Test data for exponential fits

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Introduction

To fit exponential models to TL dose-response curves, several TL dating research groups are presently using different fitting routines, some written in-house from basic mathematical principles (eg Berger et al., 1987b; Grün and Macdonald, 1989), some purchased commercially, and some written with the incorporation of "canned" procedures. Shared data sets may indicate any significant differences among these programs. We present here two data sets that can be used to compare the results from exponential fits. These data may help independent workers to determine if their fitting programs actually do what they are intended to do.

As has been amply shown in the more mature geochronological disciplines (eg Brooks et al. 1972), it is extremely important that any such differences be documented early in the use of these algorithms, so that the limitations and assumptions underpining each computation method can be appreciated. Lack of such an appreciation may lead to undesirable and unnecessary conflicts in interpretation of TL dating results.

The fitting method

We wish to compute the intersection point of two extrapolated exponential curves, as frequently encountered with the partial bleach method of Wintle and Huntley (1980). The first data set presented here was obtained from a glaciolacustrine silt, QNL84-2, described by Berger, Clague and Huntley (1987a). The second data set is from a lake sediment of Berger (unpublished). These data sets have a similar scatter (standard deviations are 4% and 3% respectively, calculated from equation 4 of Berger et al., 1987b), but differ in the percent extrapolation from the applied dose range.The form of the exponential curves applied here is

$$I = I_0 \{ 1 - \exp[- (D + D_x)/D_o] \}$$

where I is the TL intensity in photon counts, I_0 is the saturation value of the TL, D is the laboratory applied dose, $-D_x$ is the extrapolated X axis intercept, and D_o is a fitting parameter. The desired equivalent-dose value is either $+D_x$ if the additive-dose method is used, or the dose at the intersection of the two curves if the partial-bleach method is used.

The data are listed in Table 1. The best estimates of the curve parameters are calculated by three methods: a) the quasi-liklihood or iterative least-squares method described by Berger et al. (1987b) [the first data set (QNL84-2) is shown plotted in Figure 3 of that paper, but with the use of equal weighting]; b) a weighted least-squares method programmed for DJH by S. G. Cowan; and c) a weighted least-squares method using a simplex fitting routine programmed by DJH.

The error estimates in the intersection values are calculated in two ways; method (i) uses a fast delta method outlined by Berger et al. (1987b), whereas method (ii) uses a slow interval or liklihood-ratio technique (also see Berger et al. 1987b). Specifically, in (ii) different trial sets of parameters are tested for statistical "reasonableness" using a liklihood-ratio test, and the range of values of accepted parameters is then used to calculate the "error" (or chosen probability interval) in the intersection.

The weighting factors used in all three methods were those appropriate to an error model with a constant percent error in the TL intensity and no error in the dose variable [For justification see Appendix A of Berger et al. (1987b)]. In such a weighting scheme, the variance is proportional to the square of the TL intensity. It should be noted here for comparison that the simplex procedure used (only) for the additive-dose method by Grün and Macdonald (1989) makes no explicit assumption about the error model and consequently employs equal weighting.

The weighting scheme of method (a) uses the best estimate of the TL intensity (ie the intensity calculated from the fit), whereas method (b) uses the measured TL intensity. This is a subtle but important distinction in weighting schemes. This calculated intensity is required for statistical rigour in the derivation of the algorithm because the constant percent error in the TL signal is not yet known independently (but see below). However, we show below that in practice this distinction in weighting schemes produces no significant difference in results, for these data sets.

The fitting model (saturating exponential) is assumed to be a correct representation of the data. A discussion of the possibility of bias introduced by incorrect modeling is beyond the scope of this note.

Results

The data for the lake sediment are shown plotted in figure 1 with the best-fit curves of method (a). The best estimates of the curve parameters and the intersection values, where calculated, are compared in table 2. For all data, each of the estimates derived with method (a) for the parameters I_o, D_x and D_o lies

