

# Luminescence dating method for out-of-context samples

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**Abstract** – In the standard luminescence dating methodologies the general equation used to determine the age in luminescence dating is given by the ratio between the Equivalent Dose (ED) and the Annual Dose rate (AD). The ED, measured using luminescence signals, is the total absorbed dose starting from the last "zero event" while the DR, evaluated by *in situ* and *extra situ* radioactivity measurements, represents the rate at which energy is absorbed from natural radioactivity present in the sample and in the environment. For samples for which information on environmental dose contribution is lacking, which are considered out-of-context samples, this method is not applicable. However, the combination of different methodologies of luminescence dating, the fine-grain, and inclusion technique from same sample, allows age to be determined independently of knowledge of the environmental dose-rate. In this work, the method named subtraction dating is applied to an archaeomaterial sampled near Angkor Thom, Siem Reap, Cambodia. The dating results obtained using subtraction method were compared with that obtained, for each grain size, using standard approach with good results.

## I. INTRODUCTION

Absolute dating of archaeomaterials by stimulated luminescence techniques is based on the ratio of the absorbed dose (Equivalent dose) since the last zeroing event and the absorbed dose rate (Annual Dose). The Equivalent Dose (ED) is obtained in laboratory from stimulated luminescence measurements with calibrated beta source, while the Annual Dose (AD) is derived from radioactivity measurements related to the U, Th, K content present in the sample and in the surrounding environment [1]. Evaluation of the environmental dose rate component becomes a crucial point in dating since particular conditions of the site (heterogeneity, lack of structure...) could make age measurement complex and sometimes inaccurate [2-6]. In the absence of environmental data, as

with out-of-context samples, the sample age cannot be obtained. However, combination of different luminescence dating approaches on the same sample, the fine-grain and coarse methods, allows an age determination that is independent of knowledge of the environmental dose-rate.

The first to test this technique, called subtraction dating, were Fleming and Stoneham (1973) [7] who, applying the thermoluminescence technique, experimented on several terracottas of museum origin and some pottery collected from archaeological contexts without associated burial media with accuracy higher than 12% under favourable conditions. No other work that followed the one mentioned above can be found in literature. A necessary condition for the applicability of this technique is the high degree of accuracy of the absorbed dose measurements. This has been made possible in recent years by the use of some dosimetric controls introduced in the field of dating that use optically stimulated luminescence [8-10]. In this work, the subtracting dating method was tested on a sediment, named SD, taken from an archaeological site at Angkor Thom, Siem Reap, Cambodia. Absorbed dose measurements were obtained by optically stimulated luminescence on pure fine grain and coarse grain quartz; contributions to the annual dose were determined from natural radioactive isotopes concentrations through high resolution gamma spectrometry (HPGe) measurements [11].

## II. SUBTRACTION DATING

The use of different granulometric phases in luminescence dating involves different age equations. In the case of fine grain quartz fraction, we have:

$$\text{Age (a)} = \frac{ED_{FG} \text{ (Gy)}}{(k \cdot \dot{D}_\alpha + \dot{D}_\beta + \dot{D}_{\gamma+\text{cosm}}) \left(\frac{\text{Gy}}{\text{a}}\right)} \quad (1)$$

where  $ED_{FG}$  is the equivalent dose, and  $k$  is the alpha efficiency.  $D_\alpha$  and  $D_\beta$  are respectively, the annual dose contributions derived from alpha and beta decay of the radioactive contents present in the sample; together

provide the annual dose value of the sample.  $D_{\gamma+cosm}$  is the annual dose contribution resulting from gamma emissions of the radioactive material present in the environment and the cosmic dose value depends mainly on the latitude and depth from the Earth's surface [12].

In the case of Coarse Grain quartz, we have:

$$\text{Age (a)} = \frac{ED_{CG} \text{ (Gy)}}{(f \cdot \dot{D}_{\beta} + \dot{D}_{\gamma+cosm}) \left(\frac{\text{Gy}}{\text{a}}\right)} \quad (2)$$

where  $f$  is the attenuation factor which depends on the grain size [13].

