Firing temperature of pottery using TL and OSL techniques

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Abstract

Several methods of thermal analysis are used to determine in the laboratory the firing temperature of ancient ceramic sherds. These methods are based primarily on changes of physical characteristics occurring when clay minerals are heated. The luminescence properties of quartz grains in a ceramic matrix also undergo certain changes during firing. The possibility of measuring the sensitivity change (sensitization) of quartz in order to determine the firing temperature of archeological ceramic artifacts was investigated. The sensitivity change was studied for both the thermoluminescence (TL) and the optically stimulated luminescence (OSL) signal for a ceramic sample of known firing temperature. Various segments of the sample were annealed to a different temperature. Subsequently, the initial sensitivity, as well as the thermal and the pre-dose sensitization were measured for both TL and OSL at room temperature as a function of the annealing temperature. The obtained TL glow curves showed different shapes for annealing temperatures above the firing temperature. Thermal and pre-dose sensitizations also exhibited a similar, although less prominent, rise. The OSL signal was analyzed by integrating the raw signal over the initial second of stimulation. The initial sensitivity showed an abrupt change for annealing temperatures around the firing temperature. An alternative approach used for the analysis of the OSL signal involved a full-component resolved sensitization study. The same abrupt change for the initial sensitivity of both the first and second components was observed, as well as, a clear but not very prominent thermal sensitization trend for annealing temperatures above the firing temperature.

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1. Introduction

The firing temperature of ancient pottery provides a basis for understanding many aspects of ancient technology such as manufacturing techniques and functional relationships between specific resource manufacturing combinations. Several methods of thermal analysis are used in order to determine in the laboratory the firing temperature of ancient ceramic sherds, based primarily on changes of physical characteristics occurring when clay minerals are heated.

Pottery is made by firing clays, which contain 40–80% silica. Most of it is in the crystalline form of quartz, the luminescence properties of which undergo certain changes during firing. Attempts have been made to estimate the firing temperature of quartz [1,2] and flint [3]. However, while Sunta and David firmly established the authenticity of the method, Watson and Aitken observed that the procedure was not generally applicable.

The method used in these earlier attempts involved the study of the behavior of sensitivity, solely for the 110 °C thermoluminescence (TL) peak of the fired quartz, prior to and after application of a laboratory pre-dose versus the subsequent increasing temperature. The ratio of the TL sensitivity before and after the application of the pre-dose is expected to remain constant until the re-firing reaches the
firing temperature. Thereafter, it is expected to rise appreciably. However, several researchers [4,5] have expressed serious considerations concerning the feasibility of the method indicating that, although the firing episode registers its effect in an effective way in the quartz lattice, the preservation of this memory may be diluted with time. Therefore, the unlocking of the memory, if present, must replicate the conditions during the paleo-firing episode.

The present work investigates the possibility of monitoring the sensitivity changes (also known as sensitization) for both the TL and the optically stimulated luminescence (OSL) signals of quartz, attributed to: (a) the annealing treatment only, (b) the thermal activation to 500 °C and (c) the pre-dose effect, in order to determine the firing temperature of archeological ceramic artifacts.

2. Materials and methods

A ceramic sample of known firing temperature, 600 °C, was divided into seven segments. Each segment was annealed to a different temperature between 300 and 900 °C, in steps of 100 °C in order to bracket the firing temperature. After the annealing, each segment was crushed and grains of dimensions 4-11 μm were selected and deposited on aluminum discs of 1 cm² area. Subsequently, the initial sensitivity, as well as the thermal and pre-dose sensitizations were recorded for both TL and OSL at room temperature as a function of the annealing temperature.

All luminescence measurements were performed using the RISO TL/OSL reader (model TL/OSL–DA–15), equipped with a high-power blue LED light source, and a 0.079 Gy/s 90Sr/90Y β-ray source. The reader is fitted with an EMI 9635QA PM Tube [6]. All OSL measurements were performed using a Hoya U-340 filter. The power level was set at 90% of the maximum power of the blue LEDs. TL measurements were performed up to a maximum temperature of 500 °C, using a combination of a Pilkington HA-3 heat absorbing and a Corning 7-59 blue filter. In order to avoid thermal gradient, the heating rate used was 1 °C/s.

In the case of TL, in addition to the characteristic 110 °C glow peak, the behavior of the entire glow curve was studied.

