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# EFFECTS OF ALPHA DOSE AND ANNEALING TEMPERATURE

## UPON POTTERY DATING BY THERMOLUMINESCENCE

by

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### INTRODUCTION

In dating pottery by thermoluminescence (TL), the first step is to measure the natural TL (abbreviated N-TL). To determine the susceptibility of a given sample to radiation damage, the pottery is then given a fixed amount of artificial irradiation. The resultant TL, we then call A-TL. The factors which influence this response must be taken into consideration to obtain reliable TL dates.

Crystalline minerals such as quartz and feldspar are known to be the fractions responsible for producing TL in pottery. Methods have been developed and applied to date a given sample both by isolating the large crystals (Flaming, 1968) as well as taking just the fine grains of the crystals along with the clay material (Zimmerman 1971). It has been known for some time (Han and Ralph, 1971) that the response of the crystalline minerals to artificial irradiation varies with the type of radioactive particle used for the bombardment. Just recently we have learned that the response is affected also by the original firing (or annealing) temperature of the pottery.

In view of the possible existence of such problems, we separated quartz crystals from pottery for study. Two types of artificial sources, namely, alpha particles ( $\text{Po}^{210}$ ) and X-rays were used to measure the changes in susceptibility due to applied dosage.

To test quartz for dependency upon annealing temperatures as well as changes caused by radiation history (i.e. quartz embedded in pottery has been subjected to the internal radiation bombardment from the clay matrices through the life of the pottery), we turned to beach sand (quartz fraction) that had not been annealed nor subjected to this type of radiation.

Definition of TL-sensitivity "S<sup>\*</sup>".

The TL sensitivity of a given crystalline mineral is defined as the amount of TL produced for a given amount of applied radiation. It is known that this value differs with different types of radiations e.g.  $\alpha$ ,  $\beta$ ,  $\gamma$  and X-rays.

Experimental Method

The quartz ( $Q_s$ ) inclusions in a sample of pottery were first separated from the clay matrix by breaking down the fragments with an ultrasonic apparatus. To complete the sorting this was then followed by magnetic separation. The non-magnetic portion was then washed and treated with hydrochloric acid. The crystals which remained after the acid treatment were identified to be quartz by means of a 400X power polarizing microscope. Beach sand ( $S_s$ ) was obtained from Vagn Mejdahl of the Danish AEC, Denmark (this particular sand was chosen mainly due to its higher TL-response compared to our New Jersey beach sand). It was also separated magnetically and treated with HCl to remove feldspar and only the quartz was selected for this experiment.

Both the  $Q_s$  and  $S_s$  were ground to less than 10 microns in an agate mortar. Before irradiation, two portions of both  $Q_s$  and  $S_s$  were annealed, one at 500°C and the other at 900°C, each for 30 minutes. The remainder of  $Q_s$  and  $S_s$  were labelled "unannealed" even though  $Q_s$  had been annealed originally when the pottery was fired. This formed a total of six portions, 3 for  $Q_s$ , and 3 for  $S_s$ .

The finely ground samples were then cemented to our regular sample holders for the measurement of TL. (This technique of sample mounting enables the same material to be used repeatedly).

Several samples from each portion were first run through the TL reader. The unannealed portions provided measures of the N-TL for  $Q_s$  and  $S_s$ . In the course of these measurements, the samples are annealed at 450°C for less than one second. The 500°C and 900°C annealed samples yielded no TL at all, which indicated that this method of sample preparation induced no TL. All of the samples were then irradiated with a small monitor dose of X-rays (100 rads) compared with 1000 rads normally used in dating. The subsequent TL of the 320°C peak gave a measure of the initial sensitivity.