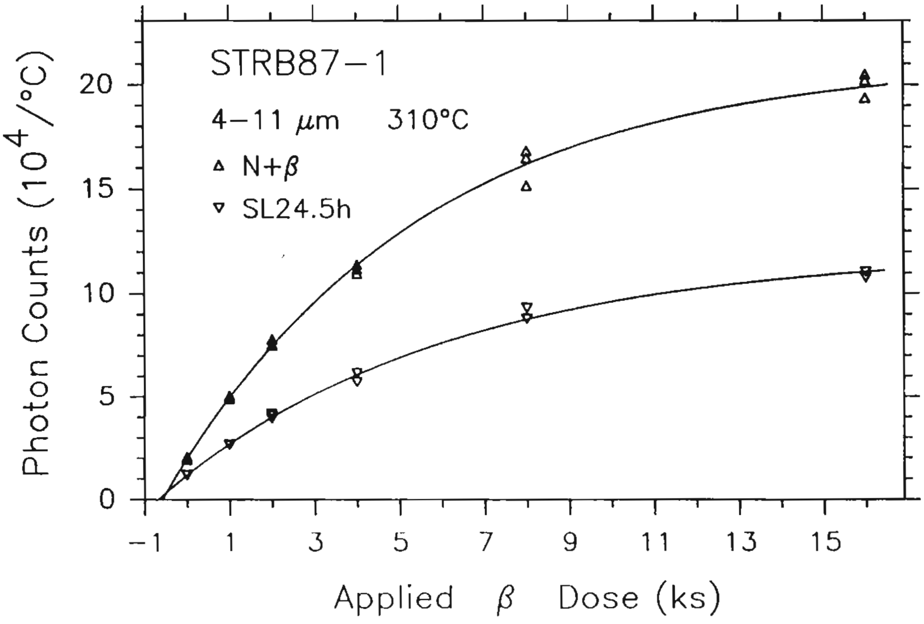

Figure 1.
Partial-bleach data and the best-fit weighted, saturating exponential curves for sample STRB87-1, computed using the method of GWB. With an unequal-weighting scheme such as employed here, high-dose points have less influence than low-dose points in determining the error in the extrapolation. For this reason the data in Figure 1 are not distributed evenly over the applied-dose range, but rather successive applied doses have been doubled.

between the two estimates calculated by the other methods. In all cases the range of these estimates was much less than their respective uncertainties, which were typically ≈3-10%. The intersection values from methods (a) and (b) also agree closely.

Thus, the exact way in which the fitting is made has no significant effect on the outcome for these data. This is reassuring, for Berger et al. (1987b) stated that with good data sets (those having >10-15 points per curve, and <5% standard deviation in the intensity values) most fitting methods should yield the same results (within error). The methods in table 2 also do not differ in the computation times for each set of three-curve parameters [3-5 s for method (a) with compiled True Basic; 3-4 s for method (b) with compiled QuickBasic, both using an 80286 CPU @ 8 MHz, without a math coprocessor].

However, the methods do differ dramatically in the computation time (under the above machine conditions) of the error in the two-curve intersection. The delta method ("a" here or "GWB" in table 2) required only ≈8 s per intersection value, whereas the interval method (b) required ≈420 s (500 trial fittings were used for the computation). A math coprocessor will reduce significantly this computation time (for both methods). For example, with an 8088 CPU @ 4.77 MHz using a coprocessor 8087 chip the error computation time for method (b) was reduced to ≈150 s, still far slower than the algorithm for the delta method run without a coprocessor, even allowing for the differences in CPUs. This dramatic difference in time (a factor of 50!) is not suprising because interval methods for the estimation of intersection errors are "numerically fierce" (Berger et al., 1987b).

Implications for the error model

We have used the scatter in the data about the regression curve to obtain an estimate of the constant percent error. However, ultimately it is desirable to estimate this error from more specific experiments, and then to use the observed data scatter to obtain a chi-squared estimate and thereby to compute a goodness-of-fit parameter (Berger et al., 1987b). A chi-squared estimate would provide an assessment of the probability that the measured scatter of data points is too large (or too small). The null hypothesis is that the scatter is due only to a random variation within a population of possible TL values whose mean is the *best-fit* TL value and whose variance is known independently (the expected error in each data point). A goodness-of-fit parameter would enable us objectively to recognise and to reject spurious data points, as routinely practiced in the more mature isotopic dating methods (Brooks et al., 1972).

In view of the apparently enormous variety of TL reponses in nature, even for one mineral type, can a sufficient knowledge of the variance in each intensity value ever be obtained? Could replicate TL measurements from many (100?) discs at a single dose value for each of several "known" mixes of minerals provide characteristic (representative) variances applicable to sediments having similar relative concentrations of minerals (estimated routinely by powder X-ray diffraction, for example)?

