grün & Macdonald (1989), this procedure may lead to slightly erroneous results because the converted data may attain different weights. They also noted that the dose response of some samples cannot be described by a single exponential function and that a function with an additional exponent:

$$I = I_{max} (1- \exp(-a(D-AD)^{\Gamma}))$$

may yield more satisfactory results (D = dose; a = fraction of unfilled defects that trap electrons per dose unit). It was subsequently emphasized by Levy (pers. comm.) that there is no physical reason for the additional exponent Γ.

During a dating study of corals from Huon Peninsula, New Guinea (where all ESR parameters were independently determined using other dating techniques) it was found that the application of a single exponential function led to systematic AD overestimations. AD assessments with an additional exponent of $\Gamma = 0.848$ did not yield "good agreement with U-series dating", but "good agreement with previous independent dating estimates" (Grün, 1990). Similar observations were also made in other laboratories (Barabas, pers. comm.).

In order to study this problem, 15 coral samples were collected from Holocene reef tracts in Kikai (Japan). Aliquots of 100 mg were irradiated in 12 steps with a calibrated gamma source and the paramagnetic centre at g = 2.0007 was recorded with a modulation amplitude of 0.05 mTpp and microwave power of 5 mW (JEOL RE1X ESR spectrometer). The ESR intensities are given in table 1. The sensitivities of the corals vary by about 50% and this may depend on the species. The AD's of all samples are well below 5 Gy, which corresponds to about 8,000 years for a surface sample. In order to eliminate individual effects and to force the dose response curve through zero (i.e. $I_0 = 0$), the natural intensity was subtracted from measured values, and subsequently normalized to the highest value (from sample 763: 686.1 Gy) and averaged. This averaged set (see table 2) was used for further statistical analysis, using the computer program FITT (Grün & Macdonald 1989). The fitting is based on the optimization of the sum of squares of the vertical distances of the data points from the calculated line SSQ.

When a single exponential function is applied to this data set, the AD increases systematically as more values are included in the regression procedure (see table 2). When using an optimization procedure for the additional exponent, the AD estimates are quite close to the expected value of zero. However, the exponent itself does not remain constant but changes systematically as more values are included. This leads to the conclusion that neither a single exponential function nor the "gamma-function" describe the dose response correctly.

Following the idea that the ESR signal at g = 2.0007 may be generated by two different paramagnetic centres, two exponential functions are optimized in the next step:

$$I = I_{max1} (1 - \exp(-a_1 (D - AD_1)) + I_{max2} (1 - \exp(-a_2 (D - AD_2))$$

First, both functions are forced through the origin (i.e. $AD_1 = AD_2 = 0$). This yields the following curve parameters:

$I_{max1} = 2660$; $a_1 = 0.0058$; $I_{max2} = 711800$; $a_2 = 0.0000129$; SSQ = 16270

When additionally optimizing for AD_1 and AD_2 the results are:

$I_{max1} = 2747$; $a_1 = 0.005559$; $AD_1 = - 1.25$
$I_{max2} = 708700$; $a_2 = 0.0000128$; $AD_2 = - 0.15$;
SSQ = 15390

In order to assess the uncertainties of these values, a jackknifing procedure was used (see Grün & Macdonald 1989):

$I_{max1} = 2740 \pm 471$;
$a_1 = 0.005559 \pm 0.0011$; $AD_1 = -1.18 \pm 1.60$
$I_{max2} = 708700 \pm 86600$;
$a_2 = 0.0000128 \pm 0.0000009$; $AD_2 = -0.15 \pm 0.72$
SSQ = 15760

Both AD values are very close to zero. The second exponential function is nearly linear in the dose range investigated here and can be approximated by the following linear function (forced through $I_0 = 0$, see also Figure 1):

$$I = 9.15\ D$$

When this linear function is subtracted from the original data set (see Figure 1), the remaining data are best fitted by a single exponential function with:

$I_{max} = 2662$; a = 0.0058; AD = -1.029; SSQ = 15730 or, when forced though $I_0 = 0$ (see also fig. 1):

$$I_{max} = 2656;\ a = 0.005885;\ SSQ = 16370$$

Note that (1 - 1/e) I_{max} is already reached at 170 Gy. It can be seen that the latter two functions have very similar parameters to the first of the two exponential functions above.

