Paleodose evaluation of porcelain: a practical regression method of saturation exponential in pre-dose technique

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Abstract A practical regression method of saturation exponential in pre-dose technique is proposed. The method is mainly applied for porcelain dating. To test the method, some simulated paleodoses of the imitations of ancient porcelain were used. The measured results are in good agreement with the simulated values of the paleodoses, and the average ratios of the two values by using the two ways are 1.05 and 0.99 with standard deviations ($\pm 1\sigma$) of 19% and 15% respectively. Such errors can be accepted in porcelain dating.

Keywords Porcelain thermoluminescence (TL) dating, Pre-dose technique, Saturation exponential regression

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1 INTRODUCTION

Pre-dose dating of the porcelain was reported by Stoneham[1] as early as 1983. Just as pointed out by Bailiff[2], it is a technique requring considerable experimental efforts to yield dose estimates due to the complexity of the pre-dose effect on which it is based. The basis of pre-dose technique is the measurement of the change in sensitivity of 110°C TL peak in quartz. The 110°C peak has a half-life of only several hours at room temperture though it does not occur in natural TL, and it has a "memory" effect. Once a piece of quartz is heated to the thermal activation temperture, the 110 ℃ TL peak can be presented and measured, because it is a highly sensitive peak and exposure to quite a small test dose (about 10~100 mGy) is usually sufficient to induce an accurately measurable TL. Because the change of 110°C TL sensitivity is a function of the paleodose or the laboratory calibrating dose, the paleodose sensitivity can be evaluated by means of the sensitivity of laboratory calibrating dose and so the paleodose can also be obtained. It has been found that the growth of 110°C TL sensitivity with increasing the dose is sublinear even if the dose is less than a few Gy in porcelain and pottery. According to the sublinear characteristic for archaeological samples, a practical regression method of saturating exponential for evaluation of the paleodose is studied.

2 RELATION BETWEEN THE DOSE D TO THE SENSITIVITY S

Concerning the pre-dose technique it is assumed that the changes in 110°C TL

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sensitivity with the dose is represented by a linear function. It is generally believed that this assumption is correct only when the dose is within the range of a few Gy. In fact, the nonlinear phenomena has been studied since many years ago. As early as 1979, Chen[3] pointed out a saturating exponential form in the sensitivity change. Later, Aitken[4], Chen[5], Bailiff[2,6], Leung et al[7] and Chen and Leung[8] further studies these problems of nonlinear response and exponential model in the sensitivity change. For porcelain dating we also made some tests for studying the nonlinearity. In particalar, the sensitivity response in the range of a few Gy was analysed. It was seen that the linear region was very narrow, and the growth of sensitivity with increasing the dose is sublinear even if the dose is within a few Gy (Leung *et al*[9]). Only in some cases the sublinearity may act as linear approximately. In these cases the error is not serious when using linear relation of S and D for evaluating the paleodose in the sublinear region, but the calibrating dose is limited because a larger additional calibrating dose will lead to a grave nonlinearity. Conversely, a small calibrating dose is not usually sufficient to induce an accurately measurable sensitivity, especially for the porcelain dating. Therefore Leung *et al*[8] suggested an exponential regression method for evaluating the paleodose the pre-dose technique and carried out some experiments using a piece of natural quartz and a piece of quartz extracted from an ancient brick as samples. A comparison of the exponential regression with the standard (i.e. linear) method was carried out. The results show that the calculated values obtaind by using the exponential regression method are very close to the actual laboratory "paleodose" (for natural quartz) and the age of the ancient brick respectively, but the values calculated by the standard method was 1.5~2 times larger than those of the actual ones, respectively (see Leung *et al*[8]).

It is easy to obtain the form of sensitivity change with increasing dose. Due to the capture of holes in traps R is random, the change of traps R with dose D is,

$$\frac{\mathrm{d}R}{\mathrm{d}D} = -\frac{1}{B}R \tag{1}$$

Where $1/B$ is the capture probability. Solving equation (1), we have $R = R_o e^{-D/B}$, where R is the amount of hole-trap uncaptured after the crystal absorbs the dose D, R_o is the sum of hole-traps, and B is a constant. It is obvious that $R_o - R = R_o(1 - e^{-D/B})$ is the amount of holes captured. Once these holes capured $(R_o - R)$ transfer into trap L, the L become luminescence center, i.e., the sensitivity S increases through the irradiation dose D. Hence

$$S = R_o(1 - e^{-D/B}) \tag{2}$$

where R_o is the largest amount of holes capured, i.e., the largest sensitivity S_∞ achieved as well. The S_∞ is expressed as the sensitivity when the dose D rising to infinity, and it is called saturation sensitivity. Then the equation (2) can be written as

