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A STUDY OF PHOTOTRANSFER IN ZIRCON, APRIL - JULY, 1978

An internal report by D. W. Zimmerman on his work during a visit to the Oxford Research Laboratory, edited by M. J. Aitken.

PURPOSES OF RESEARCH

1. To try to confirm I. K. Bailiff's finding that very deep traps in zircon do not fade (Nature 264, 531).

2. To try to improve sensitivity and to reduce the residual level in the transfer technique.

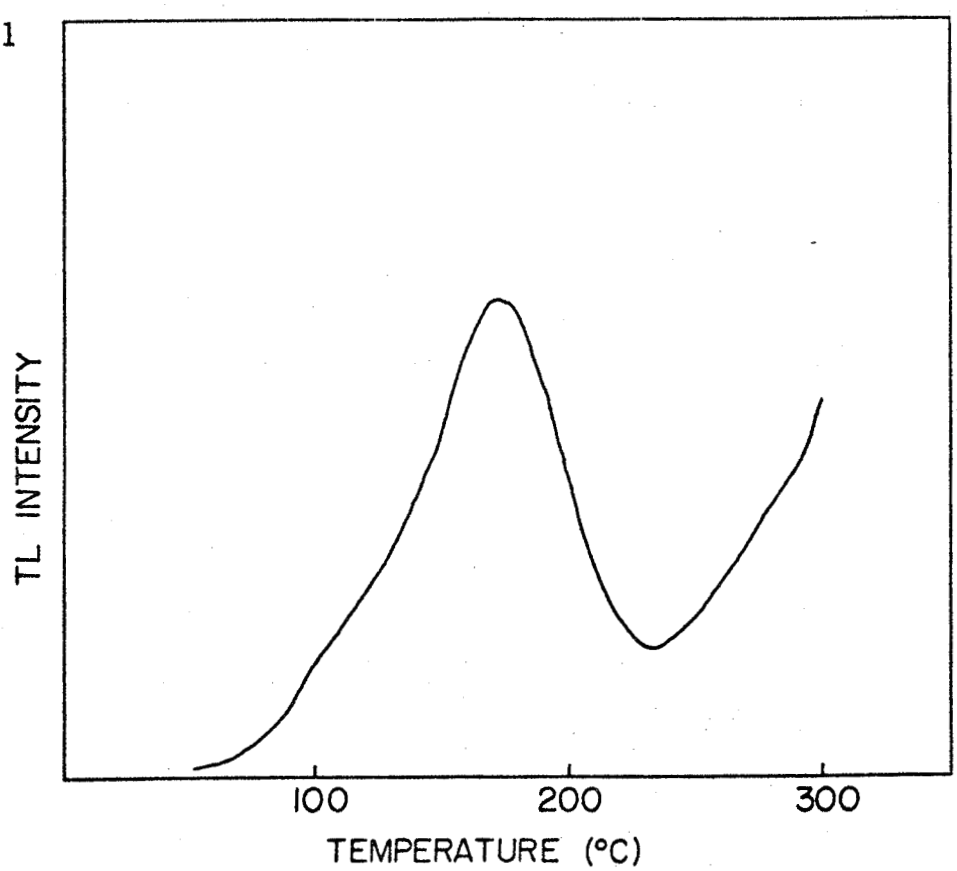
3. If 1 and 2 successful, to try transfer on zircon grains from archaeological ceramics, especially in the zircon 'natural' method (Sutton and Zimmerman, 1976, Archaeometry 18, 125).

RESULTS

A. Apparatus

Figure 1 shows a typical glow curve of transfer TL. The light was detected in all experiments using an EMI photomultiplier type 9635 without filters. Unless stated otherwise the illumination used for transfer was at a wavelength of 365 nm, and for 1 minute; this was using a 150-watt mercury lamp with a DGO Metrospec mono-chromator having an f number of 4. The set-up was that developed by S. G. E. Bowman with the sample at room temperature during transfer, except in section F.

