Ancient TL

www.ancienttl.org · ISSN: 2693-0935

Kaylor, R., Feathers, J., Gottfried, M., Hornyak, W. and Franklin, A., 1993. *Important date/ strange material.* Ancient TL 11(2): 40-44. https://doi.org/10.26034/la.atl.1993.212

Important date/strange material

R. Kaylor, J. Feathers, M. Gottfried, W. F. Hornyak and A. D. Franklin
Physics Department, University of Maryland, College Park, MD 20742 USA

Introduction

A few years ago a beautifully crafted, fossilised bone harpoon point was uncovered at Katanda near the Semliki River in Zaire (Fig.1). Two more whole points and fragments of five others, as well as an equally well crafted dagger like tool were also found in the same stratum. An abundance of large catfish bones was also present at the site. While in workmanship these specimens are not unlike those found at the very end of the Upper Palaeolithic, about 14,000 BP, geological evidence based on the site stratigraphy suggested a far older age, perhaps as old as 100,000 years. Archaeologists Alison Brooks and John Yellen, discoverers of these objects (Shreeve, 1992), aware of the requirements for TL and OSL dating procured samples of the sediments in the immediate vicinity of the specimens, collecting them excluding daylight exposure.

Procedure

Samples were prepared by defloculation followed by sieving, retaining the fraction 95 - 125 μm in diameter. The resulting material was reacted with 2:1 concentrated HC1:H_2O for 15 mins at 70°C to dissolve carbonates and iron oxides that were found to be present. In order to obtain a pure quartz fraction an etch in full 48% concentrated HF was applied for 40 min at 70°C. The resulting material was again sieved, retaining the >90 μm fraction and then density separated first with a ρ = 2.708 g/cm^3 liquid, taking the light fraction and followed by using a ρ = 2.621 g/cm^3 liquid, keeping the heavy fraction.

In spite of these measures, scanning electron microscopy, including x-ray studies, still showed some quartz grains with strongly adhering micro crystals. A wide field scan of about 250 grains confirmed that by weight the material was predominantly quartz. However, x-rays from selected small attached micro crystals indicated the presence of minerals with atomic compositions (ordered by line strength); (Si, Mg, Al), (Si, Mg, Al, Ca), (Si, Ca, Cl), (Si, Mg, Al, Ca, Cl), and even (Si, W). These results are to be contrasted to those for the relatively very pure quartz grains found in the Kalahari sand dunes (Hornyak, et al., 1992). In that case the number of grains with bonded micro crystals was considerably fewer. Their principal atomic composition found in x-ray analysis was (Si, Mg, Al, Fe) and (Si, Al, K, Na). It is not evident what these differences for the two materials would have on the TL and OSL characteristics.

The first TL technique utilised to arrive at a palaeodose for the Katanda material was to use a slowly bleaching signal. This signal was isolated by a light bleach of 10 min at 550 nm (using a 100W halogen lamp with suitable filters yielding an illumination rate of 23 mW/cm^2).

All observation of luminescence was in the UV using a Schott UG11 filter in combination with a Chance HA3 filter and an EMI 9635Q photo tube. Figure 2(a) shows the glow curve for the Katanda natural dose sample, and in Fig.2(b), the glow curve for the Kalahari natural dose sample multiplied by a normalisation factor of 2.5, and Fig.2(c) the difference (a) - (b). All these glow signals are slowly bleaching. A small admixture of peak (c) in the Kalahari data near the region A may be present. In both materials the glow peak component (b) is identified with the well known "375°C" SBP, studied extensively (Hornyak, 1992). At a heating rate of 1°C/s this peak appears at 331°C with green emission and at 312°C with UV emission. It was found that the slight anomaly at A in peak (b) if indeed due to the presence of peak (c) appeared to be a very weak contribution at all doses, in contrast to the Katanda material where peak (c) was a prominent dose dependent signal. This leaves the attribution of peak (c) to quartz uncertain, therefore only

the area in the temperature range R (320-380°C) was used to define a unique quartz signal. In view of the fact that the SBP at "375°C" behaves as if it were approximately obeying second order kinetics, all glow curves were height normalised and temperature shifted to bring the region defined by R into coincidence.

