

Developing the linear modulated OSL (LM - OSL) as a new tool for ceramic dating

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ABSTRACT Optically stimulated luminescence (OSL) is used, as well as thermoluminescence (TL), in our laboratory to investigate the authenticity of ceramic art objects from museum collections. A great advantage of the OSL is to need only a few samples using a single aliquot regeneration (SAR) technique to obtain ages with a good accuracy. On the other hand, the OSL intensity integrates the signal from various traps: some of them may be unstable. Hence a detailed investigation is needed for all new objects. The linear modulated - optically stimulated

luminescence (LM-OSL) technique could be a good alternative. The regular increase of the stimulation power permits to monitor the various traps in the crystal. The advantage of the LM-OSL is to work with low heat (125°C) reducing the risk of thermal perturbation of the crystal usually encountered with TL. Various bricks and sands are investigated. The choice of the best stimulation power depending on the type of ceramic is discussed. An example of direct dating using SAR-LM-OSL is presented and compared to TL dating obtained on the same sample.

1. Introduction

Thermoluminescence (TL) is widely used to date ceramics and terracotta since the 1970's (Aitken, 1985). As the other dating methods, TL is based on two properties of the material. It is a physical process which evolves with time and there is an initial instant (Giot and Langouët, 1984). The physical process is the accumulation of absorbed energy coming from the ambient radioactivity into the minerals. We assume that the content in radioelements (uranium, thorium and potassium) is constant and then the dose received during one year, the annual dose, is constant. The initial instant is a heat at above 500-700°C which resets to zero the anterior accumulated dose. During the TL measurement, a new heat treatment is conducted. During the heat, the previous accumulated dose, known as palaeodose, is released under light emission, the so-called "natural TL". To calibrate the emission, it is necessary to re-irradiate the sample with an artificial radioactive source before to measure again the signal. But during the first heating in laboratory, some changes in the mineralogy can occur in the sample, such as the diffusion of impurities or the phase transition from α quartz to β quartz. Then, the sample used for the calibration is, from a mineralogical point of view, not strictly the same as in the initial conditions. To avoid this problem, a particular protocol, known as additive TL (Aitken, 1985), is employed using various aliquots, some for recording the natural TL and the others to measure a mixed natural + laboratory induced TL. It is time- and material-consuming.

In the mid of 1980's, a new dating method, the optical stimulated luminescence (OSL), was developed using light (visible or near IR) to stimulate the emission, instead of the heat. Being optical stimulation an energy soft process, there is no perturbation of the

sample; then, it is possible to work with a single aliquot (Murray and Wintle, 2000). The OSL technique is then a good alternative to TL when the size of the sample is strongly limited as it is, generally, for ceramics from museums.

The usual OSL technique, or continuous wave OSL (CW-OSL), is an integrating method. Under stimulating light, all the signal is received in a short time and it is not possible to discriminate between the various kinds of emission. Only the stable signals (i.e. with lifetimes much greater than the archaeological age) are used to date and there is no straightforward way to identify them in CW-OSL. In TL, each signal is identified by a peak in the glow curve. The best temperature range is defined by the so-called 'plateau' test (Aitken, 1985). Bulur (1996) developed a technique, the linear modulated OSL (LM-OSL), in which the power of the stimulation light increases from zero to a maximum during the measurement. With this technique, it is possible to discriminate the various signals of the OSL. In this paper, known materials are investigated by LM-OSL to assess the ability of this technique to improve dating of museum objects.

2. Experimental details

2.1. Sample preparation and the number of aliquots

Sample preparation was similar to the routine procedure followed for dating. The sands and powders were crushed in an agate mortar. The tiles were sampled using a mini-drill with 1,8 mm tungsten carbide bit. After etching by HCl and washing by water, ethanol and acetone, the 4-10 μm fraction is selected by sedimentation into 8 cm height acetone and deposited on 9,8 mm diameter discs. All these operations, but the HCl etching, are automated (Zink et al., 2002).

