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Burnt flint artifacts: A new Thermoluminescence dating technique

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SUMMARY - *Burnt flint artifacts: A new Thermoluminescence dating technique* - Establishing chronologies is crucial for Palaeolithic research. The lack of chronometric ages for a given site often makes it difficult to place it within the time frame provided by chronostratigraphy and palaeoclimatology. Thermoluminescence (TL) dating of burnt flint is frequently used to determine the age of Palaeolithic sites. It is a dosimetric dating method, which employs the accumulation of radiation damage in crystal lattices through time. Flint artifacts can be dated by TL methods if they have been heated in a prehistoric fire to about 400 °C. The TL-age estimate refers to the last heating and therefore provides a direct date for a prehistoric event. Sample sizes for standard procedures require pieces of at least 10-15 g. A new TL-dating technique has been developed which uses only a few mg of material, thus reducing the minimum sample size to a few grams only, and allows the chronometric dating of sites which do not provide sample material for standard dating approaches.

RIASSUNTO - *Manufatti in selce bruciata: una nuova tecnica di datazione mediante la termoluminescenza* - Il fatto di stabilire le cronologie è fondamentale per la ricerca su Paleolitico. La mancanza di età cronometriche per un dato sito spesso rende difficile situarlo all'interno della cornice temporale fornita dalla stratigrafia e dalla paleoclimatologia. La datazione mediante la termoluminescenza della selce bruciata viene utilizzata di frequente per determinare l'età dei siti paleolitici. Essa è un metodo di datazione dosimetrica, che si basa sull'accumulazione dei danni provocati dalla radiazione subiti dai reticoli cristallini nel corso del tempo. I manufatti in selce possono essere datati con il metodo TL se sono stati riscaldati in un fuoco preistorico fino a circa 400 °C. L'età TL stimata si riferisce all'ultimo evento di riscaldamento e quindi fornisce una datazione diretta dell'evento preistorico. Le procedure standard necessitano di campioni di almeno 10-15 g, tuttavia è stata sviluppata una nuova tecnica di datazione TL che usa solo pochi milligrammi di materiale, riducendo perciò le dimensioni minime dei campioni a soltanto pochi grammi, e permette la datazione cronometrica di siti che non forniscono materiale campionato per gli approcci di datazione standard.

Key words: thermoluminescence, TL, dating, small samples, burnt flint
Parole chiave: termoluminescenza, TL, datazione, piccolo campioni, pietra bruciata

1. INTRODUCTION

Chronometric dating of Palaeolithic sites, especially beyond the range of radiocarbon (^{14}C) dating, relies to a large extend on dosimetric dating methods, like Electron Spin Resonance (ESR or EPR), Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) dating. Broad agreement is usually obtained especially between TL age determinations and independent methods (e.g. Prescott *et al*. 2007; Dykeman *et al*. 2002). Results from ESR dating of teeth often are considered to be less useful, compared to TL dating of heated flint artifacts, because the latter usually is less dependent on poorly controlled environmental parameters shared by both methods (i.e. external γ-dose from the surrounding sediment of the sample). However, the methods should be considered as complementary, because different sample types are used for dating and in many sites only either of the sample types is available. Both methods require samples of certain sizes, which can not be provided from all sites. Especially the size/weight requirements of 10-15 g for standard TL dating are frequently not met, and the respective site(s) can not be dated by TL, or not at all, if no other material for another dating technique is available either (e.g. Richter *et al*. 2000a).

2. THERMOLUMINESCENCE (TL) DATING

Thermoluminescence dating of a heated flint (or chert, hornstone, quartzite, etc.; the term flint is used here as a general descriptor of material composed of SiO2 with a low crystallinity index) determines the time elapsed since the last incidence of firing, which is usually associated with prehistoric activities. Naturally occurring fires are unlikely to be responsible for the heating of material in the vast majority of Palaeolithic sites (see also Alperson-Afil *et al*. 2007). In any case, the penetration depth of fire in sediment is very low (Bellomo 1993) and burning roots do not produce high temperatures. It is thus unlikely that artifacts were heated by natural fires to an extend required for successful TL-dating application in most cases.