$$S = S_\infty(1 - e^{-D/B}) \tag{3}$$

3 EVALUATION OF DOSE D

It is illustrated by Bailiff[2,6] that the sensitivity S changes as a result of successive dose/activation cycles using a single aliquot and a fixed dose. So long as S is an exponential function of D, ΔS_i is inevitably a linear function of S_i, where $\Delta S_i = S_{i+1} - S_i$, in which S_i and S_{i+1} are, respectively, the sensitivities of this step and next step in dose/activation cycles. Therefore, the paleodose P can be evaluated from the linear relation between ΔS_i and S_i. It is easily proved. From equation (3)

$$S_{i+1} = S_\infty(1 - e^{-D_{i+1}/B}) \tag{4}$$

$$S_i = S_\infty(1 - e^{-D_i/B}) \tag{5}$$

then

$$1 - \frac{S_\infty - S_{i+1}}{S_\infty - S_i} = 1 - e^{-(D_{i+1}-D_i)/B} \tag{6}$$

Set $\beta = (D_{i+1} - D_i)$ as a fixed dose increment administered, the equation (6) becomes the following form

$$\Delta S_i = S_{i+1} - S_i = (1 - e^{-\beta/B})(S_\infty - S_i) = S_\infty(1 - e^{-\beta/B}) - (1 - e^{-\beta/B})S_i \tag{7}$$

Let $a = S_\infty(1 - e^{-\beta/B})$ and $b = -(1 - e^{-\beta/B})$, then

$$\Delta S_i = a + bS_i \tag{8}$$

Eq.(8) shows a linear relation between S_i and ΔS_i, where a is the intercept and b is the gradient in the linear function. we obtain

$$S_\infty = -a/b \tag{9}$$

$$B = -\beta/\ln(1 + b) \tag{10}$$

By making use of S_∞ and B, we can evaluate the paleodose P. Let S_o be the initial sensitivity and S_N be the activated sensitivity of accrued natural dose, replacing β with P in Eq.(7), we obtain

$$S_N - S_o = (S_\infty - S_o)(1 - e^{-P/B}) \tag{11}$$

Solving Eq.(11)

$$P = -B\ln(1 - \frac{S_N - S_o}{S_\infty - S_o}) \tag{12}$$

Note that the measurement of the radiation quenched sensitivity $S_i \downarrow$ is unnecessary in this method.

4 EXPERIMENTS

Owing to the paleodose of ancient porcelain sample can not be clearly known, a simulated paleodose is used for testing the method. We collect a few imitations of ancient Chinese porcelain from different provinces in China. All the porcelains were last fired less than 20 years ago, the natural accumulated dose in the samples is negligible, because the natural dose is much lower than the simulated paleodose. The sampling was made by a diamond core-drill and the core was sliced into several 200μm thick slices using a precision slicing machine (Microslice 2, ULTRA TEC Mfg., Inc.). In the process of the drilling and slicing the sample was cooled with water. Giving the slice a known laboratory β dose as the equivalent paleodose P, then heating it to 150°C in order to empty the 110°C traps of the electrons acquired from the equivalent paleodose irradiated by a laboratory beta source. These equivalent paleodoses correspond to the natural accrued dose of Qing Dynasty (1323 mGy), Ming Dynasty (2646 mGy) and Tang Dynasty (5390 mGy), repectively. All TL measurements were performed by using a fully automated combined TL/OSL dating system (model Riso TL/OSL-DA-15), manufactured by Riso National Laboratory, Roskilde, Denmark. The equivalent paleodose, testing dose and calibrating dose were irradiated by using the same beta irradiator, which is mounted in the dating system attachable to the sample changer for providing software controlled irradiation to samples in situ. The radioactive beta source is an Amersham ^{90}Sr (plaque source type SIPK, 1.48 GBq). A preparatory porcelain sample that had received an equivalent paleodose was used for the following measurement procedure: (1) The sample was heated to 150°C (heating rate 2°C/s, the same below), (2) The sensitivity S_o of the 110°C TL peak was measured by using a testing dose (about 500 mGy, the same below), (3) Heat to the activating temperature (typically 650°C), (4) The sensitivity S_N was measured using the same testing dose, (5) A calibrating dose β was administered and then the sample was heated to the same activating temperature, (6) The sensitivity $S_{N+\beta}$ was measured by using the same test dose, (7) Repeat steps 5 and 6, the sensitivity $S_{N+2\beta}$ was obtained.

The response curves of the pre-dose sensitivility for sample No. 149-2 are plotted in Fig.1. The four curves from low to high intensities indicate S_o, S_N, $S_{N+\beta}$ and $S_{N+2\beta}$, respectively, where the sensitivity is expressed as intensity because all the test doses are the same. Fig.2 is the $D \sim S$ curve for sample No.149-2 and it is obviously an exponential function. Let $\Delta S_1 = S_{N+\beta} - S_N$ and $\Delta S_2 = S_{N+2\beta} - S_{N+\beta}$, and take a linear regression for the (S_N, ΔS_1) and ($S_{N+\beta}$, ΔS_2) data pairs. From Eqs.(8),(9) and (10), S_∞ and B are obtained.

