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# Ancient TL

www.ancienttl.org · ISSN: 2693-0935

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Issue 3(1) - Winter 1979: Legacy Issue  
<https://doi.org/10.26034/la.atl.vl3.i1>

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# Ancient TL

Editor: S. R. Sutton  
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St. Louis, Mo 63130 USA

No. 6 Winter, 1979

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"For to be possessed of good mental powers is not sufficient; the principal matter is to apply them well. The greatest minds are capable of the greatest vices as well as the greatest virtues, and those who proceed very slowly may, provided they always follow the straight road, really advance much faster than those who, though they run, forsake it." René Descartes, in "Discourse on the Method of Rightly Conducting the Reason and Seeking for Truth in the Sciences" (from a translation by E. S. Haldane and G. R. T. Ross).

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The preparation of this document was supported in part by National Science Foundation Grant BNS 76-82645 and in part by subscription fees.

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# PRIMARY AND INTERLABORATORY CALIBRATION OF BETA SOURCES USING QUARTZ AS THERMOLUMINESCENT PHOSPHOR

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## 1. INTRODUCTION

In thermoluminescence (TL) dating it is necessary to determine the TL sensitivity of the material used for the measurement of the so called natural TL. Since it is generally assumed that the response to gamma rays is the same as to beta rays, most laboratories use beta sources for sample irradiations, because they are easier to handle in routine work. However, beta sources introduce a disadvantage due to the difficulty of their exact primary calibration as compared to gamma sources. In previous work (Zimmerman 1971; Wintle and Murray 1977) the TL of natural  $\text{CaF}_2$  was used to compare known gamma doses with the dose delivered by a beta source. This paper describes a similar approach but with chemically pure quartz as TL phosphor to circumvent the uncertainty introduced by the calculation of the beta dose-rate delivered to ceramic material from that delivered to natural fluorite.

## 2. EXPERIMENTAL

Commercial coarse-grained quartz (Merck, Quarz feinkörnig, gewaschen und gegläht, p.A., 0.1 - 0.5 mm) was crushed and sieved. The grain size fraction of 125 - 200  $\mu\text{m}$  was etched with 40% hydrofluoric acid as in the sample preparation for the quartz inclusion technique (Fleming 1970), so that the resulting quartz sample had a grain size range of 70 - 150  $\mu\text{m}$ . After annealing at 700°C for three hours, samples were prepared for the gamma irradiations by packing about 100 mg quartz grains in small polyethylene bags so that the sample thickness was less than 1 mm. Alternatively 2 mg samples were placed in small polyethylene containers.

$^{60}\text{Co}$  gamma irradiations ( $\bar{E} = 1.25 \text{ MeV}$ ) were accomplished at the Institut für Strahlenschutz of the GSF at Neuherberg/München (Germany) and the Studienbesellschaft für Atomenergie (SGAE) at Seibersdorf (Austria). In both cases the exposure was known to an error of less than  $\pm 1\%$  at one standard deviation from calibration with a graphite cavity absolute chamber.

To achieve secondary electron equilibrium conditions the gamma irradiations were carried out behind 0.5 cm perspex absorbers at a source to sample distance of 100 cm. The small build up effect due to the perspex-quartz interface is estimated to be less than 0.5%. In addition this is partly compensated by the attenuation in the quartz grains.

The dose delivered to the sample was calculated using the ratio of the mass energy absorption coefficients  $\frac{\mu_{en}}{\rho}$  quartz and air, knowing that 1 röntgen is equivalent to 0.869 rad in air, at that energy so that

$$D = f \cdot X \quad (1)$$

$$f = 0.869 \times \frac{\frac{\mu_{en}}{\rho} \text{ quartz}}{\frac{\mu_{en}}{\rho} \text{ air}} \quad (2)$$

Where D is the absorbed dose delivered to quartz and X the exposure. The value of mass energy absorption coefficient for quartz using the values for silicon and oxygen (Attix and Roesch, 1968) was calculated to be  $0.0265 \text{ cm}^2/\text{g}$  at 1.25 MeV. The value of  $\frac{\mu_{en}}{\rho}$  for air is  $0.0266 \text{ cm}^2/\text{g}$  which yields  $f=0.867$  at 1.25 MeV.

The beta sources used were identical 40 mCi disc sources of  $^{90}\text{Sr} - ^{90}\text{Y}$ , type SIP 13, from the Radiochemical Centre, Amersham. The active area is 12 mm in diameter and 0.02 mm thick. The sources are screened with a 0.1 mm silver window, which absorbs the low energy beta radiation of  $^{90}\text{Sr}$ . The maximum energy for  $^{90}\text{Y}$  is 2.26 MeV.

The beta irradiations were performed with the quartz grains on the nichrome heating plate at a sample to source distance of 16.0 mm. Quartz is known to exhibit a predose effect not only at the  $100^\circ$  peak but also in the high temperature region (Aitken and Fleming, 1972) so that direct matching of the TL signals after gamma and beta irradiations could lead to a wrong estimation of the dose-rate delivered by the beta source. For this reason all measurements were normalized to a second standard beta irradiation. Due to the predose effect the dose-rate of the beta source is overestimated, if the beta dose is delivered after the gamma dose. This is, however, the most convenient way, because the sample should not be removed from the heating plate after the first TL measurement. This preliminary value is used in the second step of the calibration, where the normalized TL intensities after gamma irradiations are compared with the normalized signals after the beta irradiations on another quartz aliquot. The beta doses are chosen so that the ratio of gamma to beta dose is constant and nearly unity. Assuming equal predose sensitivity for beta and gamma rays, a graph of normalized TL intensities after beta and gamma doses should give a straight line ideally passing through zero. The slope of the graph is used to calculate the exact dose rate of the beta source in the following way:

$$\text{TL}_\beta = \text{DL}_\beta \cdot t_\beta \cdot E_\beta \quad (3)$$

$$\text{TL}_\gamma = X_\gamma \cdot f_\gamma \cdot E_\gamma \quad (4)$$

$\text{TL}_\beta$ ,  $\text{TL}_\gamma$  are the TL signals after beta and gamma irradiations and  $E_\beta$ ,  $E_\gamma$  are the TL efficiencies for beta and gamma radiations.  $\text{DL}_\beta$  is the dose rate of the beta source and  $t_\beta$  the beta irradiation time in minutes.  $t_\beta$  is the beta irradiation time when  $\text{TL}_\beta = \text{TL}_\gamma$  and assuming equal TL efficiency for beta and gamma radiation

$$\text{DL}_\beta \cdot t_\beta \text{ equ} = X \cdot f \quad (5)$$

so that using (1) 
$$t_\beta \text{ equ} = \frac{1}{\text{DL}_\beta} \cdot D \quad (6)$$

the inverse slope of the calibration graph (Fig. 1) yields the dose rate of the beta source in rad/min.

