

# A new technique (foil technique) for measuring the natural dose in TL dating and its application in the dating of a mortar containing ceramic fragments

C.T. Michael<sup>1</sup>, N. Zacharias<sup>1</sup>, Y. Maniatis<sup>1</sup>, D. Dimotikali<sup>2</sup>

1. Laboratory of Archaeometry, Institute of Material Science, N.C.S.R. "Demokritos", 15 310 Ag. Paraskevi, Attiki, Greece.
2. National Technical University, Chemical Engineering Department, Iroon Polytechniou 9, 15 780 Zografou, Greece.

(received 26 march 1997 ; in final form 10 september 1997)

**Abstract** A modification of the fine grain TL dating technique for measuring the natural dose is presented. In this technique (foil technique) we tried to make very thin samples and with the necessary plasticity, in order to achieve the best heating contact between sample and heater plate. Because the so prepared samples have not the same amount of powder a suitable new normalization technique is also proposed. The advantages of the proposed foil technique are such that make it quite suitable for samples with low levels of natural TL and also for authenticity testing. This technique was tested using artificially irradiated samples with known doses and applied to the dating of a mortar containing ceramic grains.

## Introduction

One of the most important steps in thermoluminescence dating is sample preparation for which two main techniques have been established: the classical fine grain technique (Zimmerman, 1971) and the quartz inclusion technique (Fleming, 1970). The present paper describes a modification of the fine grain technique (foil technique), which was mainly developed in order to overcome the spurious TL problem of samples with a relatively low level of natural TL (low natural dose or sensitivity) and also to simplify the sample preparation process.

By this technique a very good heating contact between sample and heater plate is achieved, making the use of a heat conducting gas unnecessary. This has two main advantages: a) Measurements can be made in vacuum (better than  $10^{-1}$  mbar) which avoids the use of very pure nitrogen, making the procedure cheaper and resulting in a significant reduction of spurious TL mainly in cases where the  $N_2$  purity is insufficient. The use of  $N_2$  is based on the assumption that spurious TL is usually the result of oxidation. However in some cases, spurious TL seems to have other sources such as phase

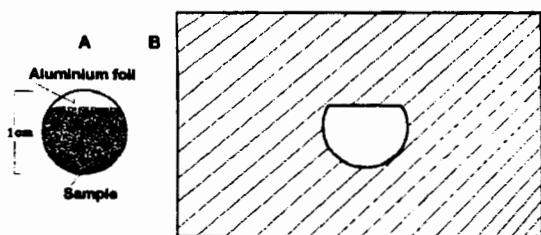
changes in carbonates due to heating. In this case the presence of spurious TL can be detected by the plateau test and must be eliminated by acid treatment. b) A possible shift of the glow curve due to a delay in heating is avoided, thus giving the possibility of using higher heating rates. This results in an increased TL signal making the technique suitable for samples with low levels of natural TL (as will be described in a future paper). This technique is quicker than the classical fine grain method and also has the advantage of avoiding the use of toxic acetone.

## Sample preparation

In order to achieve very good heating contact between sample and heater plate we tried to make very thin samples and with the necessary plasticity, so that they can follow the possible lack of perfect flatness of the heater plate surface. This lack is also possible for the hard aluminium disks (0.5 mm thick) usually used. Thus the samples prepared have a near monolayer cover of pottery powder (grains smaller than 8  $\mu$ m). The grains are well adhered to aluminium foil disks, of 1 cm diameter and 10  $\mu$ m thick, by using silicone grease (silicone DC high vacuum grease

from Riedel - de Haën). Details of the preparation procedure are given in the Appendix.

It is possible to handle these sample disks using tweezers (Fig. 1) in order to place them on the heater plate, for measuring the TL, or taken to the irradiation sources, without affecting the sample. The heater plate is pre-covered with a thin layer of silicone grease and the sample then adhered by pressing it gently with a rice-paper. In some cases, in order to eliminate the possible spurious TL from the silicone grease, it is better to take a first measurement (glow it) before the sample is added.



