

Lack of interaction between the rapidly and slowly bleaching TL peaks in an Australian quartz

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The second glow growth curve for the Rapidly Bleaching Peak (RBP, at 325°C for a ramp rate of 20°C s⁻¹) is shown to be independent of the state of bleaching of the Slowly Bleaching Peak (SBP, 375°C). This result validates the usual TL and OSL dating procedures using this second glow growth curve for the Australian sand dune quartz studied, and probably for others. Furthermore, it suggests that the corresponding two electron trap/luminescence centre systems do not interact. This raises the question whether the conduction and/or valence bands constitute the path for charge carrier transport for the thermoluminescence process for both systems in this quartz.

Introduction

Much archaeological quartz in the natural state, unexposed to laboratory irradiation, exhibits either or both of two major TL peaks, the "325°C" or Rapidly Bleaching Peak (RBP) and the "375°C" or Slowly Bleaching Peak (SBP). The temperatures describing these peaks are shown in quotes because they apply only to a ramp rate of 20°C s⁻¹. For the lower ramp rate used in this work the peaks occur at lower temperatures.

Spooner et al. (1998) have shown that even with light of wavelength greater than about 400 nm and up to about 700 nm the RBP bleaches very rapidly and apparently completely. On the other hand, the SBP is essentially unaffected unless the wavelength is less than about 400 nm, and then it bleaches much more slowly than does the RBP. Furthermore the SBP appears to bleach down only to a residual level (Wintle and Huntley, 1979). These characteristics have led to some concentration of sediment dating work, where solar bleaching is the clock resetting mechanism, on the RBP, both with TL (Prescott and Fox, 1990; Franklin and Hornyak, 1990) and with OSL (Smith et al., 1986).

For dating with either TL or OSL the second glow growth curve of the RBP is critically important, the necessary assumption being made that this curve is the same after laboratory resetting as it was at the time of

deposition. There are both experimental and theoretical reasons to be cautious about this assumption. The RBP was long ago dubbed the "malign" peak (Aitken, 1985, p.20) because of sensitivity changes after thermal resetting. There have also been reports of sensitivity changes after bleaching of OSL in quartz (Smith et al., 1990) and of TL in loess (Li and Wintle, 1992 and references therein), although loess is a complex mixture and may reflect for the most part properties of minerals other than quartz.

On the theoretical side, a number of kinetic studies have shown that the glow growth curve of a TL peak may be influenced by the state of other systems which could compete for charge carriers during irradiation (Chen and Bowman, 1978; McKeever and Chen, 1982) or for thermally-released charge carriers during heating (Kristianpoller et al., 1974; Chen et al., 1938). Thus in particular if the RBP and the SBP used the same pathways for charge transport (e.g. the conduction and valence bands) during irradiation or heating the level of occupancy of the traps and luminescence centres associated with the SBP might be expected, on the basis of such models of competition, to influence the glow growth curve of the RBP. If this were so, in order to obtain the correct second glow growth curve for the RBP the resetting procedure would have not only to eliminate the RBP but also to return the SBP to the

same state it was in on deposition (Franklin et al., 1992), a condition that might be hard to meet.

In this paper I report on an experiment designed to test in the most direct fashion possible whether the state of the SBP influences the glow growth curve of the RBP, using a reasonably typical Australian dune sand quartz. The negative result not only strengthens confidence in current dating procedures with the RBP but may also raise interesting questions for models of the TL processes in similar quartz. These implications are briefly discussed.

Experimental

The material studied was approximately 100 μm quartz, extracted by the usual procedures (Aitken, 1985, p.18) including HF treatment and density separation, from sediment from the Puritjarra rock shelter in central Australia (Smith, 1987). The extraction was done by the Archaeometry Group of the Department of Physics and Mathematical Physics at Adelaide University and the sample kindly made available by Prof. John Prescott. The intention was to compare the first glow growth curve of the RBP with second glow growth curves starting with large and small SBPs. Therefore three batches were used. In batch #1 the SBP was at its natural level, which was quite close to saturation. With batch #2 a preliminary exposure of 45 minutes to sunlight reduced the SBP to a very low level. Both of these batches were then subjected to a preheat for 1 minute at 240°C followed by a 30 minute bleach under an Oriel solar simulator using a high pass filter cutting off to 1% transmission at 475 nm. This yellow bleach was found in preliminary experiments to eliminate entirely the RBP with no measurable effect on the SBP. The preheat removed lower-lying peaks, including a small one at about 280°C. These two batches were used to produce second glow growth curves. The third batch was material in the natural state except for a 240°C preheat, and was used to produce the first glow growth curve.

All measurements were of 2.0 mg aliquots deposited on Al disks that had first been sprayed with a Silkospray silicone coating (Willy Rusch AG), using a Risø automatic TL reader with a 9635QA PM tube fitted with a UG11 filter. The ramp rate was 3.1°C s⁻¹. A preheat of

1 minute at 240°C was used before all glow curve heats. The glow curves were normalised using the integrated counts over the central 20°C of the second-glow peak at about 310°C induced by a small test dose, this peak being a combination mostly of the RBP with some SBP. This normalisation signal was found to be independent of the treatment the specimen had received prior to the test dose. Irradiations were performed with a Sr-90 beta source and are given in terms of minutes of exposure, at a dose rate of about 1 Gy min⁻¹. The starting levels of the SBP for batches #1 and #2, for the second glow growth curves, are illustrated in fig. 1. The peak height of the SBP was increased by only about 20% over the natural curve by an additional 100 Gy beta dose.

