THERMOLUMINESCENT AUTHENTICATION OF ANCIENT CHINESE POTTERY*

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ABSTRACT
A rapid and effective TL technique to authenticate ancient Chinese pottery is proposed in the paper. Twenty three samples, ranging in age from 200 to 9000 a, including multiple styles and shapes and drawn from diverse and remote areas in China have been used to establish the typical annual dose as 5.5mGy/a and its associated deviation. Ten unauthenticated samples are then appraised using the technique which, in nearly all cases, leads to satisfactory results.
Keywords TL dating, Annual dose, Ancient pottery, China

1 INTRODUCTION

China is world famous for her pottery and porcelain, indeed the word "china" is synonymous with "ceramic ware". Precious works of Chinese antiquities are highly valued internationally and, because of this, items found in famous international museums and private collections have often been found to contain a surprisingly large number of forgeries. Many of these have only been identified relatively recently and the thermoluminescence (TL) dating technique, developed in the 1960s, has offered an useful scientific approach which has made significant contributions to authenticating these ancient works of art. Within just a few years, the TL method has managed to resolve a large number of disputes among collectors and museums which had previously lasted for decades. Aitken's "TL Resolution"[1] method has provided a shocks and surprises in many museum's collection. In 1970, for example, Fleming[2] at the Research Laboratory for Archaeology and the History of Art at Oxford University identified 6 replicas out of a sample of just 9 pieces of pottery figurines previously assigned to the Chinese Six Dynasties period by using TL measurement. In 1972, of 22 pieces of supposed Warring State Period ceramic ware, unearthed in Hui County, Henan Province, none were found to be genuine[3]. In 1973, 8 contemporary relicas were identified out of 37 pieces of tri-coloured glazed pottery from the Tang Dynasty period[4]. It can be seen that the TL method is very sensitive and effective. However the reliability of its application remains subject to a number of difficulties which lead to a variety of accepted techniques which can often be time consuming or impracticable. In this paper, a reliable, rapid technique is proposed for authenticating ancient Chinese pottery.

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2 DATING PRINCIPLES

TL authentication is simply an age dating method. For precise evaluation certain information is required about the specimen–whether or not it has been buried underground and for how long, the geological nature of any burial site, associated ground water information, the water content of the piece over its history–which is not always available for items now to be found in a collection. Without this information it is not possible to accurately calculate the total environmental radiation dose received by the specimen over its history and to compensate for its water content. Hence it is not possible to determine the age accurately. However for specimens which are many centuries old, the requirements of authentication can often allow an uncertainty of up to ±30% to be acceptable in which cases the TL method is still feasible. The basis of the method is the simple equation:

$$\text{Age} = \frac{\text{Paleodose}}{\text{Annual radiation dose}} \tag{1}$$

The paleodose or archaeodose is measured from the TL yield and calibrated by administering a known beta-dose in the laboratory. In this process there is a need to incorporate the change in TL sensitivity that occurs after the first heating of the phosphor in the pottery.

The equivalent beta-dose (without supralinearity correction) can be expressed as:

$$Q = \frac{G_{\mathrm{N}}}{G_{\mathrm{N}+\beta} - G_{\mathrm{N}}}\beta \tag{2}$$

where G_{N} is the natural TL of the sample, $G_{\mathrm{N}+\beta}$ is the sum of the sample's natural TL and the TL induced by laboratory irradiation, and β is the laboratory administered beta-dose.

The equivalent beta-dose including the supralinearity correlation I is then:

$$P = Q + I \tag{3}$$

Now the annual dose is composed of four parts-alpha, beta, gamma and cosmic rays-and can be calculated using the Addition Method which incorporates the differences in TL yield expected for the different types of radiation. The effectiveness of gamma and cosmic rays in inducing TL is generally accepted as similar to that of beta radiation and so can be added directly. The effectiveness of alpha radiation in inducing TL is far lower than that for beta and is in the range 5% $\sim$ 30% relative to beta. In adding the alpha dose therefore, it is weighted by a relative effectiveness factor which is referred to as the α-value. The age A of the sample may now be written:

$$A = \frac{Q + I}{aD_{\alpha} + D_{\beta} + D_{\gamma+\mathrm{C}}} \tag{4}$$

where D_{α}, D_{β} and $D_{\gamma+\mathrm{C}}$ are the annual dose of for alpha, beta and gamma respectively.