FIG. 1

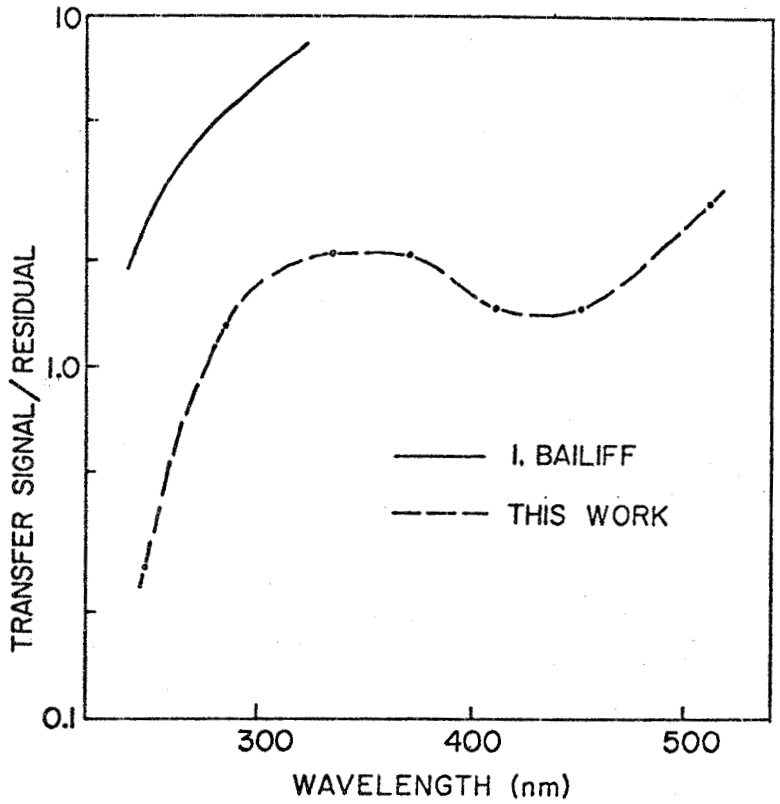


B. Wavelength dependence of transfer

(i) Instrument checks: by using various filters, it was determined that the monochromator output below 310 nm is deminated by stray light. Above 310 nm stray light is apparently unimportant, but all subeequent measurements were made with appropriate Corning color glass filter(s) in the beam to reduce stray light.

(ii) The ratio of transfer signal to residual signal was measured for Washington University (WU) sample Z-2 (geologic zircon) as a function of wavelength (Figure 2). As the quantum efficiency fell as the wavelength increased above 400 nm, the best region seemed to be about 320 to 380 nm. The intense 365 Hg line was subsequently used for most experiments.

FIG. 2



C. Fading of deep traps

WU samples Z-1 and Z-2 were beta irradiated (10 krads), heated to 475°C, the transfer signal measured 6 minutes after irradiation, and 2 days later. Corrections for bleaching during transfer were necessary. (Fading of 375°C TL = 25% (Z1) and 15% (Z2) in 2 days.)

Results:

Z-1	Fading + bleach	= 10.0 ± 0.7%
	Bleach alone	= 8.9 ± 0.3%
	Fading (2 days)	= 1.1 ± 0.8%
Z-2	Fading + bleach	= 3 ± 2%
	Bleach alone	= 3 ± 1%
	Fading (2 days)	= 0 ± 3%

(Bailiff result = 0 ± 3%, 6 months).

D. Residual signal

Bailiff (1976) reported a residual signal (annealed, unirradiated zircon) equivalent to about 10 krads. In the present work the levels were:-

Z-2, annealed 700°C, residual = 3000 rads
" " 900°C, " = 600 rads
" " 1200°C, " = 150 rads

Comparable residual levels were found (700° anneal) for Z-1, Z-12 and zircons from an Idaho baked soil. Archaeological firing may not exceed 700°C, so that is the relevant level.

(i) Optical bleaching

A wide variety of optical bleaches using various wavelengths from the monochromator and with a Hanovia germicidal lamp (Model 16) + filters. Most rapid bleaching was obtained with the Hanovia lamp plus Corning 0-52 filter (> 360 nm). Any light less than 320 nm was disastrous - it greatly increased the subsequent residual level.

Typical results with the Hanovia plus 0-52 filter were:-

700° annealed sample: residual = 3000 rads
after 1 hr bleach, " = 1500 rads
after 65 hr bleach, " = 460 rads

1220°C annealed sample: 150 rad residual not reduced by 1½ hr bleach.

