DEPENDENCE OF LUMINESCENCE CHARACTERISTICS OF IRRADIATED QUARTZ WITH THE THERMAL TREATMENT AND CONSEQUENCES FOR TL DATING

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Abstract: The dependence of luminescence properties of archaeological quartz pebbles with their thermal history is investigated and consequences for TL-dating are examined; the archaeological samples studied were collected from Solutrean layers at Laugerie Haute West rock shelter (Dordogne, France). This study is supported by a simulation experiment carried out on a natural quartz, using a combined approach by Cathodoluminescence (CL), Thermoluminescence (TL) and Electron Paramagnetic Resonance (EPR) techniques. The quartz grains used were given a high beta dose, then independent aliquots were annealed in air at a temperature varying from 300°C to 900°C. It has been observed that the TL growth with dose, after annealing and re-irradiation, evolved from a linear behaviour to a marked supralinear one according to annealing temperature linked respectively with a partial or a total thermal drainage of charges in deep traps. Consequently, during the TL-dating process of materials anciently heated at low temperature in the past (between 300°C and 500°C approximately), a special care has to be taken by adopting an annealing treatment that approaches the filling state of trapped charges that the samples had after the archaeological zeroing. This necessary new requirement strengthens accuracy and reliability of TL-dates obtained at Laugerie Haute.

1. INTRODUCTION

Recent experiments by our group (Roque, 2001; Roque *et al*., 2004) showed that TL properties of archaeological ceramics are dependent on the thermal treatment applied and particularly on the ancient firing conditions. Consequently, for dating purposes, the thermal history of the material being dated is to be addressed to define a more reliable equivalent dose (ED) measurement protocol. Recent developments led us to propose a refinement of the TL-dating procedure and data exploitation usually implemented (see for example Aitken, 1985; Guibert *et al*., 1996): additive dose technique followed by regeneration experiments on previously annealed material. The main novel contribution consists in adding, for any sample, a specific study by luminescence techniques the aim of which is to determine the more suitable annealing treatment necessarily done prior to the regeneration experiments. What is expected to find, after the laboratory thermal zeroing, is the growth of TL with dose that the investigated material had after its archaeological heating.

Methodological investigations were carried out on heated quartz pebbles excavated recently from Solutrean levels at Laugerie Haute West rock shelter (Dordogne, France). Preliminary experiments showed that the age measurement was highly dependent to the conditions of annealing (see **Table 1**, for example), extending to quartz earlier observations on the behaviour of polymineral fine grains from ceramics. They led us to examine the influence of deep traps that were not totally emptied (or radiation induced centres not totally erased) by the archaeological firing particularly on the reliability of dose determination.

A simulation experiment was then carried out on a natural quartz, using a combined approach by Cathodoluminescence (CL), Thermoluminescence (TL) and Electron Paramagnetic Resonance (EPR).

2. A COUPLED LUMINESCENCE AND ELECTRON PARAMAGNETIC RESONANCE STUDY OF A PRE-IRRADIATED QUARTZ SUBMITTED TO VARIOUS ANNEALING CONDITIONS: A SIMULATION EXPERIMENT

Sample preparation and pre-treatment

A natural quartz of industrial interest, presenting a high degree of purity (99.8% of SiO_2, according to Sifraco industry data) was firstly crushed. Fine grains (3-12 μm), which were sieved then selected by successive sedimentations, were etched by an hydrochloric solution (HCl:1M). The grains were initialized by heating in air at 650°C for 4 hours. Then a high dose simulating a geological irradiation was given by a beta source (3000 Gy). Finally different annealing treatments, variable in temperature, ranging from 300°C to 900°C by step of 100°C, for 16 hours in air, were applied to simulate an archaeological firing. The respective behaviour of these aliquots was compared to each other in order to determine the evolution of the luminescence properties with the previous thermal treatment. In the studies that follow, all luminescence intensities given are averaged over several identical replicates and normalized by mass.

