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TOWARDS LUMINESCENCE DATING OF MOSAIC GLASS

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ABSTRACT

The possibility of dating archaeological glass by means of luminescent techniques has been investigated in recent years, despite the difficulties of this application, mainly linked to the amorphous structure of the material. We focused in particular on mosaic glass, after the encouraging results obtained on byzantine and medieval samples. Further studies were devoted to the comprehension of the luminescent mechanisms in silica glasses, and to the investigation of the relationships between luminescence, colouring or opacifier ions and crystalline phase of the vitreous matrix. The results of a study on the dosimetric characteristics of thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) of a few medieval blue-green mosaic glasses from the San Lorenzo church (Milan) are presented, and the experimental protocols established to identify their suitability for dating are discussed.

KEYWORDS: Archaeological glass, Luminescence dating

INTRODUCTION

Luminescence dating (Aitken, 1985; McKeever, 2001) belongs to the class of dosimetric dating methods, and is based on the time-dependent accumulation of electric charges in insulators as a consequence of their exposure to ionizing radiation. Being the number of trapped charges proportional to the amount of absorbed energy, and being essentially constant over time the exposure to natural radiation, the number of trapped charges is proportional to the irradiation time.

In archaeological materials, such accumulation is measured as emission of light and is the result of the exposure to the low level of ionizing radiation field naturally present in nature due to natural radionuclides and cosmic rays. The luminescent signal can be set to zero by exposure to heat or light. For pottery, the zeroing takes place during manufacturing when baking in oven; for sediments, the zeroing event, referred to as bleaching, is the exposure to sunlight during erosion, transport and deposition of mineral grains. Once removed the zeroing agent (after cooling for pottery and when the sediment is covered by another layer) the luminescence signal restarts to build-up. For both pottery and sediments, the luminescent minerals used for dating are mainly quartz and feldspars.

The amount of luminescence of mineral grains extracted from a sample, measured in laboratory stimulating the sample with heat or light, is related to the time elapsed since the original archaeological or geological zeroing has occurred, and can be expressed in terms of absorbed dose of radiation, or palaeodose (energy absorbed per mass unit).

The reliability of luminescence dating stands on the reliability of the absorbed dose evaluation, i.e. on the good dosimetric characteristics of the material under study. These characteristics, on they turn, has been proposed to depend on the crystallinity of the material (Muller and Schvoerer, 1993, Sanderson et al., 1983). In an insulating crystal, in fact, due to the existence of a periodic potential, the presence of impurities and defects creates discrete energy levels in the energy gap, which act as traps for electrons, where they accumulate (McKeever and Chen, 1997). In an amorphous material, characterised only by a short range order, the presence of impurities gives instead rise to a continuum of energy. The probability of spontaneous recombination is therefore enhanced (Blasse and Grabmaier, 1994).

Archaeological glass, which is substantially amorphous silica plus variable amounts of different oxides, belongs to this second category of materials. The possibility of luminescence dating of glass has been investigated since long time, but, up to now, without satisfactory results. Recently, interesting data on Greek glass beads have been reported (Zacharias et al., 2008).

Glass mosaics, small pieces (tesserae) of glass variously coloured, are semi-transparent or opaque because they have to be looked at in reflected light. The glassy phase is associated in variable ratio to the crystalline phase. Crystals can be added to the fused phase as fine powder or separated by devetrification from the cooling of homogeneous fused glass containing suitable components. Glass colouration was obtained combining to the glassy matrix basis metal oxides with colouring and opacifying properties. Type and extent of coloration depend on the oxidation state of the oxide ions.

In the last few years, we have been involved in studies on the luminescence properties of glass mosaics (Chiavari et al., 2001; Galli et al., 2003; 2004; 2007), and we demonstrated that their relatively good TL emission is due to the relatively high crystallinity degree of the silica base and/or to the presence of crystals dispersed in it. The good luminescent sensitivity of an archaeological material is a necessary condition for its dating, but not a sufficient one. The signal stability over time, the absence of sensitivity changes and the linear growth with irradiation dose have to be verified, in order to obtain an acceptable evaluation of the absorbed dose, as illustrated in the following.

SAMPLES AND EXPERIMENTAL METHODS

We have analyzed 21 blue-green tesserae of the early medieval wall-mosaic glasses of S. Lorenzo Church (Milano, Italy). Ten of them were used to investigate and characterize the luminescent properties of this class of samples, the remaining for dosimetric experiments.

