Normalization of inclusion size quartz TL data

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A series of experiments is reported on TL observed with quartz inclusion size grains (~100 μm diameter). The relative standard deviation of the peak height of the Slowly Bleaching Peak (SBP) varies inversely as the square root of the sample weight. The rate of this variation indicates that only about 8% of the grains produces the observed TL. Little correlation was found among peak heights for the 70 °C, SBP, and the Rapidly Bleaching Peak (RBP) for first or subsequent glow cycles. These results indicate that normalization of TL data in large quartz grains by reference to any of these three peaks results in at least as large scatter as does weight normalization alone. However, a drastic HF treatment was found to strongly reduce the scatter in the TL data peak heights. Weight normalization, perhaps using some variant of this effect, with as large specimens as possible seems the best course for obtaining reliable data from inclusion size grains.

Introduction

The TL data from 100 μm quartz particles, when normalized by weight, exhibits large run-to-run scatter for aliquots from the same sample. This appears to reflect the fact that only a few of the particles in the aliquot produce most of the TL (Benko, 1983; Huntley and Kirkey, 1985; Spooner et al., 1988). This scatter represents a significant limitation on the precision obtainable in TL dating using the inclusion method (Fleming, 1979), employing 100 μm particles. In this paper we present statistical evidence for this bright/dark model, with only a small percentage of bright particles among a majority of dark ones, and then examine several possible normalization methods for improving the precision of measurements of TL intensity. These include weight normalization combined with chemical reduction of particle size and normalization not by weight but by reference to the TL intensity of various TL peaks generated by standardized beta doses (e.g. zero glow monitoring, Aitken et al., 1979).

Experimental conditions

All material used for the experiments reported here was derived from a Middle Stone Age site in the Northwest Kalahari desert. Unless otherwise noted, all were treated with 3 N HCl to remove carbonates, 30% H_2O_2 to remove organics, and unstirred 48% HF at room temperature for 30 minutes followed by 3N HCl to remove alkali feldspars. The resulting powder was sieved and the 90-150 μmportion was fractionated by density using a sodium polytungstate solution of density 2.70 g/cm^3 and centrifuging. The light fraction was retained for these experiments. The natural TL of these materials exhibits two major peaks, one at 275 °C and one at 310-330 °C (depending on filter used) for a ramp rate of 1 °C/s. These peaks can be identified with the 325 °C and 375 °C peaks reported in the literature at heating rates of 20 °C/s. The 275 °C peak is rapidly removed by bleaching with a solar simulator, and is designated here the Rapidly Bleaching Peak (RBP). The 310-330 °C peak is much more resistant to bleaching and is designated the Slowly Bleaching Peak (SBP). Complete removal of the RBP without affecting the SBP was accomplished by bleaching with the solar simulator with a Schott VG-9 (green) filter for 4 hours. The TL data were measured using a Chance HA-3 filter plus a Corning 7-59, a Schott UG-11, or a Schott VG-9 filter with an EMI-9635Q phototube operated in the single photon counting mode. The data were collected and processed digitally. All data quoted, except as noted, are counts/(°C·mg) at the maxima of various TL peaks, averaged over at least 6 aliquots.

Statistical Effects of Bright/Dark Model

Under the simplifying assumption of just two kinds of otherwise identical particles, bright and dark, the TL per unit weight (weight-normalized) should conform to a binomial distribution. Let n be the total number of grains of density 2.65 g/cm^3 in the aliquot, w the weight in mg, and p the probability that a given grain is bright. Provided that np≥5, the ratio s' of the standard deviation of the mean of the distribution relative to the mean for monodisperse quartz spheres of 100 μm diameter is given by (e.g. Li, 1957):

$$s' = 1/\sqrt{\{720w(p-1)\}}$$

Figure 1 displays a plot of s' vs. $1/\sqrt{w}$ for the SBP. A least- squares fit through the origin produced a value of $p \approx 0.08$, confirming the statistical origin of the scatter and suggesting 1 bright grain in about 10 or less. That the scatter is not instrumental was shown by exposing a similar aliquot preheated (to 500 °C) in the TL apparatus without disturbing it to 5 repeated cycles composed of an accurately reproducible Sr-90 beta dose of about 27 Gy and a TL glow run to 500 °C. The peak intensity at

about 285 °C increased about 10% in the course of these runs, approximately linearly with run number. This rise appears to reflect a small predose effect. The relative standard deviation of these data about a least squares fit to the linear increase was about 1.5%, not really different from the counting statistics value of 1.3%.