One sample from a given portion was then selected and irradiated with a large known dose of alphas, after its TL response had been read. Again a monitor dose of 100 rads of X-rays was given to the same sample to obtain a measured sensitivity (defined as  $S_e$ ). The initial sensitivity of this

particular sample is defined as  $S_e^0$ . At the same time, another sample from the same portion which was not subjected to any alpha irradiation (after an initial monitor dose of 100 rads of X-rays) was again given a monitor dose of 100 rad X-rays. The measured sensitivity is defined as  $S_c$  (c stands for control) with its initial sensitivity defined as  $S_c^0$  for this particular sample. This procedure was repeated on the same selected sample as well as on the control sample with gradually increasing large known doses of alphas of the order of less than 1 Krad up to 30 Krads for all six portions.

Similar experiments with large known doses of X-rays in place of alphas were made on four portions (excluding the annealed extracted quartz). The purpose of using a control sample was to normalize the measured changes in sensitivity each time after the sample had received a large dose of alphas or X-rays. The ratio of  $S_c/S_c^0$  represents the change in sensitivity of the control sample which is due to the monitor dose of 100 rads of X-rays. It is generally within the limits of experimental error. But the ratio of  $S_e/S_e^0$  is the change in sensitivity due to a large dose of radiation applied in addition to the monitor dose of 100 rads X-rays. The actual change in sensitivity due to the large doses only is therefore the ratio of these two, namely:-

$$\frac{S_e/S_e^0}{S_c/S_c^0} = S^*$$

\*  $S$  is the change in sensitivity of the accumulated dosage applied when repeated measurements were made on the same sample.

## RESULTS AND DISCUSSION

Quartz crystals undergo transitions at 573°C from Low-Q to Hi-Q without reconstructed change, but at 867°C Hi-Q becomes unstable at atmospheric pressure, and transforms to tridymite with a reconstructed structural change. As  $\text{SiO}_2$  is cooled from above this temperature (867°C) rearrangement of crystals will take place and thus will change the susceptibility of the quartz. This is the reason why we chose to anneal the samples of quartz ( $Q_s$ ) and sand ( $S_s$ ) at 500°C and 900°C.

The TL response was linear when alpha particles were used (Figs. 1 and 2), but with X-rays, it became non-linear above 10 Krads and showed signs of saturation between 20 and 30 Krads (Fig. 3). Not shown are the data for unannealed sand which had a response similar to  $S_{500^\circ}$ . By comparison with the sand samples, the so-called unannealed quartz was probably fired originally at some temperature above 500°C.

It is evident from Fig. 3 that when crystals are annealed above 867°C (e.g. at 900°C) the TL response from both alphas and X-rays is far greater than for crystals annealed at lower temperatures. Similar results were also reported by I.K. Kaul et al. (Kaul, Ganguli and Hess, 1972).

However the change in sensitivity  $S^*$  as calculated from the monitor dose of 100 rads X-rays between each applied large dose indicates no change was observed with accumulated alpha dose to 38 Krads. The values of  $S^*$  have a mean of  $1.0 \pm 0.15$  as

indicated by the dashed lines in Fig. 4 while  $S^*$  increases to 1.4 with accumulated X-rays above 10 Krads.

It was shown (Han and Ralph, 1971) that the efficiency of alpha dosage is only 10% as effective as the same amount of X-rays in producing TL. At 38 Krads of alphas the accumulated alpha dose is in fact equivalent to only 3.8 Krads of X-rays. For this dosage of X-rays the value of  $S^*$  in Fig. 4 is within the region of experimental error of the measured  $S^*$  for alphas which indicates that as long as one deals with low doses, the change in sensitivity is confined within a 15% range. However, if we could apply sufficiently larger doses of alphas to obtain the equivalent of 10 Krads of X-ray (i.e. 100 Krads of alphas) then it is possible that we would also see the change in the value of  $S^*$  increase. It is therefore safe to state that the change in sensitivity is independent of the accumulated radiation applied for natural doses which do not exceed the equivalent of 400 rads of X-rays. However, the TL response is definitely temperature dependent, and increases with higher annealing temperatures. This change in TL response may be important in correcting some of the samples of known age of earlier periods, which are constantly yielding older dates as shown in Fig. 5. The calibration line was drawn based on materials of the classical period (well-dated stylistically) of homogenous texture; ones which were fired to much higher temperatures, namely up to 1100°C, in most cases the purpose was to achieve the oxidation-reduction of the fine clay particles to give the so-called black glaze appearance. Because older

material beyond 1000 B.C. may not have been fired to such extent, it would have had an overall lower sensitivity. This may be the cause of erroneously old dates.

