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Research paper

Thermal characterization of ancient hearths from the cave of Les Fraux (Dordogne, France) by thermoluminescence and magnetic susceptibility measurements

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ABSTRACT

Numerous sorts of evidence of fires were observed in the cave of Les Fraux (Dordogne, France) and in particular the effects of fire on sediment were studied for a better understanding of their use centuries ago. Our present objective is the evaluation of the firing intensity by determining the past temperature (paleotemperature) attained by the topmost sediment of the archaeological fires. The principle of paleotemperature determination is based on the thermoluminescence (TL) properties of quartz and the magnetic susceptibility of the sediment. By comparing the TL signal of anciently heated quartz to the TL signal of thermal references made in the laboratory, we were able to obtain a maximal equivalent temperature attained for each sample extracted from ancient fires. The magnetic susceptibility (previously measured on the hearth surface) could thus be estimated as a function of temperature. The main result of this study is the temperature mapping of the hearth which can be used as meaningful information about the ancient firing intensity.

1. Introduction

At the cave of les Fraux, which was occupied at the end of the Bronze Age, numerous hearths were found. The question about the function of these hearths, their number, and their relation to the rock art are relevant, especially in an underground context. The study of these hearths could present new information concerning the heating intensity, the length of use of the fire structures and, consequently, their functions. In this particular case, the approach used in the study of hearths, and more precisely in the determination of the paleotemperature of the topmost sediment of the hearths, is the thermoluminescence of quartz.

Some studies have already shown an interest in the evolution of a thermoluminescence (TL) signal in relation to temperature. Valladas (1980, 1981) determined the maximal temperature attained in the past by heated sandstones, by estimating the saturation point of TL signals with the dose added (the temperature of TL curves at which natural and natural + doses overlap). This saturation point is situated at circa 100 °C beyond the expected heating temperature of sandstones. Many researchers also considered the sensitivity of the 110 °C TL peak to estimate the firing temperature on quartz (Sunta and David, 1982; Watson and Aitken, 1985; Koul et al., 1996) or on flint (Göksu et al., 1989). Another study illustrated the evolution of the geological signal with the temperature measuring TL on a sample from an instrumented experimental fire (Spencer and Sanderson, 1994). More recently, different researches were carried out on TL signal dependence with thermal treatment. They showed that the shape of TL curves and the sensitivity changed with the temperature attained by heated quartz (Roque et al., 2004a), by ferruginous sandstones (Lahaye et al., 2006) and by ceramics (Roque et al., 2004b; Vieillevigne et al., 2007). These studies led us to consider the TL signal as a whole, including its intensity and its shape, to determine past heating temperatures of heated sediment (paleotemperature).

The studied sediments came from the cave of Les Fraux, located in Dordogne in France. This cave, discovered in 1989, is a rare example of a Bronze Age site with both archaeological remains and rock art preserved (Carozza et al., 2009). The known karstic network is composed of around 1 km of narrow galleries and rooms. The preservation of this site is exceptional as the cave entrance collapsed right after its last occupation around 3300 years ago. The small rate of sedimentation left most of the archaeological remains like hearths visible. Indeed there is multiple evidence of fires such as reddened areas, ashes and charcoals. The important

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number of hearths leads us to study fires as a way to better understand the occupation of the cave. Therefore we wish to classify fires according to the importance of their effect on the sediment and thus the firing intensity.

2. Material and methods

In this paper, one hearth from the cave of Les Fraux (Fig. 1) is used as an example to present the results of the methodology developed. It consists of a clayey hearth located in the middle of reddened sediments, altered sandstones and charcoals.

Our general methodology started *in situ* by building a map of the magnetic susceptibility of the hearth, by doing surface measurements in the selected fire area. This set of measurements allowed us to choose the sampling locations for laboratory studies more precisely. Unheated sediment was also sampled to create thermal references. The latter are sediment samples with the same geological origin as that of the archaeological fires and heated according to a well defined thermal protocol in the laboratory. Then, the TL signals of all samples were measured. The comparison between the TL signals of past heated samples and the reference ones allowed us to determine the paleotemperature of each archaeologically heated sample. Finally, by calibrating *in situ* magnetic susceptibility measurements with paleotemperatures determined by TL, we obtained a temperature map of the hearth area under study.

