Study on fine quartz pre-dose techniques*

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Abstract   When using the pre-dose technique in ceramic dating, it is essential to add a calibration dose and to eliminate the background dose. For doing this measurement the sample requires multiple activation following multiple administration of a test dose to induce simulated "ancient" thermoluminescence (TL). However, the procedures introduce many factors that are difficultly corrected. This paper compares existing two kinds of measurement procedures and proposes a new procedure involving single activation following a single test dose administration. An experiment using the single activation procedure is carried out with natural fine quartz where the results obtained exhibit only 0.07 relative error. It appears that this new procedure increases the precision of the ancient TL measurement by about 0.04 and 0.11 over those of existing two kinds of procedures. In addition this method can give realistic values in TL dating for relatively "young" samples aged tens to hundreds of years where the standard high temperature TL method is relatively insensitive.

Keywords   Thermoluminescence dating, Pre-dose techniques, Ceramics

1 Pre-dose effect

In standard TL (thermoluminescence) dating the paleodose p is measured directly from the high temperature TL peak. In the pre-dose method, p is inferred from a test dose added in the laboratory to induce TL peak at low temperature. This means that "recent" TL is used to find out the past dose. The pre-dose effect is effectively a "memory" stored in the crystal that is only released after thermal activation. Fleming[1,2] discovered that when quartz is thermally activated to 500°C the 110°C TL of the next test-dose increases substantially (the amount shows the sensitivity). The increase is proportional to the total dose absorbed by the sample before activation, that is either the paleodose for the first activation or the increased dose between two activations. Thus p can be determined by the increase in TL before and after test-dose administration.

One restriction is that while mineral crystals produce a number of correlated TL peaks at different temperatures, not all these exhibit the pre-dose effect. Indeed, only the 110°C TL response peak of quartz has a significant pre-dose effect. Unfortunately, the half-life of this TL peak is very short (only 1 to 2 h at room temperature) so that this peak can be not found in the natural TL spectrum.

Where it occurs, the sensitivity of the pre-dose effect is very high. It can be used to measure paleodoses down to 0.1 Gy. That is to say it can be used to measure the age of ceramics lower than tens of years. This is valuable and useful because the sensitivity of standard TL dating using the traditional technique is very low for such young sample ages. However, the pre-dose method becomes far less sensitive at higher doses of a few Grays as the sensivitity reaches a saturation region. This limits the dating to sample aged below 2000 a. Even where this is the case the pre-dose may still be applicable to measure the paleodose in poor conditions where part of the real TL may be eliminated by spurious TL under high temperature, or is difficult to determine because of anomalous fading, or where during a repair process the pottery was heated at low temperature. The method, then, plays an important role in authentication and is in fact the effective method possible to determine the age of

porcelain by TL dating.

2 Existing two kinds of procedure of pre-dose technique

The main principle of these approaches is the fact that the dose-response of quartz at the 110°C peak, after a thermal activation, is proportional to the absorbed paleodose over the life of the manufactured ceramic. The procedures for paleodose measurement can be established as follows[3−8].

2.1 Multiple activation procedure

(i) A test-dose is added to the sample and the corresponding TL at 110°C is measured as S_0.

(ii) The sample is thermally activated to the temperature corresponding to the maximum value of thermal activation characteristic (TAC) curve, which should be measured for individual sample before the procedure[9].

(iii) An identical test-dose is added to the sample and the corresponding TL at 110°C is measured as S_N.

(iv) The laboratory calibration dose β is added to the sample.

(v) The sample is heated to 150°C to expel the 110°C electron traps formed from the calibration dose.

(vi) The identical test dose is again added and the corresponding TL at 110°C is measured as S_N'.

(vii) The sample is again activated to TAC temperature.

(viii) The identical test dose is added and the corresponding TL at 110°C is measured as $(S_N + S_\beta)$.

