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OSL DATING OF THREE PREHISTORIC CERAMICS FROM THEOPETRA CAVE, GREECE: A CASE STUDY

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ABSTRACT

Three sherds from the Theopetra cave, Thessaly, Greece have been dated by additive dose optically stimulated luminescence, using both single aliquot and multiple aliquot methods. Alternative correction procedures for the single aliquot method are found to give consistent equivalent dose values in agreement with the value from the multiple aliquot method. The relevant dose rate to convert the equivalent dose to age is discussed.

KEYWORDS: luminescence, equivalent dose, neolithic, mesolithic, pottery

INTRODUCTION

The calibrated radiocarbon dates for carbon and animal extracts from finds in the Theopetra cave, Thessaly (Kyparissi-Apostolika, 1998; 1999a,b; 2000), gave an age distribution spanning the period from the present time to 17,000 BC (Facorellis *et al.*, 2001). A human skeleton from the upper palaeolithic (c.15,000 BP) was found in this cave and a mass of unburnt clay, obviously shaped, was located in Mesolithic layers. In general, the cave was continuously occupied since at least 50,000 years ago, an important tool industry was apparent, and residues of various crops were found which had resulted from food (crop) gathering.

Three ceramic sherds from the Theopetra cave (THEOP-1, 2, 3) were derived from the Mesolithic deposit in the cave, trench D7, within a layer of 80 cm thickness. Fig.1a shows a view of the cave from outside, and Fig.1b is a schematic drawing of the sampling position at the trench D7. The question raised is whether the sherds belong to the Mesolithic layer or whether they have been carried into this deposit from Neolithic layers above. Thus, dating the ceramics is crucial for elucidation of the chronological commencement of ceramic technology in Thessaly. Should they date to the Neolithic period, a cause of their presence in an earlier level must be sought. The ages of these three ceramic sherds have been determined by the optically stimulated luminescence (OSL) method.

Experimental Method

In the OSL method of age determination, introduced for sediments by Huntley *et al.* (1985) and described in detail by, for example Aitken (1998), the age of the sample is given by, age = (equivalent dose)/(dose rate), where equivalent dose is the dose of radiation required to produce the luminescence stimulated from the sample and dose rate is the radiation dose per year to which the sample has been exposed since its formation until the present. There are thus two aspects to the age determination, one, the stimulation of luminescence from the sample along with the interpretation of the measured luminescence as an equivalent dose, and the other, the measurement of the radiation dose rate to which the sample has been exposed.

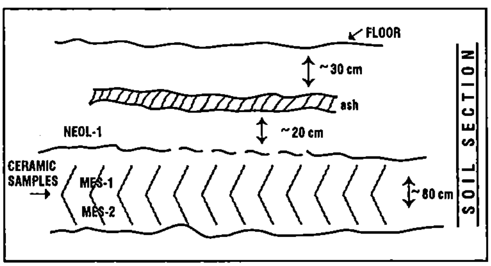
For determination of the equivalent dose, quartz grains were extracted from the ceramic sherds by crushing, stirring the resultant material with a magnet to remove any ferrous materials, washing with sodium hexametaphosphate to remove clay, sieving to a grain size of 125 – 150 μm, separating quartz by density in a sodium polytungstate solution, etching with hydrofluoric acid to remove the outer layer of the grains which would have been exposed to alpha radiation, rinsing with hydrochloric acid to remove any fluorides formed in the previous step, finally rinsing with distilled water. For stimulation of luminescence, the quartz grains were spread as a mono-layer on stainless steel discs 12 mm in diameter. A random selection of quartz samples were confirmed to be free of feldspar contamination by testing for infrared stimulated luminescence from feldspar (Spooner *et al.*, 1990).

The equivalent dose was determined from luminescence stimulated by green light (wavelength 525 nm, 40 nm FWHM) from a ring of 16 light emitting diodes, (Galloway et al., 1997), mounted on a 40-sample system which can provide sample heating, calibrated beta irradiation and measurement of OSL in any required sequence under computer control (Galloway 1991a). Luminescence, which passed through a combination of HA3 and DUG11 optical filters (pass band about 310-380 nm), was detected by an EMI type 9635QA photomultiplier.

