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ON THE FEASIBILITY OF DATING PORTABLE PAINTINGS: PRELIMINARY LUMINESCENCE MEASUREMENTS ON GROUND LAYER MATERIALS

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ABSTRACT

A typical oil painting stratigraphy consists of the canvas substrate, the ground layer, the layer of paint and eventually the varnish layer. The ground layer, a mixture of inorganic and organic material could be a very helpful tool for indirect dating. The present study presents preliminary luminescence measurements on the main inorganic constituents of the ground layers for paintings between the 15th and the 20th century. Eight different substances were selected, based on the most common materials applied throughout these centuries. Most among the materials subjected to the present study present TL glow curve with different, unique shape. Notable exceptions stand in the case of the most recently invented materials such as zinc white, titanium white and lead white. Towards direct dating purposes, a number of luminescence features, such as sensitivity, sensitization after repeated cycles of irradiation-measurement, bleaching ability as well as thermal stability were studied for both cases of TL as well as OSL. Preliminary results indicate that kaolinite and gypsum stand as very promising candidates towards luminescence dating of portable paintings. Further work is required in order to establish their usefulness.

KEYWORDS: paintings, ground layer, TA – OSL, very deep traps, kaolinite, gypsum

1. INTRODUCTION

Dating of art works stands as a challenging task since it will provide with valuable piece of knowledge for art historians, researchers and conservators. Up to present, most of the dating techniques that apply to works of art, concern the indirect dating of the artifact through both the identification of their painting layer components as well as the characterization of the technique employed by the artist. Unfortunately, application of any direct dating method has not been reported.

The ground or preparation layer is a very important and integral component for the stratigraphy of the paintings, consisting of a mixture of inert materials and organic constituents (Mayer, 1991). For many centuries, artists produced their own grounds as part of their synthesis, while upon modernization of art and introduction to industrialism, grounds became part of mass production. The most interesting and flourishing period of the preparation layer seems to be the period after Medieval painting until the late 20th century (15th-20th century, Mayer, 1991; Rousaki et al., 2010). The complicated mixtures and the variety of techniques reflect to the capability of the artists and the technological level of the society.

Most traditional recipes for the ground layers of portable paintings on wood and canvas consist of at least one extender with or without filler material along with binding media. During the past centuries, the recipes for the painting ground layers have remarkably changed, following the artistic needs of the masters of the following ages (Mayer, 1991; Rousaki et al., 2010). From the traditional gesso grounds (gypsum-$CaSO_4.H_2O$ anhydrite with or without chalk-$CaCO_3$ combined with animal glue), to the innovative and complicated mixtures of the 18th century such as barium sulfide (barite, $BaSO_4$) zinc white (ZnO), lead white ($2PbCO_3.Pb(OH)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$) with or without pigments (such as ochres; mixtures of aluminum silicates and hydrated iron oxides) together with organic media), to the light and delicate recipes of the 20th century of titanium white (TiO_2), recipes seem to be as versatile as the masters that adopted them (Mayer, 1991). Zinc white was accepted as a watercolor by 1834 but it was some years later before its difficulties in oil were overcome, while lead white is used in painting priming layer before the 18th century (Plesters, 1956).

The analytical study of the ground layers of wood and canvas paintings is a very interesting field as well as an artistic aspect of each specific artefact that has not been thoroughly researched by the scientists so far, despite the voluminous related bibliography. An ongoing research project in progress, intends to investigate the ground layers of paintings on wood and canvas by applying a variety of physicochemical techniques. Identification of the ground layer's composition, verifying thus the literature, becomes helpful providing with useful hints towards indirect dating of the artefact (Rousaki et al., 2010).

Nevertheless, direct dating for some among the paintings on wood and canvas by applying luminescence techniques could, in principle, be applied and still stands as a challenging task. In paintings it involves dating the surfaces of the ground preparation layer which relies on the optically sensitive electron traps responsible for luminescence, having been bleached by sunlight, prior to either another ground layer or the colours of the main painting being incorporated into the art piece. From the moment that any surface is no longer exposed to sunlight and put in firm contact with either another ground layer or colour, the optically sensitive electron traps are filled by electrons produced by the ionization caused from natural nuclear radiation. It is the same principal as in the case of surface dating (Liritzis, 2011). The thickness of the preparation layers vary between 10 to 50 microns, while the overlying painted layers yield much larger thickness. Therefore, since the light attenuation in rocks is up to some microns (Laskaris and Liritzis, 2011) the opaque painted layers exclude the light penetration from the underlying preparation layers, protecting the latter from solar bleaching. A thick application of paint or charcoal may thus be sufficient to seal grains from further sunlight exposure. Thus the target event, namely the date of application of paint may be contemporaneous with the optically dated event, i.e. the time since the painted grains were last exposed to light (Roberts, 1997).