TL and OSL measurements were carried out using an automated luminescence system (Risø TL/OSL-DA-15), equipped with a $^{90}Sr/^{90}Y$ beta source delivering 0.1 Gy s^{-1} (±3 %) to the sample position. TL measurements have been performed from 50°C up to 450°C, with a heating rate of 5°C/s. OSL was stimulated by an array of blue LEDs (470 ± 30 nm). Photons were detected, under constant stimulation power of 54 $mWcm^{-2}$, by a bialkali photomultiplier tube (EMI 9235QB15) coupled to a 7.5mm Hoya U-340 filter.

Sample preparation: in safe red laboratory light the tesserae were lapped to remove the first 20 μm of the external surface, exposed to sunlight. They were then cut into 4-6 slices 500 to 800 μm thick, using a diamond saw (Bueheler, Isomet type 11/1180 low-speed saw, diamond wafering blade). To investigate possible differences in luminescence due to sample size, measurements were made both on slices and on crushed material, depositing the 4-10 μm fraction on stainless steel discs following the fine-grain dating preparation procedure (Zimmermann, 1971).

For ten samples, TL and OSL growth vs. beta dose was investigated, as well as the effect of blue illumination prior TL measurement. For the remaining eleven samples, a dose reconstruction experiment was performed on single aliquots: the samples were irradiated with a known laboratory dose, subsequently measured as unknown palaeodose. We adopted a protocol derived from the standard single aliquot regeneration technique (SAR, Murray and Wintle, 2003), consisting in measuring, after every TL or OSL run, the luminescence emission due to a test dose, in order to check and take into account possible sensitivity changes. Experimental details are reported in Tab.1

RESULTS

Fig. 1 shows typical glow curves of these glasses, obtained after 30 Gy beta irradiation, representative of the whole class. They present a sharp peak around 100°C, a shoulder in the range of 120°C-250°C and another peak at around 300°C. The sample to sample TL intensity variation is about one order of magnitude. The existence of well defined peaks seems to be related to the presence of crystalline inclusions in the amorphous vitreous matrix (Galli et al., 2004), while a broad emission is typical of amorphous material. In this case, the activation energies of the traps gave a continuous distribution rather than the spectrum of discrete values typical of the crystalline materials.

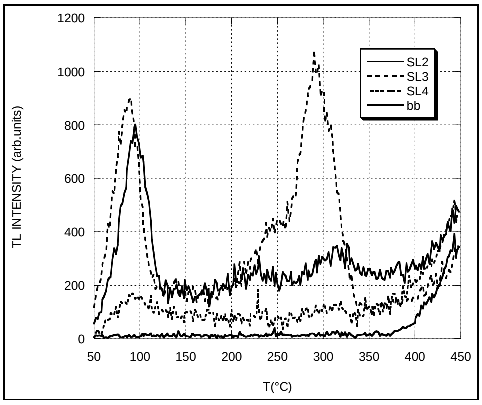

Fig. 1: Examples of TL glow curves of three glass mosaic tesserae

To investigate the relationships between TL and OSL traps, and to check the effectiveness of prior light stimulation in depleting the TL trap population, combined OSL and TL experiments were performed. They showed that the blue illumination of an irradiated sample induced an emptying of the 300°C TL peak (fig. 2), the residual OSL being strictly correlated to the extent of TL traps emptying. A strong relationship between OSL and TL traps could therefore be assumed, similarly to what evidenced in quartz (Wintle and Murray, 1997).

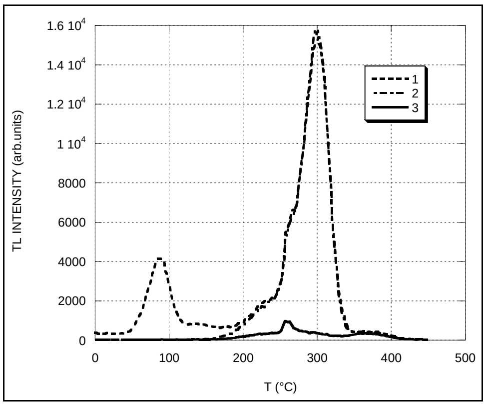

Fig. 2: Sample SL7. 1) glow curve obtained after a 5 Gy beta irradiation, 2) the same as in 1) with pre-heat at 150°C for 10s, 3) the same as in 2) with 470 nm illumination for 20 s at RT

Two typical examples of OSL shine down curves are reported in Fig. 3. They refer to measurements performed at RT and at 125°C, respectively, both after the same preheating (10 s at 150°C).

