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^{14}C Dating at the Geological Boreholes and Sedimentory in the Lower Mekong Delta

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Abstract

This paper presents the processing and chemical treatment methods for age determination of geological samples using - Task Benzene Synthesizer - and the liquid scintillation analyzer (Tri–Carb 2770 TR/SL) in the laboratory at the Institute of Archaeology (VASS-Vietnam Academy Social Sciences). From that, 15 samples of wood, peat, mollusk shell collected from geological drilling holes LKBT1, LKBT2, LKBT3 at the coastal estuary in Ben Tre were processed and determined ages. The obtained results have helped to elucidate the sedimentation of the coastal estuary in Ben Tre province from the late Pleistocene to the present.

Keywords: Radiocarbon dating; Sedimentory; Lower Mekong Deltay.

1. Introduction

Nowadays, the sea level fluctuation is a deep concern in the world and in Vietnam as well, it directly affects the environment, coastal ecosystems and has a strategic influence on the development of marine economy (Figure 1). Especially, in Vietnam, recent coastal surveillance data show that the current average sea level rise is about 3 mm/yr (1993-2008), which is equivalent to the global mean sea level rise (SLR) rate. In the last 50 years, sea level has increased by about 20 cm, and SLR is anticipated to increase 75 cm in next 100 years [4,7].

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As evaluated by geologists, in the lower Mekong basin, the sea level rise has had a strong influence on sediment deposition in coastal estuaries. Therefore, age determination of these sediments will help to reveal fluctuations of the sea level as well as sedimentation rate in the Mekong river delta over the past period of time[8,9].

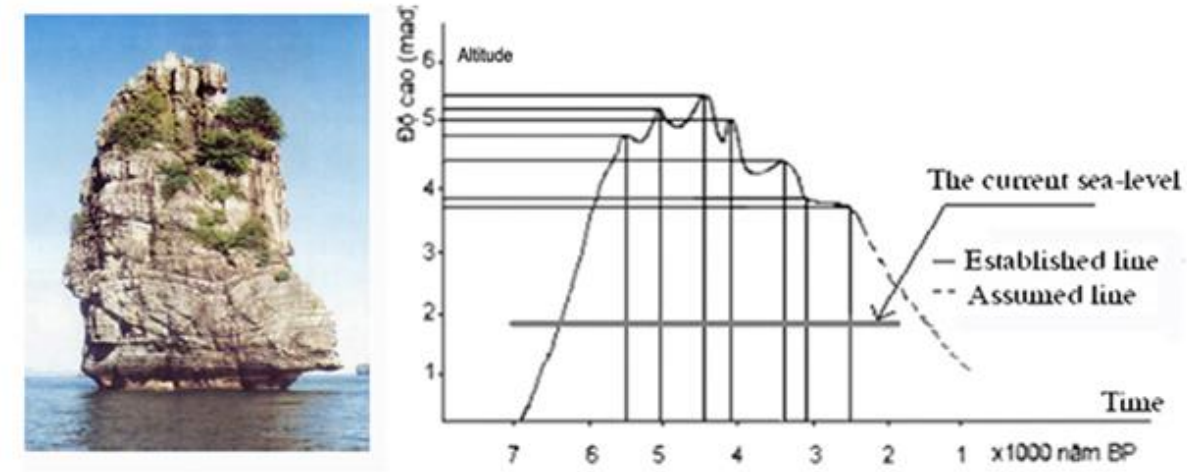

Figure 1: Traces of the oceanic fluctuations inprinted on the limestone; b) Showing on the sealevels in Holocen in the Coastal hill in Vietnam.

Source:Nguyen Quang Mien 2010b

BenTre is a province located at the end of the Mekong River, with a long coastline of nearly 65 km and a dense canal system. The province's terrain is relatively low; the sea's activity always has a strong influence on the socio-economic development of the locality. There has been still different views on the time and extent of sea level rise in the South. Determining the absolute age of sediment containing organic material, along the stratigraphy in deep boreholes, will allow an assessment of the extent and duration of sea level rise in the area [7,11]. The article present methods and results of determination of ^{14}C age of samples along three geological drilling holes: LKBT1, LKBT2, LKBT3 at the coastal estuary in Ben Tre province (Figure 2).