3 APPRAISAL METHOD

One of the problems in the age appraisal is that the method is essentially destructive so that only very small amounts of material can be made available if the sample is to remain intact. The measurement of the archaeodose P only requires several hundred milligrams so there is little difficulty at this point. However the annual dose D stems from external radiation and radiation originating from within the specimen. This measurement requires several grams of the sample and is therefore not feasible. Instead a "typical value" of D is used which needs to be compiled from data obtained of sample groups relevant to the item under investigation.

3.1 Measurement of total dose P

After scraping off the surface coating, either from the bottom or the wall of the specimen, about 200mg of is taken as a sample (powder), ground gently in agate mortar, screened for particles which are less than 60μm across using a 250 mesh sieve and subjected to a water flotation process to deposit fine particles (3–8μm) on an aluminium disc, 0.5mm thick and diameter 10mm (for further information see Ref.[5]). For most of the items investigated, 100mg of a powder sample after passing through the sieve can be processed into 10 disc sample. These samples are divided into 2 groups-one for measuring the natural TL, the other to be exposed to the laboratory administered beta-dose. [The TL and Q are measured and analyzed using a TL dating system produced by Littlemore Scientific Engineering Co.; Oxford (Type 7188)].

From the results in Table 1 it seems reasonable, in order to simplify the authenticity procedure appraisal, to omit measurement of the supralinearity correction factor I. Experiment indicates that the value of I contributes less than 10% to the total dose estimate P and hence does not significantly affect the appraisal. It can be seen from Table 1 that the mean value of the ratio I/P for 17 samples is 3.2%. Referring also to results reported by Shanghai Museum[6], only one piece from 49 samples was found to have an I/P ratio greater than 10% (15.3%) with a mean of 5.2%.

3.2 Typical value and measurement of annual dose D

Using a chemical analysis method and an α-counting method the annual doses measured for the 17 samples in Table 1 and for pottery samples of other periods are listed in Table 2. The annual α and β-dose contribution from thorium and uranium contents was obtained using a low noise level alpha counter (Type 7286 from Sci. Eng. Co., Oxford). The annual β-dose contribution from ^{40}K was measured using flame photometry. The annual environmental doses from γ and cosmic rays were measured by TLD and an α counting method. Where the sample's place of discovery is uncertain and the environmental dose rate is unavailable a typical value, $D_{\gamma+C}$ = 1.35mGy/a is used (calculated using 1.5% as the mean value of ^{40}K-content and an α-count rate 10cpks-these values obtained over 40 samples from the Shanghai Museum and the present work; and using a Cosmic ray dose of 0.15mGy/a–Ref.[1]).

The mean annual dose for 23 pottery samples, shown in Table 2, is found to be

5.49mGy/a with a standard deviation ±0.8mGy/a. (Note: while the α, β and γ+c annual doese given in Table 2 have not been corrected for water content, the final total annual dose D has been corrected.) The mean annual dose for 45 pottery samples reported by Wang and Xia[6] is 5.6mGy/a. Thus, it seems reasonable to assume a typical annual dose value D for ancient Chinese pottery of 5.5mGy/a.