TL intensities were measured using the  $375^{\circ}\text{C}$  peak maximum of the quartz glow curve. This peak shifted slightly to lower temperatures with increasing dose, but this had apparently no effect on the results.

### 3. RESULTS OF THE PRIMARY CALIBRATION

Fig. 1 shows the calibration graphs of the two beta sources now used for TL dating programmes in Heidelberg (HD) and Vienna (W). The error of the individual measurement is  $\pm 3\%$  at one standard deviation and that of the slope  $\pm 2\%$  also at one standard deviation and calculated after the method of Kerrich (Sachs, 1974). For source HD a dose rate of  $101 \pm 2$  rad/min was determined and for source W,  $125 \pm 3$  rad/min. These values are for quartz grains with a grain size of  $70 - 150 \mu\text{m}$  deposited on  $0.5 \text{ mm}$  nichrome and irradiated from a distance of  $16.0 \text{ mm}$  in the same irradiation geometry.

### 4. INTERCOMPARISON OF THE BETA SOURCES

In the same manner as in the primary calibration the two beta sources were compared with each other. The primary calibrations imply a ratio of  $0.81 \pm 0.02$  for source HD relative to source W. The experimentally determined ratio was  $0.79 \pm 0.03$  in good agreement with the primary calibrations.

### 5. DISCUSSION

It was mentioned by Dr.M.J.Aitken (Aitken 1978) that the glow curve of quartz is highly dependent on the annealing procedure. In addition other phosphors such as natural  $\text{CaF}_2$  have much higher sensitivities as compared to quartz. Therefore quartz was not considered a good phosphor for beta source calibrations.

In a preliminary check the quartz used in this study was annealed in different ways. So far only an increasing sensitivity was observed with increasing annealing temperature and time. However, the shape of the glow curve did not change as to be seen in fig.2. Since only normalized TL intensities were used in our calibration procedure, a different sensitivity should not effect the results. In addition, the quartz grains for each calibration were annealed under the same conditions.

### 6. CONCLUSION

We used quartz grains as phosphor for the primary calibration of two  $40 \text{ mCi } ^{90}\text{Sr} - ^{90}\text{Y}$  beta sources against two different  $^{60}\text{Co}$  gamma irradiation facilities. These primary calibrations were checked by a direct comparison of the beta sources. The values agreed within the experimental error limits. The dose rate values obtained by calibration with quartz can directly be used for age determinations of ceramics. This excludes any error introduced by the dose rate conversion from other phosphors to ceramic material. In addition quartz as we used it is easily obtainable in large quantities at a very low price. These advantages may outweigh the lower sensitivity, especially in cases where more material is needed than for just one calibration, such as interlaboratory comparisons.

#### Acknowledgement:

Financial support of the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung" and the Stiftung "Volkswagenwerk" is gratefully acknowledged. For the gamma irradiations and valuable discussion we thank Prof.F.Wachsmann and Dr.D.Regulla from the GSF Neuherberg/München and Dr.K.Duftschnid and Mr.Chr.Strachotinsky from the Dosimetrie-Eichlabor (DEL) at the research center Seibersdorf.

