Original Article

Dating of Freshwater Fossil Shell in the Archaeological sites at Cliff Deva Thoud-Ta Thoud-Yai, Songkhla Province of Thailand using Thermoluminescence Technique

Tidarut Vichaidid[1]*, Piyawan Latam[1]

[1]Department of Science, Faculty of Science and Technology, Pattani Campus, Prince of Songkla University, Thailand

*** Corresponding author, Email address: tidarut.v@psu.ac.th**

Abstract

Archaeological evidence indicates that a group of humans arrived in the southern region of Thailand around 40,000 years ago. Therefore, it is necessary to learn. This hypothesis is based on the discovery of human and animal bones, beads, and ceramics, as well as fossilized freshwater shells. This research used the thermoluminescence (TL) method to date freshwater fossil shells from the archeological sites at Cliff Deva Thoud-Ta Thoud-Yai in Songkhla Province. Organic compounds dependent on unpaired electrons trapped by crystal defects are required for TL dating. The method needs two factors for precise dating: annual dose and 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 the kinetics' general orders. The accumulated dose is determined by the relationship between the TL radiation intensities and the accumulated gamma radiation. Using linear regression, the dependency of TL intensity on dose was modeled. All fossil shells were dated using a temperature of 350°C TL. Our age was 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 collected this knowledge. Several archeological sites have uncovered evidence of human settlement in this region of Thailand around 40,000 years ago. This is estimated to have occurred during the Plystosine 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 them 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 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 this 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 about the dating of prehistoric material in this location. 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 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 via the TL method. 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

Sample collection. Our information is derived from 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. 72 meters above sea level, this archeological site is situated at N6^{o}30'51.145" and E100^{o}49'17.148". This site's surroundings consist of 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 shell (The 13th Department of Fine Arts, 2010) As can be seen in Figure 1, these specimens were taken from burials TP1 and TP2, respectively. (a). 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) (b).

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^{o}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 a 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 ^{o}C/s up to 400 ^{o}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 well be calculated using Eq. 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. (Engin, Kapan-Yes , Taner, Demirtas, & Eken, 206 ; Aitken, 1998; Ikeya, 1993) In the internal annual dose calculation, we assumed the efficiency of the defect production (k-value) by alpha ray in aragonite is 0.05 (Lyons & Brennan, 1991).

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

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 well be calculated using Eq. 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).

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

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 radiating 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 well be calculated using Eq. 3 (Aitken, 1998; Ikeya, 1993).

$$D = D_{in} + D_{ex} + D_c \tag{3}$$

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 expectedly these freshwater shells mainly contain aragonite and calcite. The percentage of aragonite and calcite structure may vary in the same shell, and it will depend on the mollusk and where it was developed (Chateigner, Hedegaard, & Wenk, 2000; Cano, Turbiani-Filho, Gennari, Munita, & Souza, 2013). The result obtained from the shells collected from Cliff Deva Thoud-Ta Thoud-Yai indicates that the shell has an aragonite and calcite structure. Figure 2 shows our shell sample's X-ray diffraction (XRD) result.

The concentrations of those radioactive elements are then used to estimate Din 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% 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 Fig. 3. Dose usage ranges from 0 to 80 Gy. The inset, Fig. 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^{o}C and 375^{o}C. This paper selected the signal responded to 350 ^{o}C to normalize the signal responses to the irradiation varying between 10 Gy to 80 Gy, as shown in Fig. 4. All curves have peaked around 160 ^{o}C and 350 ^{o}C, where the maximum TL signal is at the latter, possibly the response from aragonite (Tatumi, Nagatomo, Matsuoka, & Watannabe, 1993). However, these temperature responses are tricky to identify for their origin since many studies have stated differently (Takada, Suzuki, Ishii, Hironaka, & Hironiwa, 2017).

A glow-curve deconvolution (GCD) for general orders of the kinetics is 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^{o}C against the additive doses allows one to determine the accumulated dose, as shown in the x-interception. All samples dominate the linear relation between the normalized intensities and the additive doses. We, hence, obtain the accumulated dose for the samples, as illustrated in Fig. 4. With accumulated dose (AD) and annual dose rate (D) values, the age of the shells can be calculated using Eq. 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 year, respectively. Three shells were dated by the 13th Regional Office of Fine Arts Department Songkhla to compare radiocarbon results (The 13th Fine Arts Department, 2010). The ages value is shown in Table 3. The TL age values for samples SH1, SH2, and SH3 were found to be highly similar, with a standard variation of just 3%, according to the results of Table 3's age values. 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 in the burial, are discovered in graves, they reveal what people believed about the future world.