Table 1

Supralinearity correction I as a percentage of total dose value P

Sample code	Material	Source of sherds	Archaeological periods	Q/ Gy	I/ Gy	$I\cdot P^{-1}$/ %
SB146A	Pottery	Hemudu site,	Majiabang Culture	32.77	0	0
SB149	Pottery	Zhejiang Province		33.88	2.20	6.1
SB155	Pottery	Tinglin site, Shanghai	Stamped Pottery Culture	17.90	1.80	9.1
SB156	Pottery			16.55	0	0
SB158	Pottery	Tinglin site, Shanghai	Spring and Autumn Period	13.05	0.74	54
SB206	Brick	Pagoda of Yungansi, Suzhou	Five Dynasties	4.79	0.09	1.8
SB223	Brick	White Pagoda,	Qing Dynasty	1.69	0	0
SB224	Brick	Ji County, Tianjin		1.26	0	0
SB232	Pottery	Xiaokunshan site,	Liangzhu ~ Songze Culture	27.16	1.50	5.2
SB233	Pottery	Shanghai		22.73	0	0
SB234	Pottery			24.47	0	0
SB237	Pottery			34.30	0	0
SB265	Pottery	Tianyicun site,	Liangzhu Culture	19.82	1.23	5.8
SB267	Pottery	Shanghai		25.85	2.04	7.3
SB268	Pottery			23.94	1.67	6.5
SB276	Tile	Leshan Buddha Figure site, Sichuan Province	Tang Dynasty	4.37	0	0
SB278	Pottery	Changqin site, Guangxi Province	Neolethic	20.21	1.56	7.2

Considering the value of α effectiveness, 7 samples in Table 2 have the value 0.15 with the other 16 samples having a mean value of 0.146. The mean value reported by Wang and Xia[6] for 45 samples is 0.141. Under similar circumstances, it also seems practical therefore to assume a value of 0.15 for α-effectiveness when direct measurement is impossible.

Combining the findings in Table 2 and those reported in Wang and Xia[6], the range of annual dose values for ancient Chinese pottery and ceramic ware can be considered (see Table 3). The total annual dose D ranges from 3.9 to 7.4mGy/a. An indication of the effect of assuming a value of D of 5.5 mGy/a can then be estimated by calculating the two ages obtained by using the extremes of the observed range, i.e. extreme maximum age $A_{\max}$ when $D = 3.9$ mGy/a, and extreme minimum age $A_{\min}$ when $D = 7.4$mGy/a. If these values are given together with the estimated age in any authenticity appraisal a firmer basis may be provided for subsequent inference.

The maximum and minimum values of D have been obtained from a large and varied sample group, from periods ranging from 9000 a ago to 200 a ago and sites ranging from

Hemudu, Songyang Relics in Southeastern China to Zhenpiyan Relics in Southwestern China. Samples also included Neolithic Age relics and items from graves containing historic records found in Central China. The materials involved include muddy Hui Pottery, black ceramic and Jiashajiang Ceramic in many kinds of shpes and configurations-disc,