Both multiple aliquot and single aliquot additive dose methods were used with the quartz grains to determine the equivalent dose. Sample-to-sample normalization of the multiple aliquot measurements was achieved after making the additive dose measurement, by bringing all samples up to the same total radiation dose before bleaching, then applying an equal normalization beta dose and measuring the consequent luminescence, avoiding in this way any detrimental influence of preceding dose on luminescence sensitivity during normalization (Galloway and Hong 1996).

The single aliquot method requires correction of the additive dose luminescence measurements for loss of signal due to repeated use of the same aliquot (Duller 1991). Three different correction procedures were used, the original luminescence correction procedure of Duller (1991), the dose correction procedure of Duller (1994) and the iterative least squares method of Galloway (1996) as modified for quartz by Liritzis *et al.* (1997). That these three single aliquot correction methods give consistent equivalent dose values in agreement with the equivalent dose from the multiple aliquot additive dose method has been shown for 10

Fig. 1: (a) External view of the Theopetra cave, and (b) schematic map of the stratigraphy of trench D7 in which the sherds were found.



different samples of quartz (Hong et al. 2000). For determination of the dose rate to which the quartz grains have been exposed, the beta dose rate from the ceramic material was measured using a plastic scintillator (Galloway and Liritzis, 1991; Galloway 1994) and the gamma dose rate from surrounding soil was measured using a HpGe gamma spectrometer (Galloway 1991b).

Luminescence measurements: equivalent dose

Multiple aliquot additive dose luminescence measurements were made on quartz from sherds THEOP-1 (Fig.2) and THEOP-2 (Fig.3) but not for THEOP-3 because insufficient quartz was available. Three aliquots were used for each dose value and all aliquots were preheated for 5 minutes at 220°C prior to luminescence measurement at 20°C. The data points were fitted by a saturating exponential and extrapolated to zero luminescence to give the equivalent dose value, 29.7 ± 1.7 Gy for THEOP-1 and 37.3 ± 3.6 Gy for THEOP-2.

The single aliquot additive dose method was applied to 12 aliquots of quartz from THEOP-1, 10 from THEOP-2 and 6 from THEOP-3. In each case half of the aliquots were used in a single aliquot additive dose sequence of measurements with preheating for 1 minute at 220°C and the other half with preheating for 5 minutes at 220°C. Three correction procedures were applied to the measured data, the luminescence correction procedure of Duller (1991), the dose correction procedure of Duller (1994) and the iterative least squares method of Galloway (1996) and Liritzis et al. (1997). The points from each correction procedure were fitted by a saturating exponential curve, which was extrapolated to give the equivalent dose value. Figs. 4, 5 and 6 give examples of the single aliquot additive dose measurements and the results of applying the three correction procedures for THEOP-1, -2 and -3 respectively. In the single aliquot sequence of additive dose measurements, when the maximum dose had been reached (60Gy in all the present measurements) three further cycles of preheating and measuring

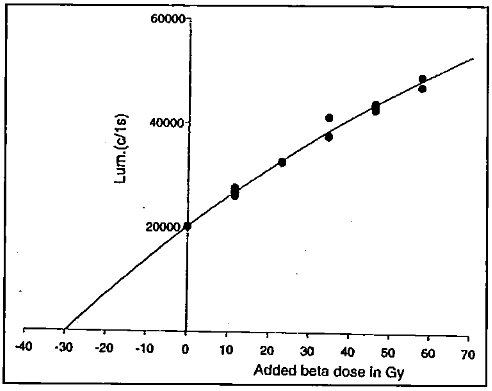


Fig. 2: Multiple aliquot additive dose growth curve for quartz from THEOP-1. Three aliquots were used for each dose value, preheating was for 5 minutes at 220°C and the curve is a saturating exponential fitted by least squares to the data points.

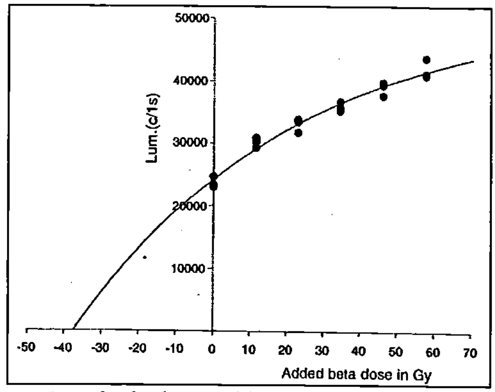


Fig. 3: Multiple aliquot additive dose growth curve for quartz from THEOP-2. Three aliquots were used for each dose value, preheating was for 5 minutes at 220°C and the curve is a saturating exponential fitted by least squares to the data points.