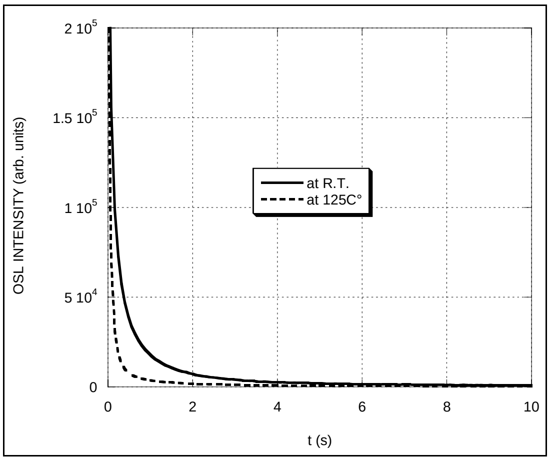

Fig. 3: Sample SL7. Solid line: OSL shine down curve obtained after 5 Gy beta irradiation, RT illumination. Dashed line: shine down obtained after 5 Gy beta irradiation, illumination at 125°C. Both curves are recorded after preheating (10 s at 150°C)

For all samples, the observed OSL decay was not a single exponential, indicating that different electron traps contributed to the process (McKeever and Chen, 1997).

The phenomenon of photo-assisted charge transfer from deep to shallow traps (phototransfer) was negligible in all the measured glasses, as shown in fig. 4: the effect of prior illumination with blue light on TL shape and intensity was a general and uniform depletion of low and high temperature traps population.

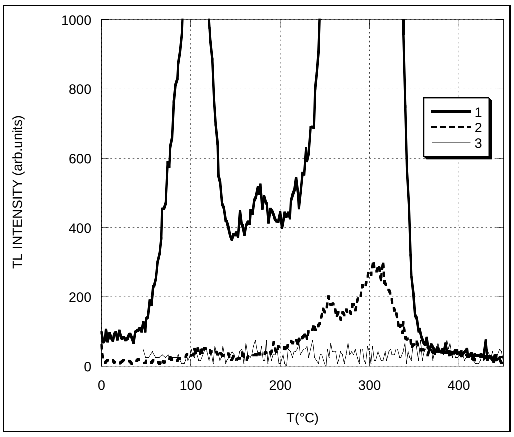

Fig. 4: Sample SL9: 1) glow curve obtained after 5 Gy beta irradiation 2) glow curve obtained after 5 Gy beta irradiation and 470 nm illumination for 20 s at RT 3) background emission.

The luminescence growth as a function of dose was studied: almost all samples showed a satisfactory linear behaviour in the range 1-10 Gy, as illustrated in Fig. 5 and Fig. 6 for TL and OSL respectively.

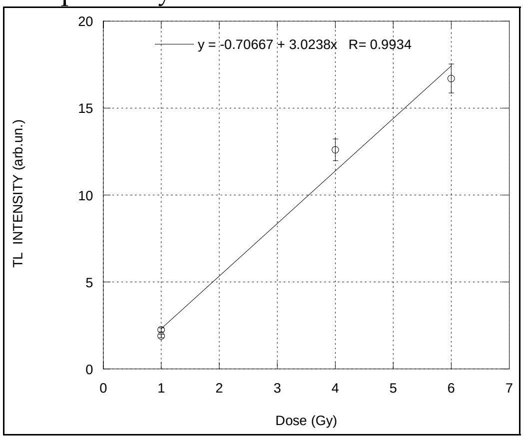

Fig. 5: Sample 7: TL growth vs. dose (TL intensity is the integral emission between 280 and 320 °C after background subtraction).

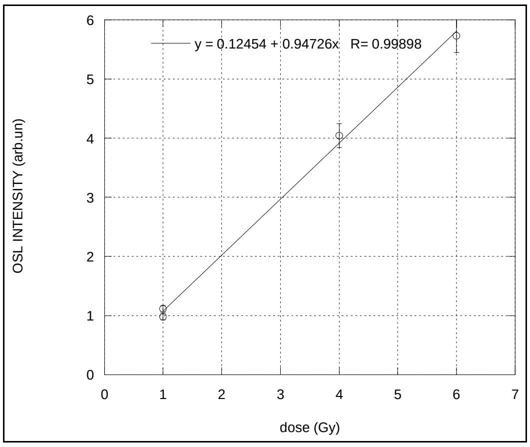

Fig. 6: Sample 9: OSL growth vs. dose. (OSL intensity is the integral emission in the first two second of stimulation, after subtracting a mean background contribution evaluated from the last 20 seconds of stimulation).

To more deeply investigate the TL and OSL characteristics of the glasses under study, and to check if they could be used for dosimetric and dating purposes, a dose reconstruction experiment was performed on further 11 mosaic tesserae. The samples, both in slices and in fine-grain form, were TL erased by heating at 500°C or OSL bleached by blue illumination (100 sec at 125°C). They were then 5 Gy irradiated, and sumbmitted to TL and OSL single-aliquot regeneration technique (SAR) protocols to recover the given dose (see Tab. 1). The dose reconstruction results are summarized in Tab. 2, in which the ratios *Given dose/Recovered dose* are listed.