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

4. Conclusions

For determining the annual doses of the samples, a gamma spectrometer equipped with an HPGe detector and able to measure radiation doses ranging from 3.24 to 3.74 mGy/y is utilized. A significant response from the sample's TL signal revealed that the temperatures were between 200 ^{o}C and 400 ^{o}C. This was discovered. The response of the TL intensity is linearly proportional to the amount of gamma irradiation that is received, which is something else to take into consideration. The calculated value of the accumulated dose sample is between 30.24 Gy and 37.56 Gy, as indicated by the findings. 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 history of the prehistoric era in southern Thailand, which will significantly assist us in achieving our goal of doing so. 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.

Acknowledgments

The authors would like to thank you for the detailed survey arranged by the Regional Office of Fine Arts Department Songkhla. We would also like to express our gratitude to the Office of Atoms for Peace (OAP) for supporting gamma irradiation exposure.

References

Aitken, M.J. (1998). *An Introduction to Optical Dating*. Oxford University Press, Oxford.

Bell, W.T. (1979). Thermoluminescence dating: Radiation dose-rate data. *Archaeometry*, 21(1), 243-245. doi:10.1111/j.1475-4754.1979.tb00258.

Brennan, T. A., Leape, L.L., Laird, N.M., Hebert, L., Localio, A.R., Lawthers, A.G., . . . Hiatt, H.H. (1991). Incidence of adverse events and negligence in hospitalized patients results of the Harvard medical practice study I. *The New England Journal of Medicine*, 324(6), 370-376. doi: 10.1136/qshc.2002.003822.

Cano, N.F., Turbiani-Filho, T.I., Gennari, F.R., Munita, S.C., & Souza, C.M. (2013) TL dating of sediments from ilha do mel, brazil. *Quaternary International,* 306 137-145. Retrieved from https://www.ipen.br/biblioteca/2013/19077.pdf

Chateigner, D., Hedegaard, C., & Wenk, H.R. (2000). Mollusc shell microstructures and crystallographic textures. *Journal of Structural Geology*, 22, 1723-1735. Retrieved from http://www.ecole.ensicaen.fr/~chateign/pdf/JSG22_1723.pdf

Engin, B., Kapan-Yes, S., Taner, G., Demirtas, H., & Eken, M. (2006) ESR dating of Soma (Manisa, West Anatolia – Turkey) fossil gastropoda shells. *Nuclear Instruments and Methods in Physics Research B*, 243(2), 397-406. dio:10.1016/j.nimb.2005.09.008

Hebert, J. (2013). Do Young C-14 Results Reflect Contamination?, *Acts and Facts,* 42 (7), 20. https://www.icr.org/article/do-young-c-14-results-reflect-contamination

Ikeya, M. (1993). *New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy*, World Scientific, Singapore.

Julie, A.D., Georgina, E.K., & Duller Geoffrey, A.T. (2015). DRAC: Dose Rate and Age Calculator for trapped charge dating, *Quaternary Geochronology*, 28, 54-61, Retrieved from http://dx.doi.org/10.1016/j.quageo.2015.03.012

Kitis, G., Gomez-Ros, J.M., & Tuyn, J.W.N. (1998). Thermoluminescence glow-curve deconvolution functions for first, second and general orders of kinetics. *Journal of Physics: Applied Physics*, 31(1), 2636–2641. Retrieved from https://doi.org/10.1088/0022-3727/31/19/037

Liritzis, I., Zacharias, N., & Polymeris, G. (2010). Surface luminescence dating of 'Dragon Houses' and Armena gate at Styra (Euboea, Greece). *Mediterranean Archaeology and Archaeometry*, 10(3), 65-81. Retrieved from http://maajournal.com/Issues/2010/Vol10-3/STYRA_LIRITZIS.pdf

Lyons, R.G., & Brennan, B.J., (1991) Alpha/gamma effectiveness ratios of calcite speleothems, *International Journal of Radiation Applications and Instrumentation. Part D. Nuclear Tracks and Radiation Measurements*, 18(1-2), 223-227. https://doi.org/10.1016/1359-0189(91)90116-Y

