OSF DOI: 10.31219/osf.io/kqhfa

Reference: Joannes-Boyau, R., Scheffers, A., Chapoulie, R., Lahaye, C., Parr, J., Orange, M., Moffat, I., and Guibert, P., 2014, Thermal behaviour of organic radicals and paramagnetic centres in chert: A case study of Bergeracois brown chert, Dordogne, France, *Quaternary Geology*, 23: 26-34.

Title: Thermal behaviour of organic radicals and paramagnetic centres in chert: A case study of Bergeracois brown chert, Dordogne, France

Authors: Renaud Joannes-Boyau, Anja Scheffers, Rémy Chapoulie, Christelle Lahaye, Jeff Parr, Marie Orange, Ian Moffat, and Pierre Guibert

In order to successfully understand the complex evolution of prehistoric societies, archaeologists require absolute dating tools, which are not only accurate but also widely applicable. Thermoluminescence (TL) dating is one such approach that has been successfully used to establish a general chronological framework for prehistoric sites and is particularly suited for use on heated lithic artefacts. Experiments conducted in this study have clearly shown the applicability of Electron Spin Resonance (ESR) isothermal modelling in combination with TL dating to constrain firing temperature. This expands the potential application for TL dating to include artefacts treated at low firing temperatures. The present study shows potential in terms of precision and accuracy for framing the “equivalent firing temperature”. At the same time, the comparison of the TL signal with the lattice-defects and aluminium centres invigorate the use of ESR dating on heated flint, especially with samples that have received low thermal treatment. The presence of organic matter in large quantity raises concern on the pyrolysis effect on the luminescence signal; however, the use of ESR isothermal and isochronal modelling could potentially lead to the ability to overcome current interferences of the organic radicals within the dating signal of TL.

Introduction

A principal concern of archaeological research is to understand the chronology of the development and changes in the material culture of prehistoric societies. Critical to this understanding is the accurate and precise dating of stone artefacts, which due to their excellent preservation potential are present in most archaeological sites. Unfortunately, direct dating of stone artefacts is problematic, and most ages for prehistoric sites are achieved using indirect dating. Frequently dates are obtained using associated materials from the same stratigraphic

layer with methods such as radiocarbon, $^{40}\text{Ar}/^{39}\text{Ar}$ and/or luminescence (e.g. Aitken, 1985, Guibert et al., 2008). This approach requires the establishment of a clear stratigraphic relationship between the dated material and other artefacts, which may be problematic in sites with reworking or complex depositional histories. Despite these difficulties indirect dating remains the preferred choice for many archaeologists because of unresolved complications in the direct dating of burnt flint.

TL dating has been extensively used since the 1970's to provide a chronology for the last heating of artefacts (c.f. Wintle and Aitken, 1977, Mercier et al., 1995, Roque et al., 2004, Richter et al., 2007) and in particular heated flints from Palaeolithic sites (i.e. Duttine et al., 2005, Mercier and Valladas, 2003). The technique is based on the premise that archaeologically heated flints will have their geological dose reset to zero. To obtain the archaeological dose, part of the sample is heated in the laboratory, this to anneal the signals before conducting the regeneration measurements ("second reading measurements"). Unfortunately, this specific firing temperature is problematic to determine and appears to have great implication on the dating protocols and age outcome, such as quartz (Roque et al., 2004) from heated pebbles. Apart from the experiments described in Duttine et al. (2005), such effect has not been investigated yet so extensively for flint dating, and the present study aims at better understanding the thermal treatment issues. The extent of this problem is of such significance that improving the procedure for the selection of samples and understanding the limitation of the dating is considered to be as one of the most profitable directions for archaeological research in the 21st century (i.e. Hiscock and Clarkson, 2000).

Despite extensive literature on the use of burnt flints for direct dating (e.g. Griffiths et al., 1982, Griffiths et al., 1983, Toyoda et al., 1993, Imai et al., 1994, Porat and Schwarcz, 1991, Porat and Schwarcz, 1995, Porat et al., 1999, Jonas, 1997, Guibert et al., 1999, Bartoll et al., 2001, Duttine et al., 2005) little has been done to rationalise the selection of suitably heated artefacts for Thermoluminescence (TL). Duttine et al. (2005) have shown an understanding of the thermal history of the sample using Electron Spin Resonance (ESR) is necessary to obtain an accurate TL age. The thermal behaviour of the ESR signals related to organic radicals and lattice defects can be used to extrapolate what could be called characteristic equivalent temperature for a suitable TL dating (e.g. Toyoda et al., 1993). TL experiments on heated quartz or flints have revealed complex sensitivity changes depending on the temperature and the heating time (Roque et al., 2004, Duttine et al., 2005) and at this stage, the contribution of ESR to characterize the thermal history of such materials is fully justified.