For the routine procedure to date museum objects, the sample is limited to 100 mg and the corresponding fine grain fraction is not enough to be split in more than twenty aliquots (or discs). Thirteen are used for additive TL measurements (Fleming, 1979), four for OSL, one for test. The last two are conserved for some possible further tests.

The main aim of the study was to see if LM-OSL measurements can be usefully incorporated in this procedure without increasing the number of aliquots. For that purpose, various kinds of materials were used, such as terracotta, as shards or powders, and sands. The powders were annealed at 500°C during several hours to eliminate all previous TL/OSL signals, before irradiation with β or X-ray source. For X-ray stimulation, 420/10 SEIFERT iso-volt X-ray tubes (Beryllium windows) were used with the sample located at 1.3 m from the tube. The β source $^{90}\text{Sr}/^{90}\text{Y}$, incorporated into the measurement apparatus, provided a dose rate of 0.13 Gy/s (at the date of 1.06.2003).

2.2. Measurement apparatus

The measurements were performed with a Risø TL/OSL DA-15 reader. The luminescence was recorded using a photomultiplier tube EMI 9235 QA with 7,5 mm Hoya U340 filter. The blue light stimulation was provided by 18 pairs of blue diode (470 nm) delivering a maximum irradiance of 19 mW cm^{-2} at the sample position. Infrared stimulation used an IR laser diode at 830 nm with a maximum irradiance of 450 mW cm^{-2} at the sample. To limit the effects of cross-irradiation and cross-bleaching (Bray et al., 2002), the discs were put only on the odd positions. All measurements were recorded by integrating one second per channel.

2.3. Experiments

A basic LM-OSL experimental sequence is described in table 1. It was adapted from a classical double-OSL measurement (Murray and Wintle, 2000).

TABLE 1

The double SAR CW-OSL procedure and the version adapted to LM-OSL.

	Basic double SAR CW-OSL	intensity observed	Adapted to LM-OSL	Intensity observed
1	Give dose D_i	—	Give dose D_i	—
2	ph 200°C os	—	ph 200°C os	—
3	IR-OSL 100s at 60°C	—	IR-OSL 200s at 60°C	—
4	BL-OSL 100s at 125 °C	Li	LM-OSL 0-100% 200s at 125 °C	Li
5	Give test dose D_t	—	BL-OSL 200s at 125 °C	—
6	ph 200°C os	—	LM-OSL 0-100% 200s at 125 °C	Lo
7	IR-OSL 100s at 60°C	—	Give test dose D_t	—
8	BL-OSL 100s at 125 °C	Ti	ph 200°C os	—
9	return to 1		IR-OSL 200s at 60°C	—
10			LM-OSL 0-100% 200s at 125 °C	Ti
11			BL-OSL 200s at 125°C	—
12			LM-OSL 0-100% 200s at 125 °C	To
13			return to 1	

The normalized response to a dose D_i ($i=\{0,1,2,3\}$) is Li/Ti for the basic double SAR and $(Li-Lo)/(Ti-To)$ for the LM-OSL double SAR.

In a first step, a dose D_0 was given to the sample. It could be a natural irradiation due to environment after the last heat, the so-called palaeodose, or an artificial irradiation made with a calibrated source in the laboratory (line 1 in table 1). The feldspar contribution was removed during the infrared stimulation (IR-OSL). The LM-OSL was recorded under blue stimulation with a power rate of $0.095 \text{ mW cm}^{-2} \text{ s}^{-1}$ (the maximum power being reached in 200s). After the LM-OSL, the sample was stimulated during 200s with the diodes at full power to eliminate all luminescence (line 5 in table 1). Then, a second LM-OSL recorded the background. To normalise the sensitivity, the cycle was repeated with a test dose (1.3 Gy). To calibrate an unknown dose D_0 , we followed a single aliquot regeneration (SAR) process. Three different regenerating doses D_i ($i=\{1,2,3\}$) were employed which interpolated D_0 . A measurement without dose gives the recuperation value, normally close to zero. The calibrations were concluded with a second measurement of D_i to test the recycling (1.00 ± 0.15 is an acceptable value). In total, the sequence displayed in table 1 was repeated six times on the same aliquot to determine the unknown dose D_0 .