2.1. Magnetic susceptibility

For *in situ* magnetic susceptibility measurements a KT-9 kappameter (Exploranium) was used. The magnetic susceptibility depends mainly on the content of magnetic minerals and their nature (principally iron oxides). Heating implies mineralogical transformations among iron oxides (Cudennec and Lecerf, 2005; Dunlop and Özdemir, 2007) depending on the nature of pristine iron oxides and the heating conditions (temperature, rates, duration, atmosphere…). In general, the higher the attained temperatures, the stronger the magnetic susceptibility. Thus, these measurements give data about the location of the hearth and about its intensity as well (Le Borgne, 1955, 1960). In this particular case, the magnetic susceptibility was used as an indicator of the perimeter of the heated zones because the variations in magnetic susceptibility were very important (at least multiplied by 100).

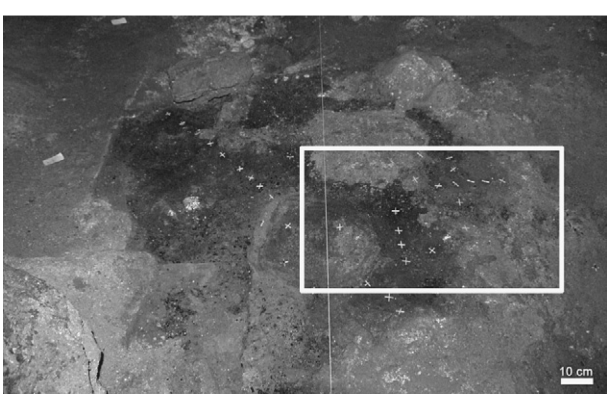

Fig. 1. Fireplace under study that is a part of a reddened area with numerous more or less altered sandstone blocks. The white rectangle represents the surface of the map of magnetic susceptibility. The white crosses show the sample locations for the TL measurements chosen along radial gradients of magnetic susceptibility. © Albane Burens, photograph published by courtesy of Edmond Goineaud, owner of the cave of Les Fraux.

2.2. Samples

The sampling locations were chosen along a radial gradient of magnetic susceptibility which was supposed to be the result of a temperature gradient. Small samples of sediments were extracted from the hearth (ca. 1 cm deep and 1 cm in diameter). An additional large sample of unheated sediment of the cave was also extracted from an unfired area of the cave with a view to making thermal references with quartz grains from the same geological origin.

In the laboratory, quartz grains were selected from the sediment by disaggregating and sieving at 80, 200, 500 μm. The fraction between 200 and 500 μm was the most abundant and thus was chosen for TL measurements. Subsequently, chemical treatments were applied: a HCl treatment (1M ≈ 3.1 w%) to dissolve any carbonates that can give rise to spurious signals while heating in a nitrogen atmosphere during TL measurements; followed by a HF (40 w%) etching for 1 h to wash the quartz grains from clay remains and dissolve feldspars; and subsequently a HCl treatment (3.1 w%) to remove potential fluorides.

2.3. Thermal references processing

A chamber furnace (Eurotherm 2416CG, Carbolite) was used to prepare the TL thermal references which would be compared to the hearth quartz samples. The unheated sediment (same geological origin than the sediment of hearth) sampled in the cave was heated according to a precisely designed heating cycle in air: (1) heating from room temperature to the maximal temperature programmed at a rate of 20 °C/min, then (2) staying for 1 h at this temperature (called also equivalent temperature) and subsequently (3) cooling until room temperature at a rate of 5 °C/min. Thus fourteen thermal references were made with different maximal temperatures that varied from 200 °C to 650 °C. We kept an unheated sample as a control. These thermal parameters were chosen to correspond to realistic heating rates and maximal temperature in a fire (Werts and Jarhen, 2007; our own experiments).