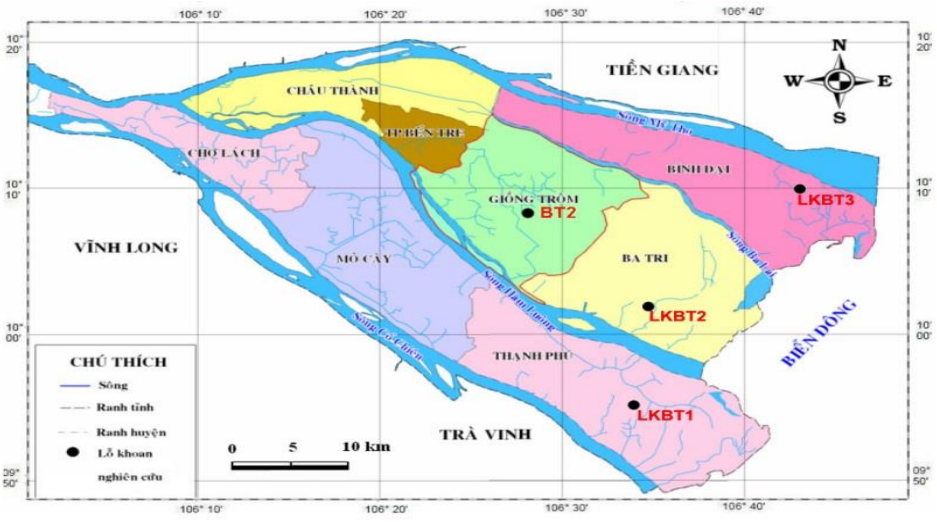

Figure 2: Distribution of geological drilling holes mentioned in Ben Tre province

(Source: Authors)

2. Experiment

2.1. Determination of research samples

In this paper, the collecting and processing of ^{14}C age measurements of 15 samples in drilling holes LKBT1, LKBT2, LKBT3 are shown in Figure 2. The characteristics such as depth, characteristics of the materials selected are described in Table 1.

Table 1: Depth and characteristics of the matherials selected for the study

No	Items	Materials	Description
1	M1	Coal	Coal gasification in LKBT1, at a depth of 0.38-0.45 m
2	M2	Wood chips	The trunk, the trunk in LKBT3, at a depth of 5.0m
3	M3	Shrub	Litter, plant in the hole LKBT2, at a depth of 10.1-11.0m
4	M4	Shrub	Litter, plant in the hole LKBT3, at a depth of 13.5 m
5	M5	Shrub	Litter, plant in the hole LKBT2, at a depth of 22.6-22.7 m
6	M6	Mollusc shell	The mollusk shell in LKBT3, at a depth of 22.7 m
7	M7	Mollusc shell	Shrimp, mollusk shell in bore hole LKBT3, at a depth of 30.0-30.7 m
8	M8	Shellfish	Shell shells, screws in the hole LKBT1, at a depth of 14.1-14.5 m
9	M9	Shellfish	The shell of the shellfish in LKBT2, at a depth of 39.0-40.0m
10	M10	Shellfish	Shell, shell shell in LKBT3, 32.8m deep
11	M11	Shrub	Litter, plant in the hole LKBT1, at a depth of 32.0-32.9m
12	M12	Shrub	Litter, plant in the hole LKBT1, at a depth of 63.4m
13	M13	Shrub	Litter, plant in the hole LKBT2, at a depth of 31.2 -31.3 m
14	M14	Shrub	Litter, plant in the hole LKBT2, at a depth of 69.9-70.0m
15	M15	Shrub	Litter, plant in the hole LKBT3, at depth 53.7-53.8m

2.2. Sample treatment and benzen synthesis for radiocarbon dating

For the remaining radioactivity of ^{14}C in the samples, the carbon content of the samples was given to the benzene compound (C_6H_6).