Towards these two tasks, (identification as well as dating of the ground layers), the present work provides with preliminary luminescence measure-

ments for the aforementioned main white extenders and fillers as well as yellow ochre for the case of portable paintings. The chemical composition of these materials, in combination with their wide spread use in the recipes for ground layers of paintings, constitute two powerful motivations for further investigation of these materials for luminescent dosimetry purposes. Moreover, no organised effort has taken place so far to characterise through luminescence analysis the components comprising the ground layers. The literature dealing with the luminescence properties of the aforementioned materials is somehow misleading; there is a voluminous literature discussing the luminescent properties of these specific materials after doping mostly with rare earth elements starting with the pioneer work of Sunta (1984) for doped Calcium Fluoride, Calcium Sulphate and Calcium Carbonate. Moreover, there is extended literature dealing with nano-powdered ZnO material specifically manufactured in order to fulfill certain requirements beyond dating. In any case, the references dealing with applications of the aforementioned naturally occurring materials, without any doping, to luminescence dating is scanty (Kiyak et al., 2010 and Kitis et al., 2010a for $BaSO_4$ as a retrospective dosimeter for large doses; Thompson et al., 2010 and Aydaş et al., 2011 for dating applications using gypsum; Correcher at al., 2010 and Garcia Guinea et al., 2010 for annealed kaolinite; Lahaye et al., 2006 for studying the thermal history of ferruginous sandstones containing ochre); a notable exception is yielded for the case of geological dating using $CaCO_3$; the reader could refer to McDougal (1968) for the early achievements as well as to Liritzis (2000), Galloway (2002), and Liritzis (2011). However, in all these cases the literature deals with geological dating with equivalent doses of several Gys. Finally the readers could refer to Roberts (1997) for a review on optical dating of prehistoric rock paintings.

2. MATERIALS AND METHODS

None of the materials subjected to the present study was obtained from original art painting object. On the contrary, these were reference materials which are manufactured and customarily sold in the market by ABIO Products, Asser Brynie. These are materials of chemical composition very similar to actual materials used by painters; the degree of purity and reproducibility between these batches was questioned in detail. Both previous conclusions were derived by applying X-ray diffraction (XRD) along with scanning electron microscopy (SEM) in batches of customarily sold materials as well as materials from original paintings kept at National Gallery-Alexandros Soutzos Museum. In all cases, artificial materials were found not to be doped, assuring thus the similarity between the preparation techniques for synthetic materials and the preparation applied by the painters. In some cases like chalk, the literature points out that, possibly, quartz inclusions are present (Liritzis et al., 2010); however this could be beneficial to luminescence dating.

Specific luminescence features, such as sensitivity, sensitization after repeated cycles of irradiation-measurement, bleaching ability as well as thermal stability and glow curve shape for both cases of thermoluminescence (TL) as well as optically stimulated luminescence (OSL), were monitored for the cases of signals subsequent artificial irradiation only. Therefore, these materials were not subjected in a study for their natural TL or OSL signal. Moreover, the presence of OSL signal emanating from very deep traps (VDT, Polymeris et al., 2010b; Polymeris and Kitis, 2012) was investigated. All materials were in powder form; Fine grained powder with dimensions between 4 and 11 microns was deposited on stainless-steel discs of 1 cm^2 area. Reproducibility in masses of all subsamples was better than 5%. In all cases of fillers and extenders, the same mass was used for all samples, in order to compare the sensitivity among the different materials.

All luminescence measurements were performed using a RISØ TL/OSL reader (model TL/OSL DA-15), equipped with a 0.075 Gy s^{-1} $^{90}Sr/^{90}Y$ β-ray source (Bøtter-Jensen et al., 2000). The reader is fitted with an EMI 9635QA PM Tube. Blue light emitting diodes (LEDs) (470 nm, 40 mW cm^{-2}) were used for stimulation. Unless otherwise stated, all TL measurements were performed using a Hoya U-340 filter (270–380 nm) of 7.5 mm thickness. However, a selected number of measurements were performed using a combination of a Pilkington HA-3 heat absorbing and a Corning 7–59 (320–440 nm) blue filter. A heating rate of 1°C s^{-1} was used in all TL readouts in order to avoid significant temperature lag, up to a maximum

temperature of 500°C. The test dose applied was 50 Gy in all cases. This specific, large test dose was applied for characterization reasons, in order to get preliminary TL glow curves of adequate signal to noise ratio, due to the different luminescence sensitivity of all materials under study. Nevertheless, given the age of the paintings, as well as the surrounding materials, archaeological doses around 1 Gy are expected. Therefore, the response of luminescence to low doses was also tested for the case of OSL.

Unless otherwise stated, all conventional OSL measurements were performed at room temperature (RT), without any preheat. Furthermore, all conventional OSL measurements were performed in the linear modulation mode (LM-OSL), the ramping rate of which was 0.04 mW cm^{-2} s^{-1}, increasing the stimulation light power from zero up to the maximum power (40 mW cm^{-2}) over a period of 1 ks.

3. RESULTS AND DISCUSSION

3.1 TL glow curve shape and intensity

The glow curves measured following artificial irradiation with the test dose of 50 Gy for the cases of barite, gypsum, kaolinite, yellow ochre and chalk are presented in Fig. 1. As this figure reveals, different TL glow curve shapes were obtained for each one among these materials.