2.4. Thermoluminescence

TL measurements were carried out with the automatic equipment that was designed and built in the Bordeaux laboratory. The main organs of this apparatus are a 24 position multi-sample holder, a beta ^{90}Sr source, a heating chamber surmounted by optical filters (a set composed of two Schott BG12 filters and one Schott IR rejector; spectral window 350–475 nm), a PM tube (EMI 9813 QA) and associated electronics that record the luminescence signals as a function of temperature. The TL signals of the quartz grains extracted from sediments are recorded while heating from room temperature to 500 °C at 4 °C/s under a neutral atmosphere (nitrogen).

The TL measurements were detailed below:

Aliquot 1:

- Reading of the remaining natural TL: ‘geological signal’
- Background
- Irradiation of 12 Gy (normalization dose)
- Reading of the normalization TL signal
- Background

These measurements were performed twice.

We recorded the TL signal that remained after the annealing treatment to make the reference material. As the sample used for making thermal references was never heated in the past, we called the remaining TL signal, ‘geological signal’. We were then able to follow its decay as a function of the annealing temperature.

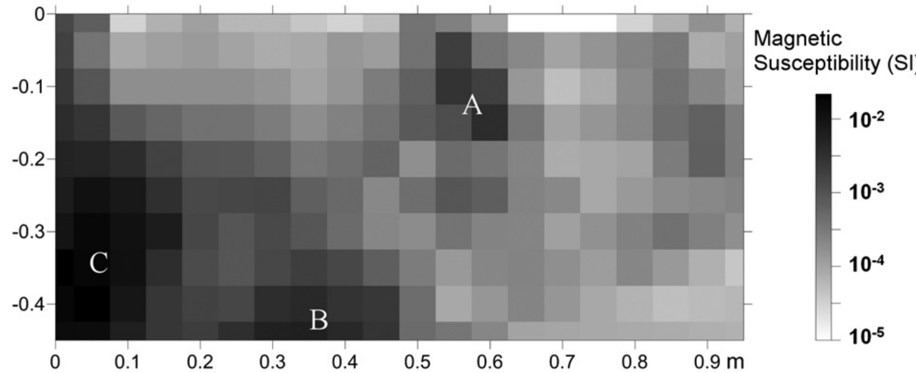

Fig. 2. Magnetic susceptibility mapping conducted in the area of the fireplace under study. Three places with strong magnetic susceptibility are visible (A, B, C).

Aliquot 2:

- Irradiation of 12 Gy following by a cut-heat at 230 °C
- Reading of the 'simulated natural' signal
- Background
- Irradiation of 12 Gy (normalization dose)
- Reading of the normalization TL signal
- Background

These measurements were also performed twice.

The TL signal named 'simulated natural' signal was recorded. To compare TL signals between references and hearth samples, it was necessary to simulate on the references the irradiation received by the archaeological samples during the time elapsed since the original fire. Therefore, a beta irradiation of 12 Gy followed by a cut-heat at 230 °C to erase low energy components of TL were performed on the reference quartz. The dose was chosen to be equivalent to the dose received since the archaeological fire (3300 years with a rate of 3.6 mGy/year, that was supposed to be a mean value for sedimentary sandy clayey material of that type in this area). The cut-heat temperature of 230 °C was determined following a trial/error procedure: the low temperature component (below 280 °C) of TL curves was compared between the thermal reference samples and the archaeological ones. Indeed, the quartz grains extracted from the hearth had a low temperature component of TL signal, around 250 °C. We observed that a cut-heat at 250 °C was too strong and erased all low temperature components (below 280 °C) of TL of thermal references. On the contrary, a cut-heat at 200 °C was too low and the remaining TL of the 230–280 °C region had too high intensity in comparison with archaeologically heated sediment. 230 °C appeared to be a reasonable compromise, even if some discrepancies were observed in the low temperature region of TL of archaeological samples.

