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# PRELIMINARY TL AND OSL INVESTIGATIONS OF OBSIDIAN SAMPLES

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## ABSTRACT

Obsidian is a volcaniclastic mineral extremely hard to break, which was used in prehistoric Greece (and elsewhere in the World), in order to provide tools, weapons, knives and arrowheads. The present work aims to characterize this extremely precious tool stone by using both thermoluminescence (TL) and optically stimulated luminescence (OSL) techniques and investigate its potential use for luminescence dating purposes. Basic TL and OSL properties, such as TL and OSL thermal and optical stability, repeatability, TL and LM-OSL glow curve shape and mainly the linearity of the TL and OSL signals as a function of beta dose were investigated. Artificially irradiated samples indicate all promising luminescence features, such as the 110 °C TL peak and dose response sub-linearity for intermediate doses, quick and effective bleaching all over the entire TL glow curve, along with quite linear CW-OSL dose response for doses larger than 5 Gy. The lack of predose sensitisation indicates the suitability of the material for single aliquot measurements. Furthermore, several features provide indications that the signal does not relate to quartz, but in fact to other silicates. Unfortunately, both lack of bleaching ability for NTL signal, along with a peculiar shape of NOSL, provide major difficulties in dating applications.

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**KEYWORDS:** Obsidian, TL, CW-OSL, LM-OSL

## 1. INTRODUCTION

Luminescence dosimetry is an important part of solid-state dosimetry and incorporates processes whereby energy absorbed from ionizing radiation is later released as light. Its applications cover various fields, such as medical, environmental, personal, and retrospective dosimetry (McKeever, 2001). Examples of the latter fall in two major categories, namely the luminescence dating and accidental dosimetry (Bailiff, 1994; Liritzis, 2000).

Both fields involve the use of natural dosimeters in order to evaluate the absorbed dose over a long period of time. In nature, there are different quartz and/or feldspars based minerals that have appropriate luminescence properties and so they can be used as dosimeters either for environmental or retrospective dosimetry. Therefore, the need of using natural materials that have appropriate luminescence properties is evident.

The objective of this study is to explore the thermally and optically stimulated luminescent (TL and OSL respectively) properties of a sample of obsidian, a widespread geological material in the Mediterranean region, in order to observe the viability of its use as radiation dosimeter.

## 2. MATERIALS & METHODS

Obsidian is a volcaniclastic mineral extremely hard to break. Due to this specific property, it was used in ancient Greece, in order to provide sharp edges for tools as well as weapons such as knives and arrowheads. Obsidian exchange systems within the Mediterranean, Europe and Anatolia consisted of large regional networks in which obsidian was procured and transported beginning in the Neolithic Period (6000 – 3000 BC). In the Aegean region, the Melos obsidian source was extensively exploited. As a result, Melos obsidian is frequently found in many archaeological contexts thought the Late Bronze Age (Stevenson et al., 2002). Prehistoric people traded obsidian from Melos island of the Aegean Sea with mainland Greece, Asia Minor, as well as all over the Mediterranean Sea. Therefore, obsidian is one of the most widely distributed natural glasses in the Aegean Region and could potentially constitute a powerful chronological tool for the study of regional archaeological sites. The recent progress in obsidian hydration dating (Liritzis et al., 2007; Liritzis and Laskaris, 2009) and characterization (Liritzis, 2006) has gained an international interest; however, luminescence dating applications of obsidian are rarely reported in the literature (Göksu and Turetken, 1979). In the present work, preliminary measurements regarding basic thermoluminescence (TL) as well as optically stimulated luminescence (OSL) properties were obtained, using natural obsidian recovered from Melos, in order to evaluate its potential use in archaeological dating and retrospective dosimetry.

As all other volcaniclastic minerals, obsidian is an amorphous glass composed largely of silicon, the presence of which was confirmed by preliminary μ-XRF measurements that were obtained from obsidian's analysis. Nevertheless, the presence of quartz inclusions inside its matrix was very recently established in the case of Melos obsidian (Liritzis et al., 2007). However, in order to study thoroughly its chemical composition, further and thorough XRD and SEM analyses are required.