The OSL signal was analyzed using two different approaches. In the first approach, the raw OSL signal integrated over the initial second of stimulation was used. The second approach involved a full-component resolved sensitization study, for each one of the components of the OSL signal. All Continuous Wave (CW-OSL) curves were transformed into pseudo-linear modulated OSL curves (pseudo LM-OSL), using the transformation initially proposed by Bulur [7] and revised by Polymeris et al. [8].

All curve fittings were performed using the MINUIT computer program [9], while the efficiency of fit was tested using the figure of merit (FOM) of Balian and Eddy [10]. The obtained FOM values were in all cases less than 2%.

3. Results and discussion

3.1. Thermoluminescence

The glow curves of various sample segments are shown in Fig. 1 for different annealing temperatures. These curves were obtained without any pre-treatment between the annealing and the read-out procedures. Therefore, they monitor the sensitivity changes occurring due to the annealing procedure.

For annealing temperatures between 300 and 600 °C, the glow curves exhibit no significant changes. However, for annealing temperatures in the range of 700–900 °C the glow curves attain a different shape due to sensitivity enhancement, which varies with temperature. As can be seen in Fig. 1, one distinct glow peak appears, centered at approximately 200 °C, and its size increases with the annealing temperature, while the high temperature region of the glow curve becomes more intense. No significant change is observed for the 110 °C glow peak. The form of the glow curve behaves similarly after both simple thermal sensitization to 500 °C, as well as pre-dose sensitization of quartz.

Normalized sensitivity changes of the glow peak at 200 °C versus the annealing temperature are presented in Fig. 2, due to: (a) purely the annealing treatment (squares), (b) thermal activation to 500 °C (circles) and (c) pre-dose effect (triangles).

Sensitivity remains stable for annealing temperatures up to 600 °C, but when the re-firing reaches the firing temperature, a prominent rise in the sensitivity is observed. This rise is steeper in the case of the pre-dose sensitization.

Annealing at a temperature of 700 °C enhances the sensitivity by a factor of 2.3 in both cases of thermal
activation and initial sensitivity and by 3.25 in the case of the pre-dose effect.

3.2. Optically stimulated luminescence: raw signal

The changes of the raw OSL signal integrated over the initial second of stimulation were found to depend on the re-firing temperature. In particular, the behavior of the initial OSL sensitivity with respect to the annealing temperature was found to remain relatively constant for re-firing temperatures in the range of 300–500 °C and to increase in the range of 600–700 °C while a small decrease appears at 800 °C. The sensitization factor at 700 °C is approximately 3.

3.3. Optically stimulated luminescence: component-resolved sensitivity study

CW-OSL curves obtained for various annealing temperatures without any pre-treatment between the annealing and the read-out procedures were transformed into pseudo-LM-OSL curves. Fig. 3 shows a number of these transformed pseudo LM-OSL curves.

As in the case of the TL glow curves, for re-firing temperatures between 300 and 500 °C, the pseudo-LM-OSL curves show no significant changes. As the annealing temperature exceeds the firing temperature, an enhancement in the sensitivity of the OSL signal integrated over not only the initial (first) second, but at least over the initial (first) 150 s of stimulation is apparent.

Fig. 4 shows the results of the component resolved sensitization study for both the C1 (squares) and C2 (circles) components of the OSL signal as a function of the annealing temperature.

The sensitization is attributed purely to the annealing treatment. The initial sensitivity of both components shows a mild change with the annealing temperature below 600 °C, and an abrupt increase above it. At an annealing temperature of 700 °C the sensitivities of the first and second components increase by a factor of 3.5 and 4, respectively. The sensitivity of the third component (C3) was found to be nearly constant and independent of the annealing temperature. The results indicated also a clear but not very prominent sensitization trend due to thermal activation to 500 °C, as well as the pre-dose effect. In particular, both phenomena result in a sensitization factor less than 1.75 for the annealing temperature of 700 °C.

4. Conclusions

In the present investigation, all TL and OSL sensitivity curves of quartz as a function of the annealing temperature...
exhibited a similar behavior. The sensitivity remains fairly constant for annealing temperatures below the firing temperature and there is a significant increase for annealing temperatures above it. These results suggest a definite relation between both TL and OSL sensitivities and the firing temperature of pottery. Therefore, either luminescence technique would be able to provide an assessment of the firing temperature. Especially, sensitivity changes attributed purely to the annealing procedure could provide a useful tool of thermal analysis. However, for antiquity samples the question of whether the quartz grains in the ceramic fabric can carry the memory of their thermal history over long time periods, remains to be resolved before a reliable measurement protocol is established.

References