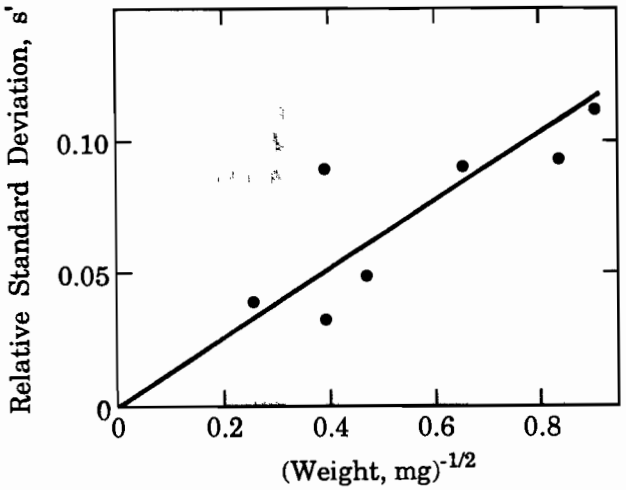

Figure 1.
Relative standard deviation (of the mean) of replicate measurements of the height of the weight-normalized Slowly Bleaching TL peak from Kalahari sample KA9-1 vs the inverse square sample weight. No laboratory doses were given, but the specimens had been exposed to the solar simulator for 30 minutes.

Chemical Reduction in Particle Size

The bright/dark model suggests that improvement in precision could be made by increasing the absolute number of bright particles per aliquot. As in the experiment quoted above, this can be done by simply increasing the aliquot weight. The relative standard deviation for a single measurement fell from a high of about 30% for 1 mg aliquots to a value as low as 10% for aliquots of 15 mg. With increasing size of the aliquot, however, goes the risk of particle pile-up.

Rather than simply increasing sample weight, the scatter might also be reduced by maintaining the weight and reducing the size of the particles making up the aliquot. Starting with a sample of the 90-150 μm fraction from "natural" material (ie without added laboratory dose) we experimented with reducing the size with a drastic HF etch, 90 minutes at 70 °C. X-ray diffraction revealed an excellent quartz pattern and nothing else. The powder remaining from the HF treatment, after washing and drying, was again sieved. New fractions were obtained from 90-150 μm (i.e. not much reduction in size) to <45 μm (i.e. drastic reduction in size). There was a small drop in intensity of the SBP with decreasing new particle size. This drop was reproduced in two separate experiments but was statistically significant only for the new <45 μm fraction.

Much more significant was an effect on the sensitivity of the 70 °C peak to a small beta dose applied before the TL run but after the etching. Because the severe HF treatment involves prolonged heating at 70 °C, a large increase in sensitivity observed for the new 90-150 μm fraction over that for the untreated material may simply reflect a pre-dose effect. However there was a drop by a factor of 3 in the sensitivity in the treated material from the new 90-150 μm to the new <45 μm fraction. The material not removed by the HF appears to possess a lower sensitivity than that removed.

The HF treatment has the desired effect of strongly reducing the run-to-run scatter when the new <45 μm fraction is compared to the untreated material. table I sets forth the percentage standard deviations for a single aliquot from measurements involving 10 aliquots for each condition.

The changes in scatter for the SBP peak are mirrored by somewhat similar changes in the scatter of the 70 °C peak. Surprisingly, the big increase in precision occurs simply with the HF treatment without a substantial reduction in particle size. Since the majority of the treated powder lies in the 90-150 μm range, the practical conclusion is that use of the drastic HF treatment to reduce scatter in the data may be worthwhile for dating with inclusion-size particles, but not because of particle-size reduction.

Zero-Glow Normalization (Normalization with the 70 °C Peak)

An alternative to weight normalization is some variant of the zero-glow technique (Aitken et al., 1979) in which a standard test dose is used to create a TL peak at 70 °C whose intensity, a measure of the amount of sensitive material in the specimen, may be used to normalize the experimental glow curve.