In general, Obsidian is a Rhyolite glass in which the common presence of Quartz, Orthoclase and Mica crystals has been generally established (Read, 1971). The chemical composition of obsidians, as known so far, in combination with its wide spread use in ancient Greece, especially in the region of the Mediterranean Sea, constitute two powerful motivations for further investigation of this material for luminescent dosimetry purposes.

The material used in the present study is a natural obsidian sample of black color, obtained from Melos island, Greece. The original piece was crushed and grains of dimensions 4 – 11 μm were selected and then deposited on aluminum discs of 1 cm$^2$ area. In order to reduce the effects of surface defects induced due to crushing, the sample was acid washed after crushing. Precipitation on discs was performed despite the problems of hydration of fine grains. Furthermore, given that obsidian is highly hygroscopic, before precipitation as well as while storing, the samples were kept at 80°C, in order to avoid possible spurious TL.

All luminescence measurements were performed using the RISØ TL/OSL reader (model TL/OSL – DA – 15), equipped with a high-power blue LED light source, a 0.0785 Gy/s $^{90}$Sr/$^{90}$Y $\beta^-$ ray source. The reader is fitted with an EMI 9635QA PM Tube (Bøtter-Jensen et al., 2000). All OSL measurements were performed using a Hoya U – 340 filter, while TL measurements were performed using a combination of a Pilkington HA –3 heat absorbing and a Corning 7 – 59 blue filter. Unless otherwise stated, all conventional OSL measurements were performed either at room temperature (RT) or 125 °C. In the former case, no preheat was applied, while in the latter case preheat at 160 °C was previously applied.

## 3. EXPERIMENTAL RESULTS

### *3.1 Natural TL*

Fig. 1A presents a glow curve of natural TL (NTL) signal of obsidian, measured up to a maximum temperature of 500 °C, using a heating rate of 1 °C/s, in order to avoid significant temperature lag between the heater plate and the samples. The main characteristic of this rather intense glow curve is that it has the form of a continuum centered on 340 °C. The FWHM of the NTL glow peak is 80 °C. These features are the same even in the case where NTL is measured using a Hoya U – 340 filter; however, this is not the case for the intensity also, since in the latter case it is greatly decreased.

According to the TL peak shape methods theory (Kitis and Pagonis, 2007), this feature provides indication for the NTL signal to consist only of one single, unique TL glow peak of second kinetic order. This result however, was not established by initial rise measurements. The initial rise technique results, presented in Fig. 1B, indicated the presence of two glow peaks to the NTL glow curve of obsidian; one main dosimetric and dominant peak in the temperature region 290–370 °C, which activation energy was estimated to be ~1.23 ± 0.08 eV. This result is in accordance to the corresponding activation energy values yielded by peak shape methods (1.18 eV). Furthermore, a second satellite TL glow peak was yielded in the temperature region 400 – 440 °C, with activation energy of 1.33 ± 0.13 eV. However, this curve does not appear clearly in the TL curve, probably due to its much lower intensity relative to main dominant one. Similar results were also yielded by the deconvolution analysis undertaken, indicating a half life of the order of 0.5 Ma.