$(S_N - S_0)$ is proportional to the paleodose p, and the increased response between steps (vi) and (viii) i.e. $\{(S_N + S_\beta) - S_N'\}$ is proportional to the calibration dose β. Therefore, p becomes

$$p = \{(S_N - S_0)/[(S_N + S_\beta) - S_N']\}\beta \qquad (1)$$

It is found that the value S_N' obtained in step (vi) is smaller than S_N obtained in step (iii). This is known as "sensitivity quenching", in that the sensitivity has been depressed. The calibration dose β is the cause of this change of sensitivity and therefore $[(S_N + S_\beta) - S_N']$

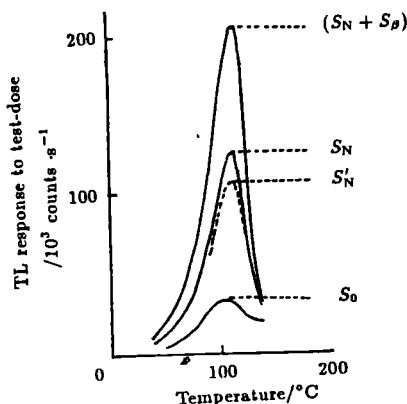is used instead of $\{(S_N + S_\beta) - S_N\}$ in Eq.(1) (refer to Fig.1).

Fig.1 The pre-dose effect in the 110°C TL peak of quartz[6]

2.2 Additive dose procedure

In the above process the sample has undergone multiple test dose administrations and multiple activation. This creates multiple quenching effects requiring multiple and uncertain correction which have been studied by Aitken[6] and Bailiff[10]. The additive dose procedure attempts to reduce this effect.

Generally, the samples are classified into two groups. One group is used to determine S_N, and the other to determine S_0 and $S_{N+\beta}$. The difference between $S_{N+\beta}$ and $(S_N + S_\beta)$ is that the calibration dose β of the latter is added after activation of the natural dose, whereas in the former it is added before activation. $S_{N+\beta}$ and S_N now involve a single activation only. However, the test dose is still used twice to measure S_0 and $S_{N+\beta}$ in the same groups.

The paleodose p becomes

$$p = [(S_N - S_0)/(S_{N+\beta} - S_N)]\beta \qquad (2)$$

The procedure eliminates both the character change of the paleodose due to heating and interference due to the quenching effect. However, a disadvantage is that the two groups of samples must be "normalized" either by weight or by S_0. Better precision is obtained through S_0. However, this is difficult when the S_0 value is relatively low. In using Eqs.(1,2) it is assumed that the pre-dose effect is linear.

3 Proposed fine quartz single acti-

vation pre-dose procedure

The procedure proposed here retains the advantages of the procedures described above, while avoiding the main disadvantages. One characteristic of this procedure is ths use of three sample groups. Each group is given an identical single test dose while the two sample groups requiring thermal activation are activated once only. This ensures that all conditions for all three groups are exactly the same for the calculation. By avoiding multiple activation, no correction is required for the quenching effect. In fact the weight deviation of fine quartz samples in dish prepared using water flotation method or acetone method is smaller than 0.05 each other. As this is the case, "normalization" between sample groups is also conveniently not required. Then the fine-grain technique can be used to pre-dose method for the young age pottery. (Whether this will remain the case' with porcelain samples is under investigation).

Using the water flotation method for sample preparation, a number of small quartz samples (NQ1) are prepared at one time. They are divided into three groups. The first group is used to measure S_0, the second group for S_N and the third group for $S_{N+\beta}$. The general steps for measurement are as follows:
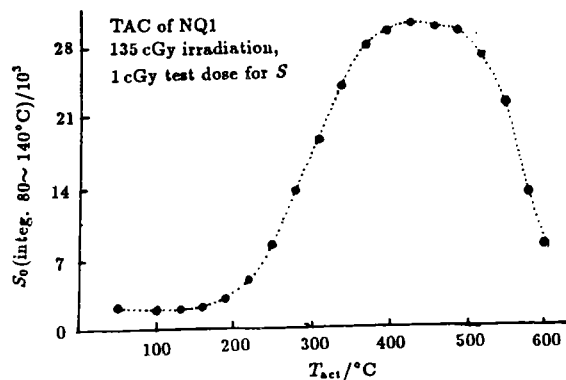

Fig.2 Thermal activation characteristic (TAC) curve of natural quartz NQ1

TAC curve of NQ1 fine quartz is measured and the maximum temperature is 500°C (Fig.2).