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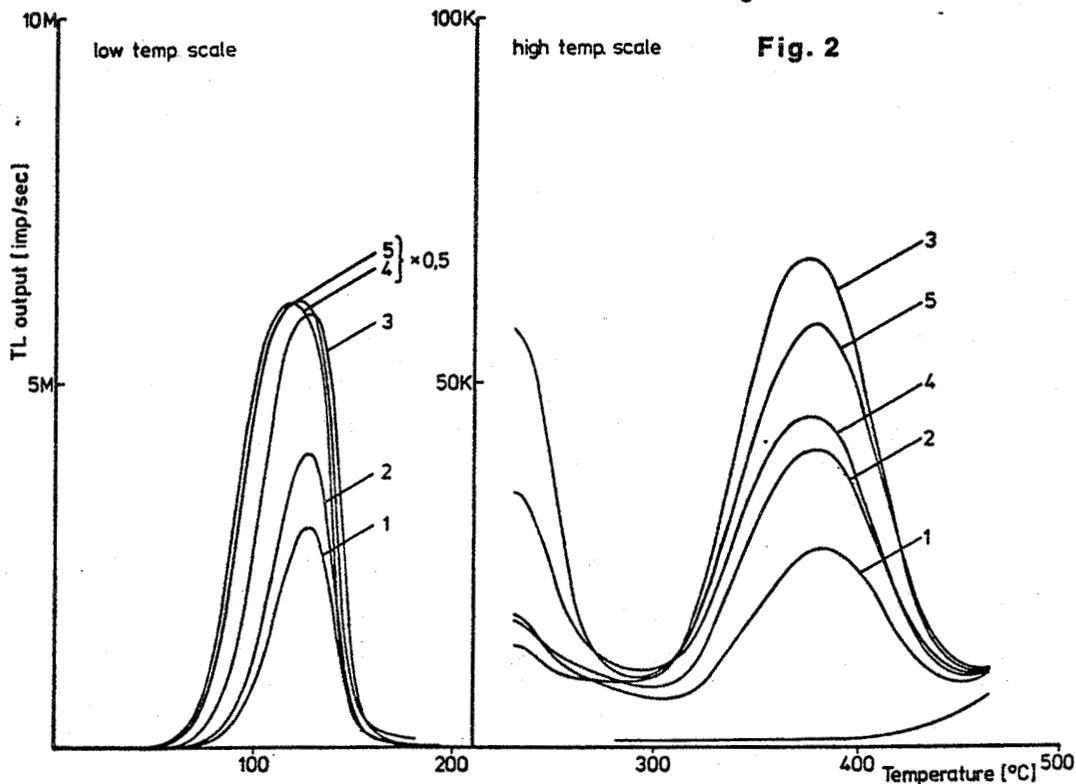
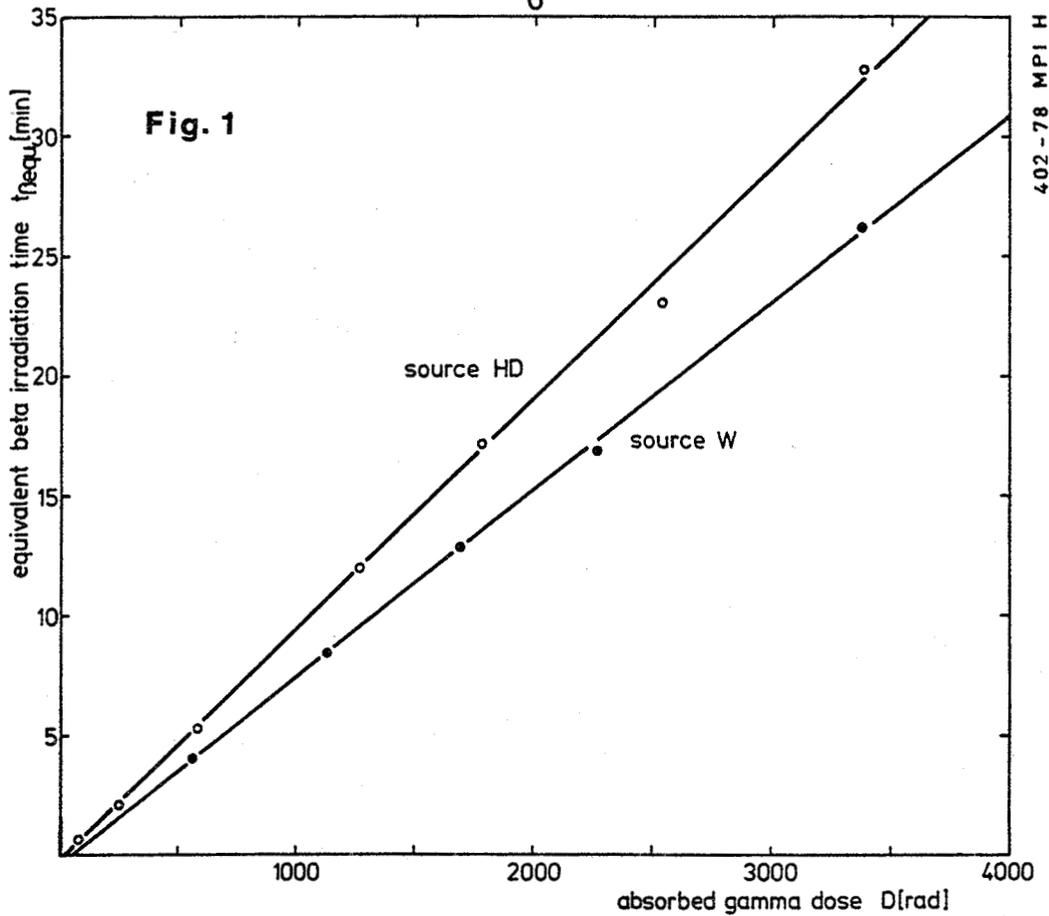
FIGURE CAPTIONS

Fig. 1: Calibration graphs of two  $^{90}\text{Sr} - ^{90}\text{Y}$  beta sources used in Heidelberg (HD) and Vienna (W) from comparison with  $^{60}\text{Co}$  gamma irradiations. The ratio of gamma and beta doses was chosen to be approximately unity to minimize predose effects. All TL signals were normalized to a second standard beta irradiation of the same sample.

Fig. 2: Glow curves of 3 mg samples of quartz grains (Merck, Quarz feinkörnig, p.A.) of the 70 - 150  $\mu\text{m}$  grain size fraction, after different annealing procedures:

- 1 - three hours at 700°C
- 2 - six hours at 700°C
- 3 - twentyone hours at 700°C
- 4 - three hours at 800°C
- 5 - three hours at 900°C

All annealings were carried out in air.



Following a suggestion by Dr. M. J. Aitken a limited number of irradiated quartz samples will be available free by May 1979. One set consists of five 200 mg samples, which have been irradiated in a  $^{60}\text{Co}$  beam to an absorbed dose of 600 to 4000 rads. A 300 mg sample of unirradiated quartz from the same batch of annealing and etching procedures will be provided.

For samples and additional information apply to Dr. E. Pernicka at the address on page 2.

## LETTER TO THE EDITOR

Removal of  $\text{CaF}_2$  contamination

We would like to report some tests we have made concerning methods of removing  $\text{CaF}_2$  contamination. Two methods were found, one rather slow but easy to carry out, the other quite fast but involving the use of concentrated acid.

The contamination was on silver planchettes and could not be removed by scraping, washing or immersion in an ultrasonic bath.

## a) Slow method

$\text{CaF}_2$  is moderately soluble in solutions of ammonium salts. A contaminated planchette was placed in a solution of ammonium chloride for about 30 minutes in an ultrasonic bath, and its TL response compared with a similarly contaminated planchette treated for 30 minutes in an ultrasonic bath in distilled water. The contaminant was natural  $\text{CaF}_2$ , MBL type S.

The heights of peaks II and III were found to have been reduced by about 50% by the ammonium chloride treatment compared with the control. Soaking the planchette overnight was even more effective, reducing the TL from the contamination by about a factor of 10. No effect was discerned on the silver after this length of time, and we would not expect any reaction to take place with the more commonly used aluminium planchettes.