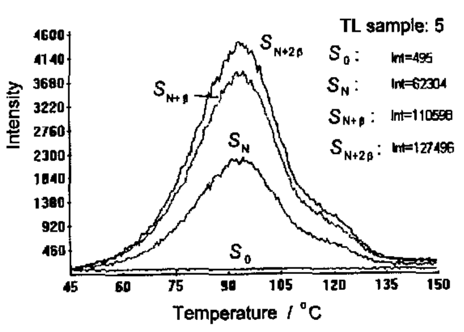

Fig.1 Response curves of the pre-dose sensitivity measured for sample No. 149-2

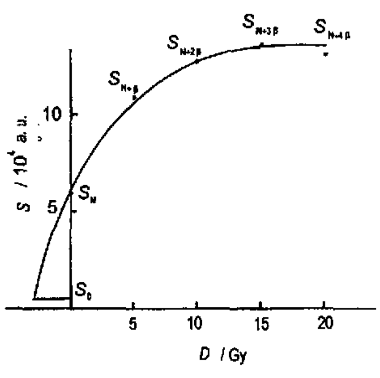

Fig.2 Sensitivity versus the beta calibrating dose curve for sample No. 149-2

Because the 110°C TL sensitivity is low, the testing dose used is greater than the usual one so as to acquire an accurately measurable TL. The large testing dose must be considerd into the calibrating dose, and be subtracted from the final result. This method is developed from Leung's method[8], in which the measurements of radiation quenched sensitivities $S_N\downarrow$ and $S_{N+\beta}\downarrow$ etc. were necessary, and $\Delta S_i = S_{i+1} - S_i\downarrow$ (for further details, see Leung *et al*[8]). For the comparison with Leung's method we also carried out a set of measurements of S_N, $S_N\downarrow$, $S_{N+\beta}$, $S_{N+\beta}\downarrow$, $S_{N+2\beta}$ and then calculated results with Leung's method[8].

This method and Leung's method are the same in principle, but the measurement is different. In Leung's method the ΔS_i is a net increment whereas in this method the ΔS_i is an apparent increment. For the age region of 100~1200 a the results obtained by the two methods are the same, but for the ages less than 100 a the present method is more accurate and for the ages greater than 1200 a Leung's method is more accurate. Each of the two methods is suitable for the ages of the upper limit or the lower limit respectively.

5 RESULTS

Table 1 gives the results of 35 measurements for 14 porcelain samples, where R is the dose ratio for the measured/known paleodses. Table 1 shows that the average value of R is 1.05 and the standard deviation ($\pm 1\sigma$)is 19% for the data. The error can be accepted in porcelain dating. The results obtained using Leung's method are shown in Table 2. The average value of the R is 0.99 and a standard deviation ($\pm 1\sigma$) is 15% in Table 2. There is reasonable agreement betweent the two methods, but the present method is a little simpler than Leung's method because the measurement of quenched sensitivity is unnecesary. In addition, the S_0 in Tables 1 and 2 are almost the same except for some sensitivities very high (e.g. No.140-1 and No.140-2 in Table 1). We found the S_o is mainly from the background of TL measurement system, true S_o from the sample is little, so it is reasonable that the S_o be subtracted from S_N and all $S_{N+\beta}$ before the regression, the results in Table 1 were obtained by $P = -B\ \ln[1 - (S_N/S_\infty)]$, but the results in Table 2 were still calculated by using Eq.(12).

The saturation exponential method is more suitable for porcelain dating, it has two advantages compared with the standard method.

(1) A good accuracy. The measurement is made in an exponential region so a larger calibrating dose can be used, such that induced TL would be raised. In addition, increasing the testing dose to 500 mGy, it can also raise the TL signal. If the sample sensitivity is low too, the testing dose can be increased to the level of detectable limit with no influence on the result, because the testing dose is subtracted from the final result. In order to increase sensitivity the best way is expanding the area of the sample by using two or three preparatory porcelain samples (3 mm in diameter for each slice) together for measuring TL if the quantity of samlpe is sufficient.