The statistical analysis of the averaged data set suggests that the general dose response in the range of 0 to 700 Gy of the paramagnetic centre at g = 2.0007 in corals can be described by a linear and an exponential function. Because of the nearly linear part in the function set, it is not very likely that the ESR intensity at g = 2.0007 is generated by two paramagnetic centres. However, this type of dose response behavior can be expected when traps are created during irradiation (see Levy 1985; 1989) where:

$$N = N_0 + K\,D$$

(N = number of traps (or defects); N_0 = number of traps before irradiation). The dose response is then described by (see Figure 1):

$$I = (N_0 - K/a)\ [1 - \exp(-aD)] + KD.$$

Following from the results above we get:

$$N_0 = 4211;\ K= 9.15;\ f = 0.005885;\ SSQ = 16395$$

If the latter formula is applied for AD-determination it seems advantageous to use jackknifing for error assessment (Grün & Macdonald 1989).

The quality of the averaged data set is not sufficient to conclude whether the production of paramagnetic centres is best described by a single trapping scheme (single exponential function) or a more complex mechanism (Katzenberger & Willems, 1988).

The measurements of these Holocene corals strongly suggest that artificial irradiation causes the production of defects and this effect has to be considered when determining the accumulated dose.

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PR Reviewer's Comments (Anne F. Skinner)

There is little question that a major bottle-neck in the successful application of ESR to dating is the absence of a sound model that explains the complex observed phenomena. Any serious contribution to this effort is therefore welcome.

This paper, part of a longer presentation at a recent conference, puts forth evidence for such a model. In the absence of full discussion of dates before and after application of the model, the evaluation rests primarily on statistical grounds. There are three alternative mathematical approaches. On going from the first ("single exponential") to the second ("gamma factor"), the SSQ drops very significantly. However, when going to the third ("double exponential"), there is no further improvement in SSQ. Given that the last equation has six parameters, and the second only four, an improvement would be expected even if the double exponential equation was no better at modelling the system than the gamma-factor equation. Of course in both cases the AD parameters are constrained to zero, both in theory and in fact, so it is perhaps more accurate to suggest that one is going from a three-parameter equation to a four-parameter one. Nonetheless, considering only statistical factors, there is no overwhelming reason to favour the concept of a double exponential fitting equation. However, one must also consider that the double exponential equation may have some basis in physical reality, whereas the gamma-factor one does not. The reference by Levy puts forth some theoretical models, and the observed results in this paper match one of his suggestions. And it is certainly possible that defects are being created by radiation, rather than simply filled. There may, of course, also be other physical models that produce the same mathematical result (such as two overlapping traps with widely differing mean lifetimes). Overall, Dr. Grun has outlined an ingenious approach to data analysis. The evidence presented is suggestive of Levy's models, although not compelling, The results, one expects, will be very useful in stimulating discussion and suggesting other lines of investigation.

Table 1: ESR intensity of the signal g = 2.0007 [a.u.] normalized on 100 mg.