2.4. LM-OSL curve deconvolutions

For a single trap of first order, Bulur (1996) described the LM-OSL curve as a function of time t by the following equation:

$$L(t) = - \frac{dn}{dt} = n_0 \frac{\sigma I_0}{\theta} t \exp \left(- \frac{\sigma I_0}{2\theta} t^2 \right)$$

n_0 is the initial trapped charge number related to the trapping probability, σ is the cross section (cm^2) related to the detrapping probability, I_0 is the maximum stimulation intensity ($I_0 = P/h\nu$ where P is the maximum irradiance — W cm^{-2} — and $h\nu$ the photon energy - eV) and θ is the total measurement time (s). The product $b = \sigma I_0$ is the frequency of optical detrapping (Hz).

For a usual sample, the LM-OSL curve is the addition of the signal from several traps. Each trap is defined by σ and n_0 . To estimate σ and n_0 , the experimental curves were fitted by the addition of several Bulur's equations. The curves were simulated using 1 to 5 components, the parameters being adjusted for each sample. The best fit was obtained by minimising the χ^2 -value ($\chi^2 = \sum_t (L_{\text{obs}}(t) - L_{\text{fit}}(t))^2$) using the SOLVER macro in an EXCEL spreadsheet.

3. Results

3.1. Properties of polymineral LM-OSL

The LM-OSL curves for various bricks and sands irradiated 47 Gy and read with a power rate of $0.095 \text{ mW cm}^{-2} \text{ s}^{-1}$ are plotted in Fig 1. Cluny B and CMB are terracotta, that is, mixtures of different minerals; it is not surprising that three peaks were found through the analysis. For sands which are dominated by quartz, the LM-OSL curve displayed almost only one peak. The corresponding parameters of the components are summarised in table 2. Similar value of σ can be noticed, especially between CMB and Sand A. The reference values in literature are very limited. Only pure quartz was actually investigated by LM-OSL under blue light stimulation (Jain et al., 2003; Singarayer and Bailey, 2003; Tsukamoto et al., 2003). Jain et al. (2003) identified seven components, called respectively ultra-fast, fast, medium, slow1, slow2, slow3 and slow4. Singarayer and Bailey found the same value of σ , but the ultra-fast and the slow1 components were not identified. The values founded by Tsukamoto et al. who made the distinction between tephric and volcanic quartz are different from the other authors who seem to work on sedimentary quartz. Our results seemed more consistent with those from Tsukamoto et al (2003). Hence, Cluny B was more consistent with tephric quartz, while CMB and sand A could be volcanic quartz. Sand B seemed a mixing of volcanic and tephric quartz.

TABLE 2

The cross section (σ) and the number of initial trapped electrons (n) of the components fitted to LM-OSL curves plotted on Fig. 1.

	$\sigma_1 (\text{cm}^2)$	n_1	$\sigma_2 (\text{cm}^2)$	n_2	$\sigma_3 (\text{cm}^2)$	n_3
Cluny B	$7.1 \cdot 10^{-18}$	$1.5 \cdot 10^5$	$2.5 \cdot 10^{-18}$	$1.1 \cdot 10^5$	$5.9 \cdot 10^{-19}$	$7.2 \cdot 10^4$
CMB	$1.2 \cdot 10^{-17}$	$5.2 \cdot 10^3$	$1.8 \cdot 10^{-18}$	$1.6 \cdot 10^4$	$2.2 \cdot 10^{-19}$	$5.0 \cdot 10^4$
Sand A	$1.1 \cdot 10^{-17}$	$1.3 \cdot 10^6$	$1.8 \cdot 10^{-18}$	$1.0 \cdot 10^3$		
Sand B	$1.5 \cdot 10^{-17}$	$9.9 \cdot 10^3$	$6.6 \cdot 10^{-19}$	$2.3 \cdot 10^3$		