Table 2

Annual dose measurement of SB samples

Samples code	Components of annual dose /mGy· a^{-1}				Water content w/%	a value	Annual dose /mGy· a^{-1}
	Alpha	Beta		γ + C			
		Th + U	^{40}K				
SB146	29.22±0.38	1.65±0.02	1.18	1.35	22±4	0.143±0.003	6.97±0.41
SB149	17.35±0.51	0.98±0.03	1.38	1.35	27±5	0.15	5.17±0.45
SB155	15.03±0.37	0.85±0.02	1.20	1.35	15±3	0.167±0.006	5.26±0.36
SB157	17.33±0.54	0.98±0.03	2.12	1.35	14±3	0.15	6.29±0.50
SB158	17.52±0.54	0.99±0.03	1.09	1.35	14±3	0.114	4.88±0.49
SB176	13.79±0.28	0.78±0.02	1.20	1.50	2.9±0.6	0.15	5.42±0.28
SB206	16.69±0.40	0.94±0.02	1.05	1.44	22±4	0.120	4.66±0.35
SB221	12.80±0.22	0.72±0.01	1.86	1.23±0.06	15±3	0.121±0.007	4.79±0.24
SB222	11.54±0.43	0.65±0.02	1.82	1.23±0.06	13±3	0.133±0.009	4.75±0.42
SB223	17.00±0.30	0.96±0.02	1.93	1.68±0.02	5±1	0.181±0.016	7.34±0.40
SB232	18.84±0.49	1.06±0.03	1.79	1.35	15±3	0.131±0.005	5.92±0.46
SB233	16.93±0.51	0.95±0.03	1.85	1.35	25±5	0.155±0.005	5.61±0.47
SB234	20.36±0.60	1.15±0.03	1.65	1.35	25±5	0.110±0.005	5.31±0.53
SB237	18.26±0.52	1.03±0.03	1.25	1.35	14±3	0.227	6.90±0.51
SB265	20.32±0.56	1.15±0.03	2.03	1.16±0.04	17±3	0.094	5.46±0.51
SB267	17.32±0.52	0.98±0.03	2.08	1.35	22±4	0.143±0.003	5.69±0.47
SB268	20.23±0.61	1.14±0.03	2.03	1.42±0.05	24±5	0.110	5.70±0.54
SB270	19.70±0.59	1.11±0.03	1.20	1.06±0.05	30±6	0.150	5.01±0.51
SB271	16.69±0.55	0.94±0.03	1.38	1.06±0.05	23±5	0.150	4.91±0.49
SB273	18.61±0.55	1.05±0.03	1.61	1.10±0.04	13±3	0.150	5.87±0.51
SB276	18.07±0.41	1.02±0.02	1.30	1.10±0.04	17±3	0.159	5.47±0.39
SB277	11.97±0.32	0.68±0.02	0.53	1.35	15±3	0.150	3.92±0.29
SB278	12.74±0.20	0.72±0.01	0.51	1.35	13±3	0.233	5.01±0.22

Table 3

Range of annual dose to Chinese pottery under normal conditions

Source of annual dose	Dose-rate (mGy/a)	Standard Deviation (±1σ)
Alpha (D_α)	11.5 –29.2	±(2–4)%
Beta (D_β)	1.2 –3.2	±(2–6)%
(from Th + U)	(0.65 – 1.65)	±(2–3)%
(from K-40)	(0.5 – 2.1)	±(1–5)%
Gamma plus cosmic ray ($D_{\gamma+c}$)	1–1.7	±(1–5)%
Total dose (D)	3.9–7.4	±(4–10)%

pot, bean, axes, tripod, quadripod, handle and figurine. It is proposed therefore that the D values measured from these pottery qualify to be chosen as generally representative of ancient Chinese pottery. Of course it is better to refine the maximum and minimum D values by taking more samples. In fact a larger or smaller extremum of D value still can be used for authenticity appraisal.