All aliquots, either reference or archaeological ones, are made with the same quantity of quartz (mass and volume). No second glow normalization was necessary to compare intensities and glow curve shapes, although normalization experiments were performed systematically.

3. Results and discussion

3.1. Map of magnetic susceptibility

The map of magnetic susceptibility (Fig. 2) shows three zones of high values corresponding to the most concentrated magnetic phases, which probably are the most heated places. They correspond to the hearth (C), to one reddened area (A) and to a third zone (B) covered with charcoals. Based on these measurements, 34 samples of sediments were taken, that are represented by white crosses in Fig. 1. Quartz grains were extracted, as explained before, for TL measurements.

3.2. Thermoluminescence results

Firstly, the TL signals of thermal references are detailed. Fig. 3 illustrates the disappearance of the 'geological' TL signal as a function of the maximal temperature. The signal seems to progressively drop and move to high temperatures. The global TL intensity decreases drastically between the unheated reference and the

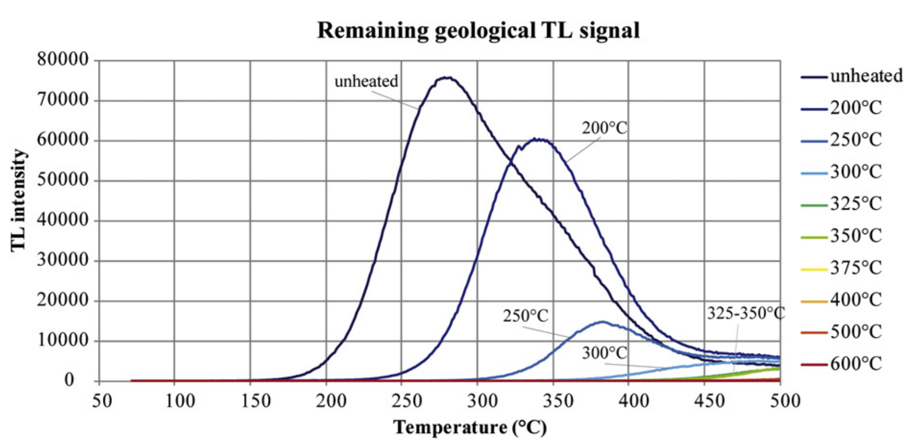

Fig. 3. Remaining 'geological' TL signal of the thermal references after annealing at various temperatures.