Study of cathodoluminescence spectra

The CL spectra of the heated aliquots were recorded using the same experimental conditions so that they could easily be compared (a progressive spectral variation of CL occurs while irradiating by the electron beam, according to Rémond *et al.*, 1992). They all exhibit three main emissions deduced from a spectral decomposition of the signals; they are centred at around 390 nm, 460 nm and 630 nm, as illustrated in **Fig. 1a**. The relative evolution of their intensities with the annealing temperature is reported in **Fig. 1b**. The relative balance of these emissions do not present important modifications with the annealing treatments, except with the one carried out at high temperature, 900°C, which causes a significant enhancement of the red and near-UV CL emissions. This result is in agreement with those reported by another sources (Huntley *et al.*, 1988; Miallier *et al.*, 1991; Hashimoto *et al.*, 1994; Rendell *et al.*, 1994; Rendell and Wood, 1994), and it has been interpreted as a modification in the population of the luminescent centres with which these emissions are assumed to be associated, i.e. NBOHC (Non Bridging Oxygen Hole Centre) and aluminium centres respectively (Stevens-Kalceff and Phillips, 1995). Note that Al centers are also involved in the sensitivity changes of near UV OSL of quartz by preheating (Murray and Wintle, 2000; Vartanian *et al.*, 2000).

In addition, we note that heating at 600°C causes a decrease of the CL intensity in all spectrum. This behaviour could be linked with the α-β reversible transition of quartz occurring at 573°C that would induce a rearrangement of defects within the crystal (Mc Keever *et al*., 1983).

Study of thermoluminescence

The evolution of shapes of glow curves and the changes in supralinearity behaviour according to the temperature of the previous heating were the principal concern of this study.

In **Fig. 2** are presented the TL glow curves recorded for each aliquot (around 1 mg deposited on brass discs, 1 cm of inner diameter) using a fixed regenerative test-dose. From the TL signals obtained after annealing at less

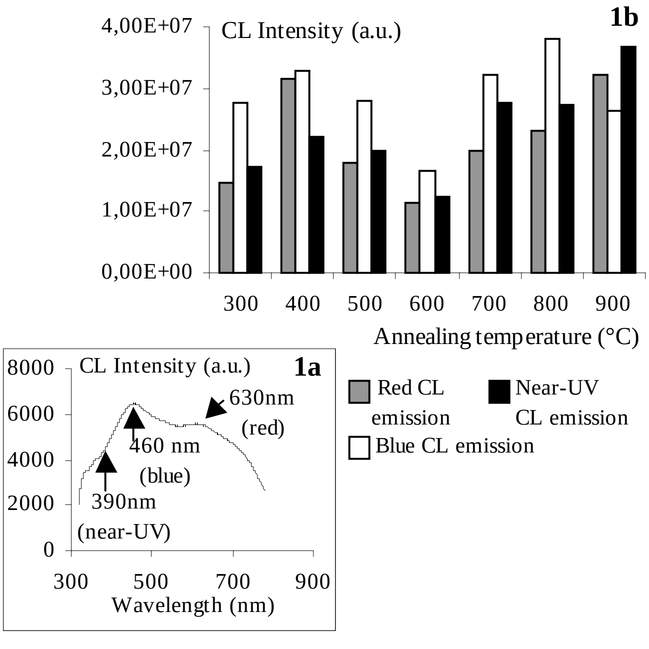

Fig. 1. Quartz crystals (from Sifraco Industries, BDX 4766): cathodoluminescence spectrum recorded after heating at 300°C (a) and relative evolution of the red, blue and near-UV emissions according to the thermal treatment (b).