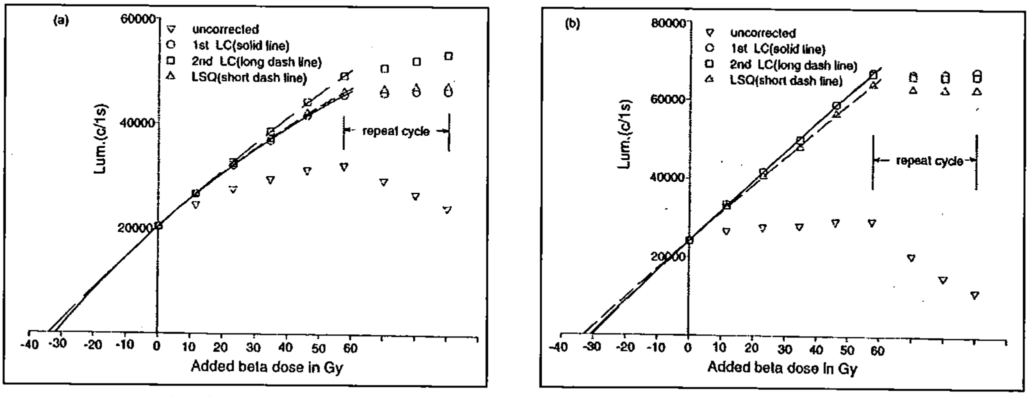


Fig. 4: An example of a single aliquot additive dose measurements on quartz from THEOP-1. The measured (uncorrected) data are shown along with the result of correcting by the procedure of Duller (1991) labelled "1st LC", the dose correction procedure of Duller (1994) labelled "2nd LC" and the iterative least squares method of Galloway (1996) and Liritzis et al. (1997) labelled "LSQ". The points from each correction procedure are fitted by a saturating exponential curve, which is extrapolated to the equivalent dose value. In (a) preheating was for 1 minute at 220°C and in (b) for 5 minutes at 220°C.

luminescence were carried out, giving four measurements for the same dose, labeled "repeat cycle" at the right hand side of Figs. 4 – 6. These measurements show a decline in luminescence with increasing number of measurement cycles, due to the loss of luminescence during each cycle of preheating and luminescence stimulation. Since these four measurements all relate to the same dose, they should, after correction, give the same luminescence value. On this criterion and looking at the corrected data overall, no correction procedure is consistently better than any other; for a particular single aliquot measurement the differences between the correction procedures is attributed to statistical fluctuations in the data used for correction. The results of all the equivalent dose determinations are summarised in table 1. For each set of single aliquot data, there is no statistically significant difference in equivalent dose value dependent on the

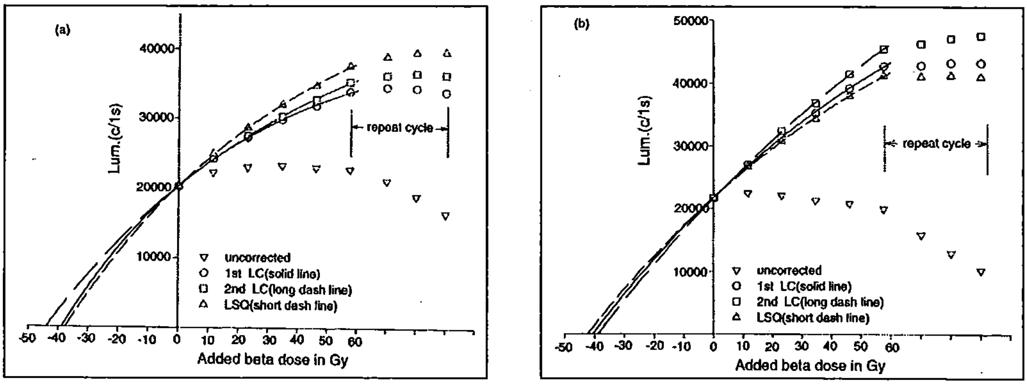


Fig. 5: (a,b) As in fig. 4, for quartz from THEOP-2.