The present study was specifically designed to investigate the thermal behaviour of organic radicals and lattice defects in heated flints using ESR, in order to better understand the thermal effect on structural centres and trapped organics. At the same time, we have investigated the use of a rational ESR signal description for the determination of the suitable TL temperature for dating purposes, while trying to correlate the variations of the organic radicals and lattice defects to the luminescence signal.

Material and methods

Sample and sample preparation

The studied Bergeracois brown cherts were excavated from the Palaeolithic site of Cantalouette II in Dordogne, France. The site was discovered while building the northern section of the RN 21 East ring road of Bergerac. The excavation of the site of Cantalouette II began in 2002 in a karstic sinkhole that was 5 m deep, 35 m long and 10 m wide and contained archaeological artefacts, under the supervision of Laurence Bourguignon (INRAP). The large dimension of the sinkhole attests the karstic activity during the Quaternary, which diminished gradually allowing the site to gradually fill with siliclastic sediments (Bourguignon et al., 2002, Bourguignon et al., 2008).

One chert sample (BDX 10173) from a Mousterian layer of Cantalouette II was used for this analysis. The large raw brown chert core shows sign of work and fragment extraction for tool shaping, however, the lack of colour and change suggests that no archaeological heat treatment was performed.

The sample was drilled, a core extracted and the cortex was set aside to avoid potential weathering interference. Material from the interior of the sample was then gently powdered with a mechanical crusher (Retsch S100) to obtain a size fraction of $<200\ \mu\text{m}$. To remove potential unwanted signal from mechanical treatment, the sample was steeped in HCl (1 M) for 1 h, then with a mixture of HCl and HF (HCl 1 M + HF 0.5 M) for 90 min to remove the $1\ \mu\text{m}$ superficial part of the grains that could retain possible contamination, or charges trapped on grain surface as a consequence of the previous mechanical treatment. By sieving, we separated the powder into several fractions, including the one selected for this study between 80 and $200\ \mu\text{m}$ (commonly used for TL experiments, Guibert et al., 2004).

Thermal treatments were carried out in a Memmert drying oven for lower temperatures, of $50\ ^\circ\text{C}$, $100\ ^\circ\text{C}$ and $150\ ^\circ\text{C}$, while for temperatures ranging between $200\ ^\circ\text{C}$ and $450\ ^\circ\text{C}$, a Carbolite RHF 1500 muffle furnace with a precision of $\pm 5\ ^\circ\text{C}$ (inner temperature gradient) was used. Samples were divided in multiple aliquots and received thermal treatment for 1 h, 2 h, 4 h and 8 h at one of the following temperatures, $50\ ^\circ\text{C}$, $100\ ^\circ\text{C}$, $150\ ^\circ\text{C}$, $200\ ^\circ\text{C}$, $250\ ^\circ\text{C}$, $300\ ^\circ\text{C}$, $325\ ^\circ\text{C}$, $350\ ^\circ\text{C}$, $400\ ^\circ\text{C}$ and $450\ ^\circ\text{C}$. All treatments were performed in air.

2.1.1. Electron Spin Resonance (ESR) analysis

ESR spectra were obtained in the IRAMAT-CRP2A laboratory in 2005 using a Bruker ESP300E spectrometer in X-band at a frequency of 9.5 GHz, with the following measurements conditions: 0.1 mW (E' , R-CH₂, CH₃, perinaphtenyl), 10 mW (Peroxy and Carbon) or 20 mW (Al) of microwave power, 0.1 mT modulation amplitude, 12 mT sweep width with a sweep time of 21 s. The spectra were accumulated from 100 consecutive measurements and normalized according to 1 mg of sample and according to ESR parameters (field modulations, scans, modulation amplitude). The intensity of the signals was calculated with the formula, where I_{pp} is the intensity peak-to-peak, and ΔB is the width of the peak. ESR analyses of the E' ($g_{\parallel} = 2.0018$; $g_{\perp} = 2.0004$), perinaphtenyl (centred at $g = 2.0027$), peroxy centre ($g_1 = 2.0088$; $g_2 = 2.0016$), CH₃ ($g_1 = 2.0158$; $g_2 = 1.9909$), amorphous carbon ($g = 2.0030$) and R-CH₂ radicals (centred at $g = 2.0032$) was carried out with a power of 0.1 mW and 10 mW at 293 K, while the Al centre ($g_1 = 2.0602$; $g_2 = 2.0083$; $g_3 = 2.0019$) was studied with a power of 20 mW at 77 K.

2.1.2. Thermoluminescence (TL)

The TL curves were obtained using a custom designed apparatus, “TL-auto 2”, which was designed at the IRAMAT-CRPAA laboratory in France.

The photomultiplier tube (EMI 9213 QKA) used for photo counting is composed by two Schott BG12 and one MTO Ta3 optical filters (between 350 and 450 nm). Irradiations were performed using a ^{90}Sr radioactive beta source with an approximate dose rate value of 74 mGy s^{-1} , with 1.5% of calibration uncertainty (1.85 GBq , AEA technology SIF1176 type). Heating was performed at a rate of $4 \text{ }^{\circ}\text{C s}^{-1}$ in a nitrogen atmosphere.

Scanning Electron Microscopy (SEM)

SEM analysis was carried out on a JEOL 6460LV at low vacuum mode, using an Energy Dispersive X-Ray Spectrometry (EDXS) INCA 300 Oxford Instruments for surface major and minor elements composition.

Errors and uncertainties

Experiments were also undertaken to assess errors and uncertainties that could come from the ESR measurements, the ESR spectrometer, the tubes and the peak-to-peak measurements. Ten distinct chert aliquots were used to investigate the heterogeneity of the artefacts while alanine dosimeter and sample powder were used to assess the error linked to tubes variations, ESR spectrometer and signal. Measurements were normalised for sample weight and sample weight loss along the process. All centres and radicals signals were measured, normalised and averaged for variation assessment. The results show less than 1% variation for the ESR measurements and the ESR spectrometer stability over the year. While differences in tube shows a small discrepancy of less than 1% with the alanine dosimeter, a variation of 2% was found using the sample powder, which most likely reflects precision in the weighting system. The larger error of 3% came from the peak-to-peak measurements, clearly induced by background and spectra resolution. All errors are well below the kinetic calculation and graphic resolution uncertainties.

Results and discussion

SEM analyses showed alteration of the outer surface (cortex), which contained most of the impurities (e.g. Na, Ca, Fe, S and Al). The typical weathering front correspond to the re-precipitation and dissolution of salts (Fernandes et al., 2007) carried by water infiltration into

the rock. Cortex is not used in TL dating. In this study we only used the unaltered part of the flint for the thermal stability study, which was identified under SEM observation and analyses.

ESR spectra of the powder revealed several radicals identifiable before thermal treatment and already described in the literature (Griffiths et al., 1982, Griffiths et al., 1983, Chandra et al., 1988, Ikeya, 1993). Fig. 1 shows all radicals and defects observed and used in the study. Five different organic radicals were identified: Peroxy (OHC), the alkyl group (R-CH₂), methyl (-CH₃), perinaphtenyl (C₁₃H₉) (only after thermal treatment) and an amorphous carbon (only after thermal treatment) (Toyoda et al., 1993) (Fig. 1A). Robins (1984) describe the later radicals as the result of cracking the long organic chain of other radicals by thermal treatment above 400 °C. The aluminium centre (Fig. 1B) corresponds to an impurity in the tetrahedron silicon (Yokoyama et al., 1985), the E' centre (Fig. 1A) also found in quartz and often used for dating purposes (e.g. Toyoda and Hattori, 2000) corresponds to a lattice defect. All radicals and impurities were trapped in the siliceous rock during the geological formation.

Effect of thermal treatment on the ESR signal

The influence of 1 h of thermal treatment is summarised in the isochrone plots Fig. 2A to D. The two lattice defect, peroxy and E' centre, behave similarly to the Al centre. The thermal treatment had virtually no influence on the E' and peroxy centre until 200 °C and 300 °C respectively where both defects show a rapid decrease. Both were undetectable after thermal treatment for 1 h at 500 °C. Clearly the two aforementioned lattice defects behave as traps that empty once a sufficient temperature for a given duration is reached. The organic radicals present a more complex pattern. The R-CH₂ radical shows the most unusual behaviour, with two distinct variations (Fig. 2). At an early stage, the R-CH₂ radical concentration decreases with temperature as low as 150 °C. On the second stage, R-CH₂ regenerates 'slightly' (increase of 166% of the relative radical concentration) between 150 °C and 275 °C before it culminates at 275 °C (NB, the relative amount of R-CH₂ has decreased by 50% between natural and 275 °C), before being completely annealed at 375 °C. The last three organic radicals methyl, perynaphtenyl and amorphous carbon show a late increase induced by thermal treatment, starting at 200 °C, 250 °C and 450 °C respectively (Fig. 2), which is followed by a rapid decline of the relative radical intensity except for the amorphous carbon.

Figure 2. Isochronous curves of each radical and lattice defect observed in the ESR spectra of BDx 10173 (A) 1 h; (B) 2 h; (C) 4 h; (D) 8 h.

While the general behaviour of each radical and centre remains the same as the heating time is increased, all defects present modifications of their maximum intensity and annihilation temperature. A clear relation between heating time and the precocity of E' annihilation temperature can be observed by comparing Fig. 2A, with Fig. 2B, C and D. E' starts to decrease at 300 °C when heated for one hour however it required eight hours of heating at 250 °C before a decrease occurred. Similar observations apply to the temperature in relation to disappearance, which occurred at 450 °C after one hour of heating compared to eight hours at 400 °C.

Both CH₃ and R-CH₂ radicals present a shift of their maximum intensities, from one hour at 275 °C to eight hours at 250 °C (compare Fig. 2A and D). Perinaphtenyl radical signal presents important modifications, with its maximum shifting to lower temperature of more than 50 °C, from 375 °C to 325 °C (Fig. 2A to D). Concurrently, the general behaviour of the radical when exposed to thermal treatment is also modified. During a period of 1 h to 8 h the pattern changes with respect to the disappearance of the pseudo-plateau to a more abrupt shape between 350 °C and 400 °C (Fig. 2). The perinaphtenyl growth is linked to the decrease of CH₃ and R-CH₂ signals, before the temperature and time reaches a certain value and start destroying the radicals. The maximum intensity recorded with ESR corresponds therefore to the optimum production/destruction budget of the perinaphtenyl radical.

Little effect is observed for the general behaviour of the peroxy centre (Fig. 2 A to D). The decreasing part of the plot shows very small differences, and the disappearance temperature remains the same. Amorphous carbon radicals were detected at lower temperatures from 450 °C after 1 h to 400 °C after 8 h of heating. These results show the existence of a competition or equilibrium between the creation and destruction of the paramagnetic defects according to the temperature and the duration of heating.

Fig. 3 represent the isothermal behaviour of R-CH₂, methyl, perinaphtenyl, peroxy, E' and the aluminium centres respectively. The influence of heating time is well illustrated by the R-CH₂ isothermal plot (Fig. 3A). The main influence of thermal treatment can be seen in the first hour, after which the signal is constant at temperatures lower than 325 °C, however, it instantly drops after four and 8 h. Perinaphtenyl radicals (Fig. 3C) behave in two phases. Firstly, the signal grows until reaching a maximum around 350 °C and then, the intensity decreases. It can be seen in Fig. 3C that the signal for 8 h at 300 °C has a premature decline compare to lower temperature. Fig. 3 shows that at 50 °C, the CH₃ intensities remain constant, whereas from 150 °C the ESR intensity is increases after one hour of heating (Fig. 3B). Between 150 °C and 300 °C it continues to increase for the full eight hours. This tendency starts to reverse from 300 °C, which corresponds to the maximum of the isochronous curve of the CH₃. It can be seen that a maximum intensity occurs around one hour of heating. For both the lattice defects E' (Fig. 3E) and peroxy (Fig. 3D) the intensity remains constant until 300 °C after which it starts to decrease. However, although the E' centre decreases in intensity with time, the peroxy signal seems to remain constant for one hour of thermal treatment at 325 °C, 350 °C, 375 °C, and 400 °C, (Fig. 3D). The aluminium centre ESR signal can only be observed at low temperature (77 K). While the first temperature does not show any significant decrease, temperatures above 300 °C start to present an almost complete annihilation after one hour. Already observed in quartz, the thermal behaviour of Al centre is strongly dependant of the sample.

Figure 3. Isothermal variation of the ESR intensity for (A) R-CH₂; (B) CH₃; (C) Perinaphtenyl; (D) Peroxy; (E) E'; (F) Al.

Expected behaviour for the paramagnetic traps corresponds to the signal intensity decreasing with time. For example, with sufficient time the amount of paramagnetic defects equal the amount of dissipating defects, hence reaching an equilibrium state. Therefore, to reach an appropriate dating centre, it is necessary to have a half life much greater than the estimated/potential age of the artefact otherwise the age could be underestimated by as much as a factor of two.

Thermal stability of organic radicals and lattice defects

The ESR signal of the lattice defect was described to be of first order kinetic (Porat and Schwarcz, 1995) and can be written as $\frac{dn}{dt} = -Kn$ which allows the description of the rate constant K as a function of T temperature and n the concentration in paramagnetic centres. By integration we obtain n as a function of time. $n = n_0 \cdot e^{-Kt}$ where n the paramagnetic centre concentration at t (n_0 at t_0)

Using the Arrhenius' relation we can extrapolate the thermal disappearance rate at ambient temperature. $k = \nu_0 \cdot e^{-(E_a/kT)}$ with ν_0 the frequency, k the Boltzmann constant and E_a activation energy.

Organic radicals such as alkyl, methyl and perinaphthenyl behave differently than the lattice defects. It needs to be kept in mind that other mechanisms are involved. For example, unstable organic components can with time transform into a different organic radical or in some case a precursor of other radicals, and thermal treatment will then have an equivalent effect as the irradiation by increasing the ESR intensity. The assumption made here is that thermal treatment has denatured some of the precursors trapped within the matrix, transforming them into a paramagnetic radical observable with ESR. As a result, isothermal curves will behave similarly to irradiation effect on lattice defect by first increasing, before decreasing with further thermal treatment.

Therefore, radical concentration calculation is slightly different and can be described by: $\frac{dn}{dt} = K_1N - K_2n$ where N represents the concentration of the unstable radical denatured by heat with a corresponding rate constant of K_1 . K_1N represent the new radical that is continuously created by heat from the precursor N . The variation of n with time corresponds to the creation by thermal processes of new radicals from specific precursors. Nevertheless, the new radicals are also unstable and tends to decay/transform with time.

Fig. 4A to E show the Arrhenius plot of the k constants of the organic radical and defects studied, while the Fig. 4F to J the extrapolated mean life around and below room temperature of the defects. The discrepancy of the data in kinetics studies always leads to large errors and uncertainties. Table 1 summarises the mean life obtained by the isothermal annealing experiments for each radical and defects at 15 °C, and ranges from 80 ka for CH₃ to 1,500 ka for the E' and Al centres. By comparison Porat and Schwarcz (1995) describe a similar value for the E' centre, in the order of magnitude 10³–10⁴ ka (Table 1).

Figure 4. Kinetic behaviour of each lattice defects and organic radicals: Figures A to E ((A) Peroxy; (B) CH₃; (C) Al; (D) E'; (E) Perinaphtenyl) are the Arrhenius diagrams for K with the slope corresponding to the activation energy. The half lives (or values of 1/K) are given as a function of temperature as shown in Figures F to J, with (F) Peroxy; (G) CH₃; (H) Al; (I) E'; (J) Perinaphtenyl respectively.

Table 1. Summary of CH₃, perinaphtenyl, peroxy, E' and Al at 15 °C mean life, using the isothermal annealing experiments. The half-life values are changing so drastically even with small variation of the ambient temperature, that the error on such values does not requires to be reported.

	CH ₃	Perinaphtenyl	Peroxy	E'	Al
$T_{1/2}$ (ka)	80	150	500	1500	1500
E_a (eV)	0.88	0.8	1.28	1.13	1.26
ν_0 (s ⁻¹)	2.4×10^{13}	1.4×10^{10}	1×10^{15}	4.3×10^{11}	2.3×10^{13}

The residual intensity of organic radical could potentially be used to estimate the minimum age of a sample while establishing the “equivalent firing temperature”. In this study, we define the equivalent firing temperature as the temperature for one hour of thermal treatment that is equivalent to the archaeological treatment. Since the initial thermal treatment can potentially correspond to different combinations of temperature and heating time, only an equivalent temperature for 1 h of treatment can be determined. By using the lifespan of all organic radicals depending on their presence/absence in the signal, potentially a rough estimation of an age could be obtained. However, a complete understanding and timing of radicals formation and half life would be required to accurately achieve even just an estimation of time elapsed since the archaeological heating.

Comparison of thermal treatment procedures

A series of experiments was conducted to accurately assess the uncertainties and errors for the equivalent temperature estimation and kinetic study of the ESR intensity measurements. Initially the cumulative firing temperatures were compared for a single thermal treatment. The intensity was compared after 2 h of heating at 300 °C and two separate one-hour heating regimes with a cooling period of 24 h between the two thermal treatments. All ESR intensity values for the organic radicals and lattice defects show no statistically significant variation. Successive and cumulative thermal treatment shows no significant difference to one equivalent heating time and temperature. The geological flint was heated at a specific temperature (300 °C) for 2 h and then successively reheated for short periods of 10 min between 150 °C and 350 °C. All temperatures between 150 °C and 300 °C show no significant influence on the ESR signal. While 10 min at 350 °C shows an intensity increase for the perinaphtenyl and a clear decrease for lattice defects. The behaviour observed here validates both the isochronal analytical approach described in Fig. 2 and the equivalent temperature identification approach, since very brief thermal treatment at lesser temperature will have no significant effect on the signal intensity. One limitation could come from the potential transformation of the ESR signal with time or other diagenetic factors. Nonetheless, under the conditions used in this study the experiment shows promising potential in terms of precision and accuracy for framing the 1-h equivalent firing temperature.

Comparative behaviour of the ESR and TL signal under thermal treatment

A thermal treatment equivalent to the archaeological firing (Lahaye et al., 2006) needs to be accurately determined in order to produce consistent TL dating on samples (Roque et al., 2004, Duttine et al., 2005). This can be accurately achieved by using precise isochronal and isothermal models built on ESR measurements of burnt flints. On the one hand, organic radicals provide a more sophisticated way of identifying the firing temperature since irradiation cannot regenerate the intensity of the radicals after being denatured by heat (Porat and Schwarcz, 1991, Duttine et al., 2005). Another approach is to use lattice defects or impurities (e.g. E' or Al centre), since both ESR signal can be regenerated with irradiation until reaching maximum temperature (see isothermal) that corresponds to structural modification (i.e. crystal modification or reorganisation, impurity and/or compensator mobility) (Duttine et al., 2005).

Given the various benefits of these approaches, the two annealing procedures have to be used simultaneously to identify precisely the equivalent firing temperature. One has to keep in mind that the temperature can only be defined with an associated firing time (i.e. temperature of 300 °C for 20 min). The use of organic radical relative intensities, in relation to their thermal treatment response, offers to bracket accurately the equivalent firing temperature. An alternative approach would be to heat the sample for short periods of times (20 min to avoid the effect of cumulate thermal treatment) at increasing temperatures, until the relative distribution of the organic radicals starts to be modified by heat, which will generally start at 50 °C under the temperature estimated with the first method. The second method will only give the corresponding temperature for a specific heating time, which can be related to the kinetic model and compare to the first estimation.

At low temperature, the geological intensity (signal accumulated before being bleached by archaeological heat) will not be completely erased, and the remaining signal for temperatures under 225 °C (1 h) are significant compare to the archaeological signal and therefore prevent effective TL dating. Between 225 °C and 375 °C (1 h) the E' centre presents a residual ESR signal from geological irradiation. This thermal stability of the E' signal as well as the peroxy signal could have had implication for TL dating of flints with potential involvements of recombination centres. Nevertheless, Duttine et al. (2005) argued that only the Al centre (380 °C TL peak) is relevant for TL dating as the E' (second electron in the oxygen vacancy) will recombine with the Al centre.

Fig. 5A presents the TL plots obtained for aliquots powdered and heated at 150 °C, 250 °C, 300 °C, 350 °C, 400 °C and 450 °C for one hour; TL curves of a natural material (non-heated aliquot) is also displayed. The natural signal provided the strongest intensity of the whole dataset. For samples annealed at 400 °C and more the intensity of the residual TL signal is negligible compared to the natural signal. Therefore, all radicals and defects have been denatured or emptied respectively. Each plot appears composed of at least two separate peaks. The 150 °C curves clearly show the disappearance of the first peak while the second peak rises. However, it should not be assumed that the intensity difference between the natural curves and the 150 °C curves can be attributed to the disappearance of the R-CH₂. While, this conclusion might be plausible because only R-CH₂ is modified at 150 °C (Fig. 3A), although it should be kept in mind that the luminescence centre (or group centres) is potentially different the paramagnetic centres. Nevertheless, it cannot be excluded that R-CH₂ potentially participates

in the luminescence activity of the artefacts, and therefore could be responsible for the depletion of the signal between the natural and the 150 °C curve. Similarly, according to the kinetic stability of the aforementioned centres, we can speculate that the 250 °C luminescence curves decrease might potentially be related to the peroxy denaturation, likewise for the 300 °C and 350 °C luminescence curves with the Al centre. The TL curves of higher temperatures (400 °C and 450 °C) samples show no significant signal while the ESR spectra had the perinaphtenyl with significant remaining intensity. It can be concluded with a relatively strong degree of confidence that the perynaphtenyl does not participate in the luminescence process at all.

Figure 5. (A) Residual TL signal recorded after 20 min of thermal treatment at 150 °C, 250 °C, 300 °C, 350 °C, 400 °C and 450 °C. (B) Background signal (second run of TL after recording the residual signal).

The background TL signal, which corresponds to the second run of the same sample with no secondary irradiation, is generally used to evaluate the zero level of TL (Fig. 5B). Aliquots previously heated at 350 °C and below continue to exhibit a greater residual intensity than the standard blackbody radiation that is emitted by sample and sample holder. On the other hand, samples that have received a thermal treatment of 400 °C and above show a negligible residual

TL signal. According to the ESR kinetic behaviour and the TL signal, the aliquots that have received thermal treatment at 350 °C and below shows a TL remaining signal most likely originating from the pyrolysis of organic radicals trapped in sample. Consequently, one should refrain itself from using flints with the equivalent temperature below 350 °C, as part of the natural signal will be generated by the transformation of organic molecules by heat treatment and not from the archaeological irradiation. In other words, a certain percentage of the signal will relate to the pyrolysis of organic matter. This will inevitably induces large error in the dose assessment of the sample. The presence of carbon radicals in the ESR signal is a fast assessment of a sufficient archaeological firing temperature. Regrettably a large portion of Bergeracois archaeological flints tested prior to this studied have provided a low equivalent firing temperature, inducing challenging TL dating.

Finally, since the amount of organic matters varies from one chert to the other (e.g. Guibert et al., 2004, Duttine et al., 2005), a standard correction for TL pyrolysis induced signal from organic matter cannot be calculated and applied systematically.

Conclusions

The ESR signal of flints is composed of several organic radicals (alkyl, methyl, perynaphtenyl and amorphous carbon impurities) as well as the aluminium centre and lattice defects (peroxy and E' centres), which are already well described in the literature. Isochronal and isothermal experiments have shown complex behaviour patterns for each of these signals. While the lattice defects shows annealing behaviour proportional to the increase of temperature, the organic radicals respond differently to thermal treatment with complex intensity variations especially for the R-CH₂ radical. Isothermal modelling has allowed us to constrain the firing temperature characterisation accurately, and reveal potential application for TL dating on low firing temperature artefacts, while isochronal experiments have shown significant differences between the mean life value for the different impurities and lattice defects that could have repercussion for the use of ESR for dating. Nonetheless, ESR dating of flints appears to be very challenging, and should be used only with great caution.

A clear link between the two lattice-defects as well as the aluminium centre with the TL signal emphasised that the potential dating range of burnt flints could reach several million years in ideal conditions. Yet, flints that have received low equivalent thermal treatment (1 h at <350 °C) should be investigated carefully with ESR as pyrolysis processes have proven to interfere greatly with the luminescence signal. Large dose estimation error could occur without proper correction for the interfering pyrolysis signal. Further studies on the TL signal compared to the ESR signal of flints could hold the key to understand and overcome such experimental limitation.

The residual ESR intensity of organic radical could potentially be used to estimate the minimum or maximum age of a sample while establishing the equivalent temperature to the archaeological firing temperature and time, supposing monomolecular kinetics of decay. One has to keep in mind that such estimation can only be achieved by assuming an average burial temperature over time, which will inevitably leads to large errors in the age approximation. Nevertheless, the use of organic radicals lifespan such as CH₃ and perinaphtenyl on

archaeologically burnt flints could give a broad estimate of age. Especially, by coupling the equivalent temperature with the measured intensity of the organic radicals, the presence or absence of one type of radical could provide in certain case very rapid minimum age estimation. Inversely, the determination of an equivalent firing temperature by using the presence or absence of organic radicals by ESR, must be examined cautiously taking into account the fact that some of these radicals thermally formed are not stable with time and could have decayed since the archaeological firing.

Acknowledgements

We would like to thank Professor Gérard Villeneuve supervisor of this work at the time, and who passed away several years ago. Gege, since, has been greatly missed by friends and colleagues in Bordeaux and Arcachon where he was living. This is the last work he supervised, before retiring and then sadly a few months later disappearing. We will always remember his kind nature, his gentle behaviour and his great sense of humour. We are also grateful to Professor Rainer Grün for his advice and input in the early stage of the manuscript. We would like to thank the Institutions in Bordeaux (Bordeaux 3 University, CNRS, Région Aquitaine) and Southern Cross University for supporting part of this work. We would like to thank also the INRAP archaeologists, especially Laurence Bourguignon, for providing samples and maps. ARC DP140100919 supported part of this research. We are deeply grateful to the anonymous reviewers who patiently through comments and suggestions improved considerably the present paper.

Editorial handling by: F. Preusser

References

- Aitken, M.J., 1985. Thermoluminescence Dating. Academic Press, London, 359 pp.
- Bartoll, J., Schwarcz, H.P., Rink, W.J., 2001. ESR studies of E' centres in geological flint. *Radiat. Meas.* 33, 893e898.
- Bourguignon, L., Sellami, F., Ortega, I., 2002. Bergerac e RN.-21 Section Nord/DFS de sondages archeologiques. INRAP, Sud-Ouest.
- Bourguignon, L., Blaser, J., Rios, L., Pradet, L., Sellami, F., Guibert, P., 2008. L'occupation moustérienne de la Doline de Cantalouette II (Creysse, Dordogne): specificites technologiques et economiques, premiers resultats d'une analyse integree. *Bull. Soc. Pr_ehistoriq. Franç.* XLVII, 133e150.
- Chandra, H., Symons, M., Griffiths, D., 1988. Stable perinaphtenyl radicals in flint. *Nature* 332, 526e527.
- Duttine, M., Guibert, P., Perrault, A., Lahaye, C., Bechtel, F., Villeneuve, G., 2005. Effect of thermal treatment on TL and EPR of flints and their importance in TLdating : application to a French Mousterian sites of les Forêts (Dordogne) and Jibouï (Drome). *Radiat. Meas.* 39, 375e385.

Fernandes, P., Le Bourdonnec, F.X., Raynal, J.P., Poupeau, G., Piboule, M., Moncel, M.H., 2007. Origins of prehistoric flints: the neocortex memory revealed by scanning electron microscopy. *Compt. Rend. Paleovol.* 6, 557e568.

Griffiths, D., Robins, G., Seeley, M., Chandra, H., Mc Neil, D., Symons, M., 1982. Trapped methyl radicals in chert. *Nature* 300, 435e436.

Griffiths, D., Seeley, M., Symons, M., 1983. Investigation of chert heating conditions using ESR spectroscopy. In: *The Scientific Study of Flint and Chert. Proceedings of the Fourth International Flint Symposium*. Brighton Polytechnic, pp. 259e262.

Guibert, P., Bechtel, F., Schvoerer, M., Rigaud, J.P., Simek, J.F., 1999. Datation par TL de sediments chauffés provenant d'une aire de combustion moustérienne. *Rev. D'Archeometrie* 23, 271e287.

Guibert, P., Perraut, A., Duttine, M., Lahaye, C., Brenet, M., Folgado, M., 2004. Datation par thermoluminescence (TL) couplée à la résonance paramagnétique électronique (RPE) de silex chauffés provenant du site moustérien des Forêts, Saint-Martin de Gurçon, Dordogne (France). *Paleo* 16, 117e128.

Guibert, P., Bechtel, F., Bourguignon, L., Brenet, M., Couchoud, I., Delagnes, A., Delpech, F., Detrain, L., Duttine, M., Folgado, M., Jaubert, J., Lahaye, C., Lenoir, M., Maureille, B., Texier, J.-P., Turq, A., Vieilleuvre, E., Villeneuve, G., 2008. Une base de données pour la chronologie du Paléolithique Moyen dans le Sud Ouest de la France. *Bull. Soc. Préhistoriq. Franç.* XLVII, 19e40.

Hiscock, P., Clarkson, C., 2000. Analysing Australian stone artefacts: an agenda for the twenty-first century. *Aust. Archaeol.* 50, 98e108.

Ikeya, M., 1993. New applications of electron spin resonance dating dosimetry and microscopy. *World Sci.* 9, 271e287.

Imai, N., Shimokawa, K., Yamamoto, M., 1994. ESR study of radiation centres and thermal behaviour in chert. *Quat. Geochronol.*, 641e645.

Jonas, M., 1997. Concepts and methods of ESR dating. *Radiat. Meas.* 27, 943e1125.

Lahaye, C., Godfrey-Smith, D.I., Guibert, P., Bechtel, F., 2006. Equivalent thermal history HE of ferruginous sandstones based on the thermal activation characteristics of quartz. *Radiat. Meas.* 41, 995e1000.

Mercier, N., Valladas, H., Valladas, G., 1995. Flint thermoluminescence dates from the CFR laboratory at Gif: contributions to the study of chronology of the middle palaeolithic. *Quat. Sci. Rev.* 14, 351e364.

Mercier, N., Valladas, H., 2003. Reassessment of TL age estimates of burnt flints from the palaeolithic site of Tabun Cave, Israel. *J. Hum. Evol.* 45, 401e409.

Porat, N., Schwarcz, H.P., 1991. Use of signal subtraction methods in ESR dating of burnt flints. *Nucl. Tracks Radiat. Meas.* 18, 203e212.

Porat, N., Schwarcz, H.P., 1995. Problems in determining life times of ESR signals in natural and Burned flint by isothermal annealing. *Radiat. Meas.* 24, 161e167.

Porat, N., Ping Zhou, L., Chazan, M., Noy, T., 1999. Dating the lower paleolithic openair site of Holon, Israel by luminescence and ESR techniques. *Quat. Res.* 51, 328e341.

Richter, D., Mercier, N., Valladas, H., Jaubert, J., Texier, P.J., Brugal, J.P., Kervazo, B., Reyss, J.L., Joron, J.L., Wagner, G.A., 2007. Thermoluminescence dating of heated flint from the Mousterian site of Berigoule, Murs, Vaucluse, France. *J. Archaeol. Sci.* 34, 532e539.

Robins, G.V., 1984. The study of heated and charred archaeological materials with ESR. *J. Anal. Appl. Pyrolysis* 6, 31e43.

Roque, C., Guibert, P., Duttine, M., Vartanian, E., Chapoulie, R., Bechtel, F., 2004. Dependence of luminescence characteristics of irradiated quartz with thermal treatment and consequences for TL-dating: application to dating of Solutrean heated quartz pebbles from Laugerie Haute (Dordogne, France). *Geochronometria* 23, 1e8.

Toyoda, S., Ikeya, M., Dunnell, C., McCutcheon, P.T., 1993. The use of ESR for the determination of prehistoric lithic heat-treatment. *Appl. Radiat. Isot.* 44, 227e232.

Toyoda, S., Hattori, W., 2000. Formation and decay of the E1 0 center and of its precursor. *Appl. Radiat. Isot.* 52, 1351e1356.

Wintle, A.G., Aitken, M.J., 1977. Thermoluminescence dating of burnt flint: application to a lower paleolithic site, Terra Amata. *Archaeometry* 19, 111e130.

Yokoyama, Y., Falgueres, C., Quaegebeur, J.P., 1985. ESR dating of quartz from quaternary sediments: first attempt. *Nucl. Tracks Radiat. Meas.* 10, 921.