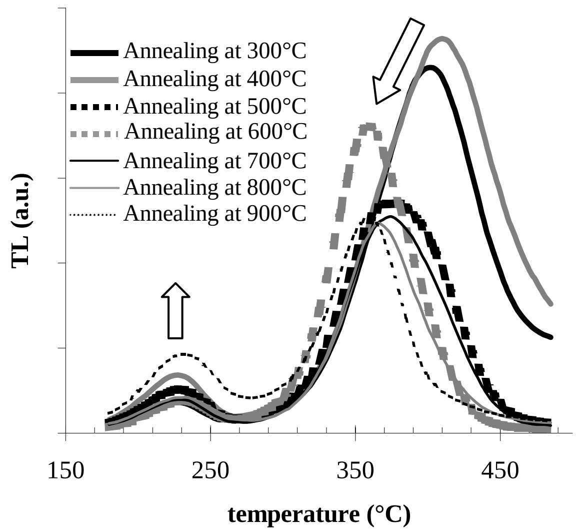

Fig. 2. Glow curves obtained on quartz crystals (BDX 4766) previously annealed in air then re-irradiated by a 6 Gy β test-dose. TL intensities are averaged over several replicates and normalized by mass. TL experiments were recorded with an automatized TL-reader built in Bordeaux, according to the following conditions: heating to 500°C at 4°C/s in nitrogen atmosphere, preheat 165°C for 2 mn, spectral window from 350 nm to 450 nm (2 BG12 Schott filters, 1 heat rejector MTO Ta2 filter, EMI 9814QKA phototube).

than 500°C, a progressive shift of the broad TL peak initially situated around 400°C towards the lower temperature region (around 360°C) is observable. Such behaviour could be phenomenologically explained by a convolution of two TL components, their maxima being at 360°C and around 420°C. The contribution of the 420°C TL emission to the global TL signal weakens after zeroing at 500°C and 600°C and, as a result, the width of the high temperature TL peak diminishes. In addition, heating between 700°C and 900°C induces an increase of the 230°C TL peak, which could be associated with the enhancement of the CL emissions in the red or near-UV regions, previously noted.

A complementary TL study has been carried out in order to determine the evolution of the TL response to dose with the previous thermal treatment. Regeneration experiments were performed on different series of aliquots annealed between 300°C and 900°C. Each set was composed of 20 aliquots and five regenerative doses were administered. The different build up curves of TL with the dose for various annealing temperatures, can be deduced from **Fig. 3** where the mean TL sensitivity (ratio of TL to dose) as a function of dose has been plotted. A strictly linear behaviour should have been represented by a line parallel to the dose axis; a supralinear one is represented by an increasing sensitivity with dose, and a saturating one by a decreasing sensitivity. Our observations show that after thermal treatments applied at 300°C and 400°C, the crystals exhibit a saturating behaviour. Then, heating at more than 500°C leads to the development of a supralinear response to dose, tending to be more marked at higher annealing temperatures.

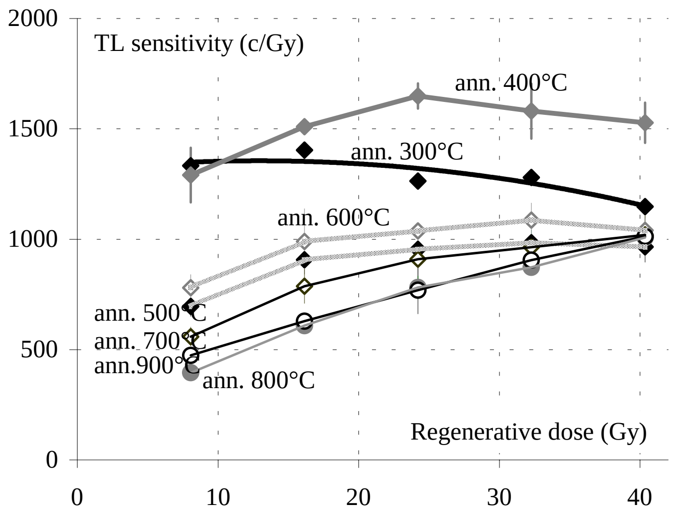

Fig. 3. Simulation experiment on pre-irradiated then annealed quartz crystals (BDX 4766). Analyse of the evolution of non linearity in the regenerated TL growth curve with dose as a function of the previous thermal treatment. The ratio (TL/dose) is the mean sensitivity of the material. A perfect proportionality between dose and TL should give a line, parallel to the dose axis; saturation effects cause a drop of the ratio and supralinear effects, an increasing ratio with the dose. TL intensities have been normalized by mass and integrated in the 280°C-450°C region.

