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Original Article

Dating of freshwater fossil shells in the archaeological sites at Cliff Deva Thoud-Ta Thoud-Yai, Songkhla Province of Thailand with thermoluminescence

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Abstract

Archaeological evidence indicates that a group of humans arrived in the southern region of Thailand around 40,000 years ago. This hypothesis is based on the discovery of human and animal bones, beads, and ceramics, as well as fossilized freshwater shells. This current study used thermoluminescence (TL) to date freshwater fossil shells from the archeological sites at Cliff Deva Thoud-Ta Thoud-Yai in Songkhla province of Thailand. Organic compounds having unpaired electrons trapped by crystal defects are required for TL dating. The method needs two factors for precise dating: the annual dose and the accumulated doses. We estimate the annual dose using the Dose Rate and Age Calculator (DRAC). Regarding the accumulated dose, we used glow-curve deconvolution (GCD) for general orders of the kinetics. The accumulated dose is determined by the relationship between the TL radiation intensity and the accumulated gamma radiation. Using linear regression, the dependency of TL intensity on dose was modeled. All fossil shells were dated at a temperature of 350°C for TL, and their ages were estimated to be 9485.96 ± 564.13 year. This outcome will ultimately help us understand more about how people in that region lived.

Keywords: thermoluminescence, Cliff Deva Thoud-Ta Thoud-Yai, freshwater fossil shell, Dose Rate and Age Calculator (DRAC), glow-curve deconvolution (GCD)

1. Introduction

Since 1912, the development of prehistoric culture in southern Thailand has been the subject of research. Both Thai and international archeologists have collected related knowledge. Several archeological sites have uncovered evidence of human settlements in this region of Thailand around 40,000 years ago. This is estimated to have occurred during the Pleistocene Epoch, which lasted from around 2,580,000 to 11,700 years ago and included the most recent era of multiple glaciations on Earth. One of the sites of interest is the Cliff Deva Thoud-Ta Thoud-Yai in Songkhla province, southern Thailand, where a change was eventually validated in 2009 by the International Union of Geological Science. This archaeological site has yielded human skeletons, animal bones, beads, ceramics, and freshwater fossil shells. This site contains evidence of rites and handicrafts, such as color paintings, ceramic fragments, whetstones, terrazzo axes, shell beads, and shellfish. Nonetheless, the archeological organization in this area has been gathering these dispersed data.

Moreover, archaeological dating is neither absolute nor precise but somewhat approximate. Therefore, it is crucial to research absolute dating to get more accurate information from the dating of prehistoric materials. Radiometric dating uses the natural decay of radioactive elements like potassium and carbon as accurate clocks to determine when things happened in the past (Marwick, *et al.*, 2017; Solheilm, 1970; The 13th Fine Arts Department, 2010).

Furthermore, as an alternative approach, electron spin resonance (ESR) and luminescence (TL or OSL), which assess the effects of radioactivity on the accumulation of electrons in imperfections, or "traps," in the crystal structure of a mineral, to determine the age of the sample, have turned

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out to be effective in this sort of research (Aitken, 1998; Ikeya, 1993; Liritzis, Zacharias, & Polymeris, 2010). Our study will concentrate on using the thermoluminescence (TL) technique on freshwater fossil shell samples. Our TL dating provides a more accurate date of around 10,000 years, unlike the archeologist's relative dating, which is 40,000 years. These results show that humans had settled before the historical period, or, more accurately, in the post-Pleistocene epoch. Since the Pleistocene era has a wide range from 2.5 million years to 10,000 years ago, this accurate result will fill the gap and help us understand more about the settlement and cultural development of the prehistoric human beings in this region.

2. Materials and Methods

2.1 Sample collection

Our information is associated with the archeological site located in Ban Kao Yang Moo 7, district of Kao Daeng, Saba Yoi county, Songkhla province, Cliff Deva Thoud Ta-Thoud Yai. At 72 meters above sea level, this archeological site is situated at N6°30'51.145" and E100°49'17.148". This site's surroundings are dominated by a 60-meter-long, 20-meter-wide limestone mountain. In addition, a natural brook flows through the cliff's face. In 2010, the Songkhla Fine Arts Department Unit 13th did a survey and collected ceramic pieces, beads, animal bones of different sizes, human skeletons, metal tool pieces, and shells (The 13th Department of Fine Arts, 2010), as can be seen in Figure 1. These specimens were taken from burials TP1 and TP2, respectively, as in Figure 1a. Freshwater fossil shell samples from TP1 were obtained at three depths, as shown in Figure 1: between 50 and 60 centimeters (SH1), 80 and 90 centimeters (SH2), and 90 and 100 centimeters (SH3) (Figure 1b).