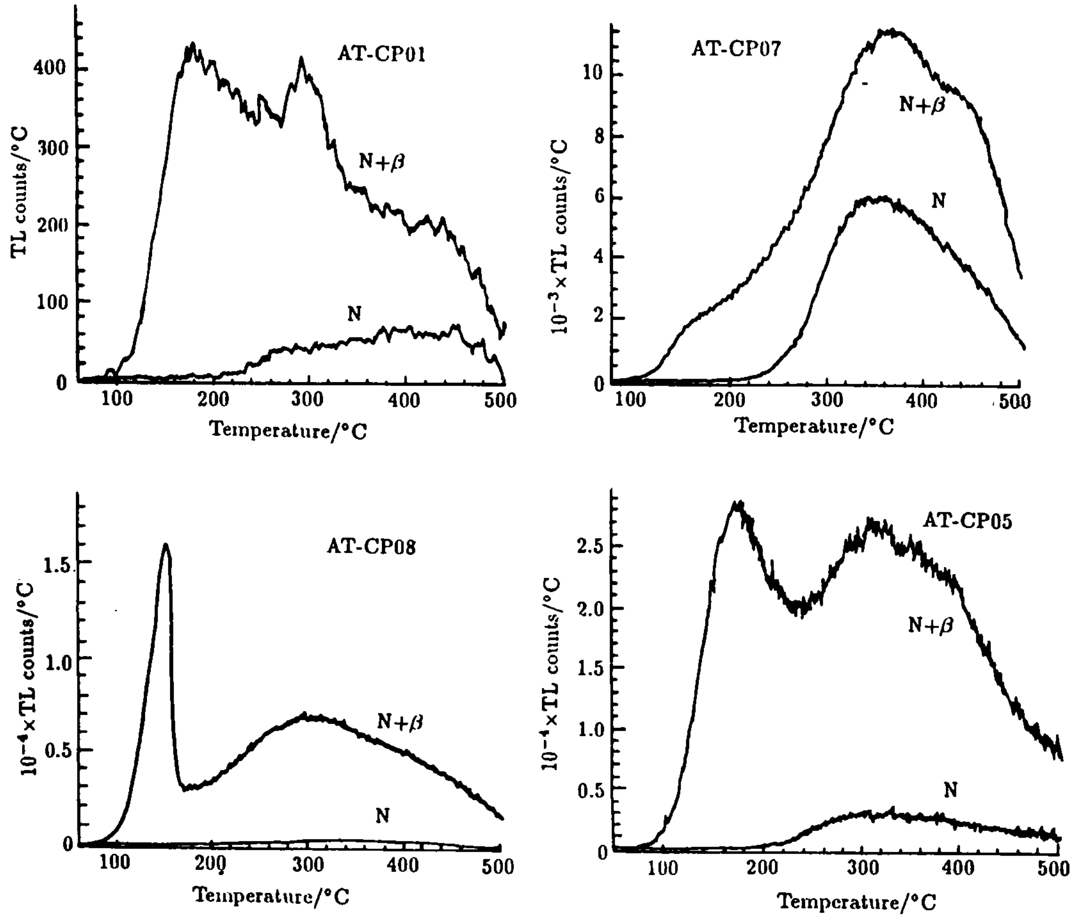
4 EXAMPLES OF APPRAISAL

Table 4 lists ten examples of authenticity appraisal of ancient Chinese pottery using the proposed rapid method. Figs 1–6 show the glow curves of some of the samples whose appraisal is listed. Here N denotes the natural TL glow curve and $N+\beta$ denotes the combined natural and induced (β irradiation) glow curve. The background has been eliminated. The amount of β irradiation used is estimated from the proposed age of the sample, based on its style. The genuineness of the sample could sometimes be simply reflected directly from these curves. Generally the sample is genuine when the intensity of the natural TL glow curve is close to that of natural plus induced glow curve, and fake otherwise.