EPR study

Room temperature EPR experiments were performed on the annealed quartz sample in order to detect the remaining E' centres, initially filled by the simulated geological irradiation. The evolution of the E' centre population is given in **Fig. 4**, as a function of annealing temperature. Still easily detectable after heating at 300°C or at 400°C for 16 hours, E' centres are not totally erased after 16 hours at 500°C and, for higher temperature treatments, not detectable.

The progressive decrease of E' centres with thermal treatment can be correlated with the evolution of TL, although no direct correlation TL peak / paramagnetic centre could be drawn by this experiment since other paramagnetic stable centres (such as peroxy, for instance) were not searched for. Nevertheless, it is important to notice that annealing at 300°C, 400°C and even at 500°C do not totally zero the electron trap centres or hole centres (recombination centres) that appeared with the simulated geological irradiation.

Interpretation of non-linearity variations and consequences for dating purposes

Modifications affecting both the luminescence properties and the filling state of trapped charges, are induced by the thermal treatment performed on a pre-irradiated quartz. From the chronological point of view, the most important result is the evolution of the TL growth with dose according to the annealing conditions: from a linear behaviour to a marked supralinear one as far as emptying deeper traps is becoming effective with an increasing annealing temperature.

Interpretations of such a change can be explained by the usual models known in the field of luminescence dating and dosimetry (Cameron *et al*., 1968; Yang and Mc Keever, 1988; Lee and Chen, 1995; Bailey, 2001). Among qualitative explanations for changes in growth behaviour,

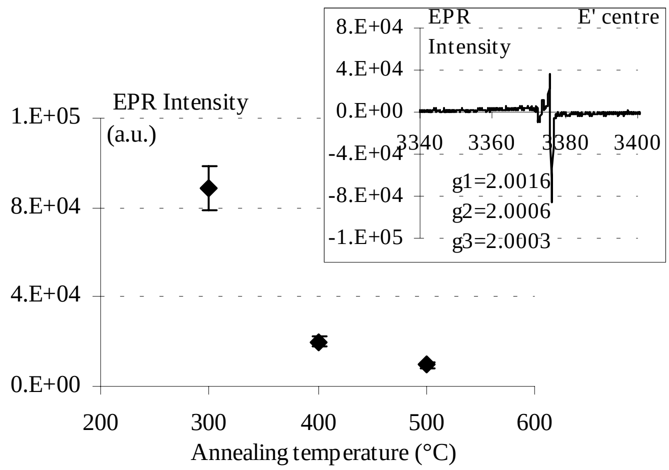

Fig. 4. Simulation experiment on pre-irradiated then annealed quartz crystals (BDX 4766). Evolution of the residual E' centre population measured by EPR, as a function of the previous thermal treatment.

all kinetics models may consider at least two active electron traps (among others) of different activation energies and some recombination centres, giving rise to luminescence or not: one of the electron traps gives a TL peak, the second is deeper and not "visible" in usual TL experiments, but it can be zeroed by annealing, provided temperature and duration of heating were sufficient. If the annealing conditions zero the former TL trap and not the second one, after re-irradiation (either archaeological or artificial in laboratory) and during the following TL process, the possibility of an electron evicted from the TL trap to recombine into the deeper one, in saturation state due to the previous geological irradiation, is not probable, thus a recombination into a (luminescent) hole trap centre is favorized, inducing an increase in sensitivity and a linearization of the growth curve. Inversely, if both electron traps are initially emptied by heating at a higher temperature, during the TL process that follows a re-irradiation (either archaeological or artificial), the recombination into the deepest trap is possible, to the detriment of luminescent recombination ways.