The two equations can also be written in the following way:

$$\begin{cases} \text{Age} \cdot (k \cdot \dot{D}_{\alpha} + \dot{D}_{\beta} + \dot{D}_{\gamma+cosm}) = ED_{FG} & (4) \\ \text{Age} \cdot (f \cdot \dot{D}_{\beta} + \dot{D}_{\gamma+cosm}) = ED_{CG} & (5) \end{cases}$$

Subtracting member to member we get:

$$\text{Age} \cdot [k \cdot \dot{D}_{\alpha} + (1-f) \cdot \dot{D}_{\beta}] = ED_{FG} - ED_{CG} \quad (6)$$

or

$$\text{Age} = \frac{ED_{FG} - ED_{CG}}{[k \cdot \dot{D}_{\alpha} + (1-f) \cdot \dot{D}_{\beta}]} \quad (7)$$

Equation (7) allows us to obtain the age even without knowing the environmental dose contribution.

All dose contributions to the annual dose must be corrected by factors that consider the sample porosity and the average moisture level of the sample during its life.

### III. MATERIALS AND METHODS

#### A. Sample preparation

The sample SD was prepared by Coarse Grain (CG) and Fine Grain (FG) technique to obtain quartz with grain size respectively  $180\mu\text{m} < \emptyset < 212\mu\text{m}$  and  $4\mu\text{m} < \emptyset < 11\mu\text{m}$ . Organic and carbonate components have been removed by  $\text{H}_2\text{O}_2$  (10%, 72 hours) and by HCl (20%, 120 min). Quartz, feldspar and other mineral fractions were separated using a high-density liquid solution of sodium polytungstate. Only for CG fraction, to eliminate the contribution of alpha radiation, the outer layer of the grains was removed by etching with 40% HF (45 min) followed by etching with 10% HCl (15 min) to eliminate any fluoride formation.

#### B. Equivalent dose determination

Before equivalent dose measurement on quartz fraction, some tests were carried out to choose the optimal dose range for the regeneration measurements and the suitable pre-heating temperature. The purity of the extracted quartz was evaluated through a feldspar contamination test. The evaluation consists in determining the following parameter:

$$R = \frac{\text{Post}_{\text{IRSL}}/T_2}{L_1/T_1} \quad (8)$$

Where the numerator is the ratio between the OSL intensity measured after irradiation stimulated with InfraRed radiation ( $\text{Post}_{\text{IRSL}}$ ) and the intensity obtained after a  $T_2$  test dose was applied. The denominator is the ratio between the OSL intensity stimulated with blue light ( $L_1$ ) after irradiation and the test dose  $T_1$ . R value should be approximately 1 with tolerance of  $\pm 0.10$ .

Equivalent dose measurements were carried out by applying Single Aliquot Regeneration (SAR) method on small aliquots [8]. The steps followed to carry out the SAR procedure have been shown in table 1. In this procedure, the OSL measurement is preceded by a pre-heating (Ph) in order to eliminate the contribution of shallow traps not useful for dating. 27 small aliquots for FG and 20 small aliquots for CG were measured.

For each aliquot of each sample, a recycling ratio and recovery test were also performed. The recycling ratio test allows to verify the presence of systematic errors in SAR procedures. At the end of each SAR sequence, the same dose as the first point is given. The recovery test consists of comparing a known dose with a dose calculated from SAR procedures to verify the accuracy of dosimetry data. Recycling Ratio and Recovery test values should be within the tolerance of  $1.00 \pm 0.10$  [9].

OSL and IRSL signals were obtained using a TL-DA-15 reader equipped, respectively, with 41 blue LEDs ( $470 \pm 30$  nm) and a laser diode ( $830 \pm 10$  nm). The stimulation units delivered about  $30 \text{ mWcm}^{-2}$  for OSL and  $240 \text{ mWcm}^{-2}$  for IRSL at 90% power. Artificial luminescence signals were induced by  $^{90}\text{Sr}$ - $^{90}\text{Y}$  calibrated beta sources integrated in the Risø systems, delivering 4.14 Gy/min.

Table 1. SAR procedure

Step	Measurement	Observed
1	Dose, 0 Gy	
2	Ph@240°C, 10 sec	
3	OSL@125°C, 40 sec.	$L_n$
4	Dose, Y Gy	
5	Ph@240°C, 10 sec	
6	OSL@125°C, 40 sec.	$T_n$
7	Dose, $X_i$ Gy	
8	Ph@240°C, 10 sec	
9	OSL@125°C, 40 sec.	$L_i$
10	Dose, Y Gy	
11	Ph@240°C, 10 sec	
12	OSL@125°C, 40 sec.	$T_i$

The procedures from step 8 to step 14 are repeated for increasing doses: 1 Gy, 3 Gy, 6 Gy, 9 Gy, 12 Gy with a test dose of 1 Gy.