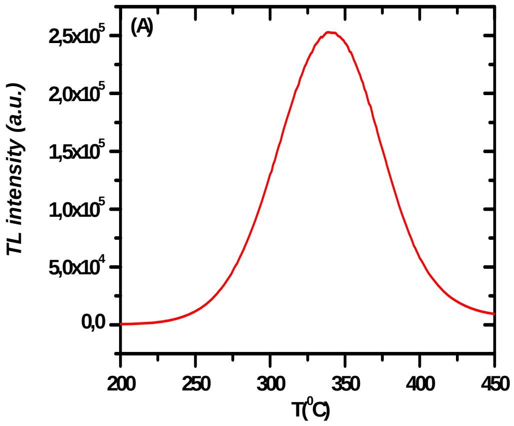

**Fig. 1A: Natural TL (NTL) glow curve signal of obsidian**

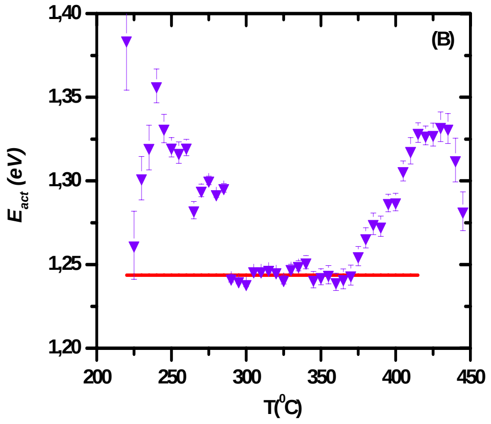

**Fig. 1B: Initial rise (I.r.) plot for the NTL signal of obsidian. For both figures, the heating rate applied was 1 °C/s.**

However, these activation energy values are probably underestimated, due to the fact that the luminescence emitted from obsidian suffers from thermal quenching. This was verified after using different heating rates, ranging between 0.25 and 4 K/s. Then, the integrated NTL signal is decreased by a factor of 0.23.

### *3.2 Bleaching of NTL*

The bleaching ability of obsidian was studied using 40 different aliquots, divided into different groups of four aliquots each. Two samples of each group were exposed to sunlight produced by a SOL – 2 simulator lamp (Dr Hönle) for the same time, while the other two samples of each group were exposed to light produced by the blue LEDs of the RISØ TL/OSL reader (emitting at 470 nm, FWHM 40 nm). 10 variable lengths of time exposure were applied, covering the range between 0 and 2 hours. Samples from the first group were measured in order to obtain the natural luminescence signal. After each exposure, the residual luminescence signal was measured for both aliquots of each sub-group and averaged. Results are presented in Fig. 2.

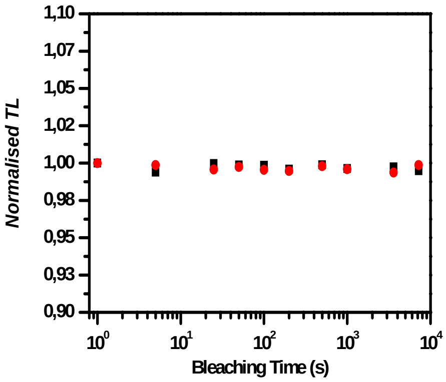

**Fig. 2: Residual level of the NTL signal, as a function of the time exposure to (a) sunlight produced by a SOL– 2 simulator lamp (Dr Hönle), (circles) (b) light produced by the blue LEDs of the RISØ TL/OSL reader (emitting at 470 nm, FWHM 40 nm, squares). Each experimental point corresponds to the mean value of the two measurements carried out in two different aliquots.**

Unfortunately, this NTL glow peak seems to be unbleachable using both blue LEDs (emitting at 470 nm, FWHM 40 nm) and/or a solar simulator SOL II (Dr Hönle). This extremely hard-to-bleach NTL signal could possibly affect the measurements of natural OSL signal (NOSL) from obsidian.

### *3.3 TL after artificial irradiation*

Fig. 3 presents a glow curve corresponding to the dose of 256 Gy $\beta^-$ irradiation in the laboratory. The NTL signal has been previously removed. Taking into account that obsidian consists mainly of silicates, its glow curve shape should be the sum of all overlapping peaks due to those minerals, such as quartz and/or feldspars. As it was further experimentally revealed, the TL signal after artificial irradiation consists of several prominent overlapping peaks, including those that are typical for silicate-dominated minerals, such as the glow peaks at $T_{max}$~90 °C (*P1*), ~165 °C (*P2*), ~200 °C (*P3*) and at ~ 255 °C (*P4*). In order to distinguish the individual glow peaks, a computerized glow curve deconvolution (CGCD) analysis should be used.

