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Post wash effects in zircon

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Introduction

In investigating the phosphorescence associated with the anomalous fading of high temperature TL in zircon, it is necessary to use a thermal wash to eliminate interference due to phosphorescence from the low temperature peaks. This thermal pretreatment has revealed two new phenomena: a short term phosphorescence not associated with the anomalous fading and a peak at 175°C whose peak area increases with time after washing.

Post wash phosphoresence

The following experiments were performed on a coarse grain sample (ref 210R2) from the Puy de Dome (courtesy of D. Miallier), mounted in a gold pan and secured with Viscasil, and a fine grain preparation of beach sand from Kerala in India (ref 210f1), mounted on a stainless steel disc. The phenomenon has been observed in several other samples of zircon, and in one sample of quartz (not necessarily pure) extracted from pottery. In no case has a sample been found not to exhibit the phenomenon.

Discovery: The sample 210R2 was irradiated (5000Gy) and left at room temperature for 30 days to eliminate any phosphorescence from the anomalously fading component of TL (Templer, 1985). The total number of TL counts to be expected from this sample was 6×10^8. Prior to giving the sample a thermal wash, the count rate was 450cps, presumed to be thermal phosphorescence. Various thermal washes of increasing stringency were tried, and the phosphorescence count rates at room temperature were recorded after each wash, both immediately (i.e. about 2 minutes after the wash) and after the phosphorescence had died down to an apparently constant level (after several hours). Results are given in Table 1: all washes consisted of a linear rise at 5°C/s, with no pause at the maximum temperature.

Table 1: Effect of different washes

Max temp of wash/°C	Immediate intensity/cps	Delayed intensity/cps
125	1000	300 ± 20
175	>250: off scale	15 ± 5
225	215	0 ± 2
225 (second wash)	30	0 ± 2

(All count rates have dark count subtracted. Immediate intensity decays very rapidly, so errors are not estimated.)

Three trivial explanations of the phenomenon were rejected:

(i) An increase in the dark count of the PMT at switch-on (the EHT was switched off during the wash): this could be ruled out because the dark count was monitored by interposing a blanking plate in the beam path.

(ii) An effect similar to spurious TL: the washes were done in high purity nitrogen, and between washes the sample was kept in vacuum.

(iii) Thermal lag: it can be seen from the time scale of the diagrams that the phenomenon lasts too long for this by about two orders of magnitude.

Given that the effect is real, it might be thought that transfer of electrons from the high temperature peaks to the low temperature peaks was happening, especially as the time dependence of the phosphorescence is similar to that of thermal phoshorescence from the low tempertature peaks (Fig 1). However, no corresponding repopulation of either the 90°C or 130°C peaks is observed. This could be explained if these peaks were thermally quenched in TL: however, a comparison of peak area with rate of thermal phophorescence at room temperature from a given dose showed that if any thermal quenching did take place, the effect was too small by a factor of at least 20 to account for postwash phosphorescence.

Further experiments were made, to find the effect of repeated washes (Fig 2): the signal is partially regenerated by reheating.

The spectrum of the phosphorescence was taken, using a series of edge cut filters in the beam path, and a subtraction technique. For comparison a similar spectrum was obtained for thermal phosphorescence from the low temperature traps. There is some correlation between the two spectra, but the emission peak at

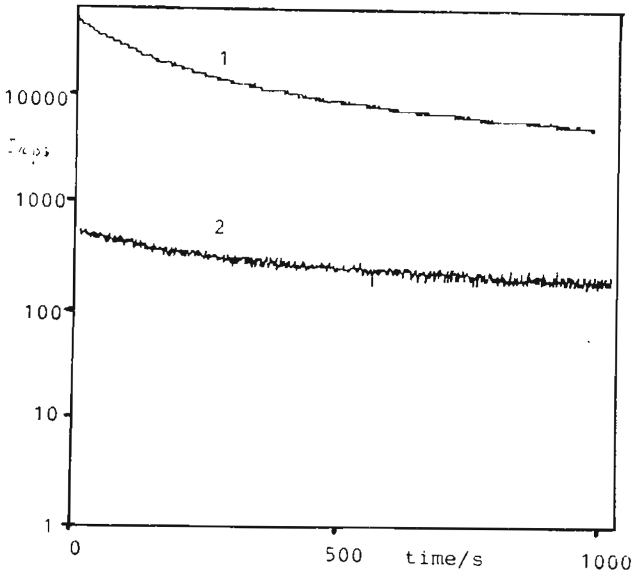

Figure 1: *Comparison of post wash phosphorescence with thermal phosphorescence from the low temperature peaks. Dose was 5200 Gy, wash was to 155°C at 5°C/s.*
1. Thermal phosphorescence.
2. Post wash phosphorescence.