Freshwater fossil shells from each site were divided into two parts. The first part was prepared under dim red light to determine the accumulated dose (AD). The second was prepared under ambient light for evaluating the internal annual dose (D_{in}). In the first part, the freshwater shells were washed and cleaned in an ultrasonic bath, followed by etching in 5% HCl for 1 hour to remove soil and the surface portion, which were exposed to a-particle irradiation in the sediment. Then they were cleaned with distilled water. After that, the samples were gently ground with a mortar, and the grains were sieved to obtain a fraction between 90 – 150 μm. The granules were again etched in 0.5% acetic acid for a few minutes to suppress spurious TL emission (Vichaidid, Youngchuay, & Limsuwan, 2007). Specimens with particle sizes of 90 – 150 μm were then washed repeatedly in distilled water and allowed to dry at 40°C. All the sample preparation steps were performed under dim red light. Each sample was divided into 9 aliquots of approximately 150-250 mg. each, and all the aliquots were irradiated for TL measurements. Artificial gamma-irradiations were carried out with a Co-60 source (GC-220E), which delivered 3.404 Gy/s, at the Co-60 gamma-ray irradiation laboratory of OAP (Office of Atoms for Peace in Thailand). The artificial dosages were given at levels of 10, 20, 30, 40, 50, 60, 70, and 80 Gy. The shell powder was put into cylindrical containers, which were then moved for TL measurements. The weight of each sample was about 150-250 mg. All the TL measurements were carried out at room temperature. The emitted TL was recorded using a Harshaw-3500 TL reader. The TL was induced by heating the sample at 5 °C/s up to 400 °C in a high-purity nitrogen atmosphere.

In the second part, the freshwater shells were washed, cleansed, and prepared with the same procedure as above, but the grains were instead sieved with a 90 μm mesh sieve to obtain a particle size range of 0-90 μm. The shells' uranium, thorium, and potassium contents were determined by a gamma spectrometry HPGe detector (Vichaidid, Youngchuay, & Limsuwan, 2007). These contents allow us to calculate the internal annual dose (D_{in}). The internal annual dose could be calculated using Equation 1. The contribution of internal gamma rays can be neglected since the shell is too thin to absorb the gamma rays emitted from the inside (Aitken, 1998; Engin, Kapan-Yes, Taner, Demirtas, & Eken, 2006; Ikeya, 1993). In the internal annual dose calculation, we assumed the efficiency of the defect production (k-value) by alpha rays in aragonite being 0.05 (Lyons & Brennan, 1991).

$$D_{in} = kD_{\alpha}+D_{\beta} \quad (1)$$

Gamma spectrometry HPGe detector was used to estimate external annual doses. The surrounding sediment was prepared in ambient light for external annual dose D_{ex} determination. The external annual dose could be calculated using Equation 2. For the estimation, the external dose rate of the sediment on calculating the alpha external dose was not considered, since the shell surface had been etched (Aitken, 1998; Ikeya, 1993). The sediment samples were gently ground with a mortar, and the grains were sieved with a 90 μm mesh to obtain the particle size range of 0-90 μm (Vichaidid, Soodprasert, Sastri, Oompathum, & Limsuwan, 2008).