Dose growth curves for TL were obtained for the Katanda material using a convenient (Sr-90,Y-90) ß-source which was calibrated against a standard Co-60 source. After each beta dose a 5 min. preheat at 170°C was done followed by the application of the above 550 nm bleach. This procedure was followed for obtaining both the additive dose growth curve (N+ß) and the regenerative dose curve, this latter obtained as described above after a 16 h bleach with the solar simulator.

After noting that the two data sets appeared to closely define a common saturating exponential behaviour, it was assumed both sets of data represented a constant dosimeter sensitivity. The cautionary note by Smith et al. (1990) that the ED from an N + ß determination did not appear to be operating here. Melding the two curves has the advantage of giving a consistent ED even taking into account the presence of the unbleachable residual signal. A saturating exponential fitting routine was used to simultaneously fit both the regenerative data points as well as the additive dose data points which were shifted in dose by constant trial dose. This was repeated for various shifting trial doses and in each case obtaining the variance generated by the fitting program. The dose shift for the lowest obtained variance was taken to be the palaeodose. Figure 3 shows the results for this optimal fit. The insert in Fig.3 shows the variance of the fit as a function of the trial dose. The resulting value of the palaeodose is 170 Gy.

The same procedure was applied to the Kalahari material, including selecting the same temperature region R for the data sets. Again, a very satisfactory melding together of the additive dose and regenerative dose data sets was possible. To a surprising extent these unified dose growth curves for the Katanda and Kalahari data matched each other as well as the additive dose curve obtained for the Kalahari material observed in the green emission when it is properly normalised. For example, the ratio for the observed TL signal at a dose of 170 Gy (the Katanda palaeodose) to that for a dose of 35 Gy (the Kalahari palaeodose) is just 2.5, the normalisation value needed in Fig. 2 to obtain the subtracted result 2(c). The success for using a single saturating exponential to fit the melded data taken in temperature range R is probably due to the exclusion of peak (c).

The strange luminescence behaviour of the material immediately became evident when TL signals based on the rapidly bleaching peak (RBP) was measured in order to establish an additive dose growth curve (N + ß). The RBP at each dose was generated by subtracting the glow curve obtained for the SBP as described earlier, from glow curves without the 10 min, 550 nm bleach (Franklin and Hornyak, 1990). The scatter in the data even after measuring many aliquots was considerable. Similar poor results were obtained for the TL regenerative dose curve using this subtraction method following a 16 h solar simulator bleach.

Figure 1.
Fossilised bone harpoon found at Katanda, Zaire.

Equivalent RBP additive dosing and regeneration dosing information was sought using the single aliquot OSL technique (Duller, 1991). The results are shown in Fig.4 both for the additive dose curve (a) and the regeneration dose curve (b). The behaviour shown for both curves is identical with the TL subtraction data set, only in this instance with virtually no scatter in the data points. Every ß-dose was followed by a preheat of 5 min., at 170°C. The OSL signal followed was for a 5 min., 550 nm exposure and observation of the luminescence was in the UV. A natural dose aliquot was given a repeated sequence of preheats and OSL reads to obtain a measure of the OSL signal loss during the entire experimental run. Ten repeated sequences gave a loss function

$$1.018 \exp(-1.797 \times 10^{-2} n)$$

where n is sequence number (n = 0 is not defined). The resulting correlation coefficient for this exponential fit is 0.9973. The data shown in Fig.4 have been corrected for this loss.

The anomalous minimum in the OSL additive dose growth curve shown in Fig.4(a), suggesting the presence of some unknown type of dose induced fading is also present in the RBP TL data based on the subtraction technique. Attempts to combine curves (a) and (b) for added doses above ~120 Gy, where a rise towards saturation is evident, in the manner that led to the Fig.2 results were unsuccessful. However, the regeneration dose corresponding to the natural OSL signal (intersection produced by line AA') yields a palaeodose of 192 Gy. It should be noted that the natural OSL signal does not properly belong in the remainder of the additive dose set. If any radiation-induced fading is involved in the procedure used, this datum point is not affected as of course would be the case with the rest of the data set.

