Mediterranean Archaeology and Archaeometry, Vol. 10 No. 1, pp. 81-87

NEW QUARTZ TECHNIQUE FOR OSL DATING OF LIMESTONES

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Received: 20/06/2009
Accepted: 15/01/2010
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ABSTRACT

The equivalent dose De determination of limestone-made ancient constructions by thermoluminescence (TL) prevents accurate measurements and requires plateau test of bleached curves. Optical stimulated luminescence (OSL) of quartz and feldspar minerals for surface dating is routinely applied for De but not for limestones. Here the OSL of present traces of such minerals removed with powder from surface limestone bleached by sunlight overcomes this issue and offers an alternative way for De. This is verified with further test examples.

KEYWORDS: Quartz, limestone, luminescence, dating, dose

INTRODUCTION

The eviction of electrons from electron traps in crystalline materials via thermal agitation or light stimulation and their refilling from ionizing radiation is the basis for zero set luminescence clock of thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) dating methods. A variant of TL and OSL has already been developed for surface dating of large carved limestone blocks (megalithic, cyclopean) of Greek monuments (Liritzis, et al 1997a; Liritzis, 2010) followed by other rock types (Habermann et al., 2000; Greilich et al., 2005; Liritzis and Vafiadou, 2005; Liritzis et al., 2010; Liritzis et al, 2008).

The surface luminescence dating of masonries concerns the inter-block surfaces of the limestone building blocks and relies on the Optically Sensitive Electron Traps (OSET) responsible for TL in the surface layer of the carved limestone block having been bleached by sunlight, prior to the blocks being incorporated into the structure. The exposure time of the surface to sunshine to a variable depth that depends upon the efficiency and time for the stonemasons to put any block in the appropriate place overlaid by another. From this moment internal surface is no longer exposed to sunlight, and OSET are filled by electrons produced by the ionization caused from nuclear radiation of natural uranium, thorium, rubidium, potassium, and the cosmic radiation. These isotopes are present in the limestone rock and the soil surrounding the sampling point.

The age equation and the procedures for luminescence dating have been reviewed elsewhere (Aitken 1985, 1998).

The OSL probes the OSET (blue or green light probes quartz and feldspar, the IR stimulation probes only feldspar), while the TL probes the Thermally Sensitive Electron Traps (TSET) but the OSET as well.

The alternative approach of De determination of limestones through quartz grains extracted thereof is presented in some indicative age studies.

Single quartz aliquot OSL dating of limestones

The extensive XRD analysis and the problems encountered with the luminescence dating of mostly limestone led to a first investigation regarding improvement in the luminescence dating of limestone buildings (Table 1) (Liritzis et al, 2007a; Liritzis et al., 2010). Since no OSL reading of limestone is as yet available (Galloway, 2002), in the conventional TL dating of calcite large scatter in the additive dose procedure for the equivalent dose (De) determination is obtained (10-30%). Such a high scatter attaches the De and solar bleaching plateau test with large error bars. Thus, the obtained luminescent data are of high scatter due to thermal alterations of calcite in temperatures up to 400 ^{o}C where the TL of $CaCO_3$ induces sensitivity changes (lattice disruption) and alteration of 275 and 350 ^{o}C TL peaks. Therefore deduced dates inheres large uncertainties in the order of $\pm$12-25% (Liritzis 2001).

The alternative technique relies on extracting traces of quartz from the removed surface powder. The detection of traces of quartz / feldspar secured the use of single aliquot / grain OSL dating of calcitic monuments, taking into account that OSL of quartz and feldspar is well established (Liritzis et al 1997b; 2008), that they are bleached fast and efficiently by sunlight (though needs more time exposure of dozen of minutes for surface layer) and errors involved in the De determined thereof could be around 5% (Aitken 1998). Therefore, surfaces are gently rubbed with a file to remove layers of powder about 1-3 mm thick taken per 0.5 mm. These polymineral grains are washed in diluted HCl to remove calcite, washed in acetone and finally sieved with a ~ 60-150 μm mesh, to gather the quartz. Preparation and quartz recovery details are given below.

Solar transmission through limestones and marble can reach depths of 0.5-1 mm and up to 16 mm respectively, depending on the opaqueness (Liritzis and Galloway, 1999). Thus, the sparse quartz grains remained as residue from the removed upper few millimeters limestone surface layer in powder form and recovered in red lighting conditions are bleached in antiquity because of solar penetration to few mm.

CASE STUDIES

The separation of trace quartz quantities from the calcitic powder, which is removed out of the carved stone via dilute HCl acid, is a straightforward procedure. We used 3.7% HCl acid, in a proportion 50ml of the acid for 1g of powder. The powder was washed for 5-6 hours.