3. PRINCIPLE OF THERMOLUMINESCENCE DATING

Dosimetric dating methods are based on structural damages/faults in the crystal lattice of minerals and an omnipresent ionizing radiation from radioactive elements from the surrounding sediment and the sample itself, as well as secondary cosmic rays. This causes a radiation dose (palaeodose or P) to accumulate in the crystal in the form of electrons in excited states. For dating application only those electrons in metastable states are targeted, which are resident over periods of time several magnitudes longer then the anticipated age. Descriptions of the principles of luminescence dating methods can be found elsewhere (Aitken 1985, 1998; Wagner 1998; Bøtter-Jensen *et al*. 2003).

The palaeodose (P) is proportional to the dose rate ($\dot{D}$ the ionizing radiation per time unit), which provides the clock for the dating application. Exposure to light or temperature causes the electrons to relax to a ground state, sometimes by emitting a photon, the luminescence. If the temperature is high enough (> ~400°C) the drainage is sufficient to relax all electrons relevant to the luminescence method used, i.e. the clock is set to zero by this event. The completeness of the resetting of the TL-signal used for dating is checked for with the "heating plateau" test in the case of heated flints. A flat ratio (Fig. 1 dotted line) of the TL-signal from unirradiated (Natural) versus TL emitted by additionally irradiated material (Natural + dose) indicates the sufficiency of the prehistoric heating event (Fig.1). The intensity of the luminescence signal (number of photons) increases with the total absorbed dose (P) in a crystal and is therefore a function of exposure time to radiation.

An age can be calculated with the following simplified formula,

$$(1) \quad age = \frac{palaeodose}{dose\ rate} = \frac{P_{(Gy)}}{\dot{D}_{(Gy \cdot a^{-1})}},$$

where the palaeodose (P) is expressed in Gy and the dose rate $\dot{D}$ in Gy per time unit (usually in a or ka).

3.1. *The Dose Rate ($\dot{D}$)*

The denominator $\dot{D}$ of the age formula consists of two parameters, the internal ($\dot{D}_{internal}$) and the external dose rate ($\dot{D}_{external}$).

$$(2) \quad age = \frac{P_{(Gy)}}{\dot{D}_{(Gy \cdot a^{-1})}} = \frac{P}{\dot{D}_{internal} + \dot{D}_{external}}$$

Any variability of one of the parameters of $\dot{D}$ through time makes it difficult to estimate the age of a heated flint (e.g. Richter 2007). All parts which are considered to be potentially geochemical instable, like cortex or patinated areas are removed from the flint samples for TL-dating.

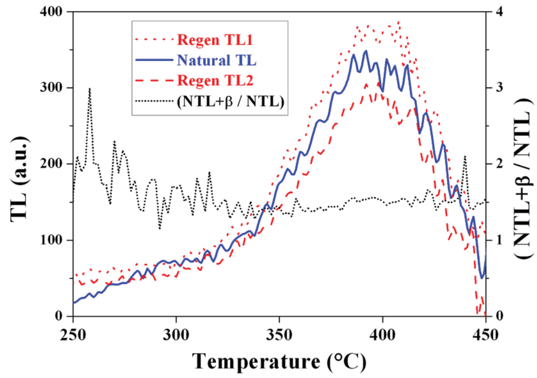

Fig. 1 - TL glow curves and heating plateau for sample AUB-168. In principle, only one aliquot is needed for the three TL-measurements: natural signal (NTL) in blue and two regeneration points (Regen TL 1 and 2) in red. The regeneration signals have to bracket the natural signal very closely. A flat ratio of natural signal which has been increased by an artificial irradiation dose (NTL+β) with NTL in the temperature region of the NTL-peak provides the information that the sample has been heated.

Fig. 1 - Curve di incandescenza TL e plateau di riscaldamento per il campione AU-168. In principio, solo una aliquota è richiesta per le tre misurazioni TL: in blu il segnale naturale (NTL); in rosso due punti di rigenerazione (Regen TL 1 e 2). I segnali di rigenerazione devono sostenere il segnale naturale molto da vicino. Un rapporto piatto del segnale naturale che è stato accresciuto da una irradiazione artificiale (NTL+β) necessita di NTL nella zona di temperatura del picco NTL fornisce l'informazione che il campione è stato riscaldato.