(power rate: $0.095 \text{ mW.cm}^{-2}.\text{s}^{-1}$; Cluny B: Roman brick 2nd century AD; CMB: a modern brick; and Sand A and Sand B: two commercial sands)

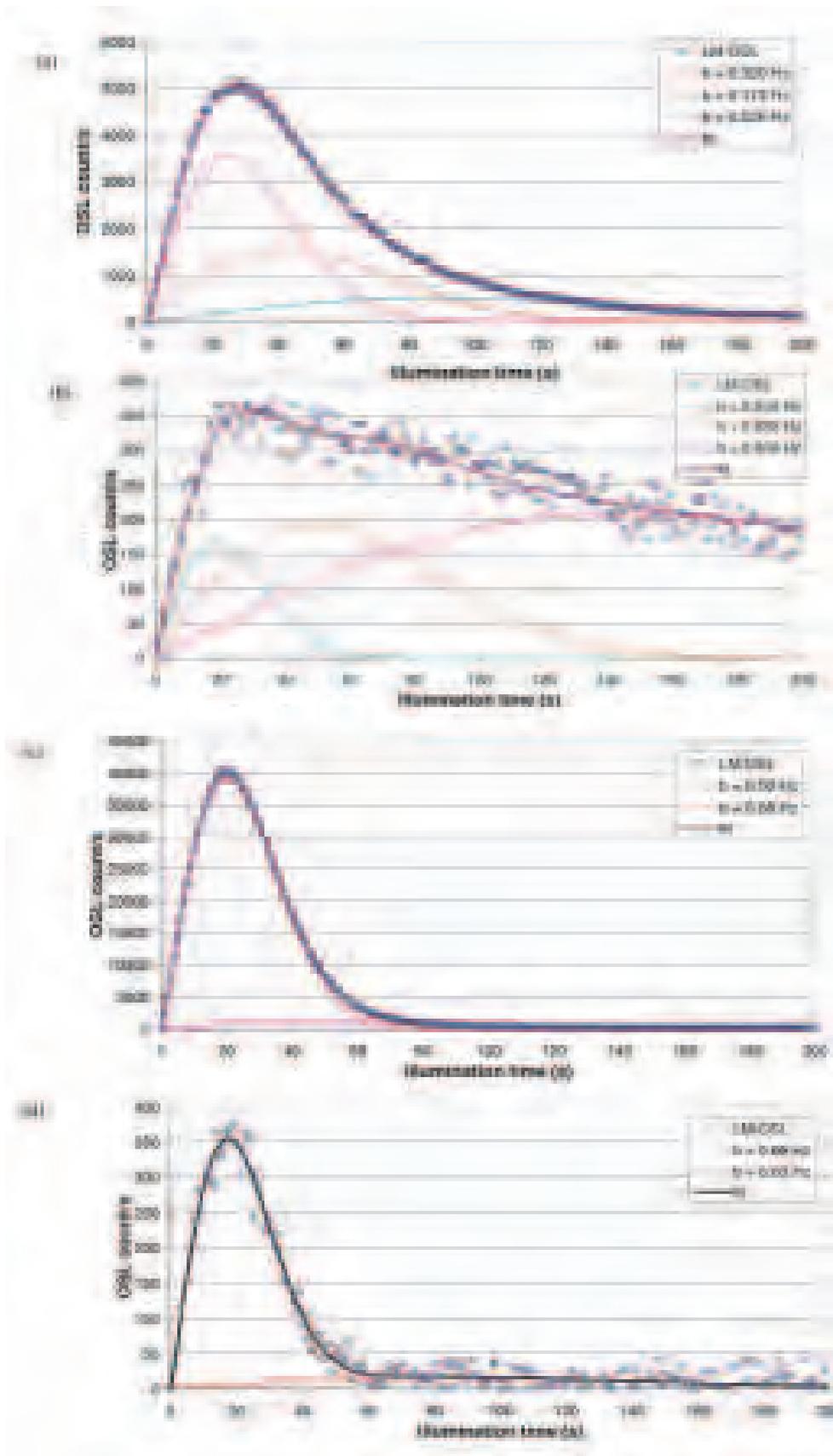


FIG. 1 – LM-OSL curves for various bricks and sands (a - Cluny B Roman brick II century AD; b- CMB modern brick 19th century AD; c-Sand A; d-Sand B). The LM-OSL component fitted and their sum are also plotted. (irradiation 47 Gy; power rate 0.095 mW cm⁻² s⁻¹)

3.2. Effect of the power rate

By increase of the total duration of the stimulation from 200 to 6000 s, we decrease the power rate from $0.095 \text{ mW cm}^{-2} \text{ s}^{-1}$ to $0.0032 \text{ mW cm}^{-2} \text{ s}^{-1}$. The measurements were made on two samples (Cluny and CMB). The values of σ were fixed for each sample to the values found for a stimulation during 200s (see above). With such an initial condition, the fit was globally satisfying. At low power rate, one to two new traps were added to optimise the fit, corresponding to traps with lower cross sections. We observed a relative stability of the charge trapped concentration.

3.3. Thermal stability

The effect of the preheat temperature was investigated for Cluny and CMB. After irradiation to a fixed dose, the sample was preheated to a temperature T between 180°C and 400°C at 20°C steps. On Fig. 2, the change of intensity of the various components are shown with a normalisation to the preheat at 180°C .