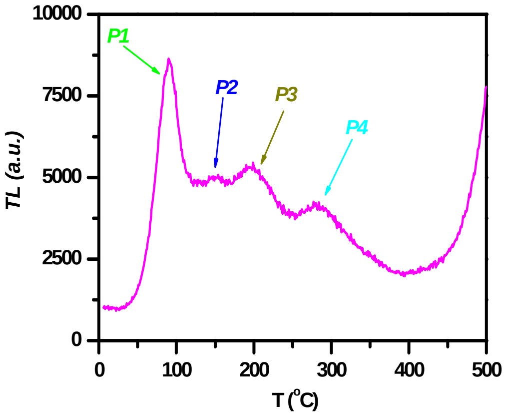

**Fig. 3: Glow curve corresponding to the dose of 256 Gy of artificial $\beta^-$ irradiation, after the NTL signal has been previously removed. TL glow peaks at $T_{max}$~90 °C (*P1*), ~165 °C (*P2*), ~200 °C (*P3*) and at ~ 255 °C (*P4*) are prominent as well as typical for silicate-dominated minerals.**

The sensitization study of obsidian was performed versus both successive irradiation – TL measurement cycles, as well as annealing temperature. In the latter case, five different annealing temperatures were applied. Results are presented in Fig. 4A, normalized over the sensitivity of the un-annealed sample. The lack of sensitization versus annealing temperatures, provides a strong argument regarding the volcanic origin of the sample. Furthermore, due to this volcanic origin of the obsidian, sensitivity of unheated sample is not changed before and after first TL measurement, implying the absence of sensitization while measuring natural and artificially irradiated signals.

In the former case, 11 successive irradiations – TL measurement cycles were applied on the same aliquot. Three different aliquots were used, each one corresponding to different dose. The doses delivered were 16 Gy in the first case, 75 in the second and 150 for the third. Fig. 4B presents the TL sensitivity for the case of glow peak (*P1*) at $T_{max}$~90 °C as a function of both the successive cycles of irradiation – TL readout, normalized over the sensitivity of the first measurement. This TL peak is typical of the quartz TL glow curve; therefore it is very interesting to study it. No sensitization is recorded, and furthermore, this sensitization pattern is similar regardless of (a) the dose delivered and (b) the glow peak studied. The TL glow peaks sensitization versus repeated cycles recorded, indicate the suitability of the sample for single aliquot TL measurements (Michael and Zacharias, 2006).

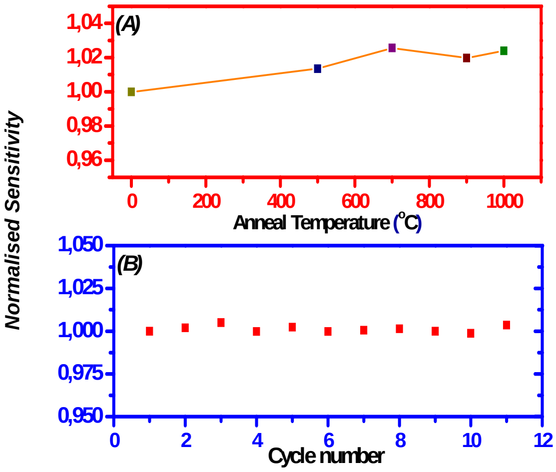

**Fig. 4: Normalised TL sensitivity as a function of (A), the annealing temperature, normalised over the sensitivity of the un-annealed sample, (B) successive cycles of irradiation – TL readout, normalized over the first cycle.**