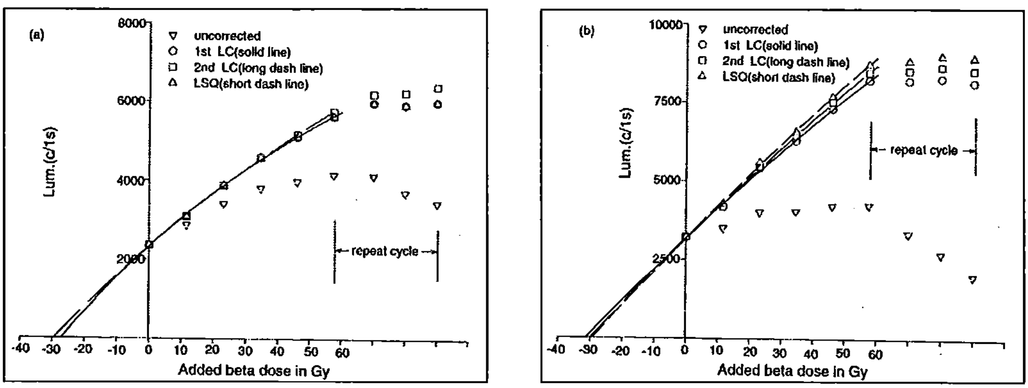


Fig. 6: (a,b) As in fig. 4, for quartz from THEOP-3.

correction procedure followed, so since there is no reason to prefer one procedure rather than another, the average of the three values is taken as the best estimate of the equivalent dose. Also, there is no significant difference in equivalent dose values between the single aliquot measurements which used 1 minute of preheating at 220°C compared with the single aliquot measurements on quartz from the same sample which used 5 minutes of preheating, although the latter have a larger standard deviation. Further, the equivalent dose values from the single aliquot and from the multiple aliquot additive dose methods are in agreement. Finally, for each sample, a weighted mean of the two average single aliquot equivalent dose values and the multiple aliquot value was taken as the best estimate of equivalent dose for the particular sample.

An interesting observation is that the equivalent dose values for THEOP-1 and THEOP-3, 30.3 ± 1.3 and 28.8 ± 0.8 Gy respectively, are consistent with one another, the equivalent dose value for THEOP-2, 38.3 ± 1.1 Gy is significantly different.

DOSE RATE MEASUREMENTS

The dose rate to be used to determine the age of a sample has three components, one due to the beta particles from the material of the ceramic itself, a second due to gamma rays from the soil which surrounded the sherd and a third due to cosmic rays.

The beta dose rates in the ceramics were measured using a plastic scintillator, Galloway and Liritzis (1991), Galloway (1994), as 2.7 ± 0.1 Gy/ka for THEOP-1, 2.6 ± 0.1 Gy/ka for THEOP-2 and 3.0 ± 0.1 Gy/ka for THEOP-3.

TABLE 1

Equivalent dose values, with standard deviations, from additive dose measurements: sa, single aliquot method; ma, multiple aliquot method. The correction procedures are, 1st LC for the Duller (1991) luminescence correction procedure, 2nd LC for the Duller (1994) dose correction procedure and LSQ for the iterative least squares correction procedure of Galloway (1996) and Liritzis *et al.* (1997).

Sample no.	No. of aliquots	Preheat at 220°C	Correction procedure	Equivalent dose Gy
THEOP-1	6 sa	1 min.	1st LC 2nd LC LSQ	31.5 ± 2.4 32.8 ± 1.7 30.7 ± 2.8 Average 31.7 ± 2.3
	6 sa	5 min.	1st LC 2nd LC LSQ	29.8 ± 2.9 28.4 ± 3.1 31.2 ± 3.6 Average 29.8 ± 3.2
	18 ma	5 min.		29.7 ± 1.7
				Weighted mean30.3 ±1.3
THEOP-2	5 sa 5 sa	1 min. 5 min.	1st LC 2nd LC LSQ 1st LC 2nd LC LSQ	37.9 ± 1.2 39.3 ± 1.6 37.6 ± 0.9 Average 38.3 ± 1.2 42.6 ± 7.5 40.2 ± 6.7 42.4 ± 6.0 Average 41.7 ± 6.7
	18 ma	5 min		37.3 ± 3.6
				Weighted mean 38.3 ± 1.1
THEOP-3	3 sa	1 min.	1st LC 2nd LC LSQ	28.0 ± 0.7 30.5 ± 1.1 28.1 ± 0.6 Average 28.9 ± 0.8
	3 sa	5 min.	1st LC 2nd LC LSQ	27.1 ± 2.9 26.5 ± 2.9 27.7 ± 2.3 Average 27.1 ± 2.7
				Weighted mean 28.8 ± 0.8

These measurements were on dry material, whereas the sherds would contain some moisture during burial. The water content of the ceramics during burial was taken as12 ± 3%, a value typical of Greek sherds (Liritzis and Galloway,1982). Correction of the measured dose rates for water content during burial used the standard equations of Zimmerman (1971) and quoted for example by Aitken (1998, p.58). Correction is also required for attenuation of the beta dose within the quartz grains, Mejdahl (1979), and the correction factor in this case was 0.95.