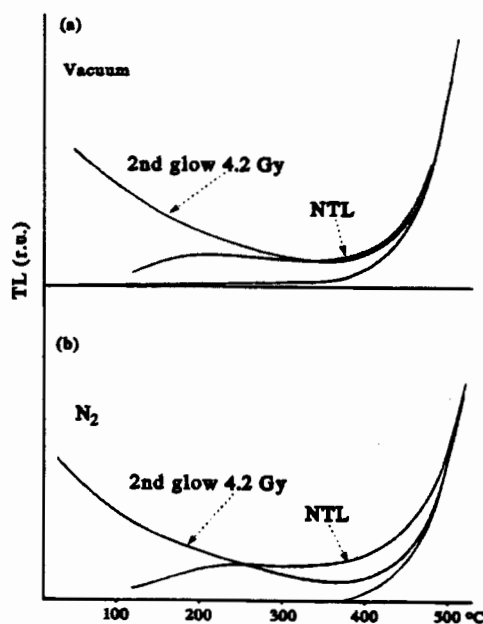
**Figure 1.**

A schematic presentation of the sample prepared by the proposed technique (A) and the aluminium foil square with the central hole (B), see Appendix. It can be seen that the upper part of the foil disk is left uncovered in order to be able to handle this by tweezers without affecting the ceramic powder

Ceramic powder with grains smaller than  $8 \mu\text{m}$  is prepared by crushing the sample in a vice and using the settlement technique. In order to avoid toxic acetone, ethylalcohol is used. Because the viscosity coefficient of the ethylalcohol is about 4 times higher than that of acetone the settling period must be increased to 8 min for a 60 mm column. This technique is quicker than the classical fine grain technique because we avoid the procedure of resuspending the separated fine grains in acetone for the deposition of pottery powder on aluminium disks, followed by evaporation of the acetone, which is the usual procedure in fine-grain technique.

Figure 2, shows glow curves of two samples of the same sherd prepared by the proposed technique. One of the samples was measured in vacuum (a) and the other in  $\text{N}_2$  atmosphere (b). In order to normalise the two samples we take the second glow for each sample by giving a monitor dose (4.2 Gy). Sample (a) shows near coincidence of the first and second glow curves, but not sample (b). This is because the level of spurious TL is higher in a  $\text{N}_2$  atmosphere than in a vacuum. It is apparent from many experimental results that for measurements

in vacuum, even if the level of Natural TL is very low, the percentage of chemiluminescence in most cases is practically eliminated (Michael *et al.* 1985). This was checked especially in the case of very low natural TL (ceramic vase two years old) as will be explicitly described in a future paper. In Figure 3, glow curves of five samples of the same sherd are shown: one prepared by the foil technique measured in vacuum, the other four prepared by the classical fine grain technique measured in a  $\text{N}_2$  atmosphere. The peak positions of the samples prepared by the classical technique show a shift as compared with the peak positions of the sample prepared by the foil technique.



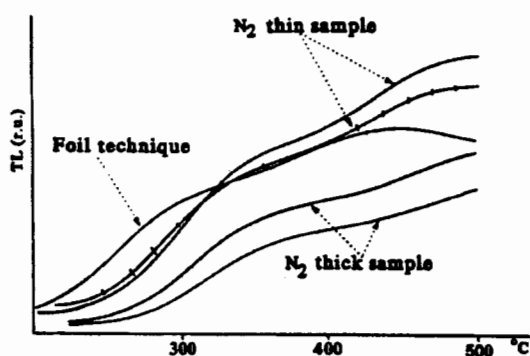
**Figure 2.**

Glow curves of two samples of the same sherd prepared by the proposed technique. One of these samples was measured in vacuum (a) and the other in  $\text{N}_2$  atmosphere (b). For normalisation the second glow for each sample was taken by giving a monitor dose (4.2 Gy).

