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USING THE TL PRE-DOSE TECHNIQUE FOR THE TL EXAMINATION OF GLASS MOSAICS

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ABSTRACT

Aiming at the evaluation of the dose absorbed by ancient mosaic glasses, we present the results of a study performed on eight glass mosaic tesserae from the two XI century byzantine World Heritage Greek monasteries of Daphni, outside Athens, and Hosios Loukas, in Phocis, 67 km from the capital. Exploiting the presence of quartz crystalline inclusions in the glass matrix, the dose was measured using the pre-dose effect associated to the 110°C peak of quartz. The preliminary encouraging results allowed the correct discrimination between the original tesserae and those related to modern restorations.

KEYWORDS: Ancient glass, mosaic, thermoluminescence dating

INTRODUCTION

The tesserae studied in this work came from the wall mosaics of the World Heritage Daphni and Hosios Loukas byzantine monasteries in Greece, located just outside Athens and 67 km from the capital respectively. They have already been object of an extensive study devoted to provide their complete characterisation (Arletti et al., 2010). The relevance of these glass decorations is double: they have been submitted to several restorations, even in the past, and the original pieces belong to a period of technology change: the samples were silica soda-lime glasses, without exclusive use of a pure mineral source of alkalis (Arletti et al., 2010).

The possibility of identifying different groups on the basis of the chemical composition is therefore a stimulating challenge. To this aim, the direct dating of the samples would be of unquestionable help. However, even if in principle thermoluminescence (TL) can be detected in glass, in analogy with ceramics, its amorphous structure makes more complex the trapping-detrapping mechanism and TL dating is not yet an assessed procedure.

In previous works (Galli et al., 2003; Zacharias et al., 2008) the dosimetric properties of mosaic tesserae related to the presence of micro-crystalline inclusions in the silica matrix were observed. In fact, the presence of a measurable natural TL signal, related to the dose absorbed in the past, arises from these inclusions. For instance, if calcium antimonate, an opacifier used since Roman times, was dispersed in the glassy matrix, the samples showed a high TL emission in the same temperatures and wavelength range of a calcium antimonate standard sample. It could be assumed that this compound plays a role in the radiative recombination processes, being probably responsible for most of the signal.

Recently, TL and optically stimulated luminescence (OSL) were applied to a set of baroque glass tesserae (Galli et al., 2011; Galli et al., 2012). It evident that the dosimetric properties of the most sensitive samples were associated to the presence of cassiterite (tin oxide) and calcium antimonate crystals. The presence of such crystals allowed the evaluation of the absorbed dose (i.e. the radiation dose absorbed by each sample during its archaeological life), by means of both TL and OSL, using Single Aliquot Regeneration (SAR) protocols (Hong et al., 2006; Murray and Wintle, 2000; Liritzis et al., 1997), even if with low precision.

In the case of the Daphni and Hosios Loukas monasteries we performed a dosimetric study on eight mosaic tesserae coming from the walls. In these glasses the only crystalline phases detected were quartz and cristobalite, a high temperature polymorph of SiO_2 (Arletti et al., 2010). In this case, the application of the well known dating protocols specific for quartz was justified. We especially focused on the pre-dose technique (Zimmerman, 1971). This method, mainly used for dating young samples and for accidental dosimetry (Bailiff and Haskell, 1983), is based on the relation between the dose absorbed by the sample and the sensitivity changes of the "110°C" peak of quartz induced by a combination of irradiation and thermal treatments (Bailiff, 1994; Liritzis, 1980).

EXPERIMENTAL

For luminescence analysis the glass was crushed in a stainless steel mortar and the 75-125 μm fraction was separated by sieving. The grains were put in aluminum cups and measured in a Risø TL/OSL-DA-15 system, equipped with a $^{90}Sr/^{90}Y$ beta source delivering 0.09 Gy s^{-1} (±3 %) to sample position. TL measurements were recorded at 5°C s^{-1}. Emissions were detected by a bialkali photomultiplier tube (EMI 9235QB) coupled to a blue filter pack (Schott BG 39, 2 mm thick; Corning 7-59, 4 mm thick).