Complementary explanations involve recombination centres: if deep trap emptying is not total after annealing, it remains potential active recombination centres, according to the electrical neutrality, the number of trapped electrons being equal to the number of trapped holes, and the probability of a luminescent recombination is then enhanced in comparison with an initial total zeroing of trapped charges.

Consequently, for TL-dating procedure, in reason of the possible partial zeroing of deeper traps according to the archaeological firing, that could cause important changes in the shape of the growth curve, it is essential that the annealing conditions required for the usual regeneration experiments have to be carefully defined, in order to approach the filling state of trapped charges that the material had after the archaeological heating. We will discuss in the following section about the relevance of different methods and tools for determining appropriate annealing conditions.

3. APPLICATION TO THE STUDY OF SOLUTREAN QUARTZ PEBBLES FROM LAUGERIE HAUTE WEST

Sample preparation and general aspects of the dating protocol

Cylinders of quartz (diameter: 10 mm) were cut in the archaeological pebbles and their 2 mm external parts were removed by a low speed diamond disc saw. The inner part of samples was crushed in an agate mortar: the 80-200μm fraction is used for beta ED determination. The grains were etched by diluted acid solutions (successively: HCl 1M, HCl 1M + HF 0.5M for 90 min., HCl 1M) for removing the superficial part of the grains (ca. 1 μm) that could exhibit possible spurious TL signals due to the mechanical treatment.

The cleaned grains were divided into two sets. Classically, the first one was employed for the "first reading" experiments, using an additive dose technique. The second one was heated in laboratory in order to erase all TL signals, according to conditions that were carefully determined (see following sections); then, the grains were irradiated by artificial beta doses and their regenerated TL was recorded. A dose – plateau test was carried out to determine the temperature range within which the TL intensity can be integrated in order to determine the equivalent dose. After treatment of the regeneration curves, a growth function was defined and fitted to the first TL reading experimental data. The intercept of this function with the dose axis gives the final value of ED, according to a slide method described earlier (Guibert *et al*., 1996).

Although the internal radioactivity of quartz is very low, the sensitivity of those material to alpha radiation was studied. The k-value determination was carried out on fine grains (3-12 μm) resulting from crushing. Grains were heated at 600°C for 1 hour in order to remove both natural TL signals and those induced by grinding. They were chemically etched (same treatment as described for the 80-200 μm grains) and deposited onto brass discs. Aliquots were given a beta dose equal to the β ED previously determined; others were administered alpha doses in order to define the alpha growth curve, TL intensity versus alpha dose. The α-ED, and the corresponding k-value, were deduced from the intersection of TL intensity from beta dosed aliquots, with the a dose growth curve. Possible changes in k-value with the thermal treatment are to be addressed. However, as the content in U and Th of quartz pebbles approaches zero, the uncertainty about k-value was considered as negligible in comparison with other sources (the alpha effective dose-rate was in all cases ranging from 1 to 5% of the total).

An example of the influence of annealing temperature on dose and age measurements of archaeological quartz pebbles

Table 1, as an example of the importance of the annealing stage of the dating protocol, presents the dose and age determination results for two quartz samples using two different annealing temperatures, 300 and 400°C (in air for 16 hours), applied before the regeneration experiments. Significant differences in dose and age are observed in each case, in agreement with the conclusions of the simulation experiments described above. Annealing at 400°C results in higher ED than at 300°C since the growth curve determined from the regenerated TL (global signal integrated between 350 and 450°C) is more supralinear, or less saturating, the additive dose data used being the same in both cases. (NB: if we had used a linear approximation to fit the experimental data, we should have obtained a greater supralinear correction after annealing at 400°C than at 300°C.)