Dose [Gy]	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777
0	63	62	57	45	24	30	25	58	49	54	29	64	50	65	48
10.7	337	331	244	214	262	263	270	336	254	236	223	315	325	374	243
21.4	593	560	415	388	468	476	474	594	454	395	422	541	569	631	432
42.9	1032	1020	795	683	865	854	866	1056	797	713	767	976	1029	1089	804
85.8	1917	1854	1408	1211	1603	1605	1607	1868	1495	1281	1415	1778	1845	1996	1441
171.5	3245	3215	2425	2170	2685	2785	2820	3145	2485	2245	2525	3060	3160	3490	2380
257.3	4395	4445	3420	2960	3665	3795	3835	4055	3330	2760	3450	4160	4225	4520	3230
343.0	5385	5390	4315	3595	4555	4765	4775	5065	4070	3825	4235	5060	5230	5730	3940
428.8	6325	6200	4980	4285	5310	5510	5460	6150	4445	4515	4940	5955	6205	6230	4670
514.6	7295	7160	5545	4855	5940	6125	6230	6670	5395	5060	5550	6710	7005	7280	5175
600.3	7995	7990	6265	5480	6750	7100	7150	7680	5855	5720	6305	7640	7925	8195	5900
686.1	8910	8645	6835	5915	7285	7685	7725	8195	6575	6230	7040	8345	8470	8820	6440

Table 2. Averaged data and fitting for the data up to the respective line.

Dose	norm.	exponential fitting		gamma-fitting		
[Gy]	average	AD [Gy]	SSQ	gamma	AD[Gy]	SSQ
0	0					
10.7	275±18					
21.4	526±29					
42.9	993±42					
85.8	1873±83					
171.5	3234±88	- 0.1±0.3	289	1	- 0.1	289
257.3	4369±144	- 0.6±0.8	1903	0.954	0.1	963
343.0	5461±101	- 1.9±1.8	14671	0.891	0.6	5190
428.8	6422±152	- 2.9±2.1	25806	0.871	0.8	6135
514.6	7189±107	- 3.2±1.9	27654	0.891	0.5	7484
600.3	8131±131	- 4.5±2.9	65907	0.850	1.1	17545
686.1	8847	- 5.6±3.0	83918	0.846	1.1	17846

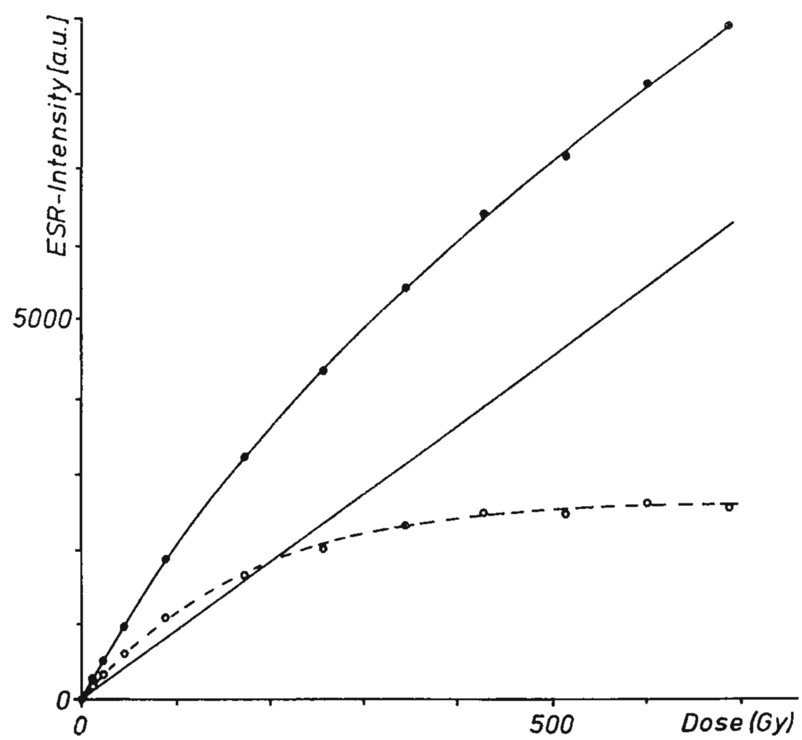

Figure 1.
Dose response of the paramagnetic centre at g = 2.0007 in corals. The closed circles show the averaged, normalized data set (see Table 2). The curve through these points is the sum of the lower two curves. The open circles result from the subtraction of the straight line from the original data set. The dotted line is the best exponential fit for the open circles.