In its original form a low-temperature peak was excited by a small in-situ ß dose prior to running the glow curve. In quartz, in our measurements at a ramp speed of 1 °C/s, the peak at 70 °C was used. This peak represents emission at 370 nm and appeared strongly with the Corning 7-59 blue filter or even the Schott UG-11 ultraviolet filter. Several similar experiments were performed, in which the counts/second at the peak maximum (peak height) for up to 15 replicate specimens were measured and the standard deviations (s') as a percentage of the mean peak height determined. Such measurements were made for the 70 °C peak and the SBP and also for their ratio, and are shown in table 2.

Table 1. Percentage Standard Deviation of a Single Aliquot

Material	Yield (%)*	s' (%)		
		SBP	70 °C	SBP/70°C Ratio
Untreated, 90-150 μm		41	23	27
HF-Treated, 90-150 μm	74	13	11	19
HF-Treated, 45-90 μm	25	18	15	13
HF-Treated, <45 μm	1	7	11	6

*"Yield" denotes the weight percent in the various fractions produced by sieving after the HF treatment.

Table 2. Relative Standard Deviations

No. Replicated	70 °C Peak, s'(1)	SBP, s' (2)	Ratio, s'(r)
14	15.1	10.1	15.9
10	11.5	16.7	14.9
15	21.2	11.4	10.8
15	15.4	18.4	12.2

If the two peaks are totally uncorrelated s' of the ratio should be given by

$$s'(r) = \sqrt{\{[s'(2)]^2 + [s'(2)]^2\}}$$

where s'(1) and s'(2) are the standard deviations of the two peaks.

If the peaks are completely correlated s'(r) should be small, reflecting only counting statistics. The experimental values of s'(r) lay between these two extremes (col. 5, table 1; col. 4, table 2), indicating some but by no means total correlation. A number of factors might contribute to the partial independence of the scatter in the two peak intensities, which we may classify as either instrumental or aliquot factors.

Instrumental factors include uncertainty in the beta dose arising from the shutter on the beta-source and variation in particle position due to motion during the run, variation in the time of waiting between the end of the beta dose and the start of the glowing out, and scatter due to counting statistics. Aliquot factors can arise because the sources of luminescence (the electron/hole traps and recombination/luminescence centers) are not the same for the two peaks and might be distributed differently among the grains of the aliquot being measured. The same grains would not necessarily be bright for the two peaks. This reasoning extends also to the pre-dose effect, which involves "reservoir" traps that also are probably not distributed uniformly across the grains. We must assume that changes in sensitivity triggered by heating the material during the TL measurement can also vary from grain to grain. Included with the aliquot factors is the effect of the distribution of the grains of the powder during measurement on the measured TL intensity because of pile-up and on the effective beta dose because of pile-up and changes in back-scattering. The instrumental factors were assessed in several experiments in which the same aliquot was left in place and repeatedly given a small beta dose and then glowed out to some maximum temperature, both the 70 °C and the SBP peaks being measured in separate experiments. There was a steady decrease in the 70 °C peak height, apparently linear in run number, for glow curves carried only to 150 °C. About the least squares line fitted to these numbers there was a scatter yielding a relative standard deviation of only 2.3%, very little different from the counting statistics value of 1.5%. For the SBP data peak, cycled to 500 °C, there was a small increase in intensity with run number, again approximately linear. The scatter about the least-squares line was 1.5%, again essentially all accounted for by counting statistics (1.3%). This experiment shows that of the instrumental errors, only the statistical counting error has much significance, but this makes only a small contribution to the observed scatter in peak intensities.

There are two major contributions to the aliquot error. One is inherent in the material itself, the variation in brightness of the grains of the aliquot, with the

possibility that different grains are bright for different TL peaks. The other contribution may arise from variations in the arrangement of the grains in the bowl. Because of entrained H_2O the arrangement of the grains can be altered, particularly during the first glow curve run. During subsequent runs with an otherwise undisturbed aliquot no further changes in arrangement should occur. Thus examining ratios of peaks from second and, especially, third glow curves should eliminate effects due to motion of the grains which might occur during the first glow curve run. Table 3 below summarizes the results of two such experiments. The same aliquot was left in place and given 3 cycles each consisting of a small beta dose followed by glowing out to the maximum temperature shown, the TL peaks being recorded in the process. A number of aliquots were treated in this way and the aliquot to aliquot scatter in peak heights and ratios examined.

With a maximum temperature of only 125 °C the 70 °C peak heights from successive cycles on the same aliquot are well correlated. The scatter in the ratios, however, is considerably larger than can be accounted for by counting statistics (~1.7% for the ratios). The scatter increases markedly when the maximum temperature in each cycle is raised to 500 °C, but is much more apparent between the first and second cycles. Some source of scatter is introduced by the heating, is greatest in the first heating, and increases with increasing maximum temperature.