Marwick, B., Van Vlack, H. G., Conrad, C., Shoocongdej, R., Thongcharoenchaikit, C., & Kwak, S. (2017). Adaptations to sea level change and transitions to agriculture at Khao Toh Chong rockshelter, Peninsular Thailand. *Journal of*

Archaeological Science, 77, 94–108. http://dx.doi.org/10.1016/j.jas.2016.10.010

Mejdahl, V. (1979). Thermoluminescnce Dating: Bata-dose Attenuation in Qyartz Grains, *Archaeometry*. 21(1), 61-72. Retrieved from https://inis.iaea.org/search/search.aspx?orig_q=RN:10451974

Murray, A.S., & Wintle, A.G. (2000). Luminescence dating of quartz using an improved single-aliquot regenerative-dose protocol. *Radiation Measurements,* 32(1), 57-73. Retrieved from https://doi.org/10.1016/S1350-4487(99)00253-X

Perrin, C., Prestimonaco, L., Servelle, G., Tilhac, R., Maury, M., & Cabrol, P. (2014). Aragonite-calcite speleothems: Identifying original and diagenetic features. *Journal of Sedimentary Research,* 84(4), 245-269. Retrieved from https://doi.org/10.2110/jsr.2014.17

Solheilm G. W. II (1970), Northern Thailand, Southeast Asia and World Prehistory, Asian Per-spectives, 13, 145-162. https://scholarspace.manoa.hawaii.edu/server/api/core/bitstreams/6194ec68-7668-4ffb-9da0-4affbefacfb4/content

Snelling, A. (2008), Radiocarbon ages for fossil ammonites and wood in cretaceous Strata near Redding, California. *Answers Research Journal*, 1, 123-144.

Takada, N., Suzuki, A., Ishii, H., Hironaka, K., & Hironiwa, T. (2017). Thermoluminescence of coral skeletons: a high-sensitivity proxy of diagenetic alteration of aragonite. *Scientific Reports*. 7:17969,1-9. Retrieved from https://doi.org/10.1038/s41598-017-18269-y

Tatumi, S.H., Nagatomo, T., Matsuoka, M., & Watannabe, S. (1993). Thermoluminescence and ESR in an Aragonite Speleothem. *Journal of Applied Physics*, 26, 1482-1486. doi:10.1088/0022-3727/26/9/022

The 13th Fine Arts Department, (2010). *Archaeological survey, and excavation from Songkhla and Satun province Unpublished report*, Thailand.

Vichaidid, T., Soodprasert, T., Sastri, N., Oompathum, C., & Limsuwan, P. (2008). Determination of U, Th and K in sediments and fossil Collected from Mae Moh Mine using gamma-ray spectrometry and neutron activation analysis (NAA), *Kasetsart Journal - Natural Science*, 42, 333-339. Retrieved from https://www.thaiscience.info/journals/Article/TKJN/10506873.pdf

Vichaidid, T., Youngchuay, U & Limsuwan, P. (2007). Dating of aragonite fossil shell by ESR for paramagnetic species assignment of Mae Moh basin, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 262(2) 323-328. doi:10.1016/j.nimb.2007.05.021

Figure

A figure caption list should precede all the figures.