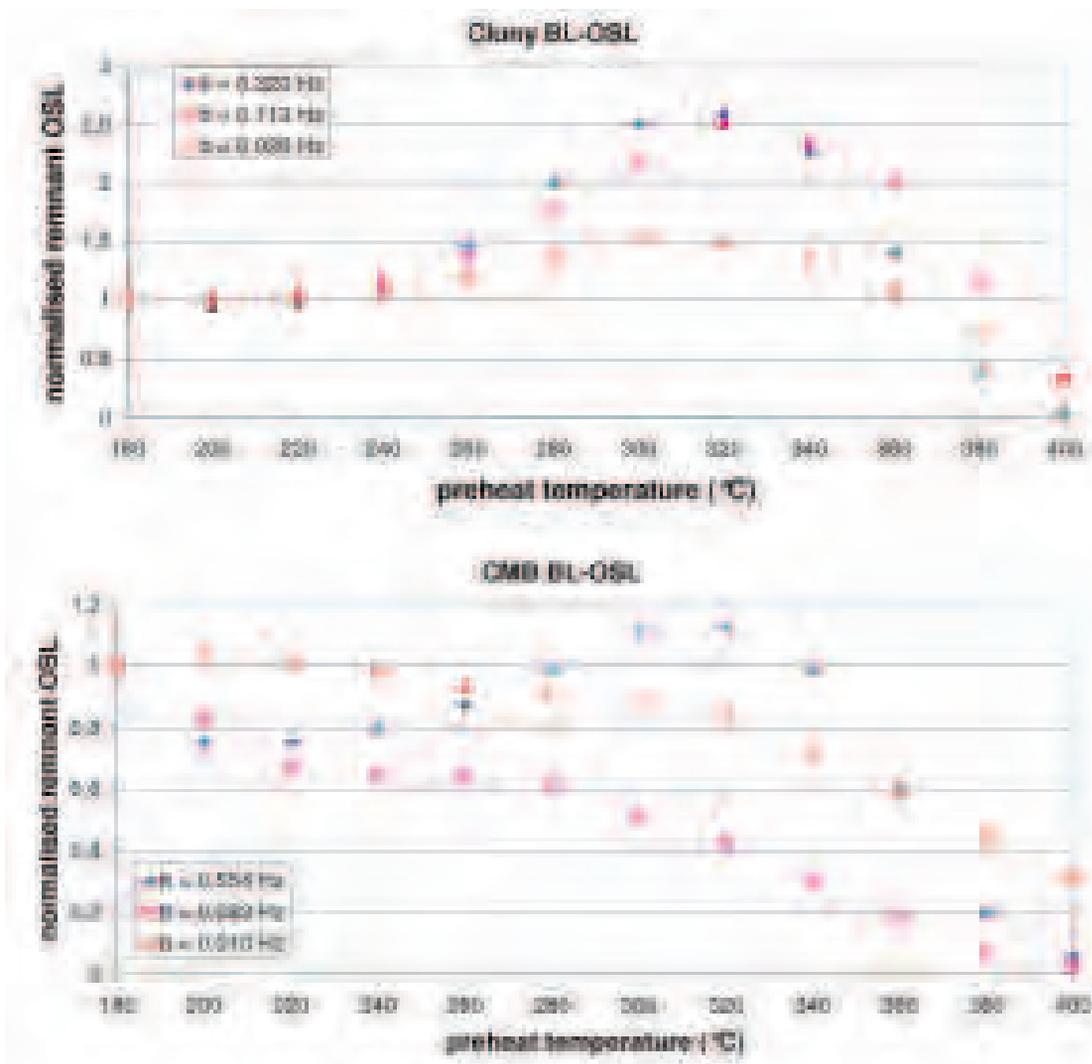


FIG. 2 – Change of intensity of the various components of the LM-OSL with the preheat temperature for a Roman brick – Cluny B and a modern brick – CMB (normalization to the preheat at 180°C)

For Cluny, the three components have the same evolution. The signals were stable until around 250°C. Then we observed a high sensitisation from 260 to 320°C, followed by a decrease. At 400°C, the component 1 is negligible, when the component 2 and 3 were reduced to around 30% of the signal for preheat at 180°C.

The evolution for CMB is more complex and the signal is less stable. The first component ($\sigma = 1.2 \cdot 10^{-17} \text{ cm}^2$) has an evolution similar to the components Cluny, with a strong sensitisation around 300-320°C. The second component ($\sigma = 1.8 \cdot 10^{-18} \text{ cm}^2$) shows two successive decays, the first below 220°C, the second above 280°C. The last component ($\sigma = 2.2 \cdot 10^{-19} \text{ cm}^2$) was stable until 240°C before decreasing.

3.4. Direct dating using LM-OSL

Singarayer and Bailey (2003) suggested to use the slower component from quartz (Slow4 following the nomenclature of Jain et al., 2003) to date all geological samples (>>100 ka). They used a SAR protocol and resolved the components of the LM-OSL curves. Such a process could be useful for old samples (the cited sample gives a palaeodose of '696±438 Gy') with a strong intensity of the luminescence. Choi et al. (2003) used indirectly the LM-OSL measurement to separate the components within the CW-OSL curve in the aim of dating. For samples with a low natural emission such as archaeological ceramics (usually 1-10 Gy), it is not possible to obtain a valuable fit, and then to separate the components. The precision on the fit is limited by the signal/noise ratio of the measurement (Fig. 3). Hence, for such a sample we suggest to use another method for which the fit is not needed.

We decided to process the LM-OSL data as for TL with the so-called 'plateau' test. After the measurement of the sample by a SAR protocol, as described above (table 1), a dose response curve was plotted for each channel (i.e. each second of illumination). Then, the palaeodose De was reported as a function of the illumination power. Analogue to the TL, we searched the power range where De is maximal and constant. We assume that for such a range, the dominant component is stable (i.e. its lifetime is much greater than the archaeological age).

We tried this method first to estimate the dose from X ray irradiated materials in the framework of a study on the effects of radiography on TL measurements (Castaing et al. submitted). Six tiles and sands were previously annealed to 550°C during few hours, and then irradiated with the X-ray source used in our laboratory for the object radiographies. The irradiation was made under 400 kV 4 mA during 90 minutes. The results (Table 3) were in agreement with the CW-OSL results.