A third method to obtain the palaeodose was using single aliquot OSL regeneration of the isothermal luminescence decay under continued illumination with 550 nm light. The procedure was to follow each dose with a 5 min, 170°C preheat, a recorded OSL luminescence decay for 300 s and a continued bleach up to 1200 s. It had been determined using the natural material that a 1200 s bleach left less than 1 percent of the original OSL signal. Decay curves were obtained for a range of regeneration doses spanning the results for the natural material. At 5 s intervals of the decay curves the regenerated dose corresponding to the natural material was determined. The results are plotted in Fig.5. The apparent decrease to an asymptotic limit at long times was simulated by a decreasing exponential function plus a constant using a computer program fitting routine. Various trial constant doses were tried with corresponding best fitting exponentials. The correlation coefficient for the fit as a function of the constant trial dose is shown in the insert of Fig. 5. The highest correlation coefficient occurred with a trial dose assumed to be equal to the palaeodose of 185 Gy.

The reason for employing the asymptotic value to represent the palaeodose is exhibited in Fig. 6. The data set labelled N is for the natural state, the set labelled ß is for a ß-dose of 185 Gy. It was found by superposing all the various ß-dose data that a fairly constant decay function shape resulted such as that shown for the set labelled ß. However, the data for the natural state shows a considerably larger rapidly decaying component to be present. This accounts for the larger palaeodose results for the earlier time slices. Fig. 6 also shows that for longer times into the decay a more all inclusive shape

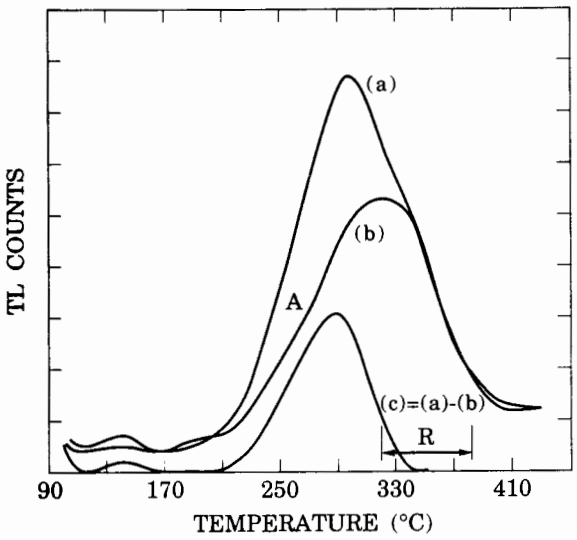

Figure 2.
Glow curves for the slowly bleaching signal observed in the UV at a heating rate of 1°C/s. (a) Katanda natural dose (about 175 Gy); (b) Kalahari natural dose (about 35 Gy) x 2.5; and (c) the result (a) - (b). The region spanned by the temperature range R was used to calculate the dose rate growth curves.

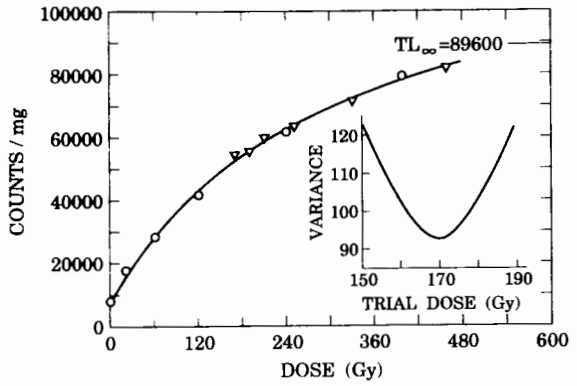

Figure 3.
The result of melding the TL additive dose growth data (triangles) and the regenerative dose growth data (open circles) for the SBP in temperature range R, when the former points are shifted by an optimal trial dose. The insert shows the variance in an overall saturating exponential computer program fit as a function of the trial dose. All data points are for 10 weight normalised aliquots. The resulting palaeodose is 170 Gy.

develops. Unfortunately using this region of time slices substantially increases the statistical uncertainties, and hence the resort to the adopted procedure.