Absorbed doses were tentatively evaluated using a pre-dose simplified protocol, described in Tab.1, in which the test-dose and the activation dose are unified. It was specifically developed for samples with low first TL sensitivity, as in this case. This protocol had previously been tested on thirty polymineral fine-grain ceramics, comparing the pre-dose EDs with those obtained using the multi aliquot additive procedure (Aitken, 1985) with good results (Galli et al., 2006).

Table 1 Description of the Pre-dose protocol adopted in this study (Galli et al., 2006).

STEP	PROCEDURE
1	Irradiation (0.9 Gy = 10s)
2	TL read-out up to 450 °C (delay between irradiation and measurements =15s). This measure gives the analogous of S0 (sensitivity after the first test-dose) in the standard protocols.
3	Repeat steps 1-2 until the saturation of the effect, measuring S_1, S_2, … S_N

This protocol is less precise than the standard one, which remains recommended when the extraction of quartz grains is practicable.

RESULTS AND DISCUSSION

All the samples showed an intense *natural* TL signal, i.e. the one due to the exposure during their archaeological life. Two representative examples are shown in Fig.1.

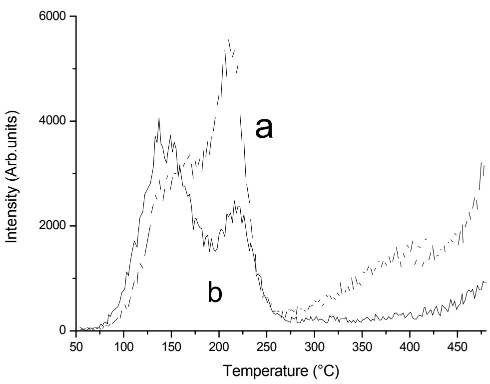

Figure 1. Typical natural TL glow curves of mosaic glass (a=F11 sample; b= F9 sample)

All the *natural* glow curves showed two peaks at low temperatures, centred at about 150°C and 200°C respectively; the TL emission over 330°C was characterized by a generally weak broad emission. The presence of the low peaks in the natural signal is anomalous: the traps at low temperature having an occupancy short lifetime (in the order of some hours), they should been emptied. The presence of these low temperature peaks could be due to charge transfer phenomena. To investigate if our samples were affected by such effect, the stability of traps at room temperature was investigated. Several aliquots of the same sample were measured: one to get the natural signal, others irradiated with the same dose, preheated (2 min at 250°C) and measured promptly or at increasing times after irradiation. Between irradiation and TL read-out, the samples were kept in the dark at room temperature.

In Fig. 2 the natural TL curve (with and without pre-heating), that obtained promptly after irradiation and preheat, and two measured after different time delays are compared.

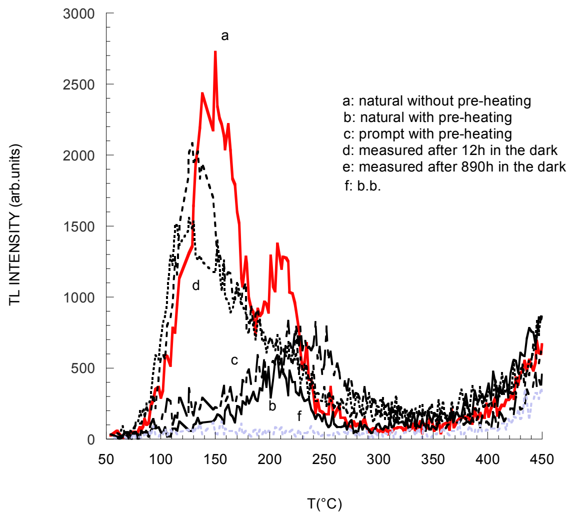

Figure 2. Sample F6. Comparison between natural glow curve (no pre-heated (a) and pre-heated (b)) and pre-heated, irradiated glow curves (c-e) kept in the dark. c) is measured promptly after irradiation and pre-heat; d) and e) after 12 and 890 hours storage in the dark respectively. Irradiation dose: 4 Gy beta; pre-heat 2 min at 250°C.