The first attempt was made on four samples: VT3 (Valley Temple, Giza, MTL3 (Mycenae, Greece), ETL5 (pyramid from Argolid, Greece) and a limestone schist from Styra Euboea Dragon House that were processed under red light condition A fifth sample from the megalithic block house in Fichtia near Mycenae, Peloponnese, Greece was also successfully prepared in natural light and trace of quartz was recovered. In fact XRD analysis had shown that BTL1 is a calcitic sample with only 3% of quartz. The treatment to remove the calcite goes as follows: initially 20g of the sample were collected and washed in 1000ml of 3.7% HCl acid for 6 hours. The solution was centrifuged several times to retrieve the residual, which was about 1.3g. Microscopic analysis has shown that the sample consists by other mineral too, but quartz (eg. biotite, mica, feldspars etc.). In the case of mica (biotite, muscovite) and other phyllosilicic minerals treatment with $Na_2S_2O_7$ was performed (Kiely and Jackson 1964, 1965). In case of feldspars, separation should be made without affecting the quartz either by concentrated HF (40%) for 40min in fraction of 180-250μm, or diluted HF (5% or 10%) for 80-120min, or H_2FSi_6 (35%) for 30h or longer (Berger et al., 1980, Rees-Jones, 1995, Prasat, 2000, Roberts and Wintle, 2001, Stokes et al., 2003a,b; Mauz and Lang, 2004, Syers et al. 1968). At the end an aliquot of mixed quartz and feldspar was successfully extracted.

For the other four calcitic samples VT3, ETL5, KAPS3 and MTL3 an amount of 0.1g from each sample was washed in 5ml of 3.7% HCl acid for 4 hours, then dried and examined by polarised light microscope (Nikon Eclipse E 200 Pol). More minerals were observed than initial XRD analysis have had shown (Liritzis et al., 2007). Any organics present were removed with hydrogen hyperoxide H_2O_2. Residues were processed and OSL readings were obtained from quartz since feldspars had a weak signal. In fact feldspars were monitored by Infra Red Stimulated Luminescence (IRSL) read out.

Luminescence measurements were performed using the fully automated RISØ TL/OSL reader (model TL/OSL–DA–15) equipped with a high-power blue LED array light source, an infrared solid state laser and a 0.076 *Gy/s* $^{90}Sr/^{90}Y$ β-ray source (Bøtter-Jensen et al., 2000). The reader is fitted with a 9635QA PM Tube. The detection optics consisted of a 7.5 mm Hoya U-340 (λ_p ~ 340 nm, FWHM 80 nm) filter that was used for all luminescence measurements. Blue light stimulation for OSL was achieved using LEDs (470 nm, FWHM 20 nm) delivering up to 40 *mW/cm²* at the sample position.

All heatings were performed using a heating rate of 1 °C/s in order to avoid significant thermal lag. In case of CW-OSL measurements, the power level was software controlled and set at 90% of the maximum stimulation intensity.

Blue light from LEDs (470 nm) are used on single aliquot for three samples. In cases that single grains are extracted, then the single grain technique may be used. The regeneration technique additive dose protocol was used (Duller et al., 2000; Murray and Wintle, 2000) and respective De results were obtained.

The applied protocol is outlined as follows:

Step 1: Regenerative dose Di (i=1 natural; i=2,3,4 three incremental regenerative doses = 20, 40 and 60 Gy respectively, i=5 zero dose for recuperation test; i=6 repeat of the first regenerative dose)

Step 2: Preheat 200 °C for 10 s

Step 3: Natural and regenerative dose OSL for 150 s at 125 °C

Step 4: Test Dose TD

Step 5: Heat to 160 °C

Step 6: Test Dose OSL for 150 s at 125 °C

Return to step 1

The results are as follows:

1) For the Valley Temple, Giza, VT3 limestone, Recycling Ratio = 1.12 ± 0.3, Recuperation = 6.47 %, De= 28±1.70 Gy, (Fig.1) of geological meaning, since the sampling was made from a deeper layer than original surface - the TL of this limestone gave a nearly saturated dose implying sampling was made on a geological layer which presumes geological age, too.

2) the Mycenean sample MTL3 from palace of Mycenae gave De= 4.00 ± 0.80 Gy (recycling ratio = 1.04±0.14 and recuperation = 64.7%) (Fig.2), and with a dose-rate of 2.80 mGy/yr it provided an age of around 1000±300 years B.C. compared with the archaeological dating of c.1250 B.C.

3) the ETL5 from the Hellenikon pyramid in Argolid, Greece (recycling ratio = 0.82±0.13 and recuperation = 11%). With the De= 1.82±0.86 (Fig.3) and a dose-rate of 2.38 mGy/yr gives a very recent age, in contrast to earlier measurements (Theocaris et al., 1996, 1997). This is due to the fact that since the initial sampling (1993) the surface was occasionally exposed to light thus subjected to unknown bleaching.