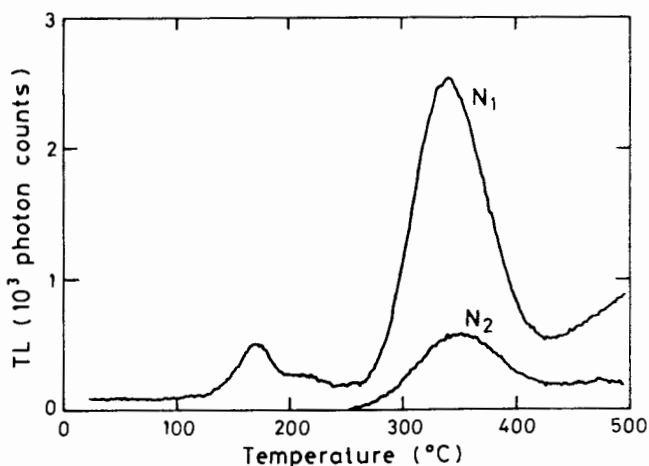


Figure 1.

Initial glow curves of batches #1 and #2 of material. $N_1 = N + P + YB$; $N_2 = N + SB + P + YB$. N = Natural, P = Preheat for 1 min at 240°C; YB = 30 min Yellow Bleach; and SB = 45 min Solar Bleach.

Samples of all three batches were then given a series of beta doses and each sample divided in half, one half being measured directly and the other measured after a yellow bleach to remove the RBP, as described above. At least 5 replicates of each measurement were made. The replicate glow curves were adjusted along the temperature axis to eliminate the temperature jitter in the apparatus, as described in a previous paper (Franklin et al., 1987). For each dose the temperature standard was the most centrally-located (in terms of temperature) glow curve measured with yellow bleach, exhibiting

only the SBP. For other yellow-bleached specimens these SBP peaks all had essentially the same shape and matching on the temperature axis by overlaying curve upon curve was straight-forward and unequivocal. For specimens given doses but no yellow bleaches the glow curves were the sum of the RBP and the SBP, with the former dominating and the overall peak shape changing slightly with dose. Temperature matching for most of these specimens was done with the same temperature standard, matching on the high temperature side only of the SBP.

For the data with the highest accumulated dose (96 min beta dose for the first glow growth curve) this procedure was not satisfactory. In this case the yellow-bleached data were treated as above but the data without the yellow bleach were temperature shifted using the overall TL peak (dominated by the RBP) with a standard consisting of the average over the temperature-corrected glow curves for the zero-dose specimens not receiving a yellow bleach. The rationale for this procedure is based on observation that the peak temperatures of the RBP glow curves produced by the standard procedure outlined above were independent of dose. The temperature-shifted replicate glow curves for each treatment were then averaged among themselves and the yellow bleached average curve, containing only the SBP, was subtracted from the corresponding unbleached curve, containing both the RBP and the SBP. This procedure produces the RBP glow curve by difference, and is illustrated in fig. 2. As shown by fig. 3, the RBP glow curves so produced do not vary in peak shape or peak position with dose, as expected for a first order peak (Wintle, 1975). A value of 0.42-0.43 for the geometric symmetry factor (Chen and Kirsh, 1981) is also consistent with first-order kinetics. On the other hand the SBP glow curves exhibited the small drop in peak temperature with increasing dose expected for a peak with some higher-order character (Hornyak et al., 1992)

Results

The integrated sum of counts over an 11°C interval centred at the peak was taken as the measure of intensity of the RBP. These intensities are plotted for all three batches as a function of dose in fig. 4. The solid line is a best fit to the second glow growth data by a

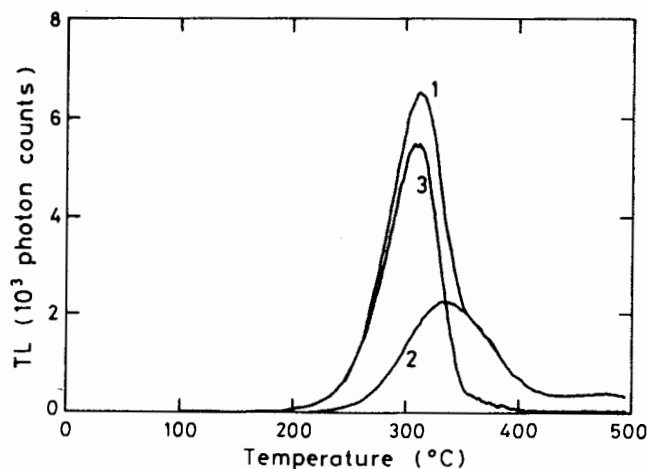


Figure 2.