2.2.1. Physical and chemical pretreatment of samples

Depending on the origin of the sample, the samples are manually treated with appropriate techniques to remove unwanted impurities [1,3]. With originally organic samples such as wood, charcoal, humus ...the following steps should be taken place. In details, firstly, neutralize with neutral water. Secondly, bleach with acid solution (usually 1% HCl acid), then bleach with alkaline solution (usually NaOH 1%), degreasing with 1% HCl acid solution. It's also written abbreviate as "A.A.A" method. Finally, the sample was cleaned with neutral water and dried drying. The shells, snaisl, samples wash, ones should be carefully cleaned to reject sticky soil. Then dry

and clean with 10% HCl solution. As the sample is added to the acid, stir until all the bubbles are gone. And, there exists a reaction to remove impurities in the form of $CaCO_3$. Illustration photos after washing are shown in Figure 3.

Figure 3: Specimens collected from the geological drilling-holes in Ben Tre province

On the one hand, after removing the impurities in the sample, the sample is taken up in benzene form, and because it is a transparent solvent and can be soluble with other solvents as well as a flashing agent (PPO-POPOP) to create and unity form. On the other hand, benzene is of a high purity and carbon ratio of over 92.31% [5,6].

2.2.2. Benzene synthesizing

The process of synthesizing benzene is performed on the Task Benzene Synthesize system, that is inlustrated in the Figure 4, and is followed by the following steps:

$$Sample \rightarrow CO_2 \rightarrow Li_2C_2 \rightarrow C_2H_2 \rightarrow C_6H_6$$

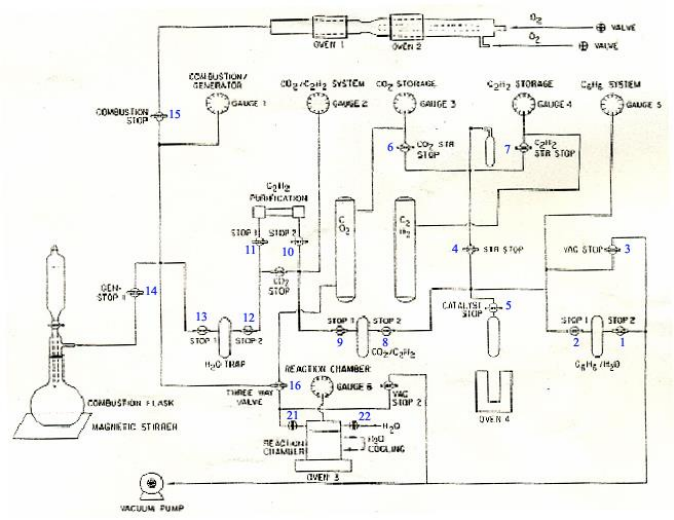

Figure 4: Diagram of TASK BENZEN SYNNTHESIZER

- ***Carbondioxide production (CO_2):*** Sample after being cleaned, dried and then put into the flask (for plant samples use bomb detonation method, while for shellfish samples use strong acids, and for humus specimens use continuous combustion method.

$C + O_2 \rightarrow CO_2$ or $CaCO_3 + H_2PO_4 \rightarrow CaPO_4 + H_2O + CO_2$

- ***Carbide production (Li_2C_2):*** The CO_2 produced in the vessel is flowed into a molten lithium metal (Li) container to form lithium carbide (Li_2C_2).

$$CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O$$

For effeciency of Li_2C_2 generation, the flask is maintained at 850°C for 2 hours, then it is cooled down gradually to room temperature.

- ***Acetylene production (C_2H_2):*** The stream of water was added to the Li_2C_2 vessel to produce hydrolysis of acetylene gas (C_2H_2).

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$$

Acetylene gas is then passed through 3 traps with liquid nitrogen to the container. Once, the catalyst in the container is discolored, add a hot water tank at a temperature of 70-80°C to immerse the catalyst. Trimerization occurs completely in the range of 3 to 3.5 hours [4,5].