It can be observed that the results obtained with TL were not satisfactory, particularly when using the sliced samples: in the majority of cases (6 samples over 11), the *Given dose* could not be measured and in the remaining cases the protocol gave scattered results.

With fine-grained samples, 9 glasses could be measured; the protocol systematically underestimated the dose.

Comparable and less scattered results were achieved with OSL, substantially regardless the sample form: all tesserae could be measured, with and a mean 10-20% overestimation.

Table 1: Details on the Single Aliquot Reconstruction protocols used for dose evaluation.

	TL	OSL
STEP		
1	Heating to 450 °C (erasure of previous TL signal)	Light Stimulation for 100 s at 125°C (erasure of previous OSL signal)
2	Irradiation with D =5 Gy	Irradiation with D =5 Gy
3	Preheat for10 s at 150°C	Preheat for 10 s at 150°C
4	Heating to 450 °C to measure TL	Measure OSL by stimulation for 100 s at 125°C
5	Irradiation with Test Dose=0.5 Gy	Irradiation with Test Dose =0.5 Gy
6	Preheat for 10 s at 150°C	Preheat for 10 s at 150°C
7	Heating to 450 °C to measure TL	Measure OSL by stimulation for 100 s at 125°C
8	Irradiation with Regeneration Dose D*	Irradiation with Regeneration Dose D*
9	Preheat for 10 s at 150°C	Preheat for 10 s at 150°C
10	Heating to 450 °C to measure TL	Measure OSL by stimulation for 100 s at 125°C
11	Irradiation with Test Dose D_t (D_t =0.5 Gy)	Irradiation with Test Dose D_t (D_t =0.5 Gy)
12	Preheat for 10 s at 150°C	Preheat for 10 s at 150°C
13	Heating to 450 °C to measure TL	Measure OSL by stimulation for 100 s at 125°C
14	Repeat steps 8-13	Repeat steps 8-13

*D = 1,4, 6 Gy

Tab.2 Dose reconstruction experiment results: Gd/Rd is the ratio *Given dose/Recovered dose* obtained on sliced or fine-grained samples using TL and OSL. Each result is the mean of at least three independent evaluations, whose mean standard deviation is 5-8%

SAMPLE	G_d/R_d, TL, slice	G_d/R_d TL, fine grain	G_d/R_d OSL, slice	G_d/R_d OSL, fine grain
SL2	1,0	*	1,2	1,1
SL3	*	0,7	1,0	1,0
SL4	*	0,9	1,3	1,3
SL6	*	1,0	0,8	1,2
SL7	1,4	0,7	1,2	1,2
SL8	*	0,8	1,5	1,3
SL10	0,4	0,5	1,0	0,9
SL11	1,1	1,2	1,3	1,1
SL13	0,8	1,1	1,6	1,3
SL14	*	*	1,3	0,8
SL15	*	1,4	1,4	1,3
MEAN±1σ (%)	0,9± 40%	0.9± 29%	1.2±16%	1.1±15%

*Dose not evaluable due to non linear behaviour or to strong sensitivity changes.

It must be noted that these results have been obtained measuring the samples immediately after the irradiation in laboratory. However, because a significant component of the luminescence signal is due to the electrons trapped in the shallow traps, the thermal fading of the signals has to be expected. This will be verified repeating the experiments introducing a time delay of a few weeks and months between the irradiation and the dose reconstruction measurements.

CONCLUSION

The luminescence characteristics of a set of medieval blue-green glass mosaic tesserae from S. Lorenzo church in Milano have been studied. A relatively high natural TL and OSL sensitivity was observed in almost all samples, showing good luminescencent properties. These characteristics sugggested to check if this class of glass was suitable for TL and OSL dating. To this aim, a dose reconstruction experiment was conducted on sliced and fine-grained sample (4-10 μm), using purposely adapted SAR protocols. The agreement between given and reconstructed dose, very poor for TL, was instead acceptable for OSL. This is considered an encouraging result toward the standardization of a dating protocol appropriate for such material.

Further investigations are planned in order to confirm these results, to explain the failure of TL as dosimetric technique, to improve the precision of dose evaluation protocols, to test the fading evaluation procedures, to measure the relative contribution of alpha particle in inducing TL and OSL in fine grains, and to accurately evaluate the internal dose rates with the limited amount of material usually available with this typology of samples.

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