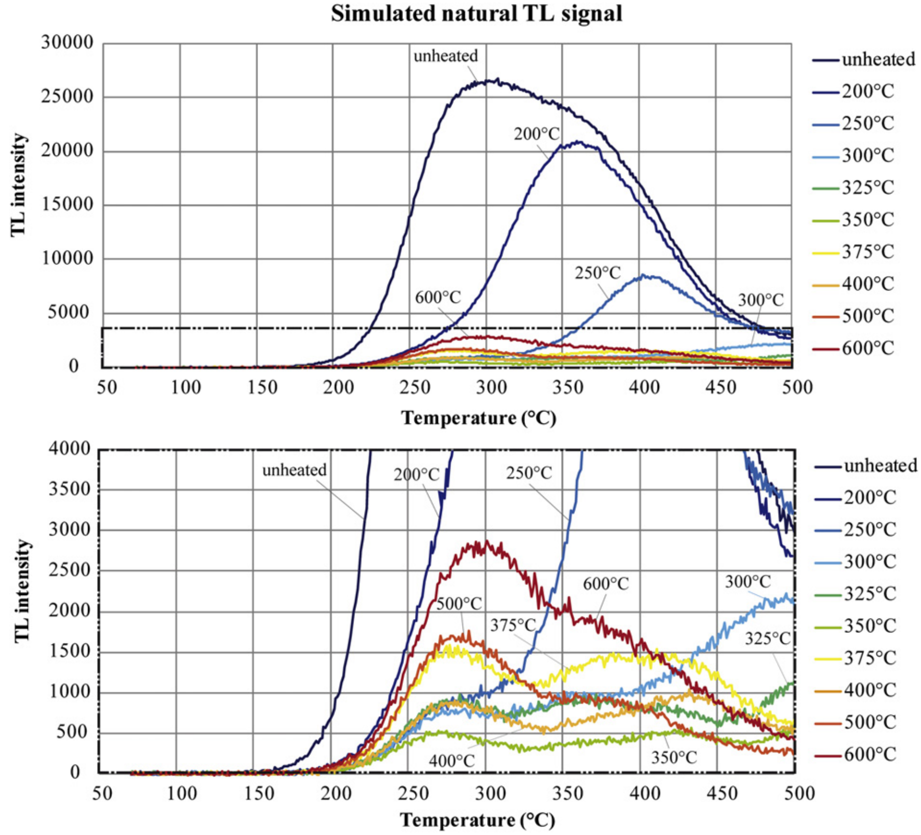

Fig. 4. 'Simulated natural' TL signal of the thermal references as a function of the previous annealing temperature.

250 °C ones. For references heated in the laboratory from 300 °C to 375 °C for 1 h, a residual signal remains in the high temperature region of the TL curves (>400 °C). After heating for 1 h at more than 375 °C, no geological TL signal remains anymore.

Fig. 4 illustrates the evolution of the 'simulated natural' TL signal. The unheated reference and those heated for 1 h at 200 °C and 250 °C are dominated by the geological signal (high intensity and saturation of TL). When the quartz was annealed below 375 °C,

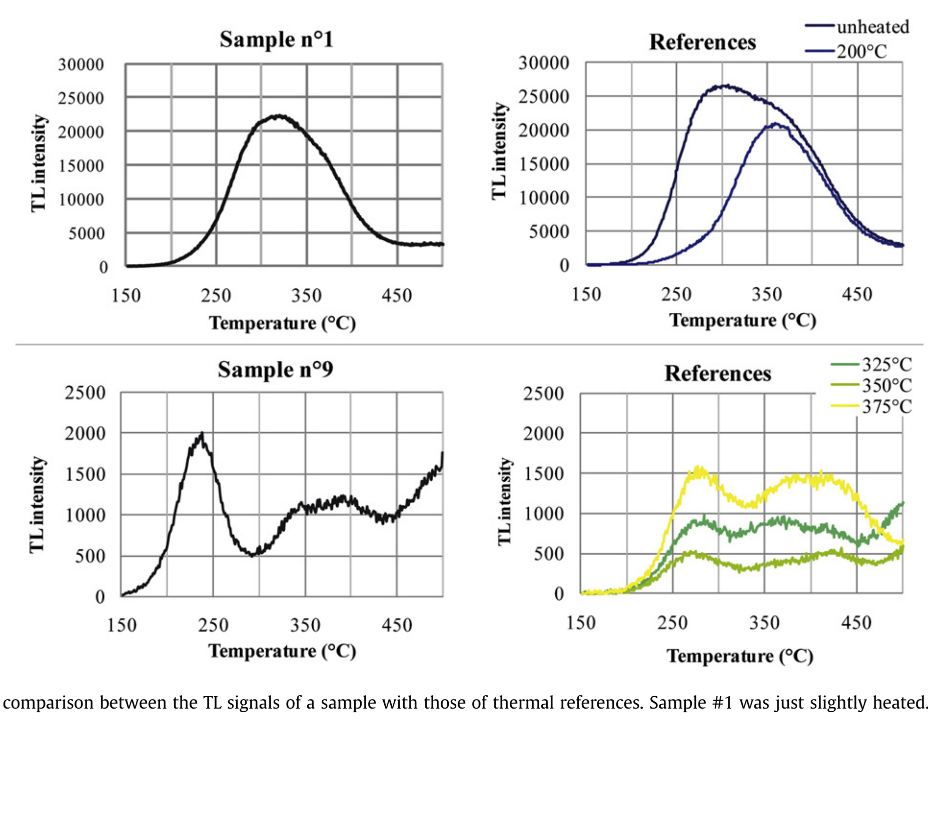

Fig. 5. Two examples of the comparison between the TL signals of a sample with those of thermal references. Sample #1 was just slightly heated. Sample #9 was heated about 350 °C.