TABLE 3

The equivalent in seconds of beta irradiation measured by linear modulated-OSL (LM-OSL) and continuous wave-OSL (CW-OSL) of an X-ray irradiation of 400 kV, 4mA during 90 minutes.

Specimen #	LM-OSL	CW-OSL	Specimen #	LM-OSL	CW-OSL
CMB-P		421 ± 50	Meggido P	339 ± 17	413 ± 21
CMB shard	338 ± 47		Sand A	286 ± 48	257 ± 10
XIX P	305 ± 21	354 ± 10	Sand B	258 ± 55	284 ± 11
Cluny P	340 ± 19	284 ± 4	Sand MNgg		276 ± 7
Average	311 ± 10	327 ± 3			

An archaeological brick from St Denis (France) was dated previously by TL and OSL in the framework of an intercalibration program between the C2RMF and the ITN, Sacavém, Portugal (Richter et al., 2003). For each methods (TL and OSL), the results (table 4) were similar for the two laboratories. But a small underestimation of the OSL compared to the TL was observed. We decided to date the brick using the LM-OSL SAR protocol (Fig. 3) with two different preheat (200 and 250°C). The signal was very low. A plateau was present between 5 and 20% power levels. Integrating the signal between 5 and 20% corresponding to the peak, we obtained an equivalent dose of $2,2 \pm 0,3$ Gy in close agreement with the CW-OSL measurements.