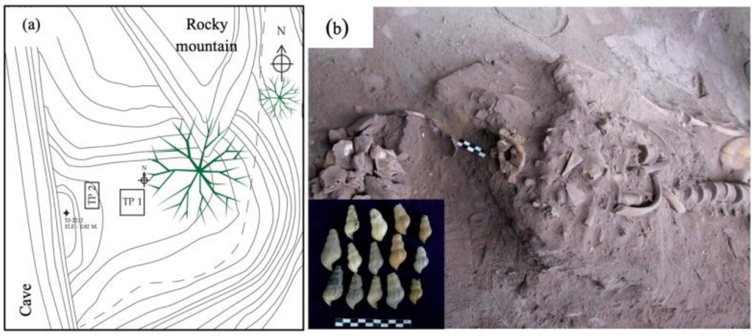

Figure 1. (a) The positions of grave holes at TP1 and TP2 , and (b) freshwater fossil shells and samples from TP1 used to perform TL dating.

$$D_{ex} = D_{\gamma} + D_{\beta} \quad (2)$$

The annual dose (D) consists of the internal annual dose (D_{in}), the external annual dose (D_{ex}), and the cosmic ray dose (D_c). The internal annual dose is caused by radiation emitted from U-238, Th-232, and K-40 in the shell, while the external annual dose is caused by radiation in the surrounding sediment. Each contribution was evaluated by determining the concentrations of radioactive elements: alpha, beta, and gamma radiation are the decay products of the U-238 series, the Th-232 series, and K-40. In addition, the dose of cosmic rays (D_c) was included in the annual dose. The cosmic rays were determined by the longitude, latitude, and altitude of the region of interest, and the depth of the sample decreased these three contributions. The annual dose could be calculated using Equation 3 (Aitken, 1998; Ikeya, 1993).

$$D = D_{in} + D_{ex} + D_c \quad (3)$$

3. Results and Discussion

The structure of aragonite is orthorhombic, with higher density and better durability than those of calcite, while calcite is rhombohedral (Murray & Wintle, 2000; Perrin *et al.*, 2014). Typically, calcium carbonate has three structural polymorphs: vaterite, aragonite, and calcite. All three polymorphs can coincide in some types of shells. In nature, aragonite and calcite are the most common forms. Therefore, as expected, these freshwater shells mainly contained aragonite and calcite. The proportions of aragonite and calcite in the structure may vary in the same shell, and it will depend on the mollusk and where it was developed (Cano, Turbiani-Filho, Gennari, Munita, & Souza, 2013; Chateigner, Hedegaard, & Wenk, 2000). The results obtained from the shells collected from Cliff Deva Thoud-Ta Thoud-Yai indicate that the shells had an aragonite and calcite structure. Figure 2 shows our shell samples' X-ray diffraction (XRD) result.

The concentrations of those radioactive elements were then used to estimate D_{in} and D_{ex} based on the online Dose Rate and Age Calculator (DRAC) (Julie, Georgina, & Duller Geoffrey, 2015) using the conversion factors from Adamiec and Aitken (Aitken, 1998), α-and β-grain size attenuation factors respectively from Bell (Bell, 1979) and Brennan *et al.* (Brennan *et al.*,1991), and β-etch attenuation factors from Mejdahl. (Mejdahl, 1979). D_c, the cosmic-ray dose rate, is derived from the geographical location and elevation of the site. Its value for each collecting site is nearly identical since they are in the same cosmic exposure area. With the mean square deviation of 1%, the combination of the three doses is the total annual dose of the fossil shells. The evaluation results of the annual dose rate are reported in Table 1.

The TL intensity glow curves of a gamma irradiated shell sample, SH1, are presented in Figure 3. Dose usage ranged from 0 to 80 Gy. The inset in Figure 3 shows the plateau, which could be derived from the ratio of the unirradiated sample to the irradiated ones at different dose levels. The plateau shown here corresponds to the temperature between 250°C and 375°C. This paper selected the signal response to 350 °C, to normalize the signal responses to the irradiation varying between 10 Gy to 80 Gy, as shown in

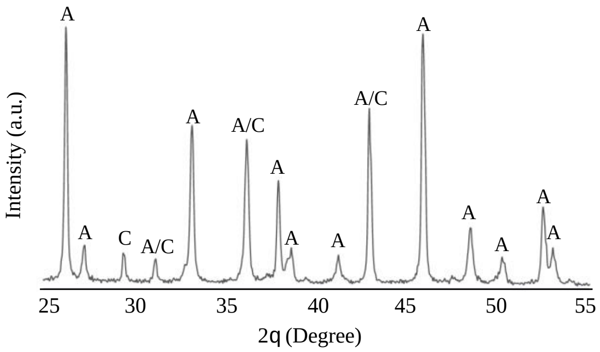

Figure 2. The freshwater fossil shells are composed of aragonite and calcite. (Aragonite, A; Calcite, C)