## b) Fast method

$\text{CaF}_2$  is dissociated by concentrated sulphuric acid. A silver planchette dropped into a test tube of this acid and left there for 10 minutes was found to have been efficiently cleaned. When the planchette was tested by being given the same dose as previously (about 700 rads), no high temperature TL was found. Testing of the liquid residue for dissolved silver showed none had dissolved, and this was confirmed by weighing the planchette before and after treatment. No change in the appearance of the planchette was seen.

Application of these methods of cleaning to contaminated heater plates, although difficult, should not be impossible. In theory nichrome heater plates should not be affected by either ammonium chloride solution or concentrated sulphuric acid, but thermocouple wires and connections to the plate would probably be attacked by the acid so the slow method seems more applicable. One possible method would be to remove the heater plate and thermocouple, and soak it overnight in ammonium chloride solution.

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## PREDOSE DATING OF A SWEDISH VITRIFIED FORT

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1. Introduction

This paper describes work on the TL dating of Swedish vitrified Fort material using the quartz inclusion predose method. A subsequent paper will describe results of the conventional method, and will compare the two.

While it is hoped that the dating will be of archaeological interest, the main feature of each paper is the interpretation of results. In this investigation, there was apparently a discrepancy comparing unetched samples with those etched in HF. This problem has been resolved.

2. Material investigated

The material was provided by F. Sandstedt of Alvsjo, Sweden, and consisted primarily of limestone from a calcinated core in a wall in a vitrified Fort. This Fort is being excavated at Torsburgen E. Gotland. It was estimated by the supplier that this core had been heated to about 1000°C.

3. Sample preparation

Samples were obtained by careful crushing in a vice, and selection of the required grain size by sieving. The whole product was used for  $\alpha$ -counting, and for estimation of  $K_2O$  content. The next step with samples for TL measurement was to remove the limestone using dilute HCl. After washing and drying, some samples were sieved again and studied at that stage, others were treated in 40% (cold) HF for 45 to 60 minutes.

4. Dose rate

The total sample had a low  $K_2O$  content, 0.13% reference (1).  $\alpha$ -counting was carried out using a ZnS powder screen on cello tape, with an  $\alpha$ -thick layer of sample of diameter 42 mm, working at an efficiency of 0.85. The  $\alpha$ -counting was carried out in this laboratory by D. C. W. Sanderson using a 4-channel counter which also had provision for pairs counting (in course of publication). The total count was 5.2 per Ks unsealed and 6.8 sealed. The pairs count is not very accurate at this stage, but indicated a Th/U ratio well below the typical pottery value of the order 3/1. A ratio of unity has therefore been assumed, which is the typical value for limestone. The unsealed  $\alpha$ -count leads to the following dose rates, using Bell's (1976) figures:

Table 1

|       | <u><math>\beta</math>-dose rate</u> | <u><math>\gamma</math>-dose rate</u> |
|-------|-------------------------------------|--------------------------------------|
| U     | 33 mrad/yr.                         | 26 mrad/yr.                          |
| Th    | 6 " "                               | 11 " "                               |
| K     | <u>9</u> " "                        | <u>3</u> " "                         |
| Total | 48                                  | 40                                   |

The corresponding  $\alpha$ -dose rate for two values of the efficiency Factor  $k$  is:

|            | <u>Fines</u> | <u>100<math>\mu</math></u> |
|------------|--------------|----------------------------|
| $k = 0.15$ | 102          | 21                         |
| $k = 0.04$ | 27           | 5                          |

For grains larger than 100 $\mu$ , or grains etched in HF, the  $\alpha$ -dose rates will be still smaller.

The  $\beta$ -dose rates in Table 1 will also be dependent on grain size, in the manner described by Mejdahl (1978).

##### 5. Results by Predose method

(a) The first samples investigated had been treated in dilute HCl but not HF. Subsequent X-ray analysis (2) showed that the main constituents were quartz and feldspar (plagioclase). Samples 4e, 8a, 12 and 14 were of this type; grain sizes and results are summarised in Table 2.

The procedure was as in Aitken and Murray, 1976. Some of the plots of TL against  $\beta$ -dose were linear to at least 600 rad, others had a slight curvature. Typical plots are shown in Fig. 1. The TL/temp. plots had a characteristic feature in that the TL signal after the first test dose, before activation, was as in Fig. 2a. There is a plateau commencing at the same temperature as that at which the quartz peak appears after activation. This plateau is present at all subsequent stages, as in Fig. 2 b, c.

It was concluded that the correct method of determining the archaeological dose in this situation was to subtract the plateau height from the total height of the quartz (100 $^\circ$ ) peak. This implies that  $S_0$  associated with quartz itself can be neglected.

(b) Samples 6, 7, 10, 11 and 13 were treated for 45-60 minutes in 40% HF following one hour in dilute HCl. These gave "clean" 100 $^\circ$ C quartz peaks as in Fig. 3. With most samples  $S_0$  was small but with 6,  $S_0$  was 35% of  $S_n$ , and with 6a it was 8%. In determining the archaeological dose with these two, the full value of  $S_n$  was used, not  $S_n - S_0$ . The values deduced were in agreement with the other samples.

X-ray analysis showed that after the HF treatment, there was no detectable feldspar.  $CaF_2$  was, however, present, in samples 6, 11 and 13 and was evidently produced by the action of HF on the feldspar. There was no detectable fluorite in 8 or 12.

It is concluded that it was the feldspar present under the conditions of section 5 (a) which led to the plateau in Fig. 2. This represents sensitivity to the test dose. It gives a spurious contribution which must be subtracted from  $S_n$ . When the 100 $^\circ$  peak is clean, however, as in Fig. 3, any value of  $S_0$  due to partial activation can be disregarded.