Moreover, the comparison of TL-ages with the known chronology of the solutrean culture or with the ^{14}C data (correction after Bard *et al.*, 1995, Stuiver *et al*., 1998) obtained at Laugerie Haute, demonstrates that the annealing parameters plays a critical part in the age determination procedure, in a similar way as we also observed in archaeological ceramics (Roque *et al*., 2004). With the examples cited in **Table 1**, erroneous results are obtained after annealing for 16 hours at 400°C.

***Table 1.** Example of the influence of annealing conditions on equivalent dose and age measurements for two quartz pebbles from Laugerie Haute. Comparison of results with radiocarbon dates obtained on bones, „fresh" or burnt (Roque et al., 2001).*

Samples and cultures	TL Dating			^{14}C Dating
	T (°C)	ED (Gy)	Age (ky)	Calendar Age
Final Solutrean Level				
BDX 5825	400	10.52±0.40	30.1±2.2	[22,600-20,500] BC[1]
	300	8.25±0.57	23.7±2.2	[24.6-22.5] ky BP[1]
Inferior Solutrean level				
BDX 5861	400	9.70±0.84	28.4±2.9	[23,400-21,100] BC[2]
	300	8.26±0.64	24.2±2.4	[25.4-23.1] ky BP[2]

T – annealing temperature. The range of calenadar age (BC or ky BP) was obtained on the basis of calibration of ^{14}C dates set with laboratory codes given in the Table.

[1] ranges were obtained on the basis of samples: GrN-4441, GrN-4605, GifA-100632, Ly-1173(OxA)

[2] ranges were obtained on the basis of samples: GrN-4446, GrN-4469, GrN-4573, Gif-100632, Ly-1175(OxA)

About the use of TL to determine appropriate annealing conditions

In practice, to search for the appropriate annealing conditions that are expected to produce equivalent effects on luminescence properties to the archaeological firing, independent aliquots of the powdered archaeological quartz were heated in air for 16 hours at 300°C and 400°C. The final annealing temperature to apply was determined by a comparison of shapes of the regenerated TL after annealing to the natural TL. The regenerative dose employed approached the equivalent dose to avoid possible dose effects in the growth of TL peaks, and subsequently possible dose-variations of the shape of glow curves. As shown in **Fig. 5**, differences in annealing temperature can produce visible changes in the glow curves; this is confirmed by plotting the ratio natural TL on regenerated TL as a function of temperature. For that sample (Bdx 5861), we adopted the following annealing conditions, 300°C for 16 hours, before the regeneration experiments were carried out, since the shape of the 300°C TL curve is the closest to the natural one.

Another technique for the evaluation of the annealing temperature has been used: in general, it is more sensitive than the glow curve shape comparison procedure, but it requires larger amounts of sample, and more experimental time, too. It is based on the dose-plateau test that takes account of all series of glow curves (first reading TL- and regenerated TL experiments): as it can be deduced from **Fig. 6** with another quartz sample (Bdx 5825), an acceptable plateau is obtained with the data of the quartz having been annealed at 300°C (for 16 hours in air) instead of 400°C.

It is important to note that, as well as shapes of glow curves and TL growth with dose, the β ED plateau is sensitive to the annealing conditions since the various parts of the glow curve originating in different traps have also different non-linearity behaviours. The dose plateau test can then be considered as a tool for evaluating the appropriateness of the laboratory zeroing conditions and age determination. The example given in **Fig. 6** shows that annealing this sample at 400°C does not reveal any plateau region, and a possible alternative (but wrong)