The internal dose-rate ($\dot{D}_{internal}$) is thus considered as being constant over the time-span of interest. This is an advantage of heated flint TL-dating over most other dosimetric dating methods, and reduces the standard deviation given for any age estimate. Most uncertainties in TL-dating of heated flint derive from the error estimates associated with the ionizing radiation from the surrounding sediment ($\dot{D}_{external}$). In order to simplify the estimation of $\dot{D}_{external}$, and thus reduce the uncertainties, each sample is carefully stripped of its outer 2 mm surface area (the range of β-radiation from the surrounding sediment) with a water cooled diamond saw prior to analysis. This leads to a minimum thickness of samples of ~6 mm, and the loss of a lot of material because of the irregular shapes of most samples. The β-dose rates from the surrounding sediment can be modeled, but at the costs of an increased uncertainty, which has to be estimated. However, this might lead to such a loss in precision that no meaningful answer to the archaeological question can be provided anymore.

3.2. *The Palaeo- or Absorbed-Dose*

The absorbed dose is commonly denominated palaeodose (P) in TL dating. This palaeodose (P) is determined from the TL signal, which is measured by heating sample aliquots at a constant rate, producing the glow curves (Fig. 1). The standard approaches for the determination of P use two series of aliquots with several mg of grains from the crushed "stripped core" of the sample (Multiple-Aliquot-Additive-Regeneration = MAAR). The sensitivity of the

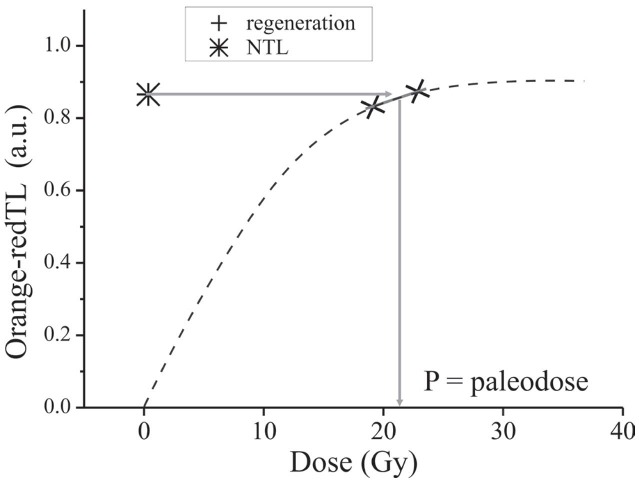

Fig. 2 - The palaeodose is determined by interpolating the natural TL-signal (star with arrow left to right) on a straight (grey) line between the luminescence signals of the two dose points (crosses) on to the dose axis (arrow downwards). Provided that these two points are set very close to each other, a straight (grey) line is a sufficiently accurate representation of the dose curve (dashed line), even for regions of strong curvature.
Fig. 2 - La paleodose è determinata interpolando il segnale della TL naturale (stella con freccia da sinistra a destra) su una riga diritta (grigia) tra i segnali di luminescenza dei due punti "dose" (croci) sugli assi dose (freccia verso il basso). A patto che quei due punti siano posizionati molto vicini l'uno all'altro, una linea diritta (grigia) è una rappresentazione abbastanza accurata della curva dose (linea tratteggiata), anche nelle zone di forte curvatura.

sample to ionizing radiation is determined by the luminescence yield after irradiation with increasing doses from calibrated radioactive sources. Some aliquots receive additive doses, while others get heated in the laboratory and then irradiated. Various regression/fitting analyses are used to determine P (see e.g. Richter 2007 for an overview). These approaches require about 500 mg of a certain grain size fraction from the crushed sample material, thus the application is limited to large samples with "core" weights of about one gram after stripping.