Table 1
Sample numbers (#) and inventory code (BDX) with short description (s.: sandstone, s.r.: reddened sandstone, c.: charcoals, s.c.: sandstone with some charcoals) and calculated equivalent paleotemperature (*T*).

Samples numbers & description			*T*	Samples numbers & description			*T*
#	BDX		°C	#	BDX		°C
1	12619	s.	25	16	12634	c.	250
2	12620	s.r.	350	17	12635	c.	250
3	12621	s.r.	425	22	12639	s.r.	450
4	12622	s.r.	325	23	12640	s.r.	325
5	12623	s.r.	425	24	12641	s.r.	>300
6	12624	s.r.	550	25	12642	s.c.	?
7	12625	s.r.	600	26	12643	s.	600
8	12626	s.r.	425	27	12644	c.	450
9	12627	s.r.	350	28	12645	c.	>300
10	12628	s.	25	29	12646	c.	600
11	12629	s.r.	400	30	12647	c.	600
12	12630	s.	25	31	12648	c.	?
13	12631	c	600	32	12649	c.	250
14	12632	c.	25	33	12650	c.	200
15	12633	c.	25	34	12651	c.	200

a part of the geological signal remained in the high temperature regions of the TL curves but the general intensity dropped. For the thermal references which were heated at more than 375 °C, the intensity of two major components of the regenerated TL (at 280 °C and 360 °C) increased with the annealing temperature. We can also note the global enhancement of sensitivity for the 600 °C curve.

To estimate paleotemperature of hearth samples, the 'simulated natural' TL signal of reference samples and the natural signal of hearth samples were compared. The comparison was based on the shape and intensity of the respective TL curves. The 34 samples presented 34 different natural TL signals which, in general, matched the thermal references quite well. We may add that the paleotemperatures determined for hearth samples are to be considered as equivalent temperatures since they are dependent on the thermal protocol parameters used to process references.

Initially, a visual comparison was made and allowed a first attribution of paleotemperature. To exemplify the comparison, the samples #1 and #9 are compared to their best-fit references (Fig. 5): sample #1 presents a curve looking like an intermediary curve in intensity and shape between unheated and 200 °C references. We can conclude that this sample had just been slightly heated. The TL of sample #9, considering the temperature region between 300 °C and 480 °C, appears to be the closest to the reference heated at 350 °C.

In addition, a hierarchic classification (SFig. 1) of the TL curves of all samples was performed (STATISTICA: the dendrogram was constructed using Euclidean distances and Ward's method, Baxter, 2003). For that purpose the 150–470 °C region of TL curves (after background subtraction) of the reference samples and the hearth ones was cut into 32 integrals 10 °C wide, and every curve was then compared to each other. The classification confirmed our first visual determination of paleotemperature.

Finally an equivalent firing temperature was attributed to a large majority of samples (Table 1). Two samples remained indeterminate because their TL curves did not match with those of the thermal references (samples #25 and #31). Two others (samples #24 and #28) were poorly thermally characterized and we denoted them '>300 °C' due to the major discrepancies in TL curve shape between aliquots of the same material (one is attributed to 300 °C, the second to 600 °C, for instance). We can then conclude that these samples were heated above 300 °C. The spatial distribution of heated or unheated samples appeared to be consistent with the fact that the samples which were heated the most correspond to the hearth and the reddened areas.

3.3. *Map of temperature*

By comparing the temperature determined by TL and the magnetic susceptibility values of samples, it was possible to deduce a relationship between these two parameters (Brodard et al., submitted for publication). Based on this relationship, an equivalent temperature mapping of the area under study was obtained (Fig. 6).