- ***Benzene production (C_6H_6):*** The amount of benzene produced is contained in the catalytic container in the form of catalyst.

$$3C_2H_2 \xrightarrow{catalyst} C_6H_6$$

To remove the benzene from the catalyst we used a trap that is also a vacuum tube soaked in liquid nitrogen. Traps are opened with a catalyst tank, heated to about 100°C to 110°C to flood the catalyst, benzene is then absorbed in the catalyst and will be gradually transferred to the trap. Benzene is trapped in the range of 3 hours to 3.5 hours [4,5]. Entire conversion process of sample carbon to benzene was carried out in a closed cycle, in vacuum with pressure less than 25" Hg, using TASK Benzene Synthesizer system provided by Athen, GA Company (USA). In addition, a mandatory requirement is that the chemicals used for sample processing must be of high purity, to ensure that the obtained benzene samples are nearly free of beta spectrum shrinking when measured by liquid scintillation counters. Accordingly, most of the carbon in the sample will be converted to benzene, with the capture efficiency corresponding to 90% [3].

2.2.3. Fabrication of liquid scintillation detector

The amount of benzene after synthesis is mixed with a solvent and luminescent material to form a flashing liquid detector and then placed in a dedicated vial box made of low-radioactive material (volume of 7 mL) as a

standard model (Figure 5).

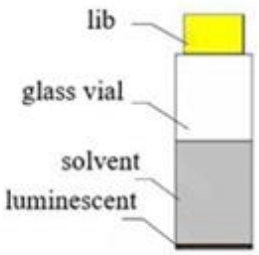

Figure 5: Liquid Scintilation detector

The beta particles in the solution collide with the solvent molecule and excite to the flashing molecules. Once the beta particles collide with such medium, they lose energy in the form of heat and ionize or stimulate molecules in the solution. The flashing liquid is going to transform the kinetic energy of beta particles into light energy that is proportional to the initial energy of the beta particle. The formedlight passes through the solvent in the detector, and reach to two photomultiplier tubes (PMT) arranged on opposite sides of the detector. At which light pulses are converted into electrical signals and transmitted to ADC circuits and then to microprocessor circuits [1]. Selectable solvent substances are capable of efficiently converting energy of the beta radiation. The absorption spectrum of the solvent does not cover the emission spectrum of the luminescent material, and is readily soluble in the sample and in the luminescence. This mixed flashing liquid has a fast luminescent effect when exposed to nuclear radiation. Previous studies have shown that PPO + POPOP blended with 6 g/L PPO and 0.2 g/L POPOP to make sure the highest recording efficiency [3,6,10].

2.2.4. Measurement of the radioactivity by Liquid Scintilation Counter

The ^{14}C radioactivity in the samples, the standard-OX sample and the back-lit sample were dissolved in the liquid-to-liquid flicker, measured on the liquid scintillation analyzer, Tri-Carb 2770 TR/SL at the Laboratory for Archaeology - Vietnam Institute Archaeology (Figure 6). This equipment is a super-clean, ultra-low-viscosity flux system, with low background and high stability [1]. To ensure statistical accuracy of the measurements, time taken for each measurement is 100 minutes and each samples were repeatedly measured for 20 times. The order of measurements, measured time, is set via the attached software.

Figure 6: a) Task benzen synthesizer b) Liquid scintillation Analyzer Tri-carb 2770 TR/SL

The entire sample processing and selection of measurement methods in the laboratory were carried out according to the procedure. The energy spectra of background (BKG), standard (OX) and research (M1) samples are presented in Figure 7.

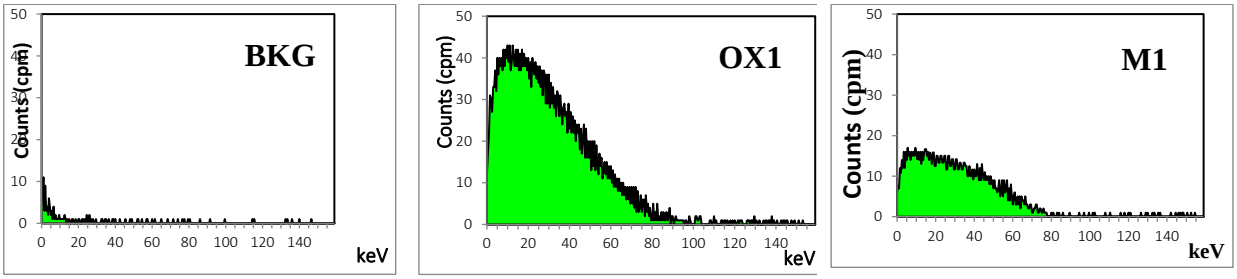

Figure 7: Energy spectra for background (BKG), standard (OXI) and research samples