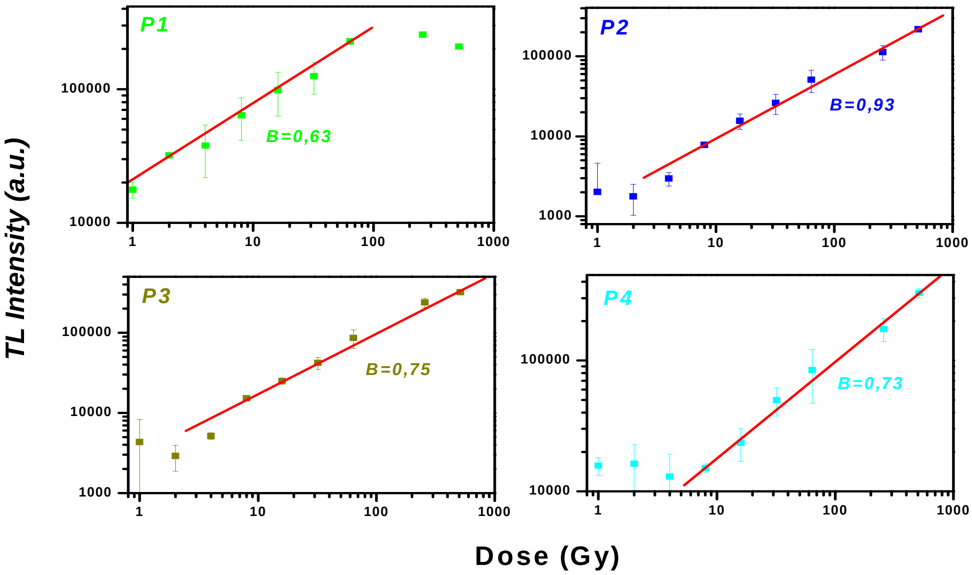

**Fig. 5: TL dose response curves for the peak heights of the four main, prominent individual glow peaks *P1*, *P2*, *P3* and *P4*. The dose region studied was between 1 and 512 Gy. Note the logarithmic axes. Solid lines represent the regression line derived from the equation $Y=A\cdot D^B$, where B values have been calculated for the linear region of each dose response curve and are presented for each figure independently.**

### *3.4 TL Dose Response*

Fig. 5 presents the TL dose response curves in the region between 1 – 512 Gy, for the four glow peaks at $T_{max}$ ~ 90 °C (*P1*), ~165 °C (*P2*), ~200 °C (*P3*) and at ~ 255 °C (*P4*) (figures A, B, C and D respectively). The 90 °C glow peak of quartz, a glow peak with unique interest in the thermoluminescence, seems to present a sublinear response in the dose region between 1 and 100 Gy. This is a typical characteristic for annealed quartz samples (Polymeris et al., 2006). The glow peaks *P3* and *P4* also exhibit sub-linear response, but in the dose region between 10 and 1000 Gy. Finally, the behavior of glow peak P2 is almost linear in the dose region ranging from 5 to 500 Gy.

### 3.5 Artificial OSL

Fig. 6 presents a selection of Continuous Wave OSL (CW-OSL) decay curves corresponding to 2, 16, 64 and 256 Gy of artificial $\beta^-$ irradiation in the laboratory, after the NTL signal has been previously removed. The CW-OSL signal of obsidian, for all doses studied, presents similar features, such as one initial and quickly decaying part, which is preceded by a second slow decaying signal, whose shape is extremely flat with very large intensity (well above 2000 counts/s), compared to the OSL background signal (~90 counts/s).

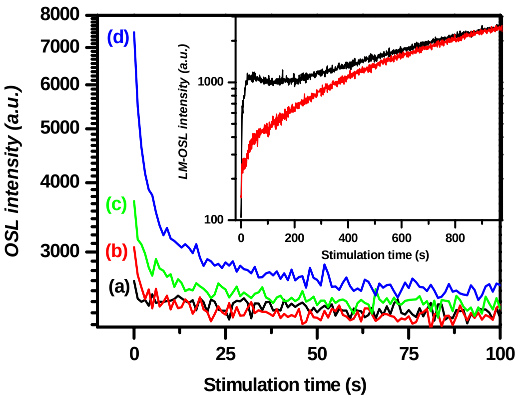

**Fig. 6: CW-OSL decay curves corresponding to beta doses of (a) 2, (b) 16, (c) 16 and (d) 256 Gy after the NTL signal has been previously removed. Inset: LM-OSL curves corresponding to the dose of 256 Gy $\beta^-$ irradiation in the laboratory, obtained at both RT and 125 °C, after the NTL signal removed.**

The inset of Fig. 6 presents LM-OSL glow curves corresponding to the dose of 150 Gy from artificial $\beta^-$ irradiation in the laboratory, after the NTL signal has been previously removed, for the two measuring temperatures described in section 2. These LM-OSL measurements were performed in order to check the bleaching ability of obsidian. Therefore, after each OSL measurement, the respective Residual TL (RTL) glow curve was received. These RTL glow curves (b and c respectively) are presented in the lower panel (I) of Fig. 7. At the same figure, in both panels, curve (a) corresponds to the TL glow curve received immediately after irradiation with 150 Gy without any bleaching. Upper panel of Fig. 7 presents the difference between bleached and unbleached TL glow curves for both measuring temperatures.