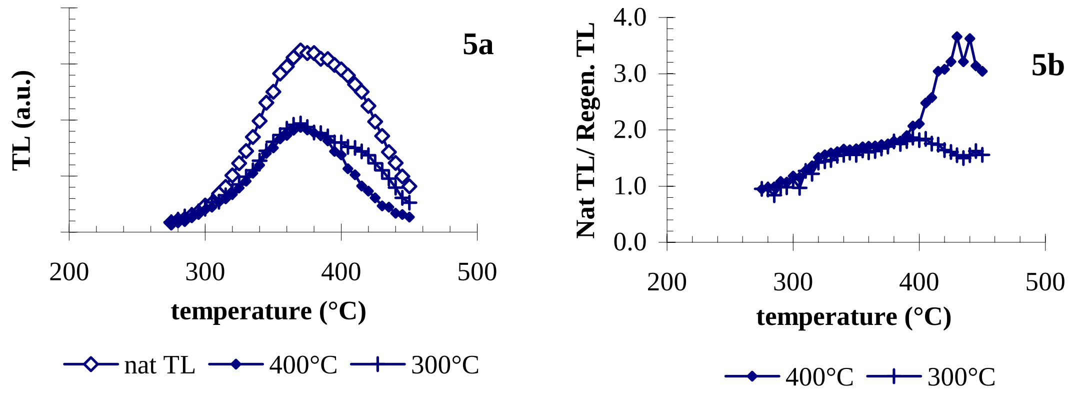

***Fig. 5.** Palaeolithic quartz pebble (BDX 5861, Solutrean culture, Laugerie Haute West, Dordogne, France): (a) TL glow curves of natural and annealed quartz grains. TL intensities are averaged over several identical replicates and normalized by mass. Same experimental conditions as in Fig. 2 except preheating temperature: 245°C. (b) Ratio of natural TL to regenerated TL as a function of temperature.*

interpretation without any alternative information, should have been that the investigated material was not heated enough in the past to give an acceptable TL date.

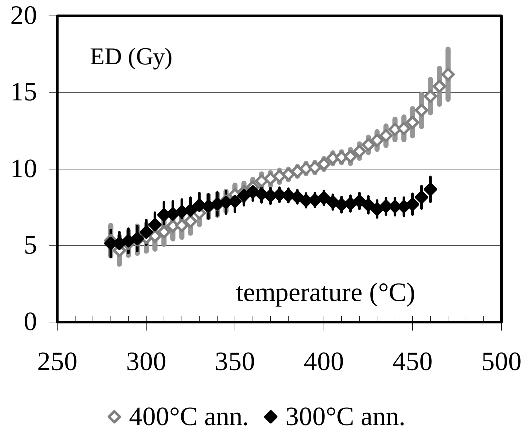

Fig. 6. *Palaeolithic quartz pebble (BDX 5825, Solutrean culture, Laugerie Haute West, Dordogne, France). Dose plateau test as a tool for checking the suitability of annealing conditions: annealing at 300°C gives the most reliable result for this sample.*

At this point of our work, we want to highlight the fact that the use of a fixed temperature or fixed conditions to anneal TL (400°C for 16 hours as we usually did in past studies, or 500°C for short whiles, using the TL thermal cycle as a very common annealing process), whatever the sample and its thermal history, is a potential source of error or dispersion in age measurements, until 25% in one of the examples cited. Our studies indicate that the annealing conditions have to be determined carefully for any sample being dated.

Laugerie Haute Solutrean TL-dates

As an illustration of the variable annealing conditions, β ED, annual dose rates and TL-dates of heated Solutrean quartz pebbles from Laugerie Haute are reported in **Table 2.** Internal dose rate was determined from low background gamma spectroscopy analyses (Guibert and Schvoerer, 1991) by using Adamiec and Aitken's data (1998). Since the archaeological layers were particularly heterogeneous, external dose rate is the result of a reconstruction calculation (Guibert *et al.*, 1998; Roque *et al.*, 2001) taking account of i) the radioactivity of lithologic elements around quartz pebbles measured by gamma

Table 2. *Laugerie Haute West (Dordogne, France): TL dates of Solutrean heated quartz pebbles. Dating results are given with their statistical and systematic uncertainties. the annealing conditions preceding the regeneration experiments were determined according to a comparison of shapes between the natural glow curve and regenerated ones. The annual dose rate is determined mainly from low background gamma spectroscopy measurements; its major component is the gamma one, evaluated using the reconstruction technique detailed in Guibert et al. (1998).*