Table 4
The examples of authentication appraisal

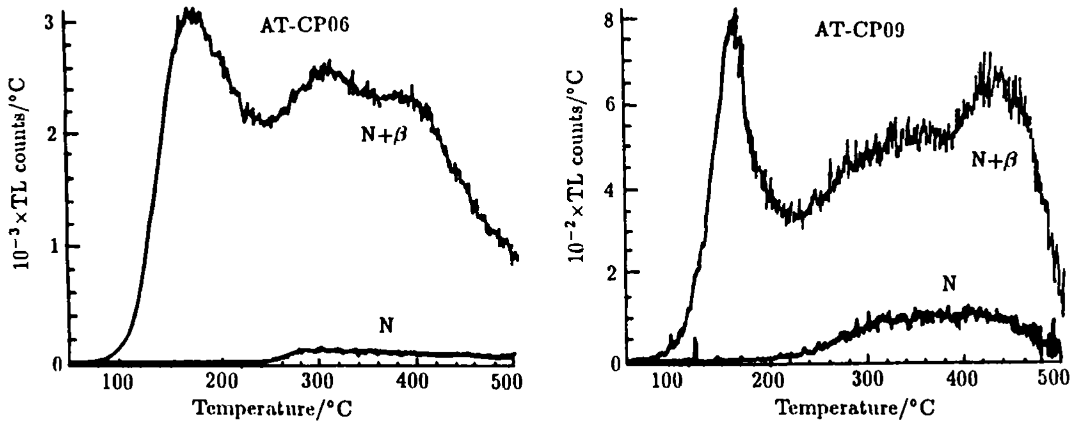
Sample code	Assumed age	Equivalent β dose /mGy	D/mGy· a^{-1} 5.5			Authenticity
			5.5	7.4	3.9	
			A/a	$A_{\min}$/a	$A_{\max}$/a	
AT-CP01	Modern brick	210	38	28	55	True
AT-CP02	Glazed tile in Qing Dynasty (1644–1910 AD)	2510	456	339	644	True
AT-CP03	Tri-colored glazed pottery of the Tang Dynasty (Camel) (618–907 AD)	90	16	12	23	False
AT-CP04	Tri-colored glazed pottery of the Tang Dynasty (women) (618–907 AD)	8840	1607	1195	2267	True
AT-CP05	Pottery Jar in Han Dynasty (~206 BC)	790	143	107	203	False
AP-CP06	Pottery figurine in Han Dynasty (~206 BC)	140	25	19	36	False
AP-CP07	Pottery pillow in Northern Song Dynasty (960–1279 AD)	6390	1162	864	1638	True
AT-CP08	Tri-colored glazed pottery of the Tang Dynasty (Small Bowl) (618–907 AD)	120	22	16	31	False
AT-CP09	Pottery Jar in Spring and Autumn period (770–476 BC)	5650	1027	764	1449	?
AT-CP10	Pottery Sherd in Qing Dynasty (1644–1911 AD)	1050	191	142	269	True

However, in order to provide more reliable quantitative conclusions the annual dose analysis can be used to give the results listed in Table 4. It can be seen that in all but



Figs.1–4 Glow curves of unknown pottery samples AT–CP01, AT–CP07, AT–CP08 and AT–CP05

one case the method enables the samples to be confidently assigned genuine or fake. Sample AT–CP03, claimed to be an example of tri-colored glazed pottery from the Tang Dynasty is obviously a modern replica. Its maximum age is estimated as no more than 23 years. Sample AT–CP05 can be confidently assigned to the end of the Qing Dynasty and not to the Han Dynasty. Sample AT–CP06 is a modern replica of Han Dynasty Pottery while sample AT–CP08 is a modern replica of a small tri-colored glazed bowl from the Tang Dynasty. Conversely sample AT–CP09, whose authenticity had once been doubted and designated as a contemporary replica, is confirmed to be genuinely old by TL appraisal. It does not however belong to the Spring and Autumn Period and as there is a large difference between the estimated maximum and minimum ages, it is difficult to ascertain the actual Period to which it belongs. It may indeed be an ancient replica rather than a contemporary piece and this case illustrates a limitation of the TL method used on its own.



Figs.5,6 Glow curves of samples AT–CP06 and AT–CP09

5 CONCLUSION

The normal TL technique used to authenticate ancient Chinese pottery may be modified and extended as outlined above. From the wide range of samples considered the typical annual dose may be established as 5.5mGy/a. Using this value and the maximum and minimum values observed from the samples, the most probable, the maximum and the minimum ages of any sample can be determined. In this way, confidence in the reliability of any authenticity attribution is greatly enhanced. Applying the method to ten unauthenticated samples gives highly satisfactory results and successful attribution, the single limitation ocurring in the precise dating of ancient replicas. In these minority of cases further investigation is required to determine the exact annual dose received by the sample in order to reduce the age uncertainty limits. It can be seen therefore that the TL technique outlined offers a relatively rapid, effective and reliable method for enabling successful authenticity appraisal of ancient pottery, tiles and bricks by determining a precise range within which the age of the artefact must lie.

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