This result stands as an extremely interesting hint towards the possibility for discriminating between these materials by solely applying TL.

However, this is not the case for zinc white, lead white as well as titanium white; all these three substances yielded TL glow curves with identical shapes, including only one TL peak with maximum temperature lower than 100°C, making thus difficult to discriminate between them by solely applying TL.

The similarity between the TL glow curve shapes of zinc white, lead white and titanium white, although their crystal structures are different, is attributed to the relatively low energy band gap as well as to the fact that these materials are not doped.

Only the TL glow curve of zinc white is plotted in Fig. 1. Additional, supplementary techniques should be applied. Fig. 1 also presents one TL glow curve corresponding to zinc white subsequent irradiation by the same test dose.

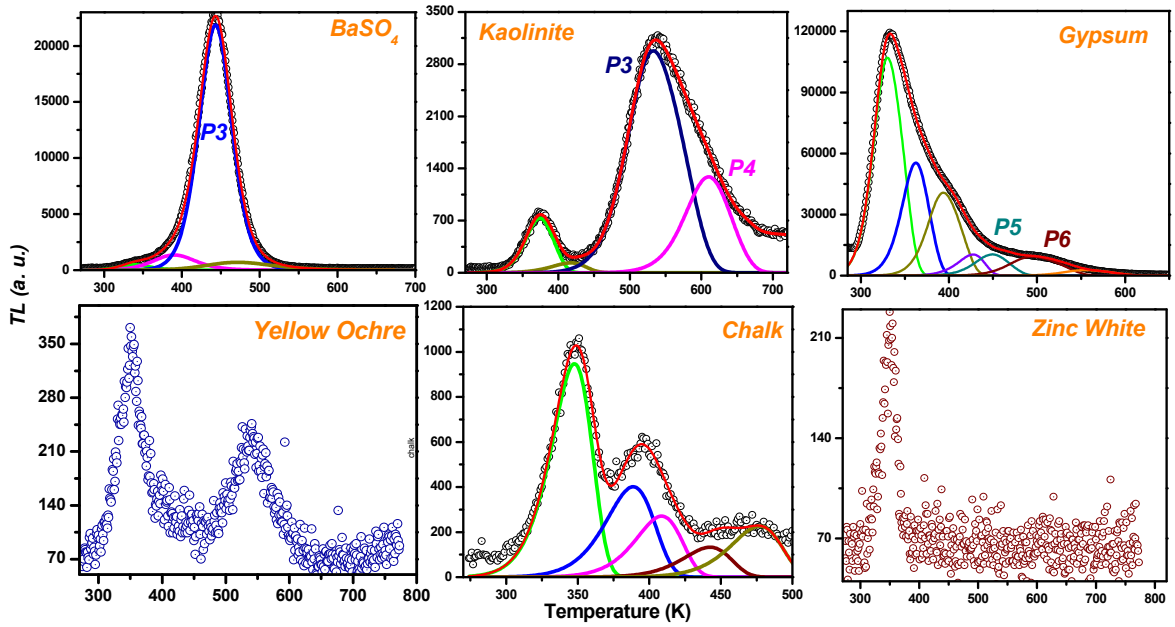

Figure 1. TL glow curves for 6 different materials. For the cases of barite, kaolinite, gypsum and chalk, the glow curves were de-convolved into their individual peaks. Open dots represent the experimentally obtained data while continuous lines correspond to de-convolution results. For each material, there are some TL peaks suggested as appropriate for luminescence dating, due to the corresponding lifetimes yielded according to the de-convolution procedure; these correspond to the labeled peaks (measurements were performed using a combination of a Pilkington HA-3 heat absorbing and a Corning 7–59 filter).

Furthermore, Fig. 1 indicates that the TL signal of the three former substances (i.e. barite, gypsum, and kaolinite) is moderately intense. Consequently the corresponding intensities could be useful for luminescence dating. This conclusion is also supported by the TL dose responses reported by Correcher et al. (2010), Kitis et al. (2010a) and Aydaş et al. (2011). All these authors present TL dose responses from doses as low as 1 Gy. On the contrary, for the cases of chalk, yellow ochre and zinc white, the intensities yielded are very poor, as one can easily resolve from Fig. 1. Similar results were monitored concerning the sensitivity of titanium and lead white.