This shift increases with sample thickness (amount of powder), although it is not exactly the same for samples of the same batch (the shift of the two thin samples is not exactly the same). It is clear that this shift is due to a delay in heating of the upper grains of the classically prepared samples with respect to the heater plate, which increases with the raising of the heating rate. On the other hand, for samples made by the foil technique, because of the immediate contact, the peaks are always at the same temperature as shown in Figure 4. The differences in the height of the glow-curves of the two samples are due to the differences in the quantity of pottery powder.

### Normalisation of the samples and calculations

Since the quantity of pottery powder in the samples is not the same, a normalisation of the samples is necessary (a procedure followed usually in inclusion dating). This can be achieved by giving all samples a monitor dose. However, because the samples have received different doses in producing the growth curves, there is the problem of the sensitivity change due to the pre-dose effect. Various techniques have been proposed to overcome the problem in the case of inclusion dating, which may be applicable in the proposed technique. The possibility of improving the accuracy of dating results by using hyperbolic or polynomial regressions on the normalised points of growth curves for materials exhibiting significant pre-dose effects was proposed by Mejdahl (1985). Also, the possibility of linear regression for materials not exhibiting significant pre-dose effect, when the initial part of the normalised growth curve is approximately linear was proposed by Michael et al. (1985).



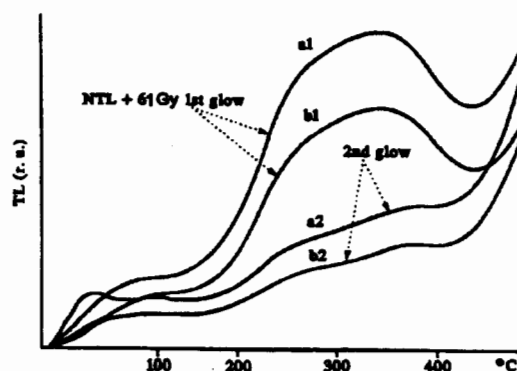
**Figure 3.**

Glow curves of samples of the same sherd. One prepared by the proposed technique measured in vacuum and four prepared by the classical fine grain method measured in  $N_2$  atmosphere (heating rate  $14^\circ C/s$ ).

The application of a small monitor dose and measurement of a low-temperature peak prior to measuring the high temperature peak (zero-glow monitoring) was proposed and applied to calcite by Aitken *et al.* (1979), to quartz by Bowman (1977) and Liritzis (1980) and to fine-grain sediments by Debenham (1985). G. A. Wagner has also proposed the equal pre-dose technique which is described by Mejdahl (1985) and Aitken (1985). An alternative normalisation technique suitable for foil technique is proposed below, which can also be applied to inclusion dating. By this technique we have a quantitative estimation of the pre-dose effect by calculating the value of  $k$  (see below - Equation 1), which can be useful for

some applications such as the dating of a mortar described below.

According to this, after the sample preparation with the foil technique, the normalized growth curve is produced as follows: for a mean value of zero point  $r_0$  (normalised natural TL) of this curve several samples are used (usually 3 to 5) for measuring their natural TL (first glow). These samples are then irradiated with a monitor dose and the second glow measured. For the other points the same procedure is repeated with samples having the natural dose plus a laboratory dose (natural +  $D_1$ , natural +  $D_2$ , etc.). Each point of the normalised growth curve represents a mean value of the ratio  $r_D$  of the TL of the first glow to the second glow (Fig. 4) at the same temperature of the plateau region, as a function of the laboratory dose  $D$ . Figure 5 illustrates a characteristic normalised growth curve.