Samples and cultures	T (°C)	ED (Gy)	D (mGy/a)	TL Age (ky)	u_1 (ky)	u_2 (ky)
Final Solutrean level						
BDX 5813	400	9.82 ± 0.54	0.450 ± 0.020	21.8±1.6	1.4	0.8
BDX 5825	300	8.25 ± 0.57	0.349 ± 0.020	23.7±2.2	1.9	1.0
Averaged TL Age (y): 22. 55 ± 1. 44					1.15	0.87
Superior Solutrean level						
BDX 5827	400	7.35 ± 0.63	0.376 ± 0.021	19.6±2.0	1.9	0.8
BDX 5828	400	9.25 ± 0.98	0.431 ± 0.025	21.4±2.6	2.5	0.9
BDX 5842	400	8.24 ± 0.47	0.313 ± 0.020	26.3±2.3	2.0	1.2
Averaged TL Age (ky): 23. 3 ± 1. 58					1.23	0.99
^{14}C chronology, F*inal and Superior Solutrean levels* **[22,600 – 20,500] BC or [24.6 - 22.5] ky BP** ^{14}C dates: GrN-4441, GrN-4605, GifA-100630, GifA-100634, Ly-1173 (OxA)						
Inferior Solutrean level						
BDX 5859	300	9.47 ± 0.67	0.452 ± 0.027	20.9±2.0	1.7	0.9
BDX 5861	300	8.26 ± 0.64	0.341 ± 0.019	24.2±2.4	2.1	1.0
BDX 5864	400	9.10 ± 0.84	0.356 ± 0.019	25.6±2.6	2.5	1.0
Averaged TL Age (ky): 23. 35 ± 1. 54					1.21	0.95
^{14}C chronology [23,400 – 21,100] BC or [25.4 - 23.1] ky BP ^{14}C dates: GrN-4446, GrN-4469, GrN-4573, GifA-100632, Ly-1175 (OxA)						

T – annealing temperature, ED - Equivalent Dose, D - annual dose rate, u_1 and u_2 - statistical and systematic uncertainities.
The range of calendar age (BC or ky BP) was obtained on the basis of calibration of ^{14}C dates set with laboratory codes given in the Table.

spectroscopy, ii) the position and iii) mass of these elements, iv) in situ measurements by TL-dosimetry of environmental dose rate of unexcavated areas in the close vicinity of the samples dated and v) cosmic dose rate measured by in situ γ spectroscopy (NaI:Tl).

The normal statistical distribution of the set of TL-dates finally obtained at Laugerie Haute on quartz pebbles (**Table 1**) and their agreement with the radiocarbon chronology strengthen the reliability of age determination and lead us to validate the procedures specially developed for ED measurements, taking into account the thermal past of samples to be dated. Such methodological improvements can be therefore applicable for a reliable and accurate TL-dating of other prehistoric sites and periods.

4. CONCLUSION

Experiments carried out on natural quartz from archaeological or industrial origin, show that various thermal treatments applied to pre-irradiated material induce variations in thermoluminescence characteristics, shape of glow curves and growth of TL with dose. According to a coupled EPR/ luminescence study, it can be stated that the modifications observed are linked to the residual filling state of trapped charges, induced by the previous thermal treatment.

Consequently, in the specific case of TL-dating of materials anciently heated adopting annealing conditions that approach the filling state of trapped charges that the material had after the archaeological zeroing (i.e. the thermal history from the trapped charge point of view) is at the present state of the TL-dating protocol, a necessary requirement in order to improve the reliability of dates. The thermal history of the archaeological artefact and/or an appropriate annealing treatment can be approached by the comparison of the shape of the regenerated TL glow curves obtained after annealing a series of aliquots at different temperatures, with the shape of the natural glow curve or by the use of the dose-plateau test. Satisfying dating results were obtained at Laugerie Haute using that procedure; TL-dates match quite well with calibrated AMS and beta counting radiocarbon dates on bones or burnt bones fragments from the same layers (Roque *et al.*, 2001).

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