Table 1.
Data for samples QNL84-2 and STRB87-1. For the former, 2-4 μm grains, for the latter, 4-11 μm grains were used. TL data are photon counts/°C. Doses are in minutes of ^{60}Co gamma radiation at 1.6 Gy/min (QNL84-2), and in kiloseconds of ^{90}Sr beta radiation at 90 Gy/ks (STRB87-1).

QNL84 - 2				STRB87 - 1			
Unbleached		Bleached		Unbleached		Bleached	
Dose	counts	Dose	counts	Dose	counts	Dose	counts
0	38671	0	20766	0	20522.2	0	11814.6
0	40646	0	21393	0	19373.6	0	11587.8
0	38149	0	22493	0	21040.6	0	11708.6
0	35836	120	31290	0	18899.1	1	26645.2
120	65931	120	33779	1	50382.5	1	26445.2
120	67887	240	43221	1	48570.2	1	26368.6
120	66133	240	43450	1	49529.5	2	41487.1
240	82496	240	41427	2	77706.6	2	39125.1
240	86708	480	51804	2	75291.3	2	40582.5
240	86580	480	59555	2	74563.8	4	61532.1
480	110978	480	54013	4	111547.5	4	57023.6
480	113807	960	75748	4	113899.1	8	93015.8
480	114192	960	76613	4	109461.1	8	87907.7
480	109652			8	164564.9	8	87655.2
960	130373			8	151504.2	16	107618.3
960	137789			8	168042.1	16	110394.2
				16	204726.5		
				16	201964.3		
				16	193457.6		

Table 2 Best-fit parameters for the two data sets

	QNL84-2 chan. 120						STRB87-1 chan.145					
	unbleached (16 pts)			bleached (13 pts)			unbleached (19 pts)			bleached (16 pts)		
Fit[a]	I_o	D_x	D_o	I_o	D_x	D_o	I_o	D_x	D_o	I_o	D_x	D_o
GWB	14.280	122.74	392.0	9.64	193.4	762	21.214	0.5832	5.96	12.043	0.6800	6.67
		±6.73			±18.8			±0.0178			±0.0226	
	intersection D_e = 86.4 ±10.1						intersection D_e = 0.4846 ±0.0368					
SC	14.246	121.86	389.9	9.67	195.2	773	21.153	0.5825	5.95	12.029	0.6823	6.68
	± 0.459	± 6.74	±30.8	±1.02	±19.5	±152	±0.483	±0.0181	±0.25	±0.320	±0.0226	±0.31
	intersection De = $85.0^{+22.1}_{-19.9}$						intersection De = $0.4814^{+0.0782}_{-0.0825}$					
S-c	14.297	123.18	393.1	9.63	192.5	757	21.243	0.5835	5.97	12.051	0.6790	6.67
S-m	14.246	121.86	389.9	9.67	195.2	773	21.153	0.5825	5.95	12.029	0.6823	6.68

Values for I_O are the photon counts divided by 10^4

Footnote a)
Four different fitting procedures were used:
1) GWB is the method of Berger et al. (1987b); 2) SC is the method of Cowan in which the variance is proportional to the square of the *measured* TL; 3) S-c is a weighted least-squares fit using a simplex routine, in which the variance is proportional to the square of the *calculated* TL value (as in method GWB); and 4) S-m, as for (3) but with the variance as in (2).
Two different methods of error estimation were used: the delta method of Berger et al. (1987b), and the interval method of Cowan. In method SC each fitting parameter was not allowed to vary by more than 2σ. Errors are quoted at the 68% confidence level (1σ) except for the intersection errors of method SC, which are computed at the 95% level (≈2σ). These 95% confidence estimates were obtained by adding in quadrature the limits due to the unbleached and bleached data, these being calculated independently. This addition is an approximate, ad hoc method for finding the intersection error for method SC, but the close agreement with the results of method GWB suggests that this is a valid approximation.

Summary

For good data and relatively small extrapolations, we observed no significant difference in results from the three different fitting routines illustrated here. However, if computation speed is important, then the delta method of Berger et al. (1987b) is much faster than the interval method in calculating the intersection error.

Acknowledgements

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