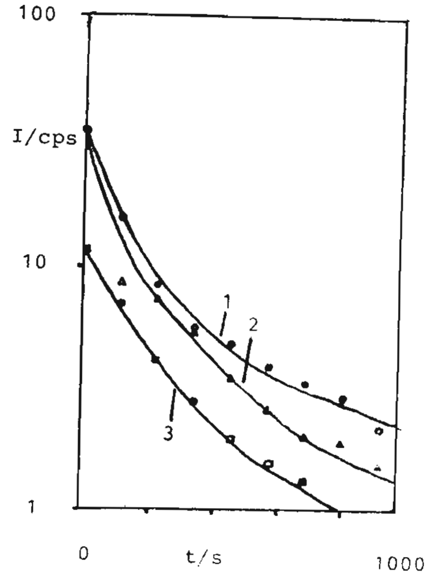

Figure 2: *Effect of repeated washes. A sample was dosed with about 70 Gy and left until thermal phosphorescence has ceased, then repeatedly washed to 100°C. The dark count of the PMT is subtracted.*

480nm in the thermal phosphorescence does not appear in the post wash spectrum, and the proportions of the emission peaks at 370, 450 and 580nm seem to differ.

A possible model for the phosphorescence is based on the idea of a reservoir trap to which some of the electrons from the deep TL traps are transferred during the wash. Because of a very low frequency factor escape of these electrons from the reservoir traps, they are not evicted during the wash, nor do they give rise to a low temperature TL peak. It is thought that a localised transition state involving the deep trap, the reservoir trap and the luminescent centre is involved (Halperin and Braner 1960), connecting the phenomenon with Templer's localised transition model for anomalous fading. Both models will be discussed in forthcoming articles by Templer and myself.

Post wash buildup

This effect was first discussed by Petridou et al (Petridou et al, 1978), for lithium fluoride, although they have observed it in other materials since. After thermally washing an irradiated sample, a TL peak at a temperature lower than the maximum washing temperature is observed, its peak area building up with time after wash. The current explanation from the same group is in terms of migrating radiation defects forming triplets with electron/hole pairs (Kitis et al.,1985).

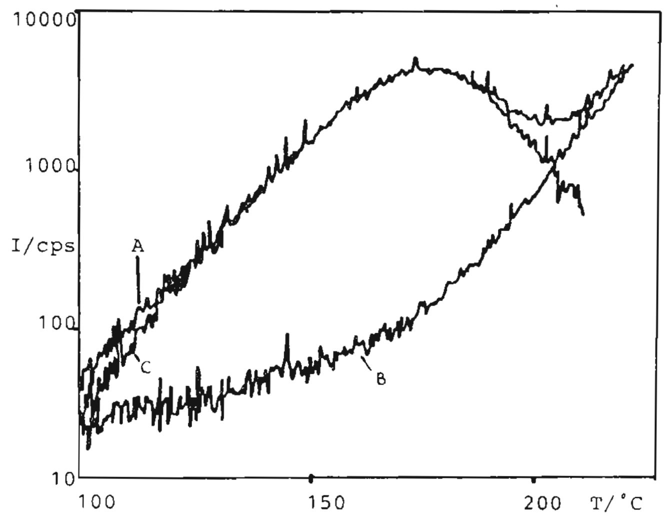

Figure 3: Post wash buildup in Zircon: 5200 Gy, 25.5 hrs after washing to 295°C. Glowed out at 5°C/s. Curve A is the delayed glow curve, B a prompt glow curve, and C the result of subtracting the two.

In the case of zircon, buildup of a peak at 172°C (for a heating rate of 5 °C/s) has been observed in the sample 210R2, which was one of the samples used for the experiments on post wash luminescence. This does not correspond to any TL peak normally observed.

In order to eliminate the possibility of spurious TL, the samples were stored under vacuum, and glowed out in high purity nitrogen. Glow curves were stored on a 4096 channel MCS so that subtraction of the prompt glow curves could be used to reveal the buildup peak (Fig 3).