Among the six glow curves which are presented in Fig. 1, four are de-convolved into their individual glow-peak-components. All curve fittings were performed using the software package Microsoft Excel, with the Solver utility (Afouxenidis et al., 2012); the general order kinetics TL equation suggested by Kitis et al. (1998) was used, while the goodness of fit was tested using the Figure Of Merit (FOM) of Balian and Eddy (1977). A different number of total glow peaks were used, depending on the sample. One notable exception is observed for the case of un-annealed kaolinite. The glow curve shape of the present study is similar to that reported by Correcher et al. (2010), despite the fact that these latter authors have applied preheat to annealed material. Moreover, these authors claim that their tests of thermal stability at different temperatures suggest a continuum in the trap distribution. Following this latter conclusion, the corresponding equation that describes the TL emission of a material with a continuous distribution of trapping states uniformly distributed over a finite energy range assuming first order kinetics (Kitis and Gomez-Ross, 2000). The glow curve corresponding to zinc white (corresponding thus also to the cases of titanium and lead white) was not de-convolved, since it consists of one unique TL peak with delocalization temperature below 100°C, corresponding to a shallow trap. There are no TL peaks at higher temperatures, as it might have been expected according to the cases of Yb-doped ZnO nanophosphors (Pal et al., 2006). In other words, the TL signal of these three latter substances is useless for dating applications, unless there is sensitization due to predose effect. On the contrary, the presence of the glow peaks at temperatures higher than 150°C makes the other materials very promising candidates towards luminescence dating. Special emphasis should be addressed to (a) the barium sulphide, where the peak P3 is around 150-175°C and should have a relatively short lifetime, (b) the case of yellow ochre, which yields a TL glow curve with quartz-like shape. Furthermore, even in the case of chalk there is one TL peak at 200°C; nevertheless its intensity is extremely low. However, this TL peak might be attributed to the presence of quartz in chalk (Göksu et al., 2001; Liritzis et al., 2010), which was identified by XRD spectrum. This specific TL peak is increasingly used for dating recent archaeological objects younger than 1000 years (Göksu and Schwenk, 2000). The presence of un-fired quartz in chalk could possibly explain the extremely low intensity of the specific TL peak. In each plot of Fig. 1, specific TL peaks are labelled and identified as appropriate for luminescent dating, based on their lifetimes yielded by the deconvolution results.

3.2 TL sensitization

A crucial step in the characterization procedure was to examine the TL sensitivity of each material as a function of successive irradiation-readout cycles. The reason is that in the case the sensitivity remains un-affected, then the use of single aliquot protocols are favoured. The suitability for single aliquot measurement protocols stands among the main outcome of the present study, as it is imposed by the sample's low quantity for the original paintings to be dated. Moreover, in the cases of titanium white, lead white and zinc white, possible sensitization could enable the application of the predose dating effect (Bailiff, 1994). In the present study, experimental sequences including five successive cycles of irradiation – TL measurements were performed for each material. Each sequence was carried out using three different test doses, namely 25, 50 and 75 Gy. Once again these doses were selected in order to get a clear idea for the phenomenon. Fig. 2 shows the re-

sults of the sequence corresponding to the dose of 50 Gy, while similar results were monitored for the other two test doses as well. Plots present the first and the last TL glow curve for each material. Generally, all signals seem to be extremely stable. A notable exception arises for the case of barite as well as the low-temperature TL peak of chalk. In those two cases a sensitization pattern is observed, especially for the case of the $BaSO_4$ sample. The latter result contradicts the findings reported by Kitis et al. (2010a), indicating thus the dependence of the luminescence properties of barite on the origin of the samples. Nevertheless, since archaeological doses around 1 Gy are expected, sensitivity changes of $BaSO_4$ were also studied after irradiation with 1 Gy. Results indicated the same qualitative sensitization pattern. Further work is required in order to study the quantitative correlation between predose and total accrued dose. For the case of chalk, this sensitization could be attributed to the presence of quartz, being beneficial for luminescence dating.

Finally, due to the presence of one unique TL peak at around 100°C, the pre-dose technique (Bailiff, 1994) would have stood as the only solution for lead white, zinc white and titanium white. Unfortunately, the lack of sensitization for this specific TL peak excludes the possibility of effectively using these two materials for luminescence dating. This lack of sensitization was somehow expected based on the lack of any quartz diffraction peak on the XRD spectra.