The mean peak intensity values for the three cycles (7000, 6720, 6770 counts/(°C·mg) give no evidence at all for a pre-dose effect stimulated by the 125 °C heating cycles. Variation in the predose effect can probably be ruled out as a source of the aliquot to aliquot excess scatter over counting statistics evident for a maximum temperature of 125 °C in table 3.

For the experiment in which the maximum temperature was 500 °C the mean peak intensities averaged over the aliquots for the 3 cycles were 7550, 29622 and 33464 counts/(°C·mg). There is strong evidence here for a predose effect stimulated by the temperature cycling to 500 °C. Most of the predose increase in sensitivity takes place as a result of the first cycle. This pattern, on the assumption that the predose effect varies from grain to grain, can account for the increase in scatter in the ratios for the 500 °C cycles relative to the 125 °C cycles, and accords with the observation that the increase in scatter is markedly less for the ratio I_2/I_3 than for the other two. The same effects are seen in the product-moment correlation coefficients. These results show that the 70 °C peak during the first glow run exhibits considerable scatter, in the range 10-20%, arising from the statistical uncertainty in the number of grains in the aliquot that are bright in this peak. For cycles to 500 °C the intensities of the second and third glow peaks do not correlate well with that of the first glow peak, primarily because of a predose effect varying from grain to grain in a way similar to, but not well correlated with, the brightness for the 70 °C peak. The second and third glow peak intensities correlate with each other somewhat better than either does with the intensity of the first glow peak.

When trying to use the 70 °C peak to normalize the experimental values of intensity in the SBP and RBP (data) peaks, a further complication is possible in that the distribution of brightness among the grains may be different for the 70 °C and data peaks. Table 4 examines the relation between the natural RBP' observed in the first glow cycles and the 70 °C peak generated by a small test dose, for 3 cycles with 500 °C maximum temperature. RBP' is primed to indicate that the observed peak is actually the RBP and SBP superimposed, in about equal proportions, as seen in natural material using a combination of HA-3 and UG-11 filters. This is the same experimental sequence shown under T_{max} = 500 °C in table 3. There is no correlation between the RBP' and the 70 °C peak from any of the cycles.

Table 3. Relative Standard Deviations of 70 °C Peak Heights and Ratios

		Cycle Number			Ratio for Cycles Shown		
T Max		1	2	3	1/2	1/3	2/3
125 °C	s',%	16.4	14.6	17.5	3.9	4.9	5.6
	r				0.972	0.966	0.948
500 °C	s',%	16.6	23.1	18.5	11.3	11.4	6.8
	r				0.854	0.818	0.961

s' = relative standard deviation; r = product-moment correlation coefficient

Second Glow Normalization

By Second Glow Normalization we mean using the data peak generated in a second glow cycle to normalize the same peak observed in the first cycle. Here we made TL measurements using a combination of a Schott VG-9 (green) with a Chance HA-3 filter. There is almost no contribution to these data from the RBP, the measured TL exhibiting essentially only the SBP. A large beta dose was administered at the beginning of the second glow cycle in order to generate a reasonably intense SBP(2). No measurement could be made of the 70 °C(2) peak, which was strong enough to saturate the PM tube. Eight replicates were measured, with the sequence first glow, beta dose, second glow without disturbing the specimen. To eliminate small run to run variations in temperature, the first glow data were shifted along the temperature axis to make each TL peak coincide with one member of the set as standard (Franklin et al., 1987). The second glow data were similarly temperature shifted using the second glow TL peak of the same member of the replicate set as a standard. Averages over all replicates were then obtained for both the first and second glow data. The ratio of the first to the second glow averages produced a reasonable plateau from 230 °C to 300 °C.

With this plateau defining the temperature range we then examined the mean and standard deviation of the counts/(°C·mg) for the first glow and second glow data and their ratio over the replicates at 10 °C intervals. The results are shown in table 5. The first and second glow peaks exhibit only partial correlation, the relative standard deviation of their ratio amounting to more than half what it would be if they were statistically independent (compare last two columns of table 5).

Indeed, the scatter in the ratios is greater than the scatter in the weight-normalized first glow data (compare columns 3 and 5). Product moment correlation coefficients for these selected temperatures ranged from 0.328 to 0.750.