3.3. Procedures

While the palaeodose can be measured even for museum specimens (unless the rock material is translucent) in the laboratory, access to the site under investigation is always needed for the measurement of the external dose-rate ($\dot{D}_{external}$), which is one of the parameters of the numerator ($\dot{D}$) of the age formula. Measurements have to be done in sections to be excavated in the future, or sections containing the same sediment as the one the dating samples are originating from (see Richter 2007 for a more detailed discussion). The measurements can be achieved by directly with a portable gamma-spectrometer within an hour or so, or by implanting small dosimeters into the profiles for several weeks up to one year. Only in very special circumstances sediment samples from old excavations are sufficient for the determination of $\dot{D}_{external}$.

4. A NEW TECHNIQUE FOR TL-DATING OF SMALL HEATED FLINT ARTIFACTS

The need to provide age estimates for sites where only small heated flint artifacts are available led to the development of a new technique of TL-dating of such material. This technique employs a regeneration protocol for the determination of the palaeodose. This can be achieved with very few aliquots, thus reducing the requirements for sample sizes drastically (Richter & Krbetschek 2006; Richter & Temming 2006).

The luminescence is detected in a more favorable wavelength band (orange-red) instead of the traditionally used UV-blue. The orange-red TL-emission does not suffer from severe sensitivity changes due to the heating during measurement, and thus allows the application of a single-aliquot-regeneration (SAR) protocol with the measurements of the natural TL, and the luminescence from two artificial doses (regeneration points) for each aliquot (Richter & Krbetschek 2006). If these two regeneration points are set very closely and produce TL-signals just below and above the natural TL-signal, then a straight line (Fig. 2, grey line) is a sufficient representation of the growth curve of the TL-signal with dose (Fig. 2, dashed line), even at doses where the curve exhibits a strong curvature (saturation). The palaeodose is determined by interpolating the natural TL-signal (Fig. 2, arrow left to right) on the straight line between the luminescence signals of the two regenerated dose points on to the dose axis (Fig.2, downwards arrow). The basic assumption of no significant sensitivity change between the measurements after the natural TL is checked by the TL output from the repetition of one of the artificial irradiations. In principle, it is possible to determine a palaeodose (P) with just a single aliquot of 4-10 mg of sample material from the "stripped core". However, in practice several aliquots are measured in order to obtain a statistically more valid result from core sizes of 100-200 mg before stripping and crushing.

5. VERIFICATION OF THE APPROACH BY LABORATORY SIMULATION

The new technique was verified by simulating the prehistoric heating and the irradiation during burial in the laboratory. Geological samples from non archaeological contexts were used in order to avoid having to make assumptions about their temperature and radiation history. The samples were heated (simulating the zeroing in a prehistoric fire) in the laboratory (500 °C for 30 min) and irradiated with calibrated radioactive β-sources with doses comparable to archaeological palaeodoses (Richter & Temming 2006). Such dose recovery tests are commonly employed to evaluate the techniques used to determine the absorbed dose.

The luminescence properties, including TL-spectra (Richter *et al.* 1999), are known for the three German samples used in these experiments. Materials from rather different geological settings and genesis from Western and Northern Europe and the Levant were selected. Various techniques were used in order to verify accuracy and precision of the luminescence techniques used, including standard protocols and the new technique (Richter & Krbetschek 2006; Richter & Temming 2006). Figure 3 shows

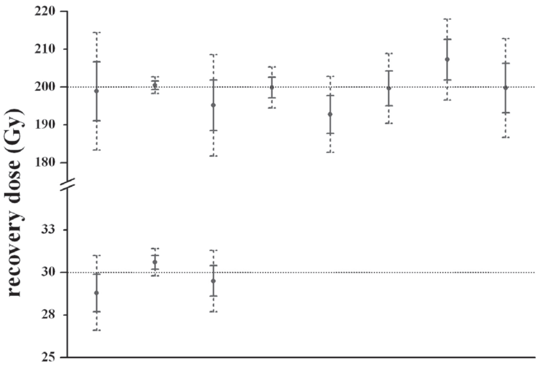

Fig. 3 - Results of the dose recovery test for the simulation with geological samples (solid 1-σ, dashed 2-σ). The dotted lines represent the applied artificial doses which had to be recovered.
Fig. 3 - Risultati del test del ritrovamento dose per la simulazione con campioni geologici (linea continua 1-σ, liea tratteggiata 2-σ). Le linee tratteggiate rappresentano le dose artificiali applicate che devono essere recuperate.