The low temperature peaks, instead of being emptied after thermal annealing at 250°C, grew after storage in the dark at room temperature. After 890 hours storage, the peaks appeared at the very same temperatures of the peaks of the natural glow curve, confirming the presence of a charge transfer phenomena, whose donor traps could not be identified, because of the absence, at least in our measuring temperature range, (50-450°C), of high temperature peaks correspondingly decreasing their intensity. The same experiment was also performed illuminating the samples during storage with solar simulator: the same qualitative behaviour observed was accelerated.

To evaluate the paleodose, the SAR (Single Aliquot Regenerative) method (Hong et al., 2006) was initially attempted. The main feature of the TL emission was the absence of thermal stable traps in the 350-375°C region, where usually the signal is integrated for calculations.

As shown in Fig.3, both natural and laboratory induced glow curves had a low, broad emission at T> 300°C, with sensitivity to radiation dose very low compared with that of the low temperature peaks (Fig.3, inset).

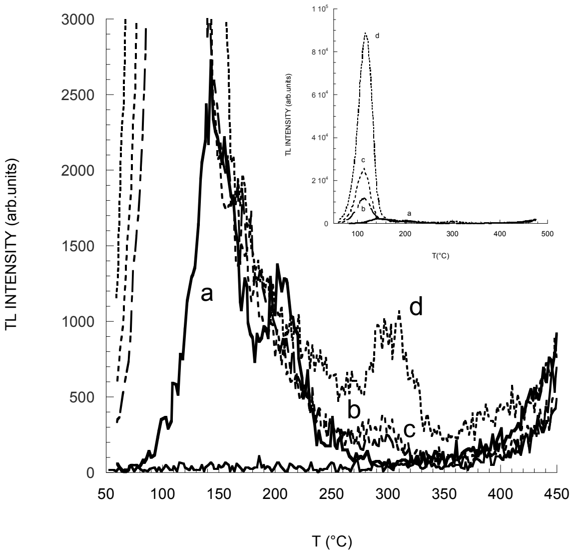

Figure 3. Sample F9. Comparison between natural glow curve (a) and irradiated glow curves (b-d). (irradiation doses: b= 2 Gy beta, c= 4 Gy beta, d= 16 Gy beta). In the inset there are the same glow curves, full scale.

The results of by XRD measurements (Arletti et al., 2010), had shown that quartz was the only mineral phase dispersed in the glassy matrix. It was then reasonable to assign the presence of the very intense TL peak centred at about 100°C to quartz and to attempt to exploit the pre-dose effect to determine the equivalent dose.

The pre-dose effect consists in a change of TL sensitivity due to the previous irradiation received by the sample combined with heating treatments. This sensitivity change, in the "110°C" peak of quartz is proportional to the previously absorbed dose. This kind of memory can be successfully used to evaluate the equivalent dose (Fleming, 1973).

Properly used it is a powerful technique, though limited in use to samples relatively recent, generally of the last 1000 years because of the early onset of saturation, usually occurring at a few Grays.

We applied a procedure (Göksu et al., 1998; Galli et al., 2006) simplified with respect to that originally proposed by Zimmermam (1971). The reason of such a choice is due to the low sensitivity of the 110°C peak in the first TL measurement. In several cases, in fact, the TL response to the small dose used as test-dose (S_0, typically hundreds of mGy) could not be detected, preventing the application of the standard measuring technique. We tried to circumvent this problem using the simplified protocol described in Tab.1 in which the test-dose and the activation dose are unified.

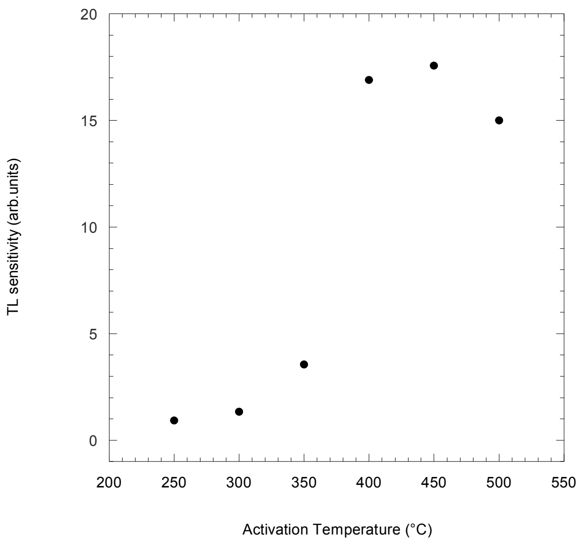

Figure 4. Sample F5: thermal activation curve

Measurements were made reading the TL emission of the same aliquot subsequent to repeated irradiations with relatively high dose (0.9 Gy) until the saturation of the effect. For a given sample, the maximum heating temperature corresponds to the temperature at which the activation of the effect is more enhanced (MAT, maximum activation temperature, in our samples ranged between 400°C and 440°C, see Fig. 4).