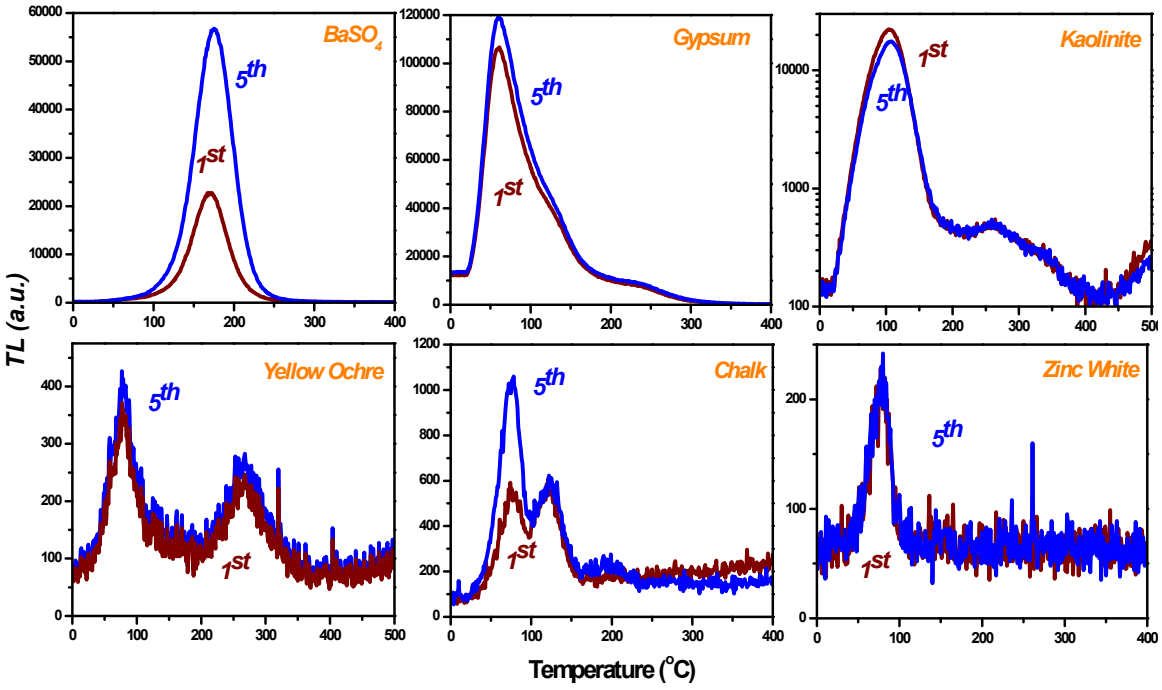

Figure 2. The first and the last (5th) TL glow cures obtained out of an experimental sequence including 5 sequential steps of irradiation – TL measurements for each material. Test dose applied was 50 Gy.

3.3 Artificial OSL – Bleaching ability

Fig. 3 presents LM-OSL curves measured following artificial irradiation by the test dose of 50 Gy for the cases of gypsum and kaolinite. A notable feature of the LM-OSL of all these substances is the presence of an intense fast OSL component, forming a peak for stimulation times lower than 150 s. One exception is noticed for the case of chalk; however, this was somehow anticipated, since chalk consists of $CaCO_3$. The presence of a fast OSL component is the corner stone for the application of OSL dating protocols. In order to study the bleaching ability of each material, an experimental protocol was applied, based on the protocol used by Spooner (1994) for natural TL, modified appropriately in order to be applied to artificial TL (Kitis et al., 2010b). The results of this protocol are presented in the inset of each plot, showing for each mate-

rial the unbleached TL glow-curves (a), the bleached ones due to the blue light stimulation (b) and finally their difference (c). The difference given by the curve (c) in all figures is a measure of the electrons evicted by the blue light stimulation from the electron traps responsible for the respective TL glow-peaks. It seems that the blue bleaching is continuous across the entire glow-curve and does not influence a certain part of the glow-curve only.

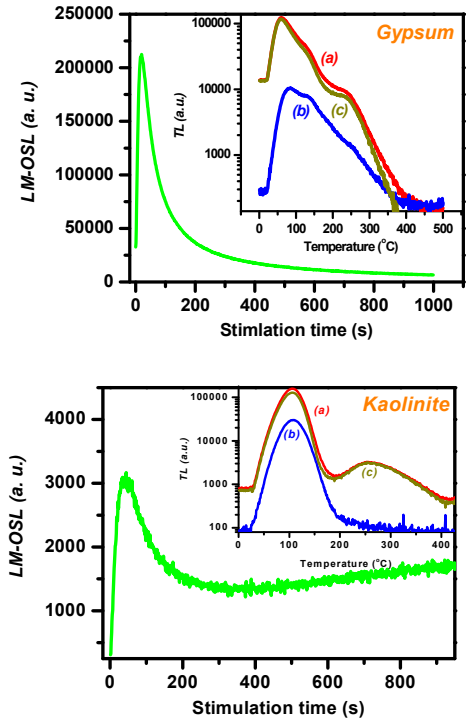

Figure 3. LM-OSL curves measured at room temperature. In all cases, a peak-like form at the beginning corresponds to the fast component(s). In each inset, the corresponding un-bleached (a) and bleached (b) glow curves are presented along with their difference (curve c).

Therefore, a fraction of the OSL signal arises from stable traps and not from shallow traps only. This is an extremely interesting feature, since it implies that the presence of a fast OSL component arising from stable traps is plausible (Polymeris et al., 2010a).

It is worth focusing on the bleachability of both yellow ochre and kaolinite; in the former case, the OSL signal results from both TL peaks, with the one located at T_{max} at ~275°C (P in Fig. 1) being of great importance since it was completely bleached. In the latter case, TL peaks at temperatures higher than 200°C are completely bleached as well. Further work, including thermal cleaning and OSL de-convolution studies is required, in order to isolate and use the most appropriate OSL signal for dating for each material.

Fig. 4 presents the continuous wave blue OSL (plot A) as well as IRSL (plot B) response of the materials subjected to present study to 1 Gy beta artificial irradiation.