It will be noted (Table 2) that samples 9 and 10 consisted of large grains selected by hand. There is then no need to use HF to remove the feldspar. Sample 9 was, therefore, simply washed and dried after the HCl treatment. The peaks were clear as for 6 and 7. 10 was etched in HF for 45 minutes to give a comparison, and there was no significant difference between 9 and 10. If there was any residue of  $CaF_2$  after HF etching of the quartz, there is no evidence of its effects on predose results.

From the results in Table 2, the average of the intercepts representing the archaeological dose in terms of  $\beta$ -irradiation time is 76 minutes, with a standard deviation of 12.9 which is 17%. The last three results for the large grains are above average, and if they are omitted, the mean is 71 and the standard deviation is 10.6 or 15%.

Table 2

| <u>Sample</u> | <u>Grain size</u> | <u>HF</u> | <u>Plot linear to</u> | <u><math>S_0/S_n</math></u> | <u>Equiv. Arch. Dose</u> |
|---------------|-------------------|-----------|-----------------------|-----------------------------|--------------------------|
| 4e            | 90-106 $\mu$      | none      | 350 rad               | 23%                         | 82 min.                  |
| 8a            | 150-355 $\mu$     | "         | 200                   | 26                          | 90                       |
| 8b            | "                 | "         |                       |                             |                          |
| 12            | "                 | "         | > 600                 | 11                          | 77                       |
| 14            | "                 | "         | > 350                 | 9                           | 60                       |

In the above, the TL/temp. plots are as in Fig. 2.  $S_0$  is the plateau height, and is attributed to feldspar, not quartz.  $S_0$  is subtracted from  $S_n$ , etc. in deriving figures in the final column.

|     |               |         |       |    |     |
|-----|---------------|---------|-------|----|-----|
| 6   | 150-355 $\mu$ | 45 min. | > 600 | 35 | 64  |
| 6a  | "             | "       | > 400 | 8  | 62  |
| 6c  | "             | "       | 200   | 4  | 75  |
| 7a  | 106-150 $\mu$ | "       | > 400 | 0  | 60  |
| 11  | 150-355 $\mu$ | "       | > 350 | 0  | 74  |
| 9   | 1 mm          | none    | > 350 | 0  | 84  |
| 10a | 1 mm          | 45 min. | 250   | 2  | 94  |
| 10b | 0.5 mm        | 45 min. | > 100 | 3  | 95  |
|     |               |         |       |    | 917 |

In the last eight samples, the TL/temp. plots have symmetrical 100°C peaks, as in Fig. 3.  $S_0$  is the height of the peak before activation. Values of  $S_0$  are disregarded in deriving figures in the final column and plots as in Fig. 1.

8b received a dose of 600 rad before taking a glow-curve, and there was then partial saturation preventing a predose estimation of archaeological dose.

|   |      |
|---|------|
| Mean of the twelve results                | 76.4 |
| Standard deviation                        | 12.9 |
| Mean of first nine results (small grains) | 71.1 |
| Standard deviation                        | 10.6 |

## 6. Age of samples

Calibration of the  $\beta$ -source was carried out by Dr. A. F. McKinlay of the Scottish Radiological Protection Board using LiF phosphors 1 mm thick. The dose-rate deduced for 100 $\mu$  grains of quartz is 2.5 rad/min. This is based on the calibration data together with the grain-size corrections (Wintle and Aitken, 1977). These corrections are not very sensitive to grain-size in the range 100 to 300 $\mu$ , so that this figure applies to all but the last three samples. For 1 mm grains the figure will, however, be reduced to 2.1 rad/min. The archaeological dose-rates in Table 1 must be multiplied by the following factors: 100 $\mu$ , 0.90; 300 $\mu$ , 0.82; 1mm, 0.61. These figures have been deduced from Mejdahl's tables (1978) allowing for the  $K_2O$ , U and Th concentrations determined in paragraph 4 above. The ages deduced are consequently as follows:

|                     |   |            |
|---------------------|---|------------|
| Samples 4 e and 7 a | - | 1820 years |
| " 6, 8, 11, 12, 14  | - | 1940 years |
| " 9 and 10          | - | 2130 years |

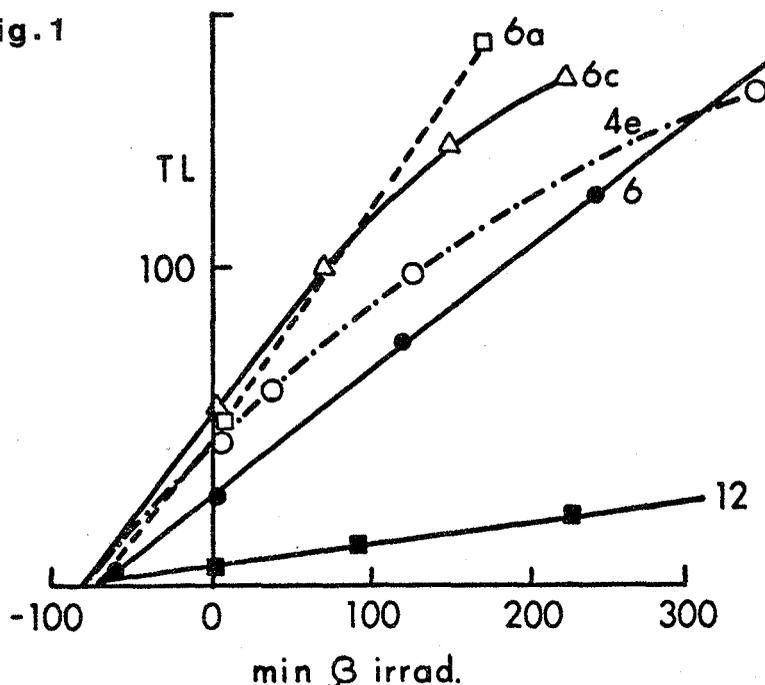
It appears that agreement comparing different grain sizes would be better if, relative to the 100 $\mu$  figures, the multiplying factors for the larger grains were either larger for the Mejdahl correction or smaller for the Wintle-Aitken correction. Taking into account the number of samples with the different sizes, the best figure for the age is 1950 years. The standard deviation is, however, not less than  $\pm 280$  years.