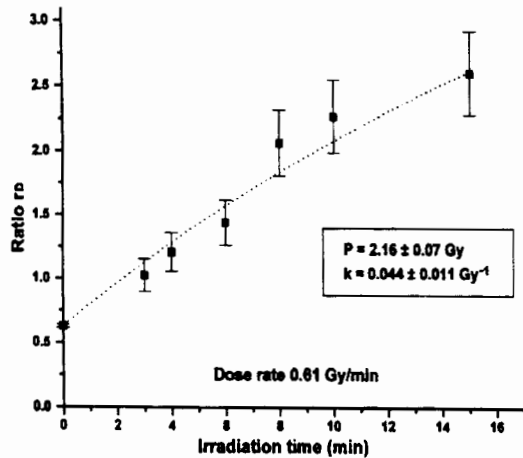
**Figure 4.**

Glow curves (1st and 2nd glows) of samples a, b of sherd 16003 (prehistoric from Macedonia) for the calculation of  $r_D$  (see in the text below) for  $\rho = 30.95$  Gy (monitor dose).

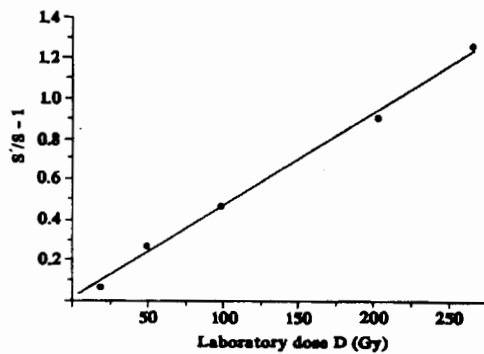
The calculation for the estimate of the natural dose is based on the assumption that the degree of sensitivity enhancement (pre-dose effect) is a linear function of the pre-dose applied (Aitken and Fleming, 1972). This assumption can be tested experimentally for every sherd and is given by the following equation (Aitken, personal communication)

$$S' = S [1 + k (P + D)] \quad (1)$$

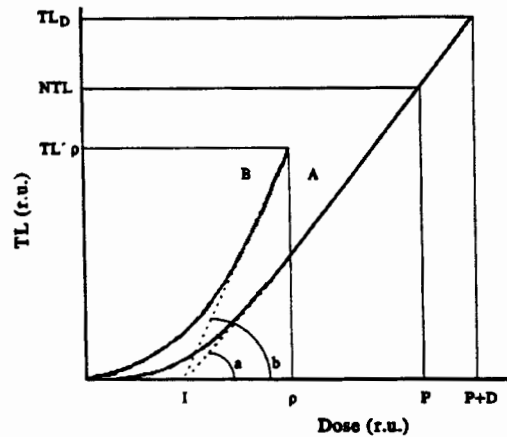
which is the mathematical expression of Figure 6 in case where  $P = 0$ . Where  $S'$  is the TL sensitivity of the second glow,  $S$  is the TL sensitivity of the first glow,  $k$  is a specific sensitivity enhancement factor and  $P$  is the natural dose (paleodose).



**Figure 5.**  
Normalised growth curve, for samples made by the 300 μm ceramic grains, existed in a cistern mortar from Heraklion Crete.



**Figure 6.**  
The second glow TL sensitivity ( $S'$ ) enhancement for the glow curve temperature 415°C versus  $D$  of sherd 3120 annealed from its NTL at 1000°C for 2 hours, so that it can be considered recently fired pottery ( $P = 0$ ).



**Figure 7.**  
First (A) and second (B) glow growth characteristic curves. NTL is the level of natural TL.

In Figure 7,  $TL_D$  is the TL for the sample which has been given a laboratory dose  $D$  (first glow) and  $TL'_\rho$  (second glow) is the TL of the same sample after the monitor dose  $\rho$ . This figure gives:

$$TL_D = S(P+D-I) \text{ and}$$

$$TL'_\rho = S'(\rho-I)t$$

where  $S = \tan a$ ,  $S' = \tan b$  and  $I$  is the supralinearity correction. Hence, taking into account Equation 1 and because  $r_D = \frac{TL_D}{TL'_\rho}$  we

take:

$$r_D = \frac{P + D - I}{(\rho - I)(1 + k(P + D))} \quad (2)$$

and for  $D=0$  we have the value of

$$r_0 = \frac{P - I}{(\rho - I)(1 + kP)} \quad (3)$$

From the Equations 2 and 3 it is possible to determine the values of  $P$  and  $k$  given by the equations (4) and (5):

$$P = \frac{D - I}{2} + \sqrt{\left(\frac{D - I}{2}\right)^2 + \frac{r_D r_0 D (\rho - I) + r_D I D}{r_D - r_0}}$$

$$k = \frac{P - I - r_0 (\rho - I)}{P r_0 (\rho - I)}$$

It is also possible to estimate the values of  $P$  and  $k$  with better accuracy using a software program in which we insert Equation 2 substituting  $\rho$  and  $I$  with their values and the values of  $r_D$  and  $D$  for each point of the normalised growth curve.

The value of  $I$  can be determined by producing the normalised second glow growth curve. For the normalisation of the samples the natural TL is used. Each point of the normalised growth curve represents the ratio of the TL of second glow to the first glow (natural TL). It is obvious that in this case the growth curve after the first supralinear part is normally linear, in contrast with the normalised first glow growth curve which is linear only when  $k = 0$  (Equation 2).

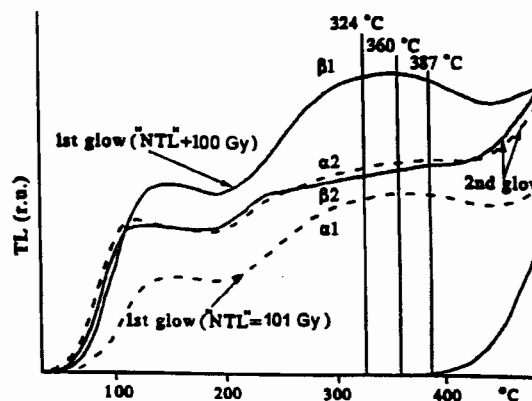
#### Experimental test of the technique

To test the accuracy of the proposed technique it was applied to prehistoric sherds from Macedonia (sample codes: 3120 and 1022) artificially irradiated with known doses. These sherds did not exhibit supralinearity or sublinearity in the range of our measurements. The following experimental steps were applied: a) a piece of sherd 3120 and of sherd 1022 were heated at about 1000°C for two hours, b) the sherds were crushed and c) samples of them prepared by the foil technique were irradiated with  $\gamma$ -dose. The artificial doses were 51 Gy for a group of samples of sherd 3120 and a group of samples of sherd 1022 and 101 Gy for another group of samples of sherd 3120. The procedure for the calculation of the natural dose was then applied to these three groups of artificially irradiated samples. Figure 8 illustrates the glow curves for the calculation of  $r_0$  (sample  $\alpha$ ) and  $r_D$  (sample  $\beta$  for  $D=100$  Gy) for samples from the group of sherd 3120 for which the exposure time was 101 Gy. The values of  $P$  and  $k$  were calculated from Equations 4 and 5 for each of the three groups for three temperatures within the plateau region (324, 360 and 387 °C).

The TL glow curves were recorded with conventional Littlemore, 711 TL equipment and a 9635QA photomultiplier with a Corning 7-59 blue filter. All TL measurements were performed with a heating rate of 14 °C/s and the irradiations were administered with a multi-KiloCurie Co-60 source (dose rate 10 Gy/min).