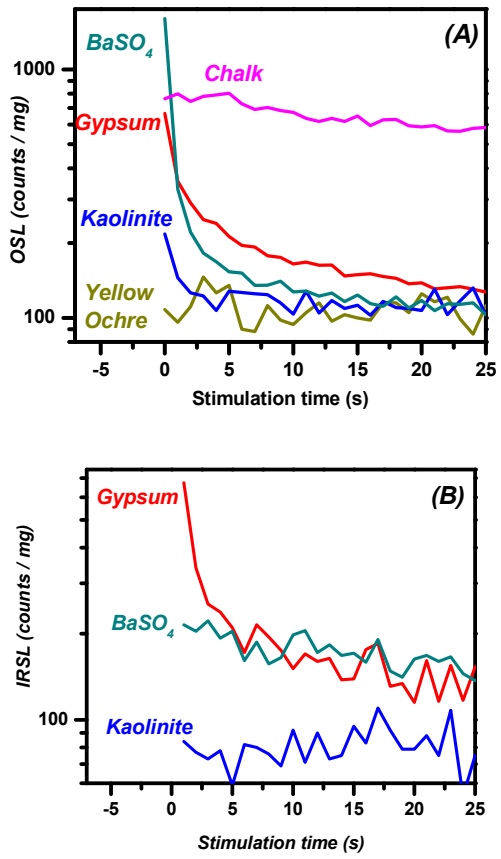

Figure 4. The blue OSL (plot A) as well as IRSL (plot B) response of the materials subjected to the present study to 1 Gy artificial beta irradiation.

All signals are presented were normalised over 1 mg mass of substance. Moreover, all blue OSL signals were measured at 125°C, and IRSL at 50°C, following the appropriate thermal cleaning in order to empty shallow TL traps according to the TL glow peaks monitored. Besides yellow ochre, the 4 remaining materials indicate sufficient sensitivity of blue OSL after 1 Gy of artificial beta irradiation. Special emphasis should be addressed to the case of chalk, where a flat, very slowly decaying part of the signal, with very large intensity (well above 800 cts s^{-1}), compared to the OSL background signal (~100

cts s^{-1}) follows an initial and slowly decaying part. Only two materials exhibit measurable IRSL signal per mg for 1 Gy irradiation, namely gypsum and $BaSO_4$.

3.4 VDT OSL

Most of TL and OSL phosphors, as wide band gap insulators, hold some deep energy level defects (Very Deep Traps, VDT hereafter), corresponding to TL glow peak having their peak maximum temperature, T_{max} beyond the 500°C. The OSL signal from VDT is accessed by a combined action of both thermal and optical stimulation over a period of 500 s, after the sample was previously heated up to 500°C in order to empty its main TL traps, resulting in the measurement of thermally assisted OSL (TA-OSL, Polymeris et al., 2010b).

Especially in the case of quartz, it was recently argued by Kitis et al. (2010c) that the lower detectable dose limit of the VDT is of the order of 1 Gy but it could be further improved. Therefore, the same rationale could be lying behind the TA-OSL of the present materials as well, if any.

Fig. 5 presents the TA-OSL curves for a selection of materials. As the upper plot of the figure reveals, zinc white indicates flat TA-OSL signal of poor statistics; in fact this signal coincides with the background signal. For the other materials, there is TA-OSL signal, presents similar features, such as one initial and slowly decaying part, which is preceded by a second slow decaying signal, whose shape is extremely flat with very large intensity (well above 2000 cts s^{-1}), compared to the OSL background signal (~400 cts s^{-1}).

One notable exception stands for the case of yellow ochre, for which the initial part of the signal decays very fast, yielding thus VDT signal with similar shape to that of ordinary quartz OSL. These deep electron traps have signals with, at least, all the benefits of the shallower traps, along with an additional un-comparable advantage, being the very low dose threshold. The preliminary results on barite, gypsum, chalk and yellow ochre indicate the VDT as a very rich source of OSL signal.

Finally, according to Correcher et al. (2010) the TL signal of kaolinite suffers from anomalous fading. Among several possible ways suggested for choosing a non-fading signal, recently Kitis et al. (2013) have suggested that the TA-OSL signal emanating from very deep traps stands as extremely promising.

This very convenient property of TA-OSL could be useful in two ways for the case of kaolinite. However, further work is required in order to check whether this signal could be effectively applied for dating purposes.

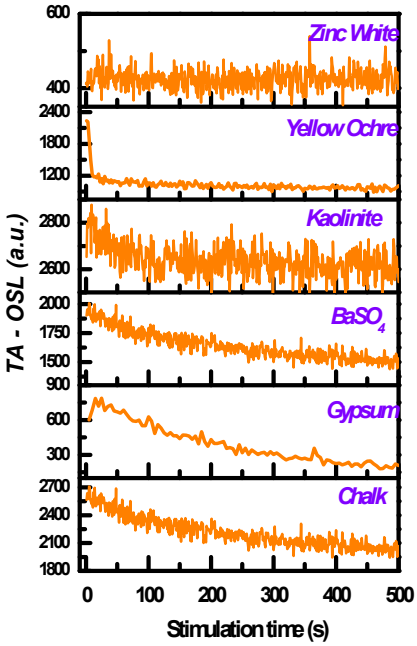

Figure 5. TA – OSL signal emanating from VDT for each material. Note the poor signal-to-noise ratio obtained for the case of zinc white, which is not indistinguishable from the background TA-OSL signal.