The evaluation of the bleaching degree allows to choose the optimal model for the ED determination: Central Age Model (CAM) or Minimum Age Model (MAM) [14]. The CAM model, is based on the hypothesis that the logs of the individual estimated EDs are evaluated by a normal distribution with a standard deviation that represents the over-dispersion of the data. In the MAM model, it is

assumed that the sample is composed of two or more populations of different bleached grains, veering towards a multimodal distribution of ED. ED values result from a truncated log-normal distribution, where the lower truncation point corresponds to the mean logarithmic value of the grains with total bleaching (Minimum Age). The Quantile-Quantile (Q-Q) plot was used to evaluate the ED distribution [15], i.e., a graphical tool for evaluating whether a set of data plausibly comes from a "normal" distribution. It is a scatter plot obtained by plotting two series of quantiles as a function of the other. Quantiles from a theoretical normal distribution are plotted on the horizontal axis and compared with a set of experimental data on the y axis. If both sets of quantiles come from the same distribution, then "normal," we should see the experimental points overlapping with the theoretical line.

### C. Annual dose determination

The contributions to the annual dose from the radioactive chains natural of U and Th, and from the radioactive isotope of K were determined from the concentrations of these elements in the sample obtained through high resolution gamma spectrometry (HPGe) measurements. For conversion from concentration (% or ppm) to dose rate (Gy/ka), the following correction factors in table 2 [16] were used:

Table 2. Concentration-dose rate conversion factors [16].

	alpha	beta	gamma
K (1%)		0.7982	0.2491
Th (1 ppm)	0.7375	0.0277	0.0479
U (1ppm)	2.6760	0.1419	0.1096

The contributions to the annual dose were corrected considering the sample humidity degree by means of the W and F factors using following equations:

$$\dot{D}_{\alpha\text{corr}} = \frac{\dot{D}_{\alpha}}{1+1.50(WF)} \quad (9)$$

$$\dot{D}_{\beta\text{corr}} = \frac{\dot{D}_{\beta}}{1+1.25(WF)} \quad (10)$$

$$\dot{D}_{\gamma\text{corr}} = \frac{\dot{D}_{\gamma}}{1+1.16(WF)} \quad (11)$$

where:

$$W = \frac{\text{saturation wet weight-dry weight}}{\text{dry weight}} \quad (12)$$

and

$$F = \frac{\text{average water content in the site}}{\text{saturation water content}} \quad (13)$$

The W factor was measured in laboratory. An average reference value equal to 0.5 was used for the F factor since,

in the absence of data related to the weight of the extraction, the saturation fraction can only be estimated.

In the case of FG quartz,  $^{241}\text{Am}$  calibrated alpha source delivering 2.7 Gy/min was used to determine the luminescence efficiency coefficient  $k$  necessary to correct the alpha dose contribution to the annual dose [1].

## IV. RESULTS AND DISCUSSIONS

### A. ED determination

For FG and CG sizes, values of feldspar contamination  $R = 0.97 \pm 0.03$  and  $R = 0.99 \pm 0.02$  were respectively obtained. Results show an adequate purity of the extracted quartz. An example of SAR for FG and CG is shown in Figure 1. Extrapolation of the  $L_n/T_n$  ratio, allows to estimate the equivalent dose (Gy).

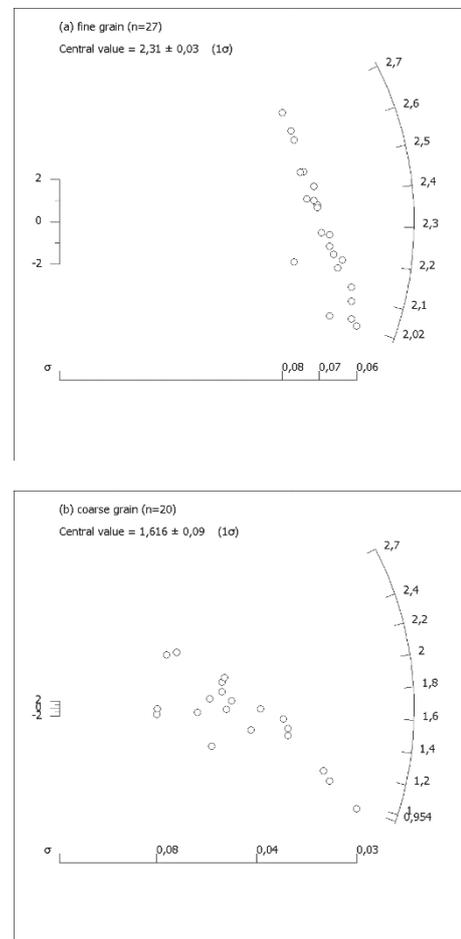


Fig. 1. SAR examples obtained by FG technique (a) e CG technique (b).