From the results shown in Tables 1, 2 and 3 it can be seen that the variations between the calculated values of  $P$  and artificially given doses are below 2.5% for all calculated values except for the value 5.28 min in Table 1 for which the variation is about 3.5%. From these Tables it can also be seen that the values of  $k$  increase as the temperature increases. This is the reason why the

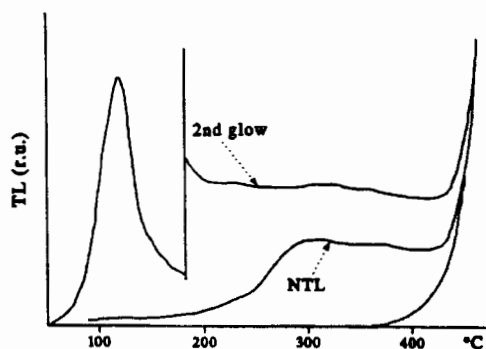
values of  $r_0$  and  $r_D$  are not the same for the three temperatures, and thus there is no plateau between the first and second glow curves, and also between second glow curves for different values of  $D$ , as is evident by comparing curves  $\alpha_2$  and  $\beta_2$  (Fig. 8). This is a general observation for most sherds studied until now (see also Fig. 4).



**Figure 8.** Glow curves (1st and 2nd glows) for the calculation of  $r_0$  (sample  $\alpha$ ) and  $r_D$  (sample  $\beta$ ). These samples are from the group of sherd 3120.

#### Dating of a mortar containing ceramic fragments

To date the mortar from a cistern excavated in Heraklion Crete, its ceramic fragments were used. The size of these fragments ranged from a few microns to 4-5 mm. After the removal of a 2 mm external layer, the mortar was crushed in a vice. The rubble produced was then treated with hydrochloric acid so that the calcitic matter was removed. In order to be able to calculate the internal beta dose-rate received by the sample, grains of size larger than 4 mm in diameter must be used. This is necessary because a 2 mm layer from each ceramic fragment must be removed. In this layer the beta dosage is transitional between that corresponding to the ceramic radioactivity and that corresponding to the surrounding material of the mortar which is lower than that of the ceramic. Since the fragment of that size available in our mortar sample were very few (about 10) we used the following technique: First we prepared 5 samples from these fragments, using the foil technique, from which the external layer of 2 mm had been removed by hydrofluoric acid (37%) treatment for 4 min. Then the mean value of  $r_0$  was estimated as described above.



**Figure 9.**

The natural TL (first glow) and the 2nd glow ( $\rho = 3.05$  Gy) of the ceramic grains (300  $\mu\text{m}$ ), from Heraklion Crete.

From Equation 3 we can calculate the value of P, when we know  $r_0$ , given by:

$$P = \frac{r_0(\rho - I) + I}{1 - kr_0(\rho - I)} \quad (6)$$

This equation involves the corrections due to the pre-dose effect and supralinearity (values k and I). As the values of k and I are dependent only on the material (independent of the fragment size), fragments of smaller size (about 300  $\mu\text{m}$ ) may be used for these estimations. These fragments are much more abundant in our material and can be selected by hand, using a suitable microscope. By applying the foil technique to pottery powder from these fragments (Figure 9) and using the software program mentioned above we found  $P = 2.16 \pm 0.07$  Gy and  $k = 0.044 \pm 0.011$  Gy<sup>-1</sup>,  $I = 0.209 \pm 0.15$  Gy. The corresponding normalised growth curve is illustrated in Figure 5. By substituting in Equation 6 the value of  $r_0 = 0.72$  found for fragments larger than 4 mm which is 14.6% higher than that found for the 300  $\mu\text{m}$  fragments and the values of k and I found above, we calculate the paleodose corresponding to the core of the larger grains which is  $2.48 \pm 0.15$  Gy. The higher value of P for the larger fragments results from the fact that the whole beta dose-rate comes from the fragment itself. This is not the case for the 300  $\mu\text{m}$  fragments, for which a part of the beta dose-rate comes from outside.