In Fig. 5, examples of the pre-dose curves of a glass sample are shown; the red curve in the inset being the response to the first test-dose (S_0), characterized in this case, but not always, by a quite good signal-to-noise ratio. The sequence S_0-S_7 shows a remarkable sensitivity enhancement after irradiation (Fig. 5).

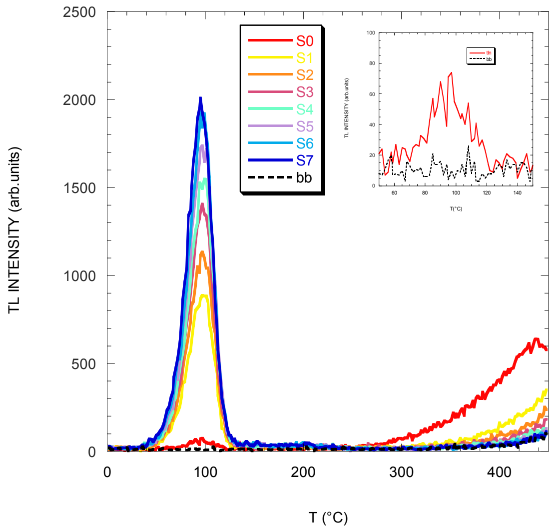

Figure 5. Sensitivity changes of 100 °C peak due to repeated β-irradiations (0.9 Gy) and heatings up to 450 °C. In the inset there are the natural glow curve and black body emission.

The plot of the ratio S_n/S_0 versus the cumulative imparted dose gave rise to growth curves like that shown in Fig. 6.

The absorbed dose is evaluated as the extrapolated intercept at $S_n/S_0 = 1$. The high error in the S_n/S_0 ratio (10%) is a consequence of the low precision in the evaluation of the net peak area in S_0.

The best fit of the experimental data was not obtained with a straight line, but with a saturating exponential, possibly indicating the presence of quenching (Bailiff, 1994) and/or the saturation of the effect. In our opinion, the latter is the most probable explanation, because the cumulative imparted dose is relatively high (about 7 Gy).