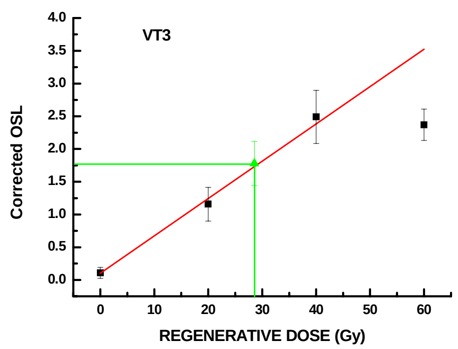

Fig. 1 Valley Temple limestone, Giza, Egypt (VT3): SAR procedure of extracted quartz

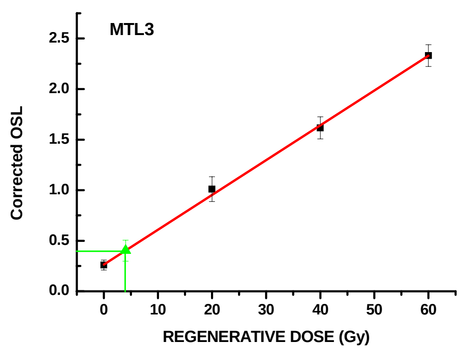

Fig. 2 Mycenean limestone from Mycenae (MTL3): SAR procedure of extracted quartz

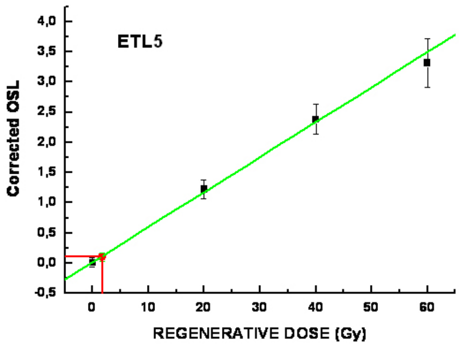

FIG.3 SAR of extracted treaces of quartz of limestone from Hellenikon pyramid, Argolid Greece

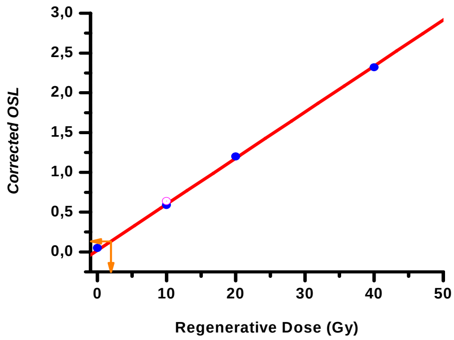

FIG.4 SAR of marble schist Dragon House Kapsala No 4 (Quartz: trace, Calcite: very abundant, Dolomite: not determined, Chlorite: trace, Muscovite: common/trace, Albite: trace)

4) the Dragon House of Kapsala, Styra, Euboea, Greece, with a De= 1.78±0.01 Gy recycling ratio 1.02±0.02, recuperation 50.6±17% (Fig.4). With a dose rate equal to 0.67± 0.05 mGy/a, the age for this megalithic house was 650±250 years B.C. The initial XRD monitor of quartz has been applied in numerous megalithic buildings (Dragon houses) at Styra, Euboia, that helped their dating procedure (see Table 1) (Liritzis et al., 2010).

TABLE 1 X-ray diffraction for dragon houses (Laka Palli, LP; Kapsala, KAPS) and megalithic gate and wall at Armena (PYARM) and a marble quarry (LAT) near LP

Sample	Quartz	Calcite	Dolomite	Chlorite	Muscovite	Albite
1-LP1	+	++++	Tr	+	++/+	+/tr
2-LP1	tr/-	++++	-	++	++	+
3-LP1	+/tr	++++	-	+++	++	-
KAPS1	Tr	++++	-	++	+++	-
KAPS3	Tr	++++	-	+	++/+	-
KAPS4	+	++++	-	+	++/+	+
2-LP2	tr/-	++++	+/tr	+	++	+/tr
1-LP4	+	++++	-	+	++	-
KAPS6	+/tr	++++	+/tr	-	+	-
3-LP3A	+	++++	-	tr	++	Tr
KAPS5	+	++++	-	+/tr	++	+
3-LP4	+	++++	-	+/tr	++/+	+
KAPS	tr/-	++++	-	-	+	-
LAT2	++	++++	-	++	++/+++	+++
PYARM	++++	-	-	tr	+/tr	-
1-LP	++	++++	-	+++	+++	+++/++
2-LP	++	++++	-	+	++*+	+
3-LP	+	++++	-	tr	++/+	+

++++: predominant, +++: abundant, ++: common, +: few quantities, tr: trace, -: not determined

DISCUSSION – CONCLUSION

The above technique has shown that quartz (and feldspar as well) separation is possible and the expected single aliquot OSL ages can be more accurate than TL of limestone. Egyptian limestones are ideal for such a work as our microscopic examination, and XRD have shown that most of them contain quartz (as detrital sand and silt grains or diagenetic chert nodules) as one of the impurity components.

Traces of quartz and feldspars in limestone blocks from Valley Temple, Egypt, and three Greek monuments, have been extracted, separated and measured as single aliquot by Blue OSL and indicative ages were given. This pilot study indicates an overcome of problems with the luminescence dating of limestone buildings, which are associated either with great uncertainties in TL or inability to getting an OSL signal and encourages applications of surface dating.

ACKNOWLEDGEMENTS

We thank A.Vafiadou for technical assistance.

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