(i) The third sample group is irradiated by a single laboratory calibration dose, β

(ii) The second and third groups of samples undergo thermal activation to 500°C separately

(iii) All three sample groups are irradiated by a test dose, and the three responses (S_0, S_N and $S_{N+\beta}$) of the 110°C TL peak are determined.

The paleodose p is then calculated using Eq.(2).

There is a problem associated with the delay-time between adding the test dose and measuring the TL response. The half-life of the 110°C TL peak in quartz is only one to two hours at room temperature. Fading will be very fast and therefore the measurements involved in step (iii) should be handled carefully. For example, if five samples of each group were measured piece by piece this would take about 45 min by which time the response peak will have faded by 50%. Therefore, the first parallel samples of three groups should be measured first, then the second parallel samples of three groups and so on. In this way the time difference for parallel samples of each group will only be of the order of 3~5 min and so fading will be small. The fading effect can also be compensated by adjusting the order of measuring S_0, S_N and $S_{N+\beta}$ (see the positions of them in Eq.2). While, in theory, the most effective method to reduce fading would be to add the test dose to only one sample (or three parallel samples) each time, this approach is inconvenient and time consuming. It is also difficult to maintain an identical test-dose for a long time. Finally, it is better to record the sensitivity of the 110°C peak responses by using the "envelope integration" method which has a smaller statistical deviation than the "peak" method. Therefore, the error of each S is not shown in Table 1, instead the standard deviation of paleodose which is the mean value of five "parallel samples" p values.

4 Results and discussion

Table 1 shows the experimental results for the fine quartz, single activation, pre-dose technique. NQ1 is natural quartz from Mainland of China. Initially, the quartz is heated to 800°C for 18 h. Fine grain samples are prepared by natural cooling. ^{90}Sr is used to supply a known dose. Storing the samples for one day after

the irradiation is for 110°C TL peak decay. In order to shorten the experimental period, prepared samples are sometimes heated to 50°C for 3 h instead of storing one day. However, the pre-dose effect is very heat sensitive so that the temperature should be certainly not exceeded 50°C and any change in the pre-dose characteristic should be carefully monitored.

Table 1 The paleodose measuring results of the natural quartz NQ1

Sample code	Irradiation dose p_0 /mGy	S_0	S_N	$S_{N+\beta}$	p /mGy	p_0/p
P17	67.5	23.8	98.0	172	67.7±8.8	1.00±0.14
P6	135	55.7	165	271	139±3.3	0.97±0.05
P8	135	38.3	120	202	135±10	1.00±0.09
P9	135	39.6	126	218	127±8.8	1.06±0.09
						mean 1.01±0.08
P14	202.5	26.9	135	232	226±23	0.90±0.10
P10	270	36.2	122	214	252±8.8	1.07±0.06
P15	337.5	28.3	152	269	357±39	0.95±0.08
P11	405	38.0	169	287	450±40	0.90±0.08
P12	540	32.3	169	292	600±41	0.90±0.08
P18	540	32.6	217	374	634±46	0.85±0.07
						mean 0.88±0.08
P13	675	31.5	181	316	748±54	0.90±0.08
P16	675	40.6	208	373	685±34	0.99±0.07
P20	675	35.4	205	358	748±42	0.90±0.07
						mean 0.93±0.07
P21	1350	39.8	308	542	1547±122	0.87±0.08
P22	2025	45.0	399	614	3375±258	0.61±0.06
P23	2700	57.8	500	795	4047±117	0.67±0.04
P24	3375	61.6	534	833	5332±245	0.63±0.04
P25	4050	69.1	634	889	8972±1166	0.45±0.06

According to Table 1, within the range of linearity (up to 1350 mGy) the results correspond to the known dose with an average relative error of about 0.07. This is small compared with the large grain, quartz pre-dose technique. This implies that the fine quartz, single activation, pre-dose technique may be applicated to date relatively "young" samples provided the quartz content is high and has good TL character. In particular in Table 1 the known dose used for samples P6, P8 and P9 is 135 mGy corresponding to an age of only tens of years. Standard TL techniques are difficult to apply in this region.