Two rates of heating (1.05 and 5°C/s) were used for glowing out the samples to allow determination of E and s values by peak shift, and two pause times were used (25.5 and 94.65 h). The E and s values were also determined by the initial rise method. Results are summarised in Table 2. The calculations were based on first order TL peaks, which is not necessarily correct: nevertheless it is noticeable that

(i) E values are very low, in the range 0.28eV to 0.52ev.

(ii) E values determined by peak shift are in all cases lower than those derived from initial rise.

(iii) s values are down by about six orders of magnitude on the values associated with normal TL peaks.

No explanation of (ii) is offered, but it may be noted that low E and s values are not inconsistent with the defect diffusion model.

Table 2

Delay/hrs	β / (°C/S)	T peak /°C	E_{ir} /eV	E_{ps}
0	any	no peak	n/a	n/a
25.5	5	172	0.443±0.013	0.292±0.10
94.65	1.05	109	0.519±0.022	0.282±0.012
94.65	5	174	0.350±0.04	0.352±0.018
25.5	1.05	117	0.380±0.017	

Abbreviations: β = heating rate
ir = initial rise
ps = peak shift

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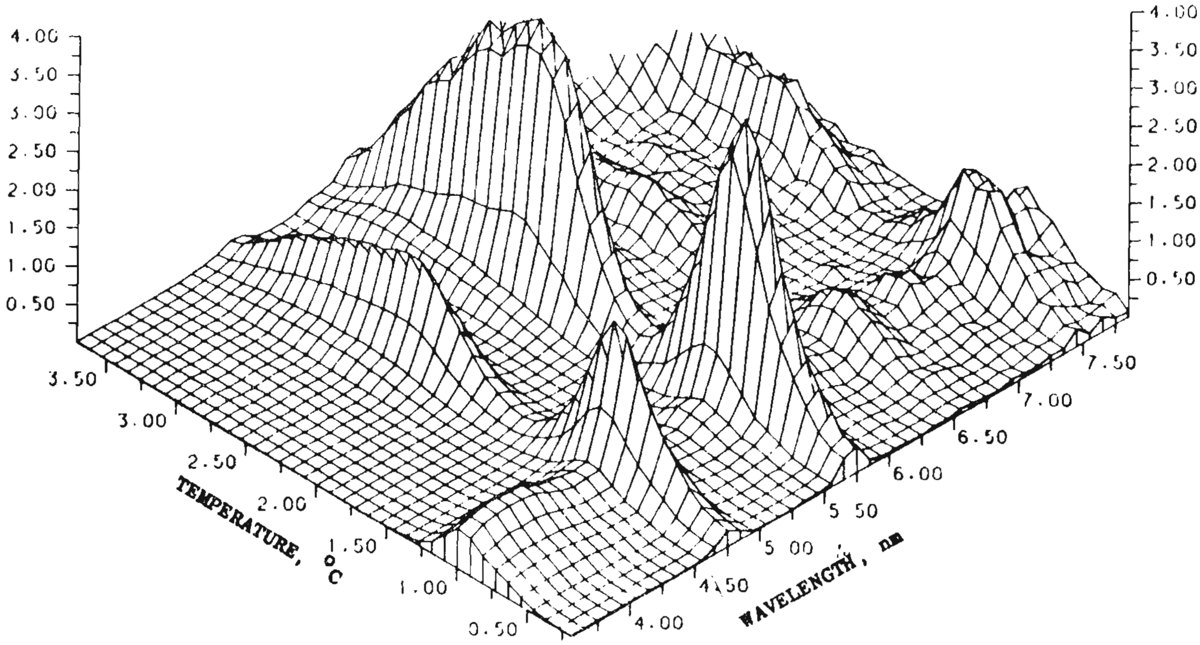
P.I. Reviewer's Comments (Peter Townsend)

It seems a pity that the term thermal wash has come into common usage since thermal anneal is more appropriate. *(Ed; 1 agree)*

Based on spectral results we have obtained in our laboratory (see below), we have reached a similar conclusion concerning the possibility of a diffusion stage the zircon TL signal change. In fact this process is probably quite common, but often ignored.



TL spectrum of a green zircon taken at 20°C per min. Low T blue peak (400nm) is from a different impurity from the others and fades faster, bleaches at a different rate and is sample dependent. Current suggestions include evidence for a regeneration of the 100°C/575nm feature from the decay, or movement of other traps. The peak appears even after 30 days storage. Subtle changes occur in the higher temperature peak spectra on storage. A paper is planned which will show more of these details.

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