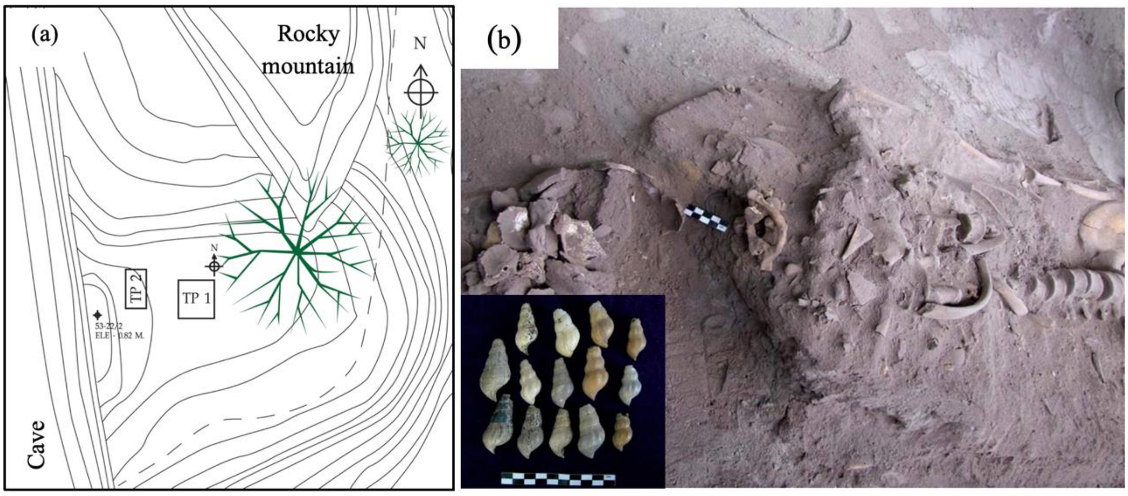

Figure 1. (a) Show the position of grave holes at TP1 and TP2 (b) We used the freshwater fossil shells and samples from TP1 to perform TL Dating.

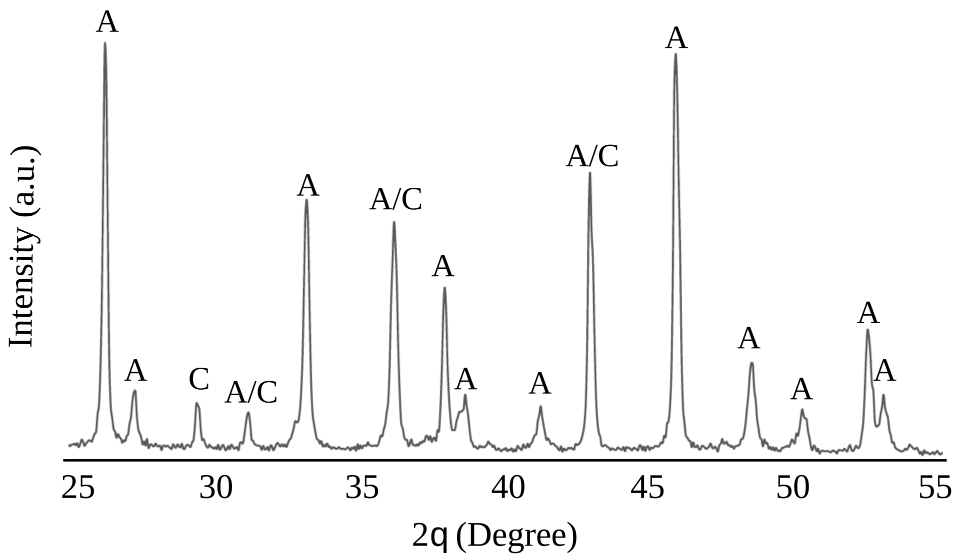

Figure 2. The freshwater fossil shells are composed of aragonite and calcite.

(**Aragonite, A; Calcite, C**)