In Figure 2, the results in terms of histogram and Kernel Density Estimate (KDE) for the obtained ED values are shown. KDE is a non-parametric way to estimate the probability density function of a random variable. Kernel density estimation is a fundamental data smoothing problem where inferences about the population are made,

based on a finite data sample.

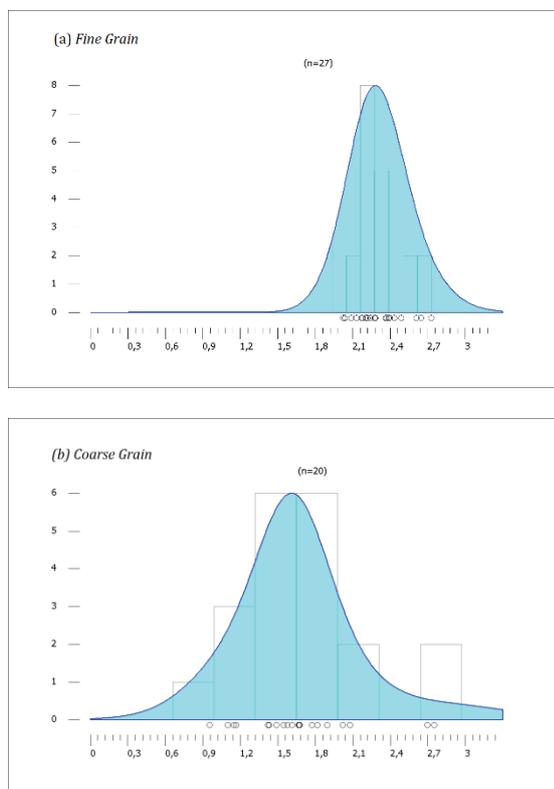


Fig. 2. Histogram and KDE for ED values obtained by FG (a) and CG (b) techniques.

The Quantile-Quantile (Q-Q) plot was used to evaluate the ED distribution for each group (CG and FG) (fig. 3).

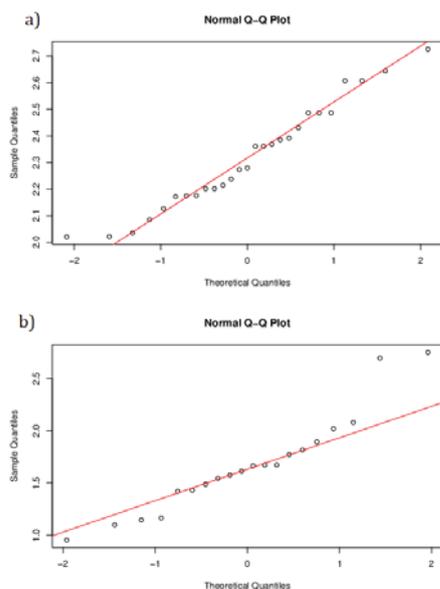


Fig. 3. Q-Q plot of FG sample (a) and CG sample (b).

For both FG and CG samples, the experimental points

follow the theoretical line; the behaviour suggests that the data are normally distributed. For ED calculation useful for dating, the use of the CAM model is therefore suggested.

The results obtained by radial plot with CAM are reported in figure 4.