4. CONCLUSIONS

With respect to luminescence signals obtained from the materials analyzed and their dosimetric characteristics, the conclusions of the present study can be summarized as follows:

1. TL could easily identify most of the fillers, since each one among them presents TL glow curve with different, unique shape. Notable exceptions stand in the case of zinc white, titanium white and lead white; all these three yielded glow curves of identical shapes.
2. Moreover, these three aforementioned materials yielded TL glow curves with one, unique

TL glow peak at around 100°C without any pre-dose sensitization pattern indicating their uselessness for luminescence dating measurements. This uselessness is also supported by the low intensity of both OSL and TA-OSL emanating from VDT.

3. $BaSO_4$ and chalk are not so promising for ordinary TL dating, due to strong sensitization pattern and extremely low sensitivity respectively. Nevertheless, they both yielded TA-OSL signals of very high statistics. TL dating application using $BaSO_4$ may be more accurate if based on multiple aliquot protocols. Due to the presence of quartz inclusions in quartz, further work is required in order to study the effective application of predose effect.
4. Besides these three substances, in all other cases, the OSL exhibits fast components, and even at room temperature, stimulates traps corresponding to the entire TL glow curve. Moreoever, kaolinite, gypsum and $BaSO_4$ yield in ascending form the best responses of blue OSL to 1 Gy artificial irradiation.
   Chalk yields OSL signal of strange shape, where a flat, very slowly decaying part of the signal follows an initial and slowly decaying part.
5. Special caution should be addressed to yellow ochre. Specific luminescence features such as the bleaching ability of the ochre's TL glow peak with T_{max} at ~275°C as well as the intense TA-OSL signal stand as promising hints, besides its low sensitivity and lack of sensitization.
6. Gypsum and kaolinite stand as very promising candidates towards IRSL dating, based on the very good IRSL response of those materials to 1 Gy artificial beta irradiation. However, further work is required in order to establish their usefulness.
7. The intense TA-OSL signal of kaolinite could possibly provide a correction way for the anomalous fading effect.

Finally, in order to utilize the observed characteristics for the practical application of luminescence in dating paintings, further studies are required to assess the effects of light exposure on these materials, and the adequacy of light protection by different paints and painting techniques.

REFERENCES

Afouxenidis, D., Polymeris, G.S., Tsirliganis, N.C., Kitis, G. (2012) Computerised curve deconvolution of TL/OSL curves using a popular spreadsheet program. *Radiation Protection Dosimetry*, vol 149 (3), 363–370.

Aydaş, C., Engin, B., Aydin, T. (2011) Radiation-induced signals of gypsum crystals analysed by ESR and TL techniques applied to dating. *Nuclear Instruments and Methods in Physics Research B*, vol. 269, 417–424.

Bailiff, I.K. (1994) The pre-dose technique. *Radiation Measurements*, vol. 23 (2/3), 471-479.

Balian, H.M. and Eddy, N.W. (1977) Figure Of Merit (FOM): An improved criterion over the normalized Chi-squared test for assessing goodness of fit of gamma-ray spectral peaks. *Nuclear Instruments and Methods*, vol. 145, 389-395.

Bøtter-Jensen, L., Bulur, E., Duller, G.A.T., Murray, A.S. (2000) Advances in luminescence instrument systems. *Radiation Measurements*, vol. 32, 523–528.

Correcher, V., Garcia-Guinea, J., Crespo-Feo, E., Rodriguez-Lazcano. Y., Prado Herrera. P. (2010) Dose–response of thermoluminescence in natural kaolinite. *Thermochimica Acta*, vol. 503–504, 12–15.

Garcia-Guinea, J., Correcher, V., Rodriguez-Lazcano, Y., Crespo-Feo, E., Prado Herrera. P. (2010) Light emission bands in the radioluminescence and thermoluminescence spectra of kaolinite. *Applied Clay Science*, vol. 49, 306–310.

Göksu, H.Y., Schwenk, P., Semiochkina, N. (2001) Investigation of the thermal stability of 210°C TL peak of quartz and dating the components of terrazzo from the monastery church of Tegernsee. *Radiation Measurements*, vol. 33, 785–792.

Göksu, H.Y., Schwenk, P. (2000) Thermoluminescence dating of bricks and terrazzo from the monastery church of Tegenseee (Bavaria-Germany) using 210°C TL peak of quartz. *Radiation and Environmental Biophysics*, vol. 39, 301–308.

Galloway, R.B. (2002). Does limestone show useful optically stimulated luminescence? *Ancient TL*, vol. 20, 1 – 7.

Kitis, G., Gomez-Ros, J.M., Tuyn, J.W.M. (1998) Thermoluminescence glow-curve deconvolution functions for first, second and general orders of kinetics. *Journal of Physics D: Applied Physics*, vol. 31, 2636-2641.