Example of glow curves used to obtain RBP by subtraction. 1 = without YB, 2 = with YB, and 3 = RBP by difference.

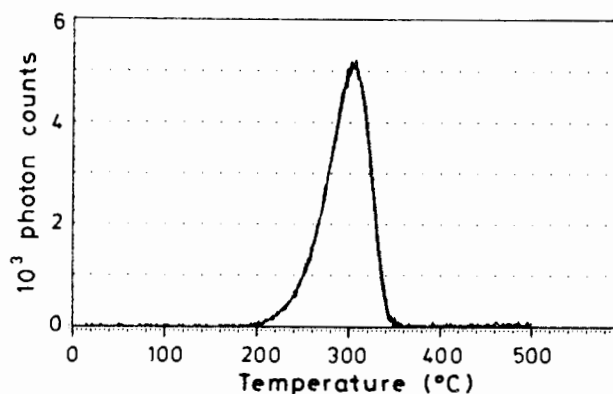


Figure 3.

RBP glow curves for first glow growth. Curves for 0, 24, 48 and 72 min beta doses are scaled to the same height and plotted together. $N_3 = N + P$.

satürating exponential. The first glow growth data have been shifted along the dose axis by +73 min as an estimate of the ED to illustrate the consistency of the first and second glow growth curves. The result is clearly that the variation in the initial state of the SBP has had no observable influence on the glow growth curve of the RBP. Because the experiment was so arranged that the lower-temperature peaks below the

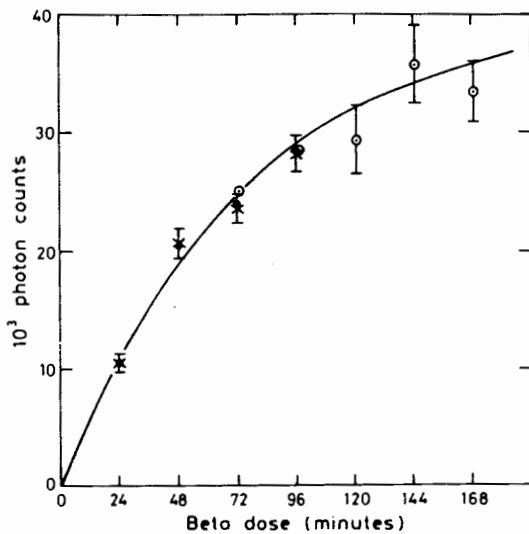


Figure 4.

Glow growth curves for the three batches of material. Data points are identified as: • = N_1 , × = N_2 and ○ = N_3 , with N_1 and N_2 as in caption to fig. 1 and N_3 as in caption to fig.3. The error bars represent two standard deviations for N_2 (up to 96 min beta dose) and N_3 (above 96 min beta dose), the errors for N_1 being about the same as those for N_2 . The solid line is the unweighted least squares fit of a saturated exponential to the N_1 data.

RBP were very small or absent, it has not tested interaction between these peaks and the RBP. However, in the field at the time of deposition the traps associated with these peaks are reasonably certain to be empty so that this interaction should not be a problem in any event.

Discussion

The result shows that there is no observable change in the glow growth curve of the RBP in this quartz when it is solar-bleached and one can conclude that for dating purposes it does not matter how bleaching is done, provided it eliminates the RBP, before the second glow growth curve is obtained. This conclusion certainly applies to this particular quartz and probably also to a wide range of Australian quartz and perhaps other

quartz exhibiting primarily the RBP and the SBP. The situation is sufficiently complex, however, that the present conclusion of no interaction between the RBP and SBP should be extended to other materials only with caution, particularly in the light of mention by Smith et al. (1990) that sensitivity changes in the OSL of quartz have been observed as a result of bleaching.

The apparent lack of interaction between the RBP and the SBP in this quartz raises the question whether the two systems use the same pathways for charge transport. Different pathways would certainly account for the observed apparent lack of interaction. Perhaps both systems do not transfer charge carriers through the conduction and valence bands, but rather at least one involves transfer in some other way, in the sense describe by Townsend and Kirsh (1989). Kinetic treatments of the irradiation and glow-out processes in this latter system would then have to take this into account.

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PR Steve McKeever

The author poses an important and interesting question, namely does the degree of bleaching of the slowly bleached TL peak (SBP) in quartz affect the growth curve (i.e. sensitivity) of the rapidly bleached peak (RBP)? The data presented clearly indicate that it does not, for the particular sample of quartz under study. However, since the mechanism that causes the bleaching of the TL signals in quartz is still uncertain, and under considerable debate, we should be cautioned about extending this conclusion to all quartz samples (a point noted by the author). Similarly, we should also be careful about the inferences that may be drawn from these data concerning kinetic models.

Nevertheless, models aside, the present data are clearly relevant to general concerns regarding possible sensitivity differences between samples that have received only a selective bleach in the laboratory (e.g. "yellow bleach" referred to in this paper) versus other less selective bleaches (e.g. a solar bleach, or a natural sunlight bleach). It would perhaps be fruitful for all laboratories engaged in this type of research to carry out similar tests and in this way the question regarding the generality of the results, raised by the author in the Discussion section, could be examined in greater depth.