Conclusions

We conclude that most of the scatter in the 70 °C peak, RBP, and SBP in 100 μm quartz aliquots arises from differential grain brightness and that this distribution in brightness among the grains of an aliquot is not the same for any of the three peaks. Furthermore, when several glow cycles to 500 °C are repeated on the same aliquot the response to the predose effect is distributed among the grains in still a fourth way, so that even the ratios of the 70 °C peaks from two glow cycles exhibit considerable scatter. This is particularly true for ratios involving the 70 °C peak from the first glow curve.

It follows that in general normalization of the data peaks

Table 4. Relative Standard Deviations of RBP' and 70 °C Peak and Their Ratios

Glow Cycle		1		2	3			
Peak		70 °C	RBP'	70 °C	70 °C	RBP'(1)/70(1)	RBP'(1)/70(2)	RBP'(1)/70(3)
s',%		16.6	13.1	23.1	18.5	19.3	21.7	23.7
r						0.098	-0.109	-0.355

Table 5. Relative standard deviations of SBP peaks and their ratios

Temp.	Glow Cycle Peak	1 SBP(1)	2 SBP(2)	Ratio SBP(1)/SBP(2)	$\sqrt{SBP(1)^2+SBP(2)^2}$
230	s',%	23.0	44.4	25.0	50.1
240	s',%	20.4	40.5	23.9	45.4
250	s',%	18.5	38.3	25.2	42.5
260	s',%	17.6	37.0	27.3	41.0
270	s',%	18.3	36.7	31.0	41.0
280*	s',%	18.0	35.9	31.9	40.2
290	s',%	18.5	35.0	29.7	39.6
300	s',%	19.1	42.0	28.4	46.1

from 100 μm particles using the 70 °C peak from any glow cycle offers no improvements over, and mostly less precision than, weight normalization. There appears to be little correlation between the RBP' and the SBP. Since the RBP' is a superposition of the RBP and the SBP this suggests these two also involve different bright grains and the RBP' cannot be used to normalize the SBP and vice versa. Finally, even the SBP observed during a second glow cycle does not correlate very well with the SBP from the first cycle. The SBP cannot be used to normalize itself with second glow normalization.

It appears that weight normalization, perhaps using large specimens, or some form of the drastic HF treatment, produces the most satisfactory TL data with "inclusion" size particles. These experiments were carried out using quartz from a single source but the characteristics involved seem so general that the conclusions probably apply to any "inclusion" size quartz powders derived from natural sediments.

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References

Aitken, M. J., Bussel, G.D., and Driver, H.S.T. (1979), Zero- glow monitoring, *Ancient TL* **9**, 13-15.

Benkö, L. (1983), TL properties of individual quartz grains, *European PACT* **9**, 175-181.

Fleming, S. J. (1979), *Thermoluminescence techniques in archaeology*, Clarendon Press, Oxford.

Franklin, A. D., Hornyak, W. F., and Tschirgi, A. (1987), Experimental TL techniques for the inclusion method, *Ancient TL* **5(3)**, 9-10.

Huntley, D. J., and Kirkey, J. J. (1985), The use of an image intensifier to study the TL intensity variability of individual grains, *Ancient TL* **3(2)**, 1-4.

Li, J. C. R. (1957), *Introduction to Statistical Inference*, Edw. Brothers Inc., Ann Arbor, MI, p. 396.

Spooner, N. A., Prescott, J. R., and Hutton, J. J. (1988), The effect of illumination wavelength on the bleaching of the thermoluminescence (TL) of quartz, *Quaternary Science Reviews* **7**, 325-329.

PR Reviewer's Comments (John R. Prescott)

Although photoluminescence dating techniques are becoming increasingly used, there is still considerable scope for traditional TL. There is therefore a place for studies aimed at improving the precision of TL and this is such a study. The conclusions are somewhat disappointing, at least to the extent that none of the normalization procedures based on TL itself seem to work. This reviewer can add the result of our experience with "self" - normalization of the RPB peak itself. This is successful: with a standard calibration dose of 7 Gy, administered after the first series of glows, and with due allowance for pre-dose sensitization of this dose, the relative standard deviation is typically improved from 5-7% to 3-5%. It may seem like a trivial matter, but mass normalization is unecessary if all disks are prepared with the same mass. The extra work involved is not onerous.