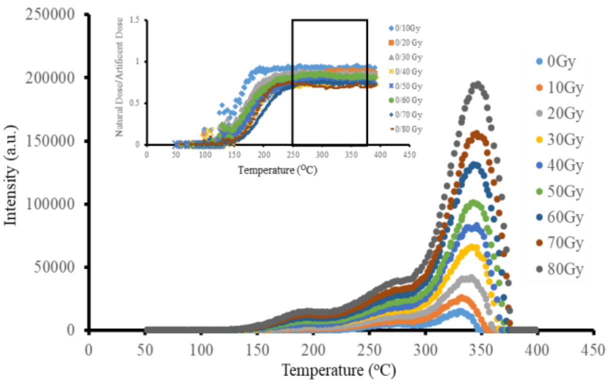

Figure 3. Thermoluminescence (TL) intensity responses as functions of temperature for SH1 subsamples exposed to different doses (Gy).

Figure 4. All curves have peaked around 160 °C and 350 °C, where the maximum TL signal is at the latter, possibly as response from aragonite (Tatumi, Nagatomo, Matsuoka, & Watannabe, 1993). However, these temperature responses are tricky to identify for their origin since other studies have stated differently (Takada, Suzuki, Ishii, Hironaka, & Hironiwa, 2017).

A glow-curve deconvolution (GCD) for general orders of the kinetics was then employed to fit the curves based on those temperatures (Kitis, Gomez-Ros, & Tuyn, 1998). The area under the curve of such a peak gives the total emitted photons. Plotting the area under the curve at 350°C against the additive doses allows one to determine the accumulated dose, as shown in the x-intercept. All samples showed a linear relation between the normalized intensities and the additive doses. We, hence, obtained the accumulated dose for the samples, as illustrated in Figure 4. With accumulated dose (AD) and annual dose rate (D) values, the age of the shells can be calculated using Equation 4.

$$\text{Age} = \text{accumulated dose (AD)} / \text{annual dose rate (D)} \quad (4)$$

The results are shown in Table 2. The freshwater fossil shellfish at SH1, SH2, and SH3 have ages of 9067.33 ± 531.33, 10044.54 ± 610.80, and 9345.99 ± 550.25 years, respectively. Three shells were dated by the 13th Regional Office of Fine Arts Department Songkhla to compare

Table 1. Concentrations of U, Th and K in the samples used to calculate the annual dose rate (D) of the samples.

Sample	U-238 (ppm)	Th-232 (ppm)	K (%)	Cosmic ray (mGy/year)	D (mGy/year)
SH1	1.18 ± 0.53	2.35 ± 0.23	0.31 ± 0.04	0.18 ± 0.01	3.36 ± 0.20
SD1	1.70 ± 0.66	3.27 ± 0.46	0.22 ± 0.01	0.18 ± 0.01	
SH2	1.43 ± 0.34	3.56 ± 0.38	1.10 ± 0.05	0.18 ± 0.01	3.74 ± 0.17
SD2	0.96 ± 0.16	3.15 ± 0.28	1.73 ± 0.15	0.18 ± 0.01	
SH3	0.67 ± 0.17	1.76 ± 0.29	1.03 ± 0.22	0.18 ± 0.01	3.24 ± 0.17
SD3	1.04 ± 0.44	2.09 ± 0.68	0.10 ± 0.01	0.18 ± 0.01	

Table 2. Shells' ages obtained using TL method.