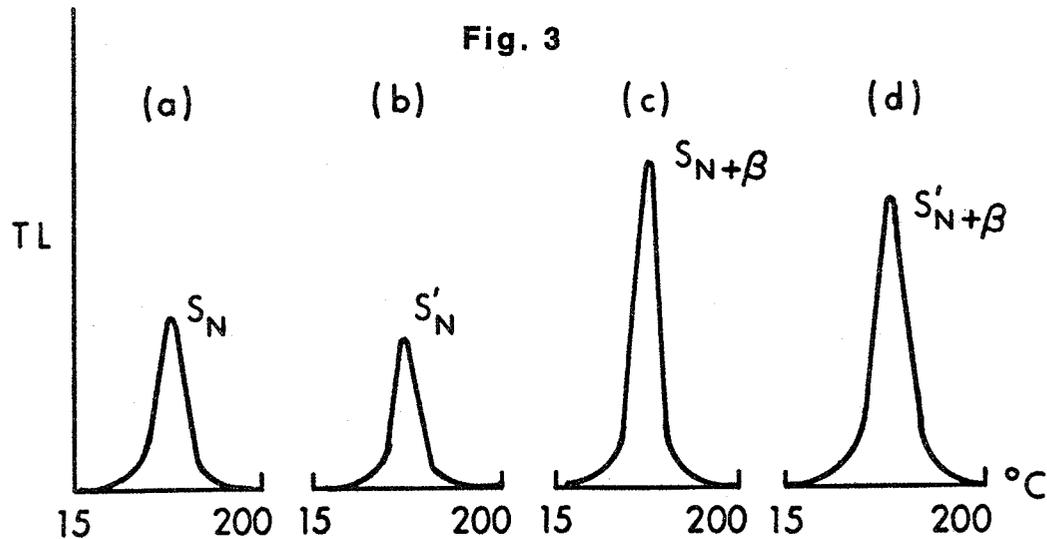
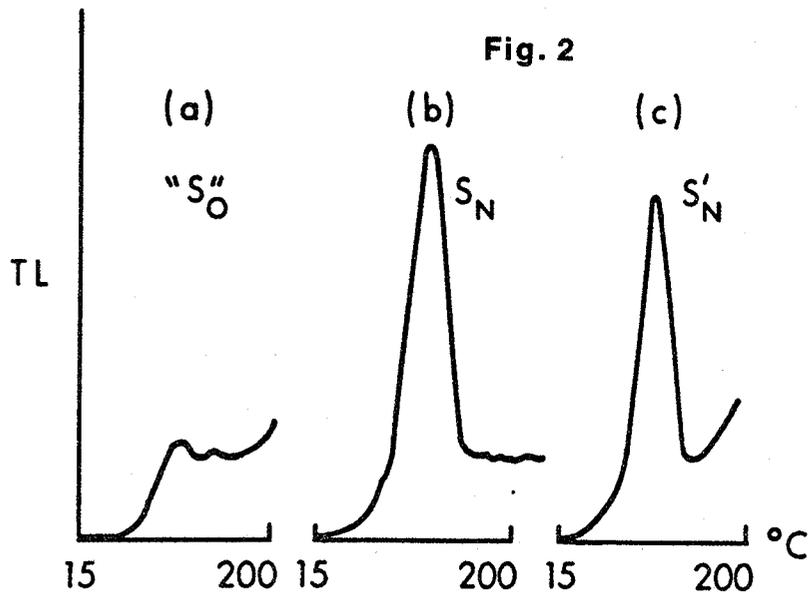
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- (2) X-ray analysis was carried out by R. G. Hardy, Geology Department, University of Durham.

|                               |       |   |
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Fig. 1





### A REMINDER TO CONTRIBUTORS

Send your contributions for Ancient TL to the editor at the letterhead address. Instructions for manuscript preparation may be found in issue No. 1. To help minimize publication costs, it is also requested that single spacing be used, as in the articles of this issue.

# A NOTE ON THE PLATEAU TEST AS USED IN THERMOLUMINESCENCE DATING

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## Abstract

Attention is drawn to effect of the presence of non-first-order TL kinetics upon the production of a TL "plateau".

## 1. Introduction - the "plateau test"

The "plateau test" is a useful criterion for determining if the localized energy levels (traps) associated with a given temperature interval thermoluminescence (TL) glow-curve are deep enough for long-term retention of the charge carriers (electrons or holes) during antiquity. In principle, the glow-curve of the natural TL (TLN) is compared with that of the TL resulting from artificial irradiation (TLA), and a plot is made of the ratio TLN/TLA against glow-curve temperature. Those traps which do not have the necessary stability are indicated by a non-constant value for the TL ratio with glow-curve temperature. The region of stable traps is indicated by a constant ratio - or "plateau" (Aitken, 1974).

In practice, however, samples tested in this fashion often produce poor plateaus, or may sometimes fail to show a plateau at all. One reason for this is a change in the TL sensitivity induced in the sample which has been heated prior to artificial irradiation. To circumnavigate this problem, the procedure most widely adopted is to artificially irradiate a previously undrained sample and a glow-curve corresponding to the artificial plus natural TL (TL(A+N)) is then produced. The plateau test is then carried out by plotting the ratio  $TLN / (TL(A + N) - TLN)$  against glow-curve temperature (e.g. Aitken and Fleming, 1972; Seeley, 1975; Aitken, 1978).

Other difficulties which may give rise to a poor plateau are supralinearity, anomalous fading, and non-radiation-induced ("spurious") TL. Indeed, the presence of spurious TL is often tested for by means of a "plateau test".

## 2. Second-order kinetics

Another, although perhaps as yet, not fully appreciated, effect arises as a simple consequence of the presence of non-first-order TL kinetics during the recombination process. A TL peak which is governed by pure first-order kinetics will always appear at the same glow-curve temperature, no matter to what level the traps are initially populated. Second-order kinetics, however, result in a shift in peak position with varying initial trap-populations, in particular the peak temperature  $T^*$  increases as the initial trap-occupancy  $n_0$  decreases (Garlick and Gibson, 1948). In general, TL peaks obeying non-first-order kinetics show an increase in  $T^*$  with decreasing  $n_0$ , the degree of increase in  $T^*$  depending upon the exact order of the kinetics.