Fig.3 shows the linearity test for NQ1 quartz. (Each experimental point in the figure represents an average of five p values by measurement; the dotted line represents the pseudo linearity of the sample at 2366 mGy). As indicated, the linear range is samll (less than 2 Gy). If the annual-dose is 4.0 mGy, the oldest age that can be measured is only 500 a. This means that the pre-dose method is mainly use-

ful for samples aged from tens to hundreds of years (the upper limit depends on the characteristics of the quartz) and the standard high temperature TL dating method should be used for older samples where it is already proven.
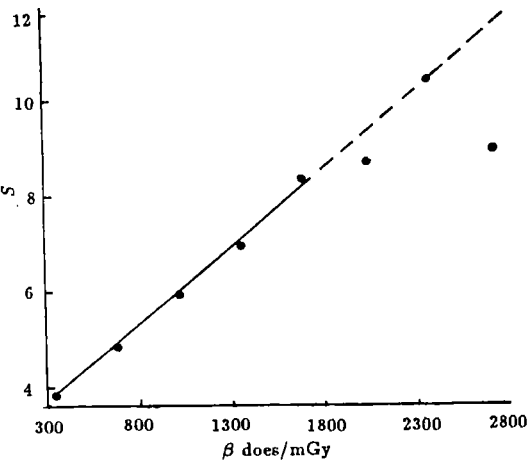

Fig.3 Linearity check of NQ1 quartz sample

It should be clarified here that only 0.05

of the annual α-dose is used to calculate the age in this pre-dose technique. The α-dose response of the 110°C TL peak is lower than the high temperature response by one to two orders of magnitude. This gives a typical k value of about 0.01 for the annual-dose calculation compared to 0.15 used for the standard method.

5 Comparison among 3 procedures

The samples were divided into three groups, the first group undergoing multiple ac-

Table 2 Comparison of pre-dose results among three kinds of procedure in quartz NQ1 experiment

Procedure	Irradiated dose p_0 /mGy	S_0	S_N	S'_N	$S_{N+\beta}$ or $S_N + S^*_\beta$	p /mGy	p_0/p
Multiple activation (1 piece)	337.5	758	26488	22322	36166*	289.5	1.17
Additive dose (2 pieces)	337.5	746	26488	—	39297	303.5	1.11
Single activation (3 pieces)	337.5	734	25859	—	38841	315.5	1.07

Table 3 Comparison of pre-dose results among three kinds of procedures in brick power experiment   mGy

Irradiated dose	Multiple activation	Additive dose	Single activation
100	45	109	164
200	245	292	190
300	225	262	353
900	925	812	899
1500	1969	1454	1717

tivation (see 2.1), the second undergoing additive dose analysis (see 2.2) and the third undergoing single activation (see 3). NQ1 quartz was again used for this comparison. The results are shown in Table 2 and confirm the previous analysis. The highest precision is obtained using the proposed single activation procedure, the additive dose procedure and the multiple activation procedure follow it, compared with the known dose. The proposed procedure raises the precision about 0.04 to 0.11. Comparison also extended to the real brick sample, after heating to 800°C for 15 h powder of which was used for the experiment as the same as the NQ1 quartz. The results are shown in Table 3. They are discrepant for different irradiation doses, but overall single activation procedure seems to be the best. Nevertheless, the fine grains, single activation, pre-dose method does appear to provide increased precision in dating relatively "young" pottery samples.

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