3. Calculation of radiocarbon age

3.1. Equation of radiocarbon age

The ^{14}C age of carbon-containing objects is clearly understood to be the time from death of organisms (without metabolism process with the surrounding environment) up to the present. In case of living organisms, the $^{14}C/^{12}C$ ratios in such objects are constant and equal to the $^{14}C/^{12}C$ ratios in the medium. Once that organism dies, the biological metabolism stops, the amount of radioactive isotope in the organism is reduced exponentially, resulting in the $^{14}C/^{12}C$ ratio in the sample decreasing exponentially as well. As a result, the specific radioactivity of ^{14}C in carbon taken from the samples containing carbon also decreases exponentially, according to the following equation [3]:

$$A = A_o exp \frac{-0,693}{T} t \qquad (1.1)$$

where A_o and A are the radioactivities of ^{14}C in 1g of carbon taken from the sample at the initial time and t-time needs determining in term of dpm/1gC, and T - the half-life of ^{14}C is 5730 ± 40 years [5]. Based on the International Association for Radiocarbon Age (ICRA), the A_o value is officially announced as 13.56 dpm/gC with the corresponding original date in 1950 AD. From the equation (1.1), the specimen's age is estimated by

the following equation:

$$t = \frac{T}{ln2}\ln\frac{A_o}{A}. \quad (1.2)$$

where: t is calculated in years BP (Before Present). In the formula (1.2), we considered the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios to be the same for all living things. However, due to the selection effect between light and heavy isotopes, the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios will vary slightly depending on the source of the carbon-containing materials [2,3,4]. Therefore, the specimen's age is mathematically calculated by the formula as the effect of fractionation is taken into account [6]:

$$t = \frac{T_{1/2}}{Ln2}.Ln[K_{NBS}.\frac{A_{st}}{A_s\left[1-\frac{2(\delta C^{13}+25)}{1000}\right]} \quad (1.3)$$

where $T_{1/2}$ is the half-life of ^{14}C; K_{NBS} is normalization factor for Oxalic Acid II, and equal 0.7459; A_s and A_{st} are radioactivity in the tested sample and in the standard sample, respectively (A_{st} is the international standard factor for contemporary radiocarbon, is NIST Oxalic Acid SRM 4990-C, it's also called OXI or NOX); δC^{13} is $^{13}C/^{12}C$ fractionation factor of samples and Oxalic Acid II (measured by mass spectrometry) with respect to Belemite americana from the PeeDee formation in South Carolina, commonly referred to as PDB [3]. The value of the above $\delta^{13}C$ index is usually determined by mass spectrometer. Since, we don't have access to this kind of equipment in Vietnam, so the value of $\delta^{13}C$ is obtained from the tabulated data of the given element following recommendations of the radiocarbon dating association in the world [5,6,10].

3.2. Determination of counting efficiency and detection thresholds

From the data obtained in Table 2, the counting efficiency of analyzer was calculated by the following equation:

$$\varepsilon = \frac{n_{st}}{m_{st}.A_{0st}}\, x\ 100\% = 67.2\% \quad (1.4)$$

where ε is counting efficiency of the analyzer, n_{st} is net count rates of the standard sample (it was subtracted the count rates of the background sample), m_{st} is mass of the standard sample, with A_{ost} is the radioactivity of the standard sample, From that, limit of detection, it's also called detection thresholds of the analyzing system with time measurement of 100 minutes and 20 times, is determined by the formula:

$$A_{\min} = \frac{3}{\varepsilon}\sqrt{\frac{n_\phi}{kt}} = 0.083 \text{ dpm/