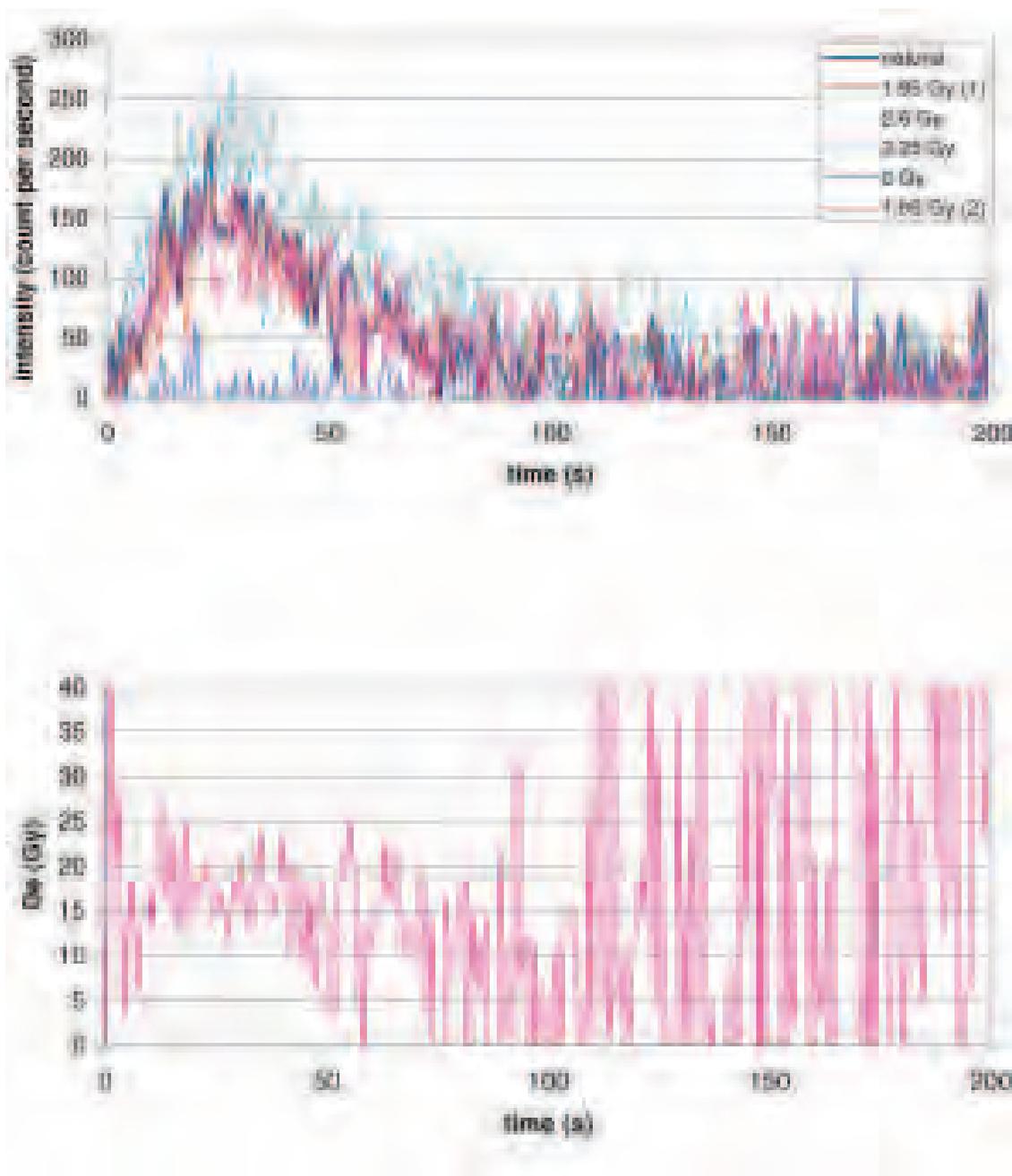


FIG. 3 – Single aliquot regeneration protocol applied to the LM-OSL signal of a medieval brick (St Denis 57a). Top curves: LM-OSL curves. Bottom curve: the equivalent dose (D_e) as function of the irradiation time, the so-called 'plateau test'.

TABLE 4

Equivalent dose (in Gy) for a medieval brick from St Denis (France, 13th century) by various methods and dating techniques at the C2RMF (Paris) and at the ITN (Sacavém). The LM-OSL results are presented and commented in the present paper.

LM-OSL plateau	LM-OSL σ_1^*	LM-OSL σ_2^*	LM-OSL σ_3^*	CW-OSL C2RMF	CW-OSL ITN	TL** C2RMF	TL** ITN
2.2±0.3	2.1±0.3	2.3±0.3	0.4±0.4	2.2±0.3	2.39	2.6±0.3	2.70±0.08

* Component 1: $\sigma_1 = 9.2 \cdot 10^{-18} \text{ cm}^{-2}$

Component 2: $\sigma_2 = 2.9 \cdot 10^{-18} \text{ cm}^{-2}$

Component 3: $\sigma_3 = 4.4 \cdot 10^{-19} \text{ cm}^{-2}$

** For the discussion on the TL results see Richter et al. (2003).

We applied also a component-resolved method (see section 2.4). The parameters for the St Denis brick were based on LM-OSL measurements of coarse grains irradiated with 31 Gy after bleaching 5 minutes under blue light. Three components were identified. The first two components corresponded to the main peak and agreed together (Table 4). On the other hand the slow component 3, responsible of emissions at high power radiance, showed a very low value of the equivalent dose 0.4 ± 0.4 Gy. It is not surprising that the plateau range excluded the slow component. Due to its low intensity, the component 3 did not yield to a large underestimation of the CW-OSL dating which integrates the three components. It explains the good agreement between LM-OSL and CW-OSL dating.

4. Conclusions

LM-OSL is a simple experimental approach to detect the presence of various traps. Varying the measurement conditions gives the possibility of choosing the best signal for the purpose of dating. Our LM-OSL measurements showed that the CW-OSL signal from polymineral fractions extracted from ceramics or sands can not be easily reduced to quartz signals. Hence a LM-OSL study is useful for all new samples before dating measurements. Moreover the LM-OSL can be used directly to date. For such a purpose, a simple plateau method can be used, giving results in agreement with the more complex component-resolved method. The plateau method is particularly useful for ceramic dating where the luminescence signal is low.

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NOTES

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