A radioactivity assay of 15 g of sample material was measured using a large volume and a thin intrinsic Ge γ–ray detector. Over 20 γ-ray line strengths obtained spanning the entire radioactive Th and U chain of elements were directly compared with those from National Bureau of Standards certified pitchblende-sand and monazite-sands standards. No decay chain disequilibrium was detected. The assay results were Th-232, 4.11±0.07 ppm; U-238, 0.76±0.02 ppm; and K-40, 1.49±0.02 ppm.

Weight loss measurements were conducted for etching with 48% concentrated HF at 70°C as a function of etch time for pure Kalahari quartz sand (90 - 125 μm diam.) believing that the major luminescence was produced by the quartz component in the Katanda material. This measurement gave an equivalent etch depth of 6 μm for 40 min of etch time. Using the estimations of the α and ß-ray reduction in irradiation effectiveness produced by the etch loss as contrasted to that for γ-rays given by Fleming, 1979, leads to a dose rate of 2.08±0.01 Gy/ka at a confidence level of 95%.

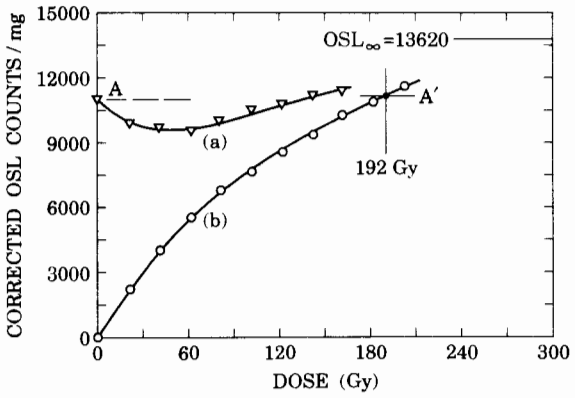

Figure 4.
(a) The single aliquot OSL result for the additive dose growth data and (b) the result for the regenerative dose growth data. The data sets for the two separate aliquots used are weight normalised. The standard procedure for determining the palaeodose is also shown, resulting in a value of 192 Gy.

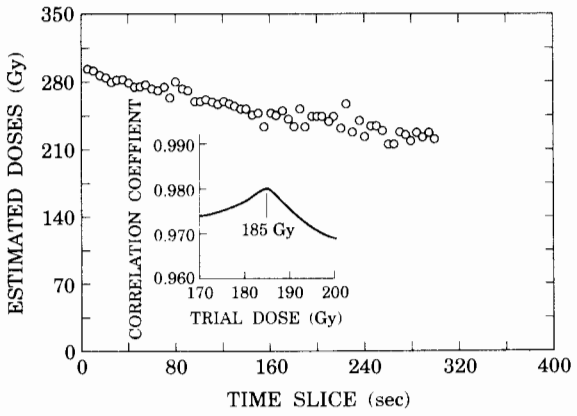

Figure 5.
The result for the time slice determination of the palaeodose from 17°C isothermal decay data obtained under continual illumination with 550 nm light using a single aliquot. A fit to this data was performed using a program with a decaying exponential plus a trial asymptotic constant combination. The insert shows the correlation coefficient to the program fit as a function of the trial constant. The optimum fit occurs for a palaeodose of 185 Gy.

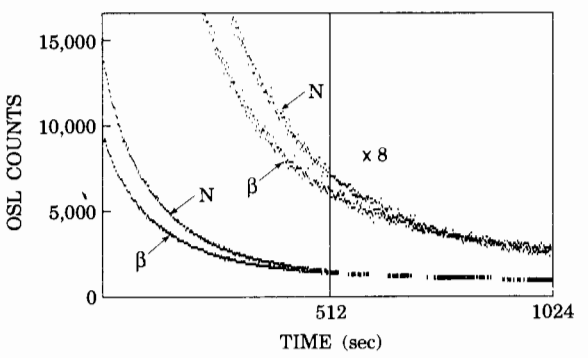

Figure 6.
The family of isothermal decay curves used in Fig.3 all have very similar shapes to that labelled ß, which is reproduced for a dose of 185 Gy. The decay curve for the natural sample labelled N is uniquely different showing an additional rapidly bleaching component. The two sets appear to merge at longer bleach times suggesting a common asymptotic limit. Background counts in these runs are less than 100 per channel.