Table 1 Measured results of the simulated paleodoses of the porcelains using the saturation exponential method

Sample	S_0	S_N	$S_{N+\beta}$	$S_{N+2\beta}$	S_∞	B/Gy	R
128-1	383	3109	6080	7268	7676	5.495	0.86
128-2	391	4040	7492	9007	9801	6.115	1.05
129-1	483	11336	20404	25196	30083	7.896	1.35
129-2	396	10728	19965	23426	25104	5.130	0.99
135-1	373	2542	4421	5323	5782	6.862	1.20
135-2	364	2674	4480	5136	5146	4.972	1.10
136-1	381	7991	14713	17133	18113	4.929	0.98
136-2	349	7728	13355	15913	16642	5.385	1.18
137-1	464	5214	10573	13626	17204	8.950	1.07
137-2	357	5636	11555	14162	15875	6.141	0.89
137-3	451	4529	9659	12424	15231	8.184	0.92
137-4	381	6062	8347	9436	10061	6.833	1.14
138-1	373	3636	6146	7283	7851	6.359	1.36
138-2	392	3286	5735	6646	6794	5.092	1.04
138-3	399	3543	6059	7085	8046	6.891	1.30
140-1	802	48500	154040	223252	354313	11.936	0.56
140-2	780	42781	107276	147550	213736	10.695	0.83
143-1	325	11510	22148	26304	28643	5.358	0.96
146-1	448	7528	14162	18123	23544	9.765	1.33
148-1	370	6168	14678	21795	57231	27.811	1.10
148-2	409	5603	13496	20164	56262	30.007	1.07
148-3	379	5340	12622	19240	84821	52.671	1.19
148-4	354	6171	14617	21325	46861	21.858	1.07
149-1	541	43410	91527	114378	134503	6.763	0.94
149-2	495	62304	110598	127496	136095	4.795	1.07
149-3	463	42171	87399	110544	134598	7.561	1.03
149-4	467	59784	90773	106041	120402	7.114	0.95
150-1	437	2722	5140	5949	5918	4.599	0.78
150-2	417	2061	3774	4722	5479	8.512	1.13
150-3	405	1743	3226	4327	7106	16.960	1.35
150-4	368	2520	4615	5522	5848	6.015	1.01
150-5	373	1151	2517	3072	3078	5.591	1.04
161-1	440	1791	4037	4847	4864	4.938	0.51
161-2	382	2634	4713	5472	5525	4.997	0.95
161-3	400	2521	4256	5134	6533	7.393	1.33
164-1	433	3224	9147	11507	12637	5.473	0.81
164-2	431	3266	8936	11526	13273	6.427	0.96
164-3	354	3411	9027	11798	14139	7.125	1.13
166-1	432	3493	6656	8248	9438	7.335	1.07

Note: The porcelain slice samples were given equivalent paleodoses, respectively, as follows: 150-5 and 164-3 correspond to Qing Dynasty; 137-4 and 149-4 correspond to Tang Dynasty; all the others correspond to Ming Dynasty.

Table 2 Measured results of simulated paleodose on porcelain using Leung's method[8]

Sample	S_0	S_N	$S_N\downarrow$	$S_{N+\beta}$	$S_{N+\beta}\downarrow$	$S_{N+2\beta}$	S_∞	B/Gy	R
136-5	368	7010	3514	10050	5526	11371	22545	11.969	0.83
136-6	344	4451	2284	7977	4535	9589	22338	15.082	1.17
136-7	351	2272	1306	7068	3835	8375	13230	7.629	1.00
137-4	330	5595	3011	8790	5151	10369	25055	16.565	0.77
148-5	374	4137	3623	10620	9869	16495	121421	82.240	0.94
148-6	396	5009	4483	12661	11856	18688	49279	24.983	0.87
147-7	389	4371	3879	10202	9474	14903	43450	28.926	1.04
148-8	407	4606	4095	11557	10813	16790	37852	20.159	0.85
149-5	365	53274	36544	97952	72870	117721	171273	8.277	1.14
149-7	510	41766	30519	83944	63980	102479	149887	8.468	1.00
149-8	493	51785	35451	103320	77471	126821	189447	8.666	1.00
149-9	518	45702	31802	87449	64986	106583	163231	9.146	1.10
149-10	436	54442	36666	100220	73204	118191	161734	7.097	1.07
149-11	495	54047	38887	75580	58510	86413	120801	8.476	0.99
150-5	360	2034	1039	3619	2056	4141	6339	7.551	0.89
150-6	390	2098	1076	3906	2144	4328	5754	5.423	0.71
150-7	342	1160	648	2747	1630	3659	30094	68.099	1.27

Note: The samples were given equivalent paleodoses, respectively, as follows:

136-7 and 150-7 correspond to Qing Dynasty;136-5,137-4 and 149-11 correspond to Tang Dynasty; all the others correspond to Ming Dynasty

(2) Expanding measurable age. In pre-dose effect, S rising with D is quick, the linear region is very small at the beginning, it may act as linear approximately only when D is much less than B (for details, see Leung *et al.*[8]). Therefore, the application of the standard method is limited, and it is mainly suitable for authentification of modern imitation. The exponential method expands the range of measurable age and the porcelain made 1500 years ago can also be dated.

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