Soil samples for gamma spectrometry were collected from around where the ceramics were found. Sample MES-2, whitish in colour, calcitic, came from the undisturbed Mesolithic layer, sample NEOL-1, blackish in colour, came from the Neolithic layer and sample MES-1, intermediate between the other two in colour, came from a disturbed Mesolithic layer.The water content of the three soil samples, measured 20 days after collection was, 10% by weight for MES-1, 10% for MES-2 and 15% for NEOL-1. The three soil samples were dried and the gamma dose rates measured by Hp Ge gamma spectrometer as 1.10 ± 0.03 Gy/ka for NEOL-1, 1.37 ± 0.03 Gy/ka for MES-1, and 1.36 ± 0.03 Gy/ka for MES-2. The measured dose rates were corrected for the measured water content. The cosmic ray dose rate was taken as 0.15 ± 0.05 Gy/ka, Aitken (1998, p.44).

DATING THE SHERDS

Due to the fact that the three ceramic sherds, broadly characterized as Neolithic, were found in the Mesolithic deposit (fig.1a) although their exact origin within the disturbed stratigraphy is unknown, two extreme possibilities were examined. In the first, it is assumed that they have always been buried in the Mesolithic deposit, and in the second, that they have until very recently been buried in the Neolithic deposit. Thus, the gamma dose rates from the respective soil deposits were used in each case for the age calculations. The gamma dose rates from the disturbed and undisturbed Mesolithic deposits were similar and equal to 1.36 ± 0.03 Gy/ka, while that for the Neolithic deposit was 1.10 ± 0.03 Gy/ka.

The age equation is, Age = Equivalent dose / (Db + Dg + Dc), where, Db is the beta particle dose rate corrected for moisture content and attenuation within the quartz grains, Dg the gamma ray dose rate corrected for moisture content and Dc is cosmic ray dose rate.

If all the ceramics belonged to the Mesolithic deposit, then they would date to,
THEOP1, 6500 ± 500 years BC,
THEOP2, 8940 ± 500 years BC,
THEOP3, 5540 ± 400 years BC.

If all the ceramics belonged to the Neolithic deposit, then they would date to,
THEOP1, 7300 ± 700 years BC,
THEOP2, 9970 ± 700 years BC,
THEOP3, 6180 ± 500 years BC.

DISCUSSION

The above dates indicate that if the sherds belong to the Mesolithic layer, they are younger than if they belong to the Neolithic layer, a clear absurdity! Consequently, the probable interpretation is that the sherds originated in the Neolithic layer and moved into the Mesolithic deposit, with the alternative dates above indicating the extreme dates of origin for each sherd.

THEOP-3 has the lowest equivalent dose and highest Db. The age span of the two extreme dates, 5,150-6,700 years BC, suggests that this sherd is of early Neolithic origin, and that it must therefore have been carried from the Neolithic level down to the disturbed Mesolithic layers. In this regard it can be noted that the floors in the cave often slope, and that the first metre below the present surface is rather disturbed.

Similarly for the THEOP1 sherd, the age span of 5,900-7,900 years BC can be interpreted as indicating an origin in the Neolithic.The third ceramic, THEOP-2, seems under the present suggested hypotheses to be much older than the known early Neolithic period in Thessaly and Greece as a whole. The age span of 8,300-10,700 BC possibly implies one of the earliest attempts at producing pottery in Greece, perhaps about 7,00-1,000 years earlier than early Neolithic.However, the hitherto unknown presence of such an early ceramic technology in Greece, makes the result dubious, although at present we can not explain the cause of error.

CONCLUSION

The OSL dating technique, by both single and multiple aliquot methods, has been successfully applied to three ceramics from the prehistoric cave of Theopetra, Thessaly, Greece, with ages ranging between 6,000-9,000 B.C. The alternative correction procedures used in the single aliquot method gave consistent equivalent dose values in agreement with the value from the multiple aliquot method and the repeatability of the results was excellent.

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