The relevance of this to the "plateau test" is simply that a natural glow-curve (which may be the result of an absorbed dose in antiquity of  $10^4 - 10^6$  rad) cannot be compared with an artificial glow-curve when the artificial TL has been produced by irradiation with  $10^2 - 10^3$  rad only - if the kinetics of the TL process are higher than first-order. The differences in trap-occupancy are such that significant differences in  $T^*$  will result, and thus by comparing the natural TL curve with the artificial curve we are not comparing "like-with-like". A plot of natural TL/artificial TL will thus result in a very poor plateau.

To demonstrate this I have constructed a glow-curve, shown in Figure 1, using the normal TL glow expression, assuming second-order kinetics (e.g. see Chen, 1976). The values used for the trapping parameters are  $E_1 = 1.0$  eV;  $S_1 = 1.3 \times 10^{13} \text{ s}^{-1}$ ;  $n_0 = 5.0$  arbitrary units;  $E_2 = 1.2$  eV;  $S_2 = 1.0 \times 10^{13} \text{ s}^{-1}$ ;  $n_0 = 10.0$  arbitrary units;  $E_3 = 1.4$  eV;  $S_3 = 8.7 \times 10^{12} \text{ s}^{-1}$ ;  $n_0 = 8.0$  arbitrary units.

Curve (a) represents the "natural" glow-curve, in which there has been some thermal fading of the less stable traps during "antiquity" (equivalent to having heated the sample to 250°C). Curve (b) represents the "artificially" irradiated sample, having been given a dose of radiation ( $D_A$ ) equal to its natural dose ( $D_N$ ). Curve (c) is that glow-curve obtained with  $D_A = 2 D_N$  and curve (d) is with  $D_A = D_N/2$ . Curve (e) is equivalent to superimposing an artificial dose  $D_A = D_N$  on top of the natural dose. (Note that  $e \neq a + b$ ).

The "plateau tests" obtained by dividing curve (a) by the other curves, is shown in Figure 2. Only when the natural curve is divided by an artificial curve which has an artificial dose equal to the natural dose, is a good plateau obtained. Poor plateaus, or no plateau at all, result with all the rest.

### 3. Importance of non-first-order kinetics in TL dating

It is fortunate that, with quartz (perhaps the most often dated archaeological material), the complications of second-order kinetics do not appear to be a problem. The results of both Aitken and Fleming (1972) and Levy (1978) imply that the kinetics of the TL process in quartz are almost pure first-order. Natural fluorite (Aitken and Fleming, 1972) also exhibits first-order kinetics. However, Levy (1978) finds second-order kinetics for the TL of albite and suggests that the TL from all other feldspars will follow second-order kinetics. Prôkic (1977) finds that a kinetic-order of 1.5 best describes the TL from natural barite. Wintle and Aitken (1977) observed that isothermal decay experiments on one of their flint samples caused the peak to shift to a higher temperature as the sample was thermally drained. In addition, when an artificial dose is superimposed on the natural dose, the resultant glow-curve shows a peak which is at a lower temperature than the corresponding peak in the natural glow-curve. This is strongly indicative of non-first-order kinetics and this, in turn, may be partially responsible for the lack of a plateau for this sample. (It should be pointed out that M. J. Aitken (private communication) considers that the shift in the TL peak, with isothermal decay, in this flint sample is more likely to be due to a spread in trap energies. However, non-first-order kinetics should not be ruled out.)

### 4. Conclusions

In addition to the effects of sensitivity changes on heating, supralinearity, anomalous fading and spurious TL, the presence of non-first-order kinetics may be a contributing factor in the difficulties met with when attempting a "plateau test" in some materials. Unless considered, non-first-order kinetics may give rise to misleading interpretations - for example, they may lead one to suspect the presence of spurious TL. Some samples, which may be otherwise suitable for TL dating, are often discarded on the basis of a poor plateau. Complications due to non-first-order kinetics should be borne in mind, and rejection of some samples may not prove necessary.

### Acknowledgements

The author wishes to thank the Science Research Council (UK) for the award of a Postdoctoral Research Fellowship tenable at the University of Birmingham. The author is also grateful to Dr. S. A. Durrani.

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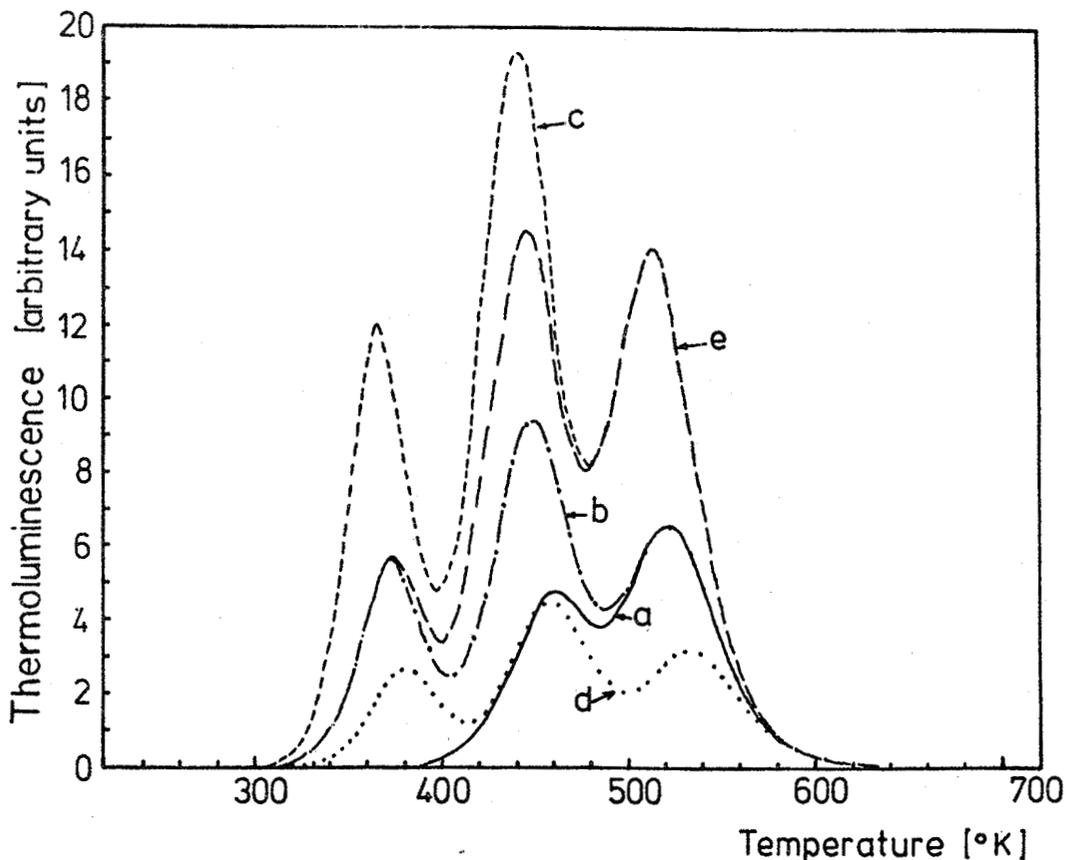