Sample	D (mGy/year)	AD (mGy)	Age (years)
SH1	3.36 ± 0.20	30.49 ± 0.05	9,067.33 ± 531.34
SH2	3.74 ± 0.17	37.56 ± 1.55	10,044.50 ± 610.79
SH3	3.24 ± 0.17	30.24 ± 0.79	9,345.99 ± 550.25

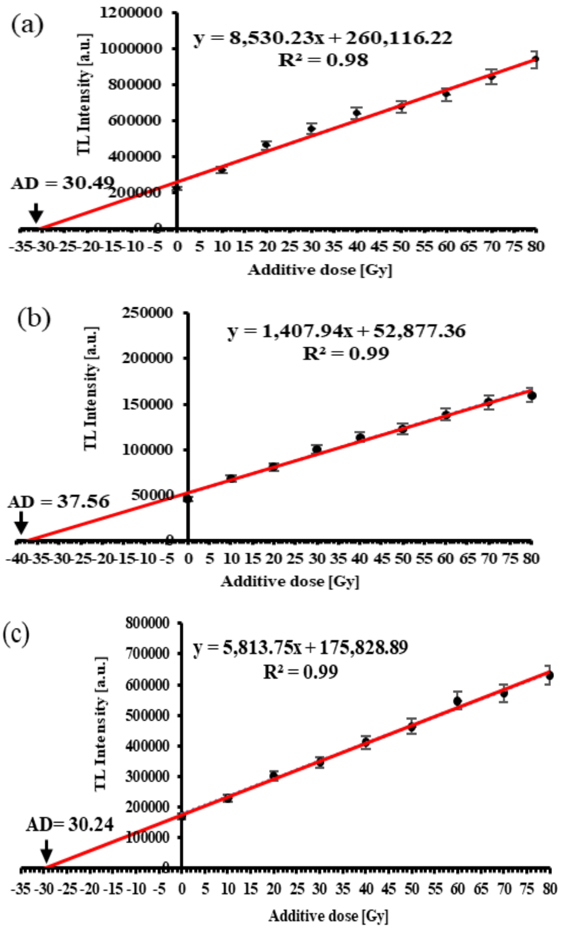

Figure 4. TL analyses of accumulated dose (AD) for SH1-SH3 are displayed from (a) to (c), respectively, based on TL responses at 350ºC.

radiocarbon results (The 13th Fine Arts Department, 2010). The ages are summarized in Table 3. The TL based age estimates for samples SH1, SH2, and SH3 were found to be highly similar, with a standard deviation of just 3%, according to the results in Table 3. The age estimates provide accurate age information for the archaeological site. This indicates that people historically inhabited the region. Because food, jewelry, tools, and pottery, which were used every day, were included in the burial are discovered in the graves, they reveal what people believed about the future world.

Table 3. Comparison between radiocarbon and TL dating results

Sample	C-14 Age (years)	TL Age (year)
SH1	6,610 ± 1,140	9,067.33 ± 531.34
SH2	10,700 ± 570	10,044.50 ± 610.79
SH3	10,130 ± 540	9,345.99 ± 550.25

The C-14 technique took only shell samples for age analysis, and the samples of shells from each region will have different levels of environmental contamination around them. The study yielded different age estimates despite the fact that the samples were apparently of the same age. As a result, the age estimates of SH1 as determined by the C-14 technique were below those for SH2 and SH3 samples, which, assuming the analytical procedure was accurate, did not exclude the possibility of adjustments for various environmental contaminants. This will lead to age estimates that are inconsistent with reality (Hebert, 2013; Snelling, 2008). The TL technique of age determination employs both the shells and their surrounding environmental samples. It is observed that the age estimates obtained using the TL technique for the same sample site are in a close agreement.

4. Conclusions

For determining the annual doses of the samples, a gamma spectrometer equipped with an HPGe detector, able to measure radiation doses ranging from 3.24 to 3.74 mGy/y, was utilized. A significant response in the samples' TL signals revealed that the appropriate temperatures were between 200 ºC and 400 ºC. The response in the TL intensity was linearly proportional to the amount of gamma irradiation received, which is worth consideration. The calculated estimates of the accumulated doses were between 30.24 Gy and 37.56 Gy. It has been determined that the ages of fossil shellfish discovered in freshwater range from 9067.33 to 10044.54 years. Radiocarbon dating reveals a gap of 6.29 percentage points between these two sets of findings. This specific date will help us confirm a study of the prehistoric era in southern Thailand. Based on these discoveries, one can conclude that human settlement occurred before the historical period, or more precisely, during the post-Pleistocene epoch. This accurate result will help fill in the blanks and assist us in learning more about how ancient people lived and how their culture evolved in this region. Specifically, it will help us learn more about how people used to live in this region.

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