(ii) Bleaching at elevated temperature

Bleaching for 5 min at 400°C was tried with three wavelengths; Hanovia plus 0-52, Hanovia plus 7-59, and Hanovia with no filters. All produced a small (about 50%) increase in the residual. Also, bleaching for 5 min at 700°C was tried with the Hanovia lamp plus 0-52 filter. It increased residual by x 3.

E. Sensitivity

The intensity of the transferred TL (from above 500°C) was compared to the direct TL (350°C) for three geologic zircon samples (annealed 700°C, then irradiated).

	transfer		direct		transfer
Sample	Dose (rads)	Peak ht. (cps)	Dose (rads)	Peak ht. (cps)	direct
Z-1	12K	11K	100	30K	1/300
Z-2	"	6K	"	80K	1/1600
Z-12	"	12K	"	35K	1/350

The sensitivity can be increased by x 20 using longer or more intense illumination.

F. Transfer at low temperature

Measurements on Z-2 were made in co-operation with S. Mobbs using her apparatus at about 20° above liquid nitrogen temperature. No significant change (compared to room temperature) was seen in the transfer signal intensity either of the residual or of a 2.3 Krad signal.

G. Alpha efficiency

All measurements above were made with beta irradiation (for convenience). One measurement on Z-2, annealed 700°C, 100 μm dia. grains in monolayer, was irradiated with a curium -242 source. The estimated dose was 8000 rads (one-fifth of the dose to fine-grains), within a factor of two. The alpha efficiency of the transfer TL and the direct 300° TL were found to be approximately the same, namely about 0.2.

H. Idaho Soil Zircons

Measurements were made on zircons from a 'pseudo' archaeologic sample - a lava baked soil from Idaho having an age of about 2300 years according to C-14 and quartz TL. The sample was about 1 mg of zircon in the size range 10 to 100 μm.

Results:

		Peak ht.
1.	Natural TL to 450°C	196 k cps
2.	Transfer (1 min, 365 nm)	45 k cps
3.	Beta irradiation, 5 krads	
4.	TL to 450°C	152 k cps
5.	Transfer	55 k cps
6.	Heat to 700°C	
7.	Transfer (residual)	2.0 k cps
8.	beta 5 krads	
9.	TL to 450°	133 k cps
10.	Transfer	2.2 k cps

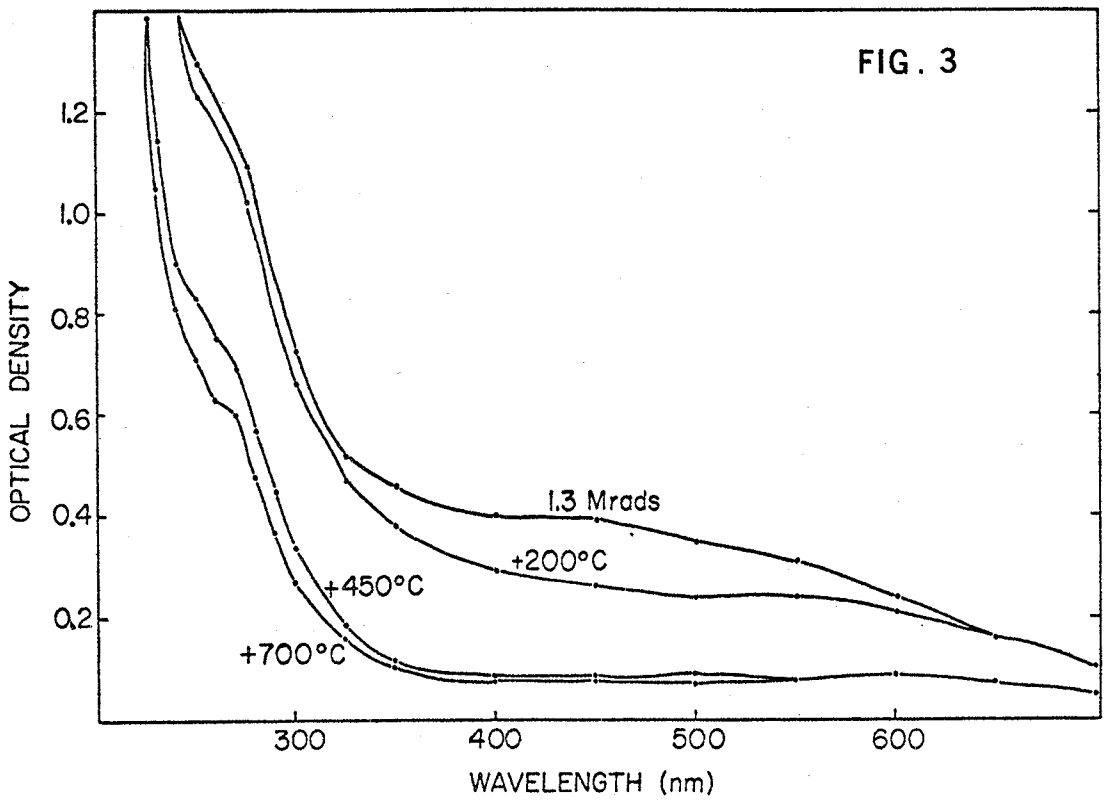
Comment:

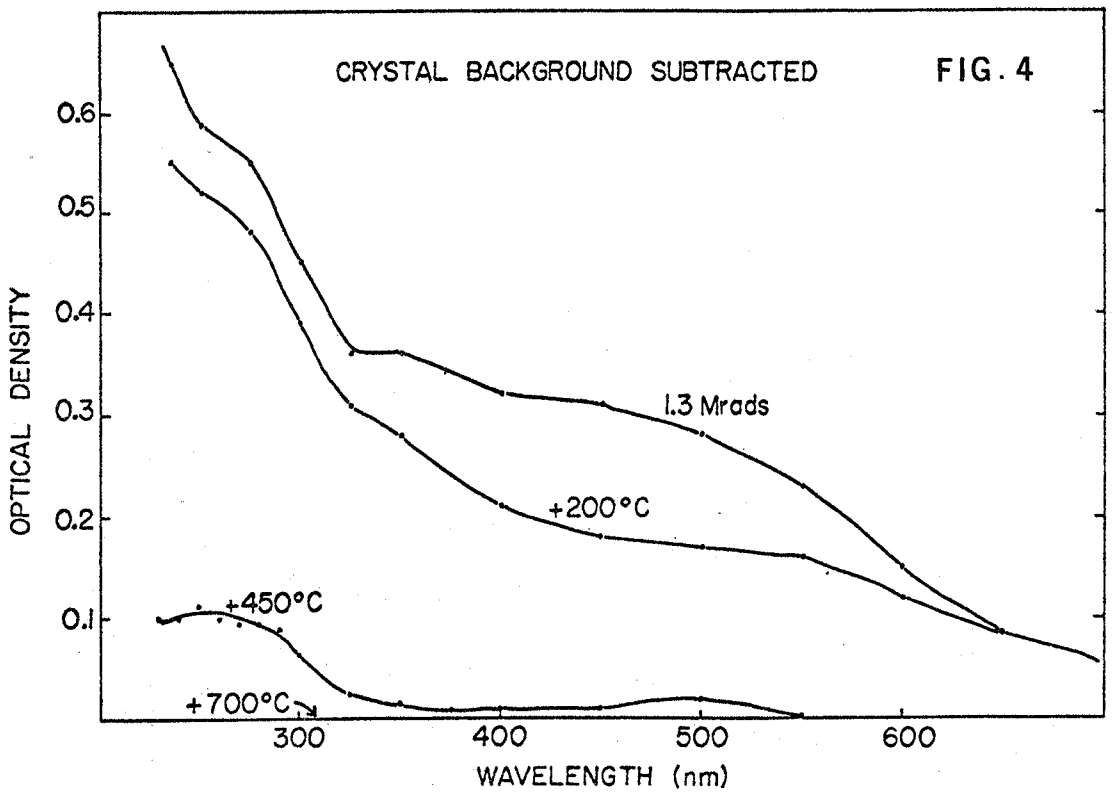
Transfer (from 5 krads) = 0.2 k cts/sec, direct TL (from 5 krads) = 125 k cts/sec. Therefore direct TL is at least 500 times more sensitive than transfer (in agreement with studies of geologic zircons, section E). The large transfer signal from the natural (step 2 above) was presumably from the geological dose, suggesting that the sample had not been heated high enough by the lava for resetting. If it had been, it appears that the sensitivity would have been marginal for measuring even the natural.