Figure 1 An imaginary glow-curve consisting of three peaks, constructed using  $E_1 = 1.0\text{eV}$ ;  $E_2 = 1.2\text{ eV}$  and  $E_3 = 1.4\text{ eV}$ . Values for  $S$  and  $n_0$  are given in the text. Second-order kinetics are assumed for each peak. Curve (a) represents the "natural" glow-curve; curve (b) represents the "artificial" glow-curve obtained after imparting an "artificial dose"  $D_A$  equal to the "natural dose"  $D_N$ . Curve (c) is obtained with  $D_A = 2D_N$  and curve (d) is with  $D_A = D_N/2$ . Curve (e) is equivalent to superimposing an artificial dose  $D_A = D_N$  on top of the natural dose. (Note that  $e \neq a + b$ )

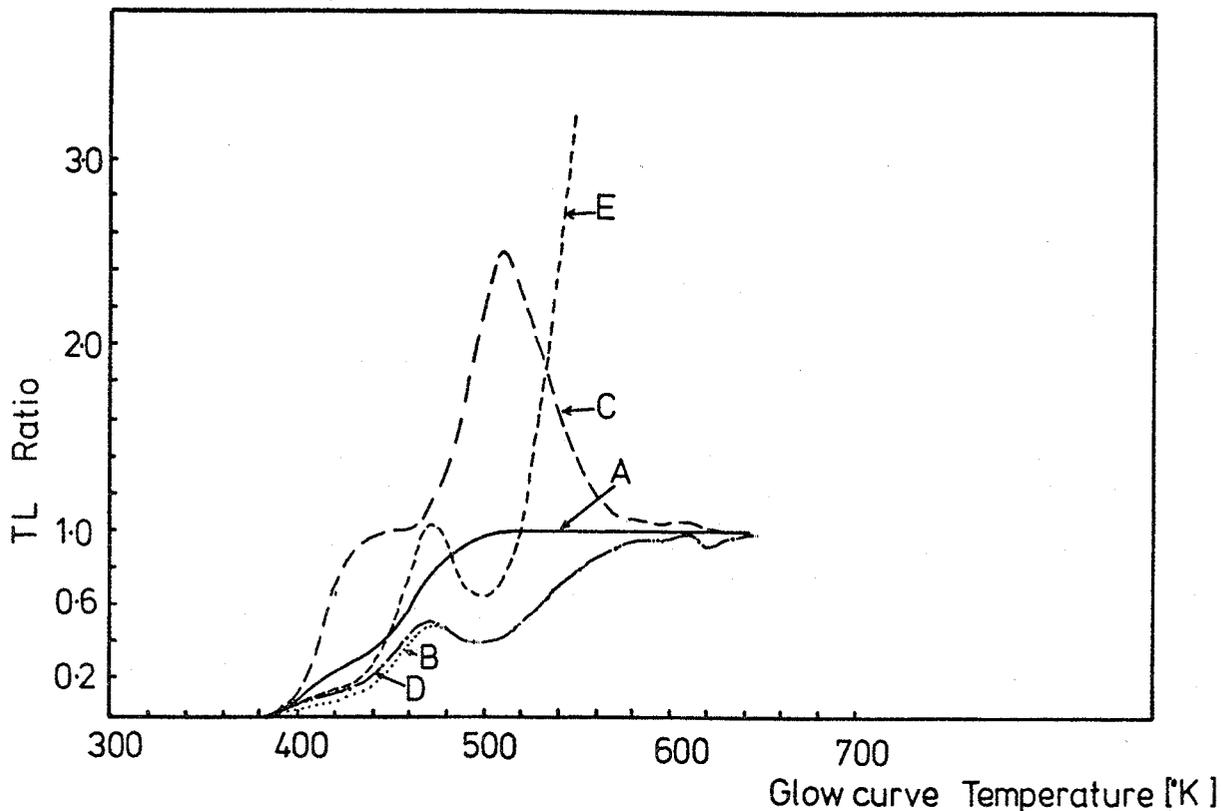


Figure 2 The "plateau tests" obtained by dividing curve (a) from Figure 1 by each of the other curves.  $A = a/b$ ;  $B = a/c$ ;  $C = a/d$ ;  $D = a/e$ ;  $E = a/(e-a)$ .

[Editor's Note: Measurements by Singhvi and Zimmerman ( *Archaeometry*, Volume 21 (1), 1979, p. 73-77 ) indicate that the dominant luminescent mineral in some fine grain pottery samples is feldspar. Such samples may exhibit non-first-order kinetics and, as a result, have poor plateau characteristics as described above.]

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