Since the presence of quartz inside obsidian's–matrix was previously established, it is expected that the LM-OSL signal measured at RT should include the component corresponding to the 110°C TL peak in quartz (Kiyak et al., 2008; Polymeris et al., 2009).

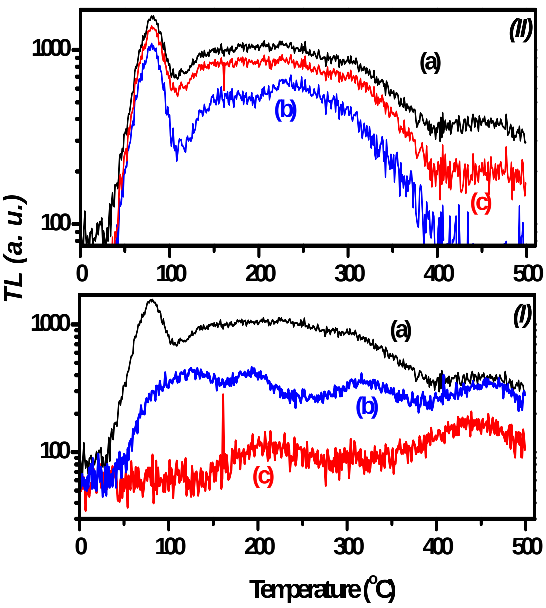

**Fig. 7: Panel (I) presents RTL curves after no LM-OSL (a), LM-OSL at RT (b) and at 125 °C (c). Panel (II) presents the respective unbleached minus bleached glow curves.**

This is also further supported by both inset of Fig. 6 as well as by both panels of Fig. 7. However, while measured at 125 °C, the LM-OSL signal seems to be featureless, indicating a strong amorphous phase. Nevertheless, it seems that blue bleaching seems to be continuous, all over the entire TL glow curve, without affecting selectively a specific part of the latter. The high-temperature part of the TL glow curve, i.e. for temperatures >400 °C is bleached as well. Uniform bleaching of regenerated TL across a wide glow curve temperature range, in conjuction with the absence of any predose enhancement for P1, is often taken as an indication that the signal does not relate to quartz, but in fact to other silicates (Galli et al., 2006). However, Kitis et al., (2010) has recently demonstrated that uniform and not trap selective bleaching occurs even in quartz samples. Pulse annealing experiments could possibly be more selective in terms of locating OSL signal origins.

Fig. 8 presents the OSL dose response curves in the region between 1 – 512 Gy. In order to get this curve, the initial OSL intensity during the first second of stimulation was used, after subtraction of the final second as a background signal. Despite this extremely flat CW-OSL signal, with very large intensity “tail”, the dose response curve seems to be fairly linear for doses larger than 10 Gy.

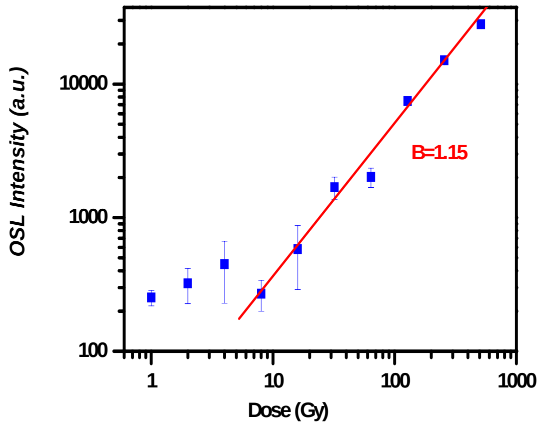

**Fig. 8: CW-OSL dose response curve. Note the logarithmic axes. Solid line represents the regression line derived from the equation $Y=A \cdot D^B$.**

### 3.6 Natural OSL

Natural OSL (NOSL) signal was investigated and found to consist of one component, whose shape is rather peculiar and extremely flat with intensity as large as 20 times the OSL background signal. This is exactly similar to the CW-OSL tail after artificial irradiation. This NOSL signal is presented in Fig. 9, together with a background OSL signal for comparison. The latter corresponds to an OSL measurement received after TL measurement. The shape of NOSL was already expected, since bleaching of the NTL signal was not efficient according to Fig. 2. NOSL does change neither shape nor intensity, even after 20 ks of illumination using commercial blue LEDs, implying that this shape could possibly be attributed to the presence of intense photoluminescence signal.