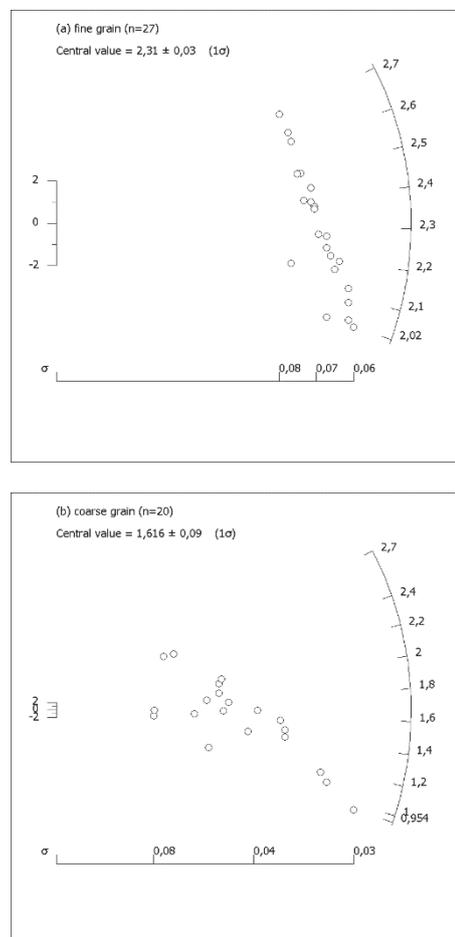


Fig. 4. Radial plot with CAM for FG (a) and CG (b) samples.

ED results, for both samples, are shown in Table 3

Table 3. ED values and relative uncertainties obtained for the two measured samples.

ED <sub>FG</sub> (Gy)	ED <sub>CG</sub> (Gy)
2.31±0.03 (1σ)	1.61±0.09 (1σ)

### B. Dose rate determination

The contributions to the annual dose from the radioactive chains natural U and Th, and from the radioactive isotope of K were determined from the concentrations of these elements in the sample obtained by gamma spectrometry measurements at high resolution (HPGe) (Table 4).

Table 4. Concentration of U, Th and K.

Sample	U (ppm)	Th (ppm)	K (%)
SD	0.23±0.01	1.25±0.04	0.10±0.01

The contributions to the annual dose were corrected considering the sample humidity degree by means of the W and F factors. For SD sample  $W = 0.13 \pm 0.01$  was obtained. An average reference value equal to 0.5 was used for the F factor since, in the absence of the data relating to the weight of the extraction, the saturation fraction can only be estimated.

Table 5 shows the annual dose contributions corrected for humidity.

Table 5. Contributions to annual dose corrected for humidity.

Sample	$D_{\alpha\text{corr}}$ (Gy/ka)	$D_{\beta\text{corr}}$ (Gy/ka)	$D_{\gamma\text{corr}}$ (Gy/ka)
SD	1.40±0.11	0.13±0.01	0.10±0.01

For FG, from comparison of optically stimulated luminescence response between alpha and beta irradiation, the  $k$  value of  $0.07 \pm 0.01$  was obtained. For CG, a mean attenuation factor ( $f$ ) related to a grain size of 0.90 was used.

### C. Age determination

Table 6 shows, for each technique, ED value, Annual Dose (AD), and age through the equation (1) for FG, (2) for CG, and (7) for Subtraction method (Sub).

Table 6. Equivalent Dose (ED), Annual Dose (AD) and Age for each technique.

	ED (Gy)	AD (Gy/ka)	Age (ka)
FG	2.31±0.03	0.33±0.02	6.91±0.42
CG	1.61±0.09	0.22±0.01	7.22±0.58
Sub	0.70±0.09	0.11±0.01	6.31±0.44

Obtained ages with the three techniques, within the range of experimental errors, are in good agreement with each other (fig. 5).

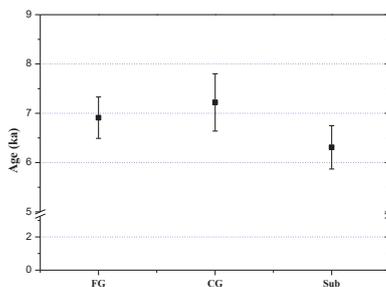


Fig. 5. Obtained Age for SD sample by the three different

techniques: FG, CG and Subtraction.

## V. CONCLUSIONS

The purpose of the presented work was to show a method for the solution dating of out-of-context samples. Obtained results show that this is possible if equivalent dose measurements are accompanied by appropriate dosimetric control tests. Specifically, the purity of the quartz was first tested with a feldspathic contamination test, then the dose test was used to monitor changes in the sensitivity of the quartz during the readout and irradiation phases and the recycle test for the detection of any systematic errors in the ED determination. Finally, the recovery test allows the dosimetric accuracy of the equivalent dose measurement to be evaluated. The possibility of applying subtraction dating methods could effectively eliminate the need to know the environmental dose rate, an important factor in dating objects excavated many years earlier and now in museum collections.

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