Attempts are being made to substantiate these findings by annealing at higher temperatures before artificial irradiation and checking sensitivities in the usual manner (with 1000 rads X-ray), as well as by applying methods that will give information concerning the original firing temperature of these samples. At present, we have some results from DTA (Differential Thermal Analysis) and TGA (Thermogravimetric Analysis) performed with a few objects that show promise of giving the needed information. For example, samples with erroneously early TL dates exhibit large endothermic peaks between 650° and 700°C (DTA) and large weight losses (TGA). Ones with TL dates in good agreement with C<sup>14</sup> dates show only small endothermic and exothermic peaks, and weight losses are small. Further study with the samples in question may bring us to a better understanding of the process that causes low response in induced TL. Thus a correction may be applied to these samples of known age (and eventually to samples of unknown age) with the hope that they will be brought closer to the calibration line.

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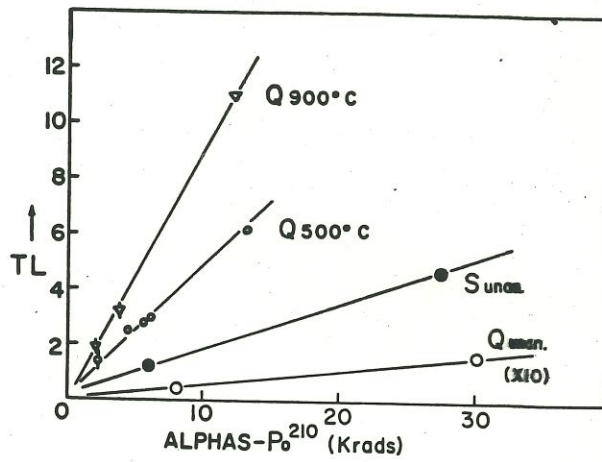