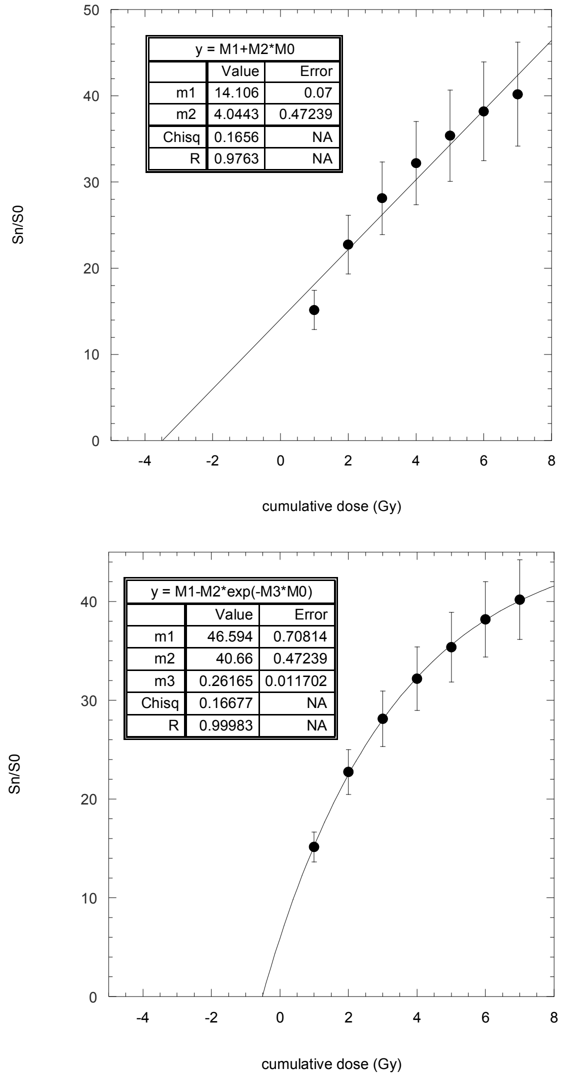

Figure 6. Sample F9. Changes in TL sensitivity as a function of irradiation dose and measurement cycles. The graph reports the TL emission of the 100°C peak for 0.9 Gy of beta dose, normalized to the TL emission due to the first irradiation (S_n/S_0), as a function of the cumulative dose. 6a, linear fit; 6b, exponential fit .

In the paper of Chen (1979), and in a more recent work of Burbidge et al. (2010), is stressed that quenching phenomenon does not affect the absorbed dose evaluation when the sensitivity of the 110°C peak grows linearly with the dose. However if the sensitivity growth is exponential, a correct evaluation is only obtained when the laboratory imparted dose is similar to the natural one, even if the quenching correction has been performed. In our experimental procedure the absorbed dose is higher than the hypothesized natural absorbed dose, being mandatory the application of the simplified pre-dose protocol. A new protocol that accounted for radiation quenching is however under study.

In order to check the reliability of the technique, a dose recovery experiment was performed. 2 Gy of additional beta laboratory dose were imparted to the samples and the pre-dose simplified protocol was applied. The expected results should therefore be 2 Gy higher than that obtained with the unirradiated samples. Recovered doses were then interpolated with both saturated exponential and linear regression. In the first case, the recovered dose was systematically lower than 2 Grays, indicating the non suitability of the exponential interpolation, while satisfactory results were obtained with the linear interpolation using only the linear part of the growth, corresponding to an accumulated laboratory dose of the order of magnitude of the natural one (Imparted dose/recovered dose = 0.90 ±20%).

The archaeological absorbed doses were then evaluated using the linear regression of experimental data, up to about 3 Gy of cumulative dose. The weighted results were in the range 1.5-3 Gy (see Table 2), in good agreement with the values expected for Byzantine glass, and allowed the discrimination between the original tesserae (D9, D17_2, D33_2, F6, F9, F11) and that related to modern restoration (D12). Sample D27, not analyzed with XRD, did not show any pre-dose, probably due to absence of quartz.

Table 2. Results of the absorbed dose evaluation

SAMPLE		Crystalline phase	#Aliquot	ED (Gy)
D9	Daphni, original (IX century)	Quartz and crystobalite	49	2.55±0.2
D12	Daphni, non original (XIX century)	Not analysed	52	<0.5
D17_2	Daphni, original (IX century)	Quartz and crystobalite	38	2.15±0.2
D27	Daphni, original (IX century)	Not analysed	18	-
D33_2	Daphni, original (IX century)	Quartz and crystobalite	20	2.05±0.2
F6	Hosios Loukas, original (IX century)	Not analysed	13	2.60±0.2
F9	Hosios Loukas, original (IX century)	Quartz and crystobalite	14	1.50±0.2
F11	Hosios Loukas, original (IX century)	Quartz and crystobalite	14	1.65±0.1

To definitely assess the suitability of the pre-dose technique for dating our mosaic glass samples, it will be necessary to complete the experimental evaluations for the annual dose-rates, to compare the TL dating result with the archaeological ones. The measurements are in progress, and particular care will be given to the aspects related to the external contribution. This appears to be an arduous task, for the complexities linked to the possible inhomogeneity of the local gamma field, difficult to evaluate without direct access to the archaeological sites.

CONCLUSION

The Pre-dose technique is potentially applicable to glass mosaic rich in quartz inclusions, but the initial low TL sensitivity of the low temperature peak can be a complicating factor.

The simplified protocol here applied allowed to circumvent this problem, and gave values of absorbed dose in good agreement with those hypothesized on historic and compositional grounds. Even if the dose evaluation was characterized by low precision (10-15%), a successful discrimination between the original tesserae and one related to modern restoration was possible.

Moreover, the application of this protocol may be prevented in presence of quenching effects, and could give unreliable results at the onset of the saturation of the effect.

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