I. Optical Absorption Measurements

To obtain a better idea of what is happening, optical absorption measurements were made on a large single crystal of Z-12 (about 10 x 5 x 4 mm). The crystal was annealed for 1 hr at 700°C, mounted in araldite, and then ground on coarse sandpaper to expose two parallel faces. These were given a smoother grinding (600 grit on glass) and then polished (by R. Holland, Dept. of Geology, in charge of thin-section preparation). The sample (now 10 x 5 x 2 mm) was then removed from the araldite.

The sample was then run on a Cary 14 recording spectrophotometer (in Inorganic Chemistry, thanks to the co-operation of Dr Peter Day and Dave Woodwark). Figures 3 and 4 show the absorption curves obtained for a 1.3 megarad dose with annealling at the temperatures indicated.





Results:

(i) Irradiation produces absorption bands over the entire region 240 to 700 nm but the bands are extremely broad and unresolved.

(ii) As a function of temperature the bands are also very broad.

R.T. to 200°C	325 to 575 nm
200 to 450°C	240 to 650 nm
450 to 700°C	240 to 325 nm
700°C	240 to 300 nm

(iii) The 1.3 mega rad (no annealing) sample was also run at liquid nitrogen temperature - no measurable change.

Comment:

The results are in reasonable agreement with the transfer characteristics. The greatest efficiency for transfer from the 500 to 700° traps is around 250-300 nm. However, the well annealed crystal (700°C) also has a large absorption there giving rise to the large residual transfer. The rapid rise in absorption at 250 nm is presumably the fundamental absorption edge. The shoulder at 270 nm could be either from structural defects and impurities, or from still higher temperature traps filled by previous irradiation.

The broad nature of the bands and lack of structure implies that there is no gain to be found in measuring the transfer characteristics in smaller wavelength increments.

The overlap of the different temperature regions may explain some non-linearities and the saturation observed in transfer as a function of bleaching time.

J. High Temperature TL

An attempt was made to measure the 500-700° TL directly using Z-2, Z-3, Z-8 and Z-12. The normal TL equipment was used, heating rate 10°C/sec and an EMI type 9635 photomultiplier with two corning 5-58 and two HA3 filters.

Of these samples, Z-12 was the best, giving 5 k cts/sec at 550°C for a 5000 rad dose. The blackbody background was 1 k cts/sec. However the TL at 550° was 20 times less that the TL at 350°C. The TL from the other samples fell more rapidly still at high temperatures. That, combined with the loss in intensity from the extra filters, results in too low a signal to be useful for dating.

General conclusions

(i) There do seem to be non-fading deep (500-700°) traps.

(ii) They are probably in significant numbers - around 10^8/mg at 100 rads.

(iii) Optical transfer is not the way to measure them. The residual is 3 orders of magnitude too large for the 'natural' method. This appears to be a fundamental limitation arising from the impurity of the crystals. The sensitivity is also low, though that may not be a fundamental limitation.

Acknowledgement

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REDUCTION OF SPURIOUS TL IN ATMOSPHERES

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It is well-known that the so-called "Spurious TL" component of a glow curve can be reduced by heating samples in inert atmospheres having very low oxygen and moisture concentrations. The exact reasons for this have so far defied detailed explanation but it is quite clear that the lower the oxygen content of the gas in the TL system, the less likely is spurious TL to occur (see e.g. Sutton and Zimmerman, 1977). This suggests that some further improvement might be achieved with the use of chemically reducing atmospheres. Additionally, as an economic factor, the need for the use of high-purity gases might be avoided, or at least one might be able to tolerate a somewhat greater oxygen content in the gas used. A range of samples of archaeological and geological interest has been tested in a mixture of 5% hydrogen plus 95% nitrogen. (Manufacturer's specifications state: less than 10 ppm oxygen, less than 25 ppm moisture). Comparison was made with commercial high purity argon (less than 6 ppm oxygen, 12 ppm water). The samples tested included aboriginal hearthstones, baked clay, apatite, calcite, fluorite, zircon, pottery samples, various quartzes, as well as a variety of TLD phosphors. No great improvement was noted but in no case was the result worse than that obtained with the high purity argon. A mixture of 10% methane plus 90% argon, called P-10 and commonly used for filling gas counters (15 ppm oxygen 25 ppm moisture) did not give improved performance for any sample.