Fig. 1

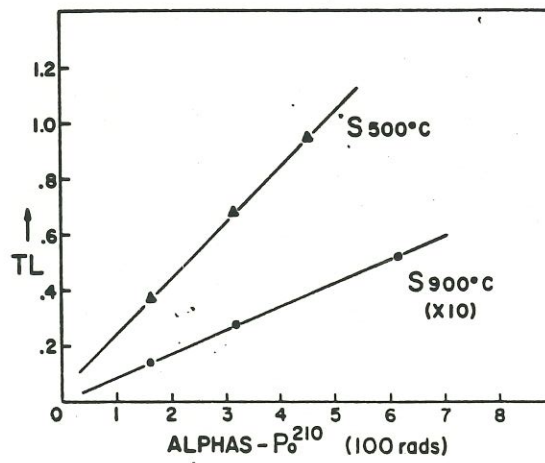


Fig. 2

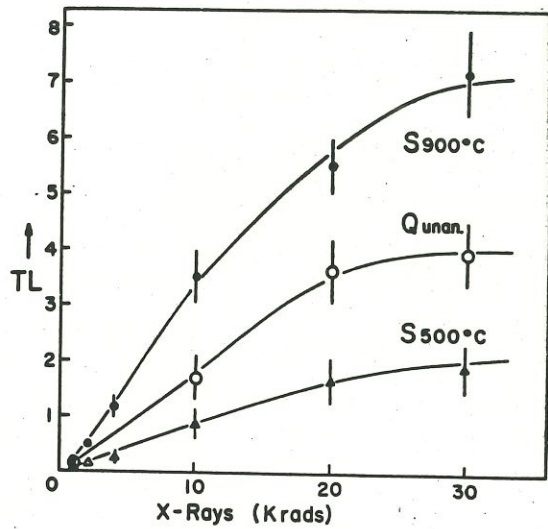


Fig. 3

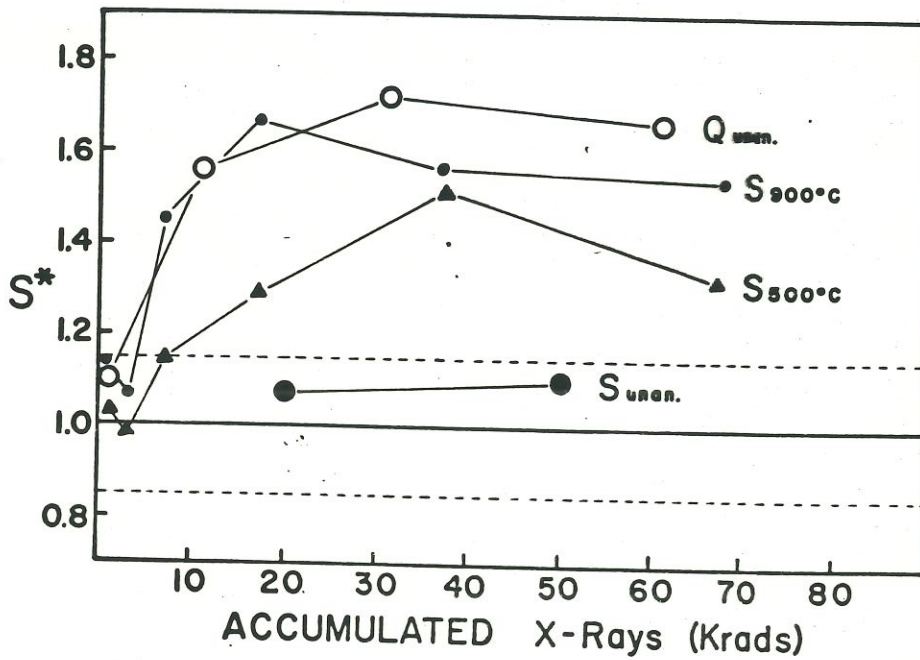


Fig. 4

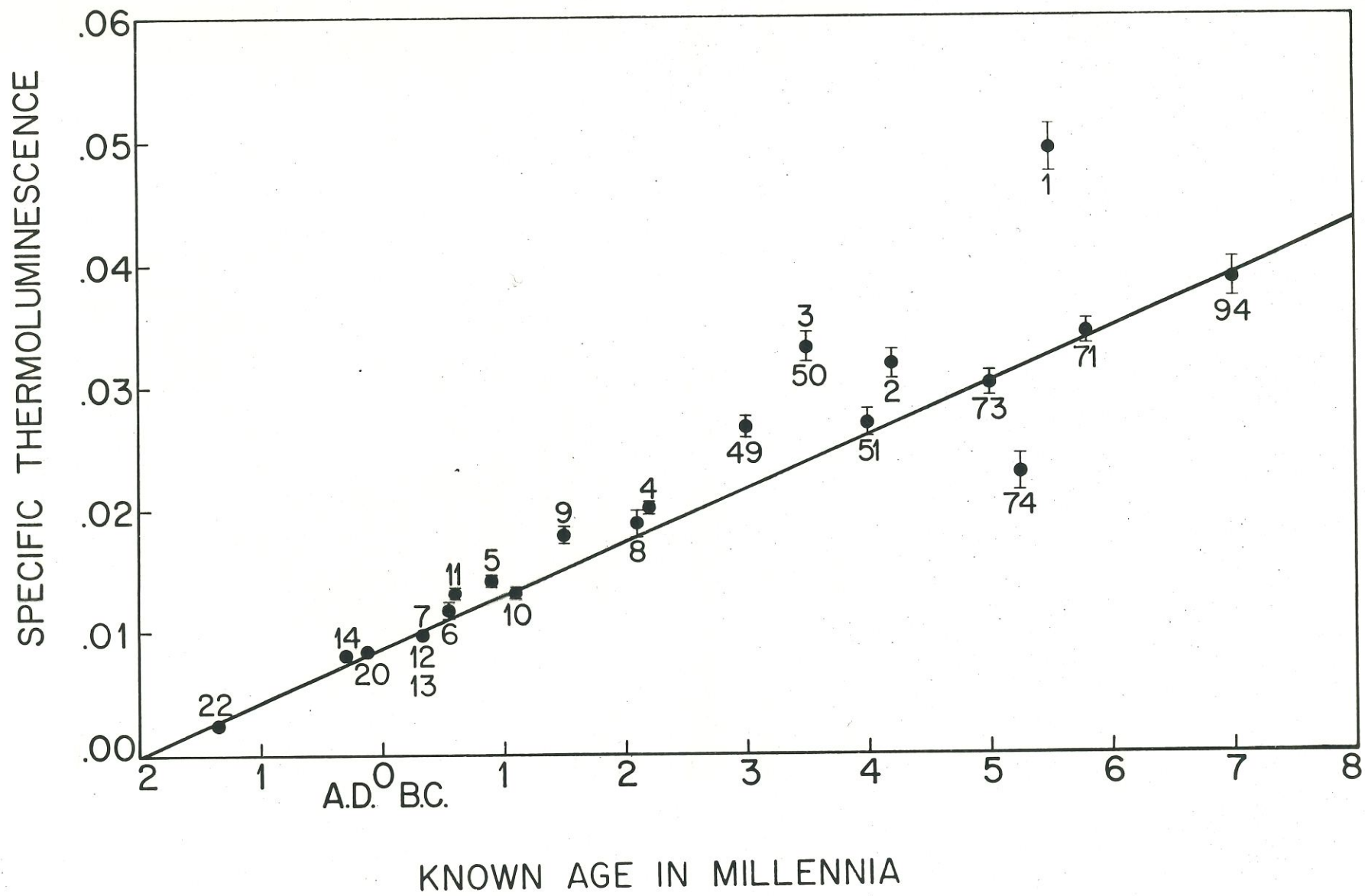


Fig. 5

- Fig. 1 TL induced artificially by alphas from  $Po^{210}$  for unannealed sand (Sunan) and extracted quartz from pottery annealed at  $500^{\circ}C$  ( $Q_{500^{\circ}C}$ ) at  $900^{\circ}C$  ( $Q_{900^{\circ}C}$ ). The unannealed quartz Qunan (X10) represents 1/10 of its measured TL (about the same as  $Q_{500^{\circ}C}$ ). TL in arbitrary units.
- Fig. 2 TL induced artificially by alphas from  $Po^{210}$  for sand annealed at  $500^{\circ}C$  ( $S_{500^{\circ}C}$ ) and  $900^{\circ}C$  ( $S_{900^{\circ}C}$ ). TL in arbitrary units.
- Fig. 3 TL induced artificially by X-rays (at the rate of 1 Krad per minute) for unannealed quartz (Qunan) and sand annealed at  $500^{\circ}C$  ( $S_{500^{\circ}C}$ ) and  $900^{\circ}C$  ( $S_{900^{\circ}C}$ ). The unannealed sand had results similar to  $S_{500^{\circ}C}$ .
- Fig. 4 The change in sensitivity  $S^* = \frac{S_c/S_e^0}{S_c/S_c^0}$  due to accumulated doses of X-rays. For accumulated doses of alphas all the values of  $S^*$  fall within the region bounded by the dashed lines.
- Fig. 5 Calibration chart of TL measurements of pottery of known age. For samples older than 1000 B.C., their known-age was provided by corrected  $C^{14}$  dates of associated materials.