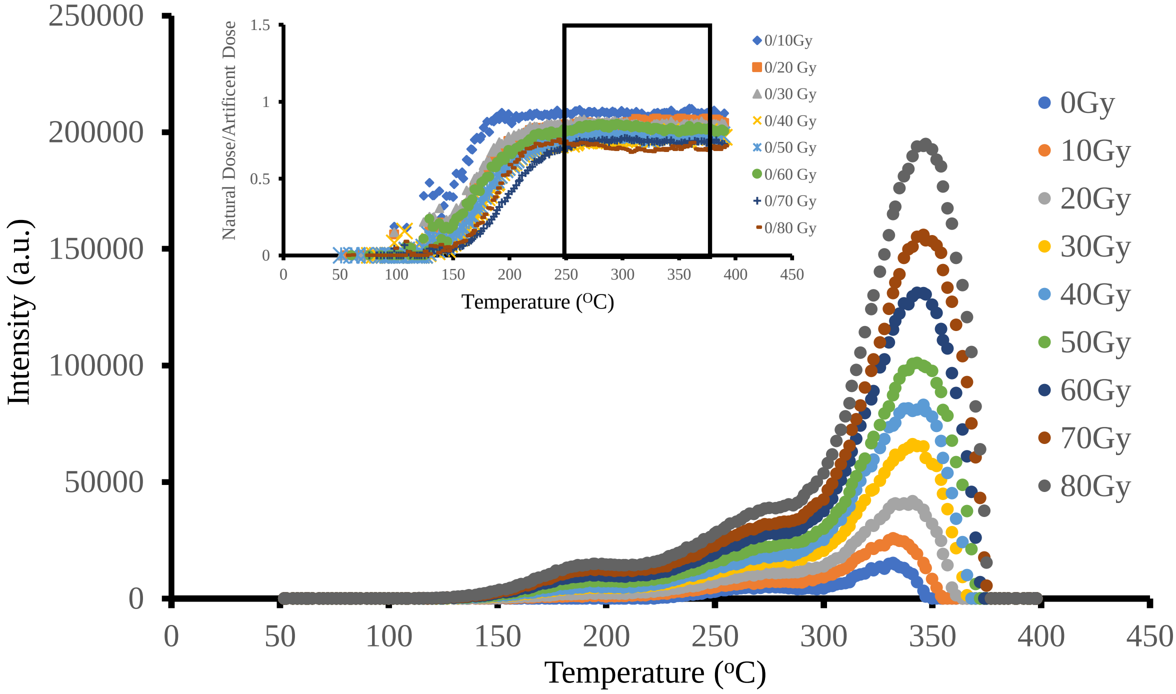

Figure 3. Intensity of the thermoluminescence (TL) response as a function of temperature of SH1 sample exposed to different doses (Gy).

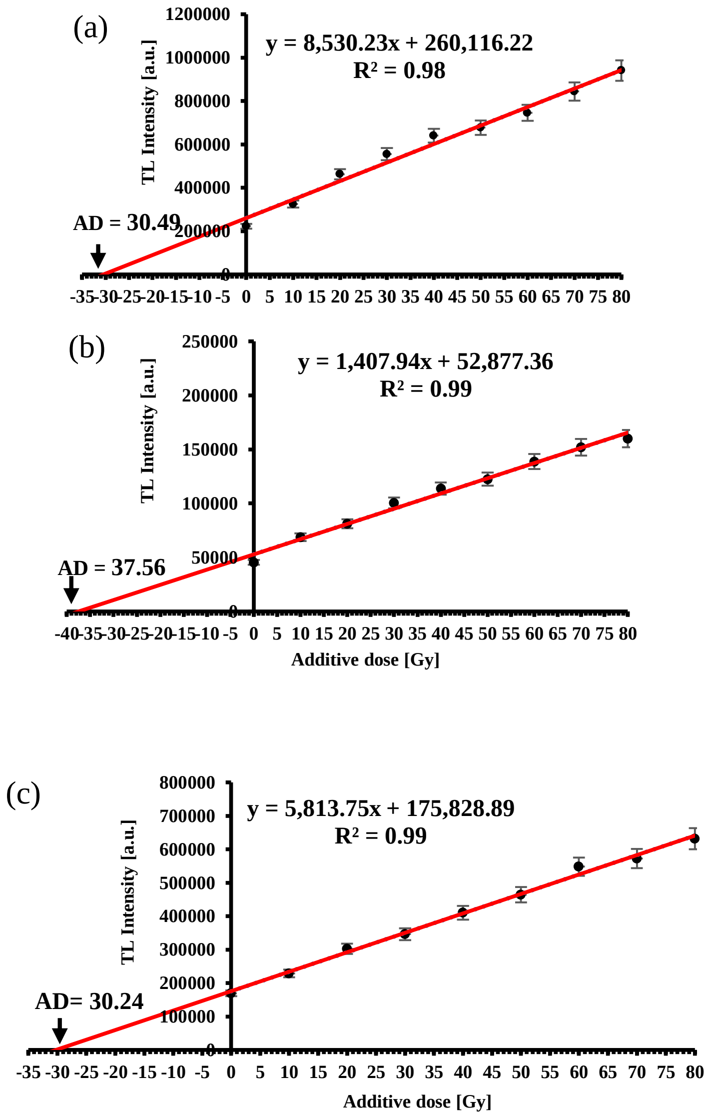

Figure 4. TL analyses of accumulated dose (AD) for SH1-SH3 are displayed from (a) to (c), respectively, based on TL responses at 350^{o}C.

A table file containing all the tables (including title, description, footnotes).

Table 1 Concentration 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 (year)
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

Table 3 Comparison between Radiocarbon and TL ages.

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