For the estimation of the a-value we also used samples made by the 300  $\mu\text{m}$  fragments and the estimated value is:  $0.115 \pm 0.02$ . The U, Th and K concentrations were measured using all the separated ceramic fragments independently of their size, and their concentrations were found to

be:  $4.96 \pm 0.43$  ppm and  $7.72 \pm 1.22$  ppm for U and Th respectively ( $\alpha$ -counting) and  $1.46 \pm 0.15$  % for K (AAS). The resulting dose rates from these concentrations are: For alpha particles  $16.10 \pm 0.52$ , for beta particles from U and Th  $0.94 \pm 0.04$  and for beta particles from K  $1.20 \pm 0.12$ , all values in mGy/year (Liritzis *et al.*, 1992). The environmental dose rate was recorded with a portable NaI scintillator. Its value is  $0.406 \pm 0.08$  mGy/year. Taking into account the reduction due to the water content (saturation content 0.25 and fraction of saturation  $0.5 \pm 0.3$ ) the total dose rate is 3.82 mGy/year. Finally the age of the cistern was found to be  $650 \pm 95$  years BP which is in agreement with the historical date (Venetian period 1206 - 1669 AD, A. Karetsou personal communication).

### Conclusions

The foil technique was tested by the use of artificially irradiated samples with known doses and the accuracy found to be satisfactory. Also, this technique allows the dating of the mortar, which is not possible using any of the other TL dating techniques because there were too few ceramic fragments of sufficient size in our mortar sample.

### Acknowledgements

The authors are indebted to Dr. J. Tomlinson and Dr. Y. Facorellis for help in the preparation of the text and figures.

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### Tables

**Table 1:** Values of  $r_D$ ,  $r_0$ , P and k for sherd 3120.  
D= 150 Gy,  $\rho$ = 151 Gy,  
P= 51 Gy (Artificial irradiation).

T (°C)	$r_D$	$r_0$	P (Gy)	k (Gy <sup>-1</sup> )
324	1.106	0.314	49.7	0.00098
360	1.089	0.323	51.6	0.00112
387	1.060	0.327	52.8	0.00131

**Table 2:** Values of  $r_D$ ,  $r_0$ , P and k for sherd 3120.  
D= 100 Gy,  $\rho$ = 101 Gy,  
P= 101 Gy (Artificial irradiation).

T (°C)	$r_D$	$r_0$	P (Gy)	k (Gy <sup>-1</sup> )
324	1.492	0.857	101.1	0.00166
360	1.453	0.853	102.8	0.00180
387	1.381	0.828	102.8	0.00224

**Table 3:** Values of  $r_D$ ,  $r_0$ , P and k for sherd 1022.  
D= 61 Gy,  $\rho$ = 101 Gy,  
P= 51 Gy (Artificial irradiation).

T (°C)	$r_D$	$r_0$	P (Gy)	k (Gy <sup>-1</sup> )
445	0.902	0.453	50.35	0.00199
463	0.885	0.455	51.35	0.00228
481	0.859	0.453	52.17	0.00269

### APPENDIX

Samples are made by first covering a glass plate with a thin layer of silicone grease, and then placing an aluminium foil disk on it. The disk is pressed using rice-paper until its surface becomes flat and smooth (all ripples disappear), and the disk and glass surface are then cleaned with a paper tissue. After that, a 50  $\mu$ m thick aluminium foil square 5x5 cm having a central hole of 1.1 cm diameter is used to cover the glass surface around the disk leaving the disk uncovered. Next, a rice paper is covered with silicone grease using a small wire, and the disk covered with a thin layer of the grease by pressing it with the paper. The use of the aluminium foil square is essential in order to avoid silicone grease remaining on the glass around the disk and thus to avoid a loss of pottery powder on the glass plate (see below). This is necessary in case of authenticity testing where the amount of pottery powder is usually very small.

After removing the aluminium foil square, pottery powder of grain-size less than 8  $\mu$ m is spread on the aluminium disk using a small paintbrush. In order to check whether the surface of the disk is completely covered with powder a rice-paper is pressed on the disk. If the paper shows no traces of silicon grease or pottery grains the sample is ready for measuring, otherwise a small amount of powder is added and the sample rechecked. The disk is loosened from the glass plate with the help of a sharp thin blade.

Reviewer  
Gunther A. Wagner