Kitis, G., Gomez-Ross, J.M. (2000) Thermoluminescence glow-curve deconvolution functions for mixed order of kinetics and continuous trap distribution. *Nuclear Instruments and Methods in Physics Research B*, vol. 440, 224–231

Kitis, G., Kiyak, N.G., Polymeris, G.S. (2010a) Thermoluminescence and optically stimulated luminescence properties of natural barites. *Applied Radiation and Isotopes*, vol. 68, 2409–2415.

Kitis, G., Kiyak, N.G., Polymeris, G.S., Pagonis, V. (2010c) Investigation of OSL signals from very deep traps in unfired and fired quartz samples. *Nuclear Instruments and Methods in Physics Research B*, vol. 268, 592–598.

Kitis, G., Kiyak, N.G., Polymeris, G.S., Tsirliganis, N.C. (2010b) The correlation of fast OSL component with the TL peak at 325°C in quartz of various origins. *Journal of Luminescence*, vol. 130, 298–303.

Kitis, G., Polymeris, G.S., Pagonis, V., Tsirliganis, N.C. (2013) Anomalous fading of OSL signals originating from very deep traps in Durango apatite, *Radiation Measurements* 49, 73-81.

Kiyak, N.G., Polymeris, G.S., Kitis, G. (2010) TL/OSL properties of crystalline inclusions from heavy, barytes loaded, concrete. *Radiation Measurements*, vol. 45, 543–545.

Lahaye, C., Godfrey Smith, D.I., Guibert, P., Bechtel, F. (2006) Equivalent thermal history (H_E) of ferruginous sandstones based on the thermal activation characteristics of quartz. *Radiation Measurements*, vol. 41, 995 – 1000.

Laskaris, N., Liritzis, I. (2011) A new mathematical approximation of sunlight attenuation in rocks for surface luminescence dating. *Journal of Luminescence*, vol. 131, 1874- 1884.

Liritzis, I. (2000) Advances in thermo- and opto- luminescence dating of environmental materials (sedimentary de-posits): part II: applications. *GLOBALNEST*, vol. 2 (1), 29-49.

Liritzis, I., Drivaliari, N., Polymeris, G.S., Katagas, Ch. (2010) New quartz technique for OSL dating of limestones. *Mediterranean Archaeology and Archaeometry*, vol. 10 (1), 81 – 87.

Liritzis, I. (2011) Surface dating by luminescence; an overview. *Geochronometria*, vol. 38 (3), 292 – 302.

McDougal, D.J. (1968) *Thermoluminescence of geological materials.* London University Press.

Mayer, R. (1991) *The artist's handbook of materials and techniques*. 5th ed.rev., S.Sheehan. New York: Viking Press.

Pal, U. (2006) Thermoluminescence properties of ZnO and ZnO:Yb nanophosphors. *Applied Physics Letters*, vol. 89 (18), 183118 – 183123.

Plesters, J. (1956) Cross-Sections and Chemical Analysis of Paint Samples. *Studies in Conservation*, vol. 2 (3), 110-157.

Polymeris, G.S., Kitis, G. (2012) Thermally assisted photo transfer OSL from deep traps in Al_2O_3:C grains exhibiting different TL peak shapes. *Applied Radiation and Isotopes*, vol. 70, 2478–2487.

Polymeris, G.S., Raptis, S., Afouxenidis, D., Tsirliganis, N.C., Kitis, G. (2010b) Thermally assisted OSL from deep traps in Al_2O_3:C. *Radiation Measurements*, vol. 45, 519–522.

Polymeris, G.S., Gogou, D., Afouxenidis, D., Raptis, S., Tsirliganis, N.C., Kitis, G. (2010a) Preliminary TL and OSL investigations of obsidian samples. *Mediterranean Archaeology and Archaeometry*, vol. 10 (4), 83 – 91.

Roberts, R.G. (1997) Luminescence dating in archaeology: from origins to optical. *Radiation Measurements*, vol. 27 (5/6), 819-892.

Rousaki, A., Kouloumpi, E., Terlixi, A., Moutsatsou, A.P., Polymeris, G.S., Paraskevopoulos, K.M. (2010). Application of traditional recipes for the preparation of the paintings – Physicochemical characterisation and study of the ageing mechanisms towards luminescence dating, In: International Symposium 'Works of Art & Conservation Science Today', Thessaloniki, November 26-27, p. 85.

Spooner, N.A. (1994) On the optical dating signal from quartz. *Radiation Measurements*, vol. 23 (2/3), 693–700.

Sunta, C.M. (1984) A review of thermoluminescence of calcium fluoride, calcium sulfate and calcium carbonate. *Radiation Protection Dosimetry*, vol. 8 (1/2), 25 – 44.

Thompson, J.W., Burdette, K.E., Inrig, E.L., DeWitt, R., Mistry, R., Rink, W.J., Boreham, D.R. (2010) Optically stimulated luminescence dosimetry with gypsum wallboard (drywall). *Radiation Protection Dosimetry*, vol. 141 (1), 1–9.