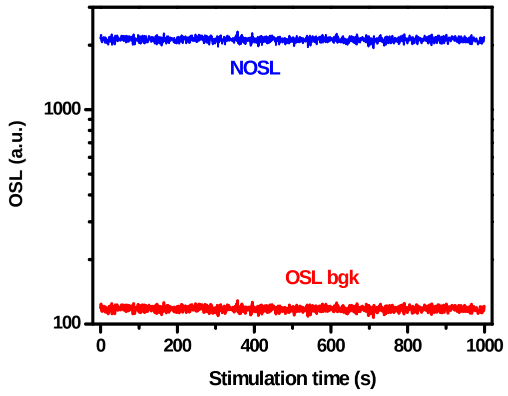

**Fig. 9: Natural OSL signal of obsidian, measured at 125$^{o}$C**

In order to check for photoluminescence, several fresh aliquots were prepared and subsequently were irradiated with varying doses, without previously removing the natural luminescence signal. A selection of CW-OSL curves in the framework of this additive dose OSL procedure is presented in Fig. 10.

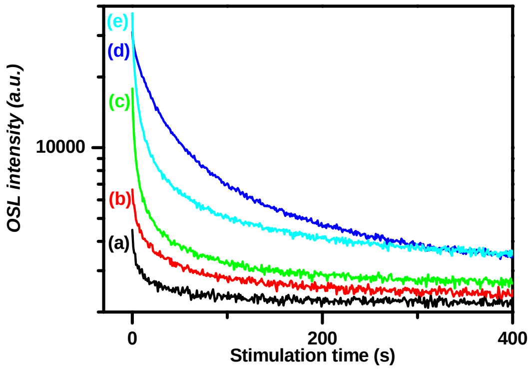

**Fig. 10. NOSL plus artificial $\beta$ signal decaying curves of obsidian for (a) 32, (b) 64, (c) 128, (d) 128 and (e) 512 Gy**

As the this Fig. reveals, adding extra doses over the natural OSL signal causes an increase of the latter. This result could imply that this shape and intensity of NOSL signal could not be attributed to photoluminescence. Alternatively, it could be explained in the framework of the presence of an extremelly slowly decaying OSL component, exhibiting quite large lifetime. However, this component could possibly not be related to eviction of charge from a colour centre, since the color of the samples does not change following heating or bleaching. Study of absorption spectra before and after bleaching and heating could be very useful.

## CONCLUSIONS

Basic thermally and optically stimulated luminescent (TL and OSL) properties of obsidian were studied in the present work.

The natural TL signal consists of one single TL peak of second order kinetics, centred at about 340 °C, along with a satellite peak of much lower intensity at ~ 420 °C. This TL peak was proved to be unbleachable using both blue LEDs (emitting at 470 nm, FWHM 40 nm) and/or a solar simulator SOL II (Dr Hönle), while it suffers from thermal quenching. The artificially irradiated TL signal from obsidian yields all TL features of silica dominated materials, such as the 110 °C TL peak and dose response being sub-linear for intermediate doses. However, the lack of sensitisation indicates the suitability of the material for single aliquot measurements.

Artificially irradiated samples seem to be easily and effectively bleached all over the entire TL glow curve, even in the high-temperature part of it. CW-OSL dose response is fairly linear for doses larger than 5 Gy. However, the presence of a large and hard to bleach natural signal, which contrasts with easily bleachable signals induced by laboratory irradiation, provides major difficulties in dating applications.

Further work is required towards the origin of OSL signal, in order to seek for an alternative and suitable zeroing mechanism. Finally, anomalous fading from the glassy structure, the orthoclase, mca, and/or quartz microcrystals should also be checked.

## ACKNOWLEDGEMENTS

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