Conclusions

The palaeodose for the quartz component of the Katanda material is only taken from the SBP results to be 170±10 Gy. In this instance the quoted error is in the nature of a limit of error based solely on the methodology used in the data analysis. Combining this palaeodose with the above value for the dose rate gives an age of 82±8 ka. Due to the uncertainties in the dosemeter material behaviour the quoted error is perhaps no better than a "standard deviation". Particularly uncertain is the role played by the non quartz-like contaminants in the TL and OSL responses. In spite of these problems the two OSL results for signals that may properly be associated with quartz give some supportive evidence for the more unambiguous quoted palaeodose of 170 Gy particularly when noting that bleaching sensitisation effects may be present in the OSL determinations (Li and Wintle, 1991). It is to be noted that the same RBP and OSL experiments conducted with our pure quartz material from the Kalahari did not show any of the anomalies observed with the Katanda material.

Tentative results using ESR dating of a hippopotamus tooth found in the same stratum as the harpoon tips has yielded a possible age ranging between 60 and 110 ka (Henry Schwarcz, private communication).

In any event, the barbed harpoon tips are in fact much older than might have been expected from a comparison with other dated archaeological objects of similar sophistication.

Acknowledgements

The material used in this research was provided by Alison Brooks and John Yellen (see postscript) who also provided much information on the stratigraphy of the archaeological site and the disposition of the objects and the surrounding matrix. We are also indebted to Scott Treude for assisting with some data taking. We wish to acknowledge the NSF support of this project under contract #BNS-9107652.

References

Duller, G. A. T. (1991) Equivalent dose determination using single aliquots, *Nucl. Tracks Radiat. Meas.* **18(4)**, 371-378.

Fleming, S. (1979) *Thermoluminescence Techniques in Archaeology,* Clarendon Press, Oxford.

Franklin, A. D. and Hornyak, W. F. (1990) Isolation of the rapidly bleaching peak in quartz TL glow curves, *Ancient TL* **8**, 29-31.

Hornyak, W. F. et al. (1992) Thermoluminescence characteristics of the 375°C electron trap in quartz, *Phys Rev B* **46(13)**, 8036-8049.

Li, S-H and Wintle, A. G. (1991) Sensitivity changes of luminescence signals from colluvial sediments after different bleaching procedures, *Ancient TL* **9(3)**, 50-53.

Shreeve, J. (1992) The dating game, *Discover* **13(9)**, 76-83.

Smith, B. W. et al. (1990) Optical dating of sediments: initial quartz results from Oxford, *Archaeometry* **32(1)**, 19-31.

PR S.W.S. McKeever

The unusual behaviour of the optically sensitive signals from this material (i.e. the RBP TL peak and the OSL signals) are a pertinent reminder of the complexity of TL and OSL processes in natural samples. This is especially so since one might look at the benign behaviour of the SBP TL signal and be seduced into thinking that the processes are straightforward and easily understood. The data and discussion clearly indicate that, for the Katanda material, whenever there is a natural component present in either the RBP TL signal (i.e. the additive dose and the continuous OSL decay curves), unusual behaviour is noted. One is tempted to speculate, after examining the glow curves and reading the discussion regarding the incomplete removal of non-quartz components, that the difficulties encountered may be a result of the unwanted admixture of extraneous minerals. If so, one may perhaps have faith in the date produced since the authors have wisely limited their conclusions to what appears to be the quartz only fraction. Arriving at a physical explanation of the observed properties of the optically-sensitive components, however, will have to wait.

Postscript

John Yellen, the anthropologist who found the artefact, has provided the following comment:

This work is important because it sheds light on the question of when and where behaviorally modern humans first appeared. It suggests, in concert with paleontological information, that this transformation took place in sub-Sahara Africa prior to 50,000 years ago.