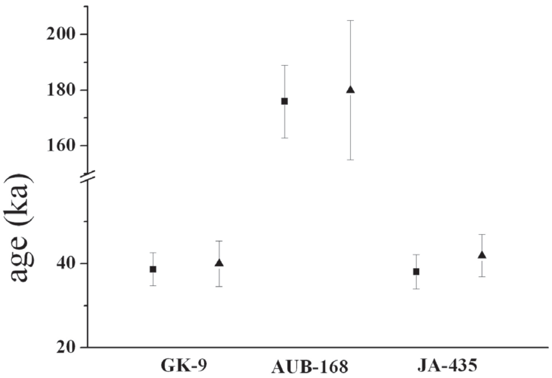

Fig. 4 - TL-ages obtained for archaeological samples using standard UV-blue (squares) and the new orange-red SAR (triangles, mean of 8 aliquots) techniques (1-σ).
Fig. 4 - Età TL ottenute per i campioni archeologici usando standard UV-blu (quadrati) e le nuove tecniche (1-σ) SAR rosso-arancio (triangoli, media di 8 aliquote).

that the applied artificial doses can be recovered successfully with the new technique. For the majority of the samples the obtained doses agree at the statistically significant level of 68% probability (1-σ with the applied dose (Fig. 3). All samples gave the right results at the probability level of 95% (2-σ). Two samples were rejected because they did not meet the quality criteria (e.g. recycling ratio) used to evaluate the applicability of the technique, which points to the sufficiency of these criteria to screen out samples which can not be dated by this technique.

However, the dose rates used in the simulation, and thus the time length of the artificial irradiations is shorter by several orders of magnitude then the natural one. This could lead to long term differences which can not be tested for because of the time involved. It is essential to test any new dating method or technique on samples of known age. Such a requirement is notoriously difficult to meet, because truly independent age estimates are available for very few sites only. Therefore, the comparison here has to be limited so far to the results obtained by standard TL-techniques which had been verified to provide good age estimates for other sites. However, it is possible to check the new technique by using identical archaeological samples and compare its results directly with the ones obtained by established standard techniques.

6. VERIFICATION OF THE NEW TECHNIQUE WITH ARCHAEOLOGICAL SAMPLES

A set of flint samples from various archaeological contexts which had already been measured using standard TL (UV-blue) methods (Richter *et al.* 2000b; Lebel *et al.* 2001; Richter *et al.* 2002) were dated with the new technique. Samples from the Middle and Early Upper Palaeolithic sites of Bau de l'Aubesier (AUB) in France, Jerf al'Ajla (JA) in Syria and the Geißenklösterle (GK) in Germany were used. For some of these associated radiocarbon data is available as well, which is in agreement with the results obtained by standard TL-dating for these samples with *a priori* unknown irradiation and thermal histories.

The ages obtained with the new technique on 8 aliquots (of ~6 mg) agree very well within 1-σ uncertainty with the ones derived on 400-800 mg by standard techniques (Fig. 4). It has to be noted, that the uncertainties obtained with the new technique can be reduced significantly by using more aliquots.

7. CONCLUSIONS

Many Palaeolithic sites do not yield samples of heated flint large enough for standard TL-dating approaches, and the sites thus may remain undated. Chronometric ages can now be provided for small samples of heated flint with a new orange-red SAR TL-technique. However, in order to achieve a better precision the outer 2 mm surface of the samples should still be removed, which determines the minimum size of samples (few grams) and is the major constrain for sampling. Furthermore, the necessity to determine the external dose-rate usually on the site (availability of sediment profiles) applies to this new technique.

The principal applicability of the technique is shown by the successful dose-recovery tests, where a prehistoric fire and the burial irradiation are simulated in the laboratory. Furthermore, the comparison with dating results obtained with standard TL-techniques gives perfect agreement of the results as well and thus confidence in the new technique. The dating results with the new technique are of comparably good accuracy, while providing a sufficient precision for answering many archaeological questions.

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