First of all, we may notice that places which were heated the most (heated above 350 °C) emerge from a background due to the intrinsic variations of the mineralogy of the sediment. Secondly, we may observe that the magnetic susceptibility exhibits significant changes only for the material that was heated at more than 350 °C (equivalent temperature determined by TL). Nevertheless, the first enhancement of magnetic susceptibility is expected around 250–300 °C (Cudennec and Lecerf, 2005; Dekkers, 1990; our own experiments on the sediment of the cave of Les Fraux: Brodard et al., submitted for publication). To explain this discrepancy, one of the likely hypotheses is the differences in investigation volume and depths of both *in situ* magnetic measurements (around 2 cm deep, 5 cm in diameter) and sediment sampling for TL studies (less than 1 cm deep and 1 cm in diameter): magnetic measurements investigate a greater depth of sediment and, by averaging, a less heated material than the quartz sampled. Thus the temperature determined by TL is higher than the average temperature due to the depth gradient.

Nevertheless, it was possible to reconstruct a paleotemperature mapping of the hearths studied. The three zones of high magnetic susceptibility are now represented by zones of the most elevated temperatures. The B and C zones exhibit the most heated sediment

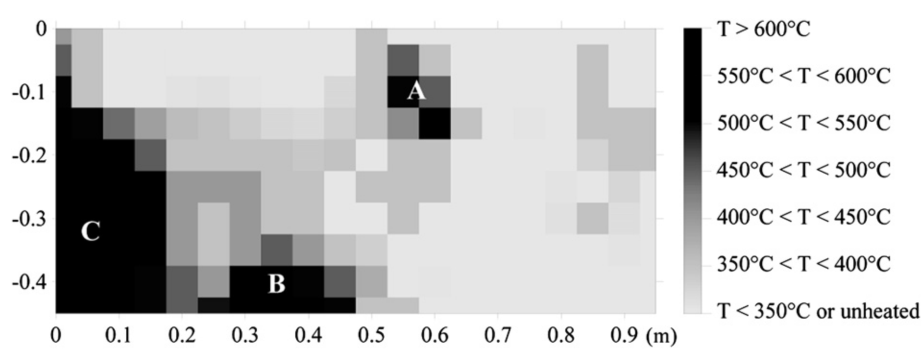

Fig. 6. Map of the equivalent temperature obtained after the calibration in temperature of the magnetic susceptibility values.

with paleotemperature equivalent to 600 °C. The temperature attained by the sediment of the reddened area (A) is lower, between 400 and 550 °C. Finally the heated places show up very clearly in contrast with the unheated or slightly heated sediment.

4. Conclusions

TL measurements of quartz allow determination of paleotemperature of anciently heated quartz. This is, naturally, to be considered as an equivalent temperature referencing to a particular thermal protocol. The combination of TL measurements with magnetic susceptibility makes the temperature mapping of important areas possible. As long as the sediment is the same (i.e. same geological origin of quartz, qualitative composition of the sediment), thermal references and calibration of magnetic susceptibility with temperature are usable. Only this methodology is transferable to another site but thermal references have to be recreated for each new material, each new site.

The integration of TL and magnetic susceptibility measurements on burnt sediments allowed the quantitative study of ancient hearths. The temperature attained by the topmost sediment is thus a first indication of the firing intensity. To better understand the heating marks let by ancient fires in the sediment, experimental fires have to be set up and monitored by series of thermocouples to record the temperatures attained at different locations and depths below the surface of the fire. This is the following step of this research, currently in progress.

In addition to the evaluation of the agreement in determining by TL the equivalent annealing temperature of quartz grains with a known thermal history, these fires also allow us to estimate the necessary quantity of wood for a chosen duration of heating. Finally, the combination of thermal characterization results with experimental fires will help to create a numerical model of fire adapted to our study. Its further integration in the three dimensional model of the cave of Les Fraux will allow a better characterization of the living environment in terms of light, heat, and certainly smoke, during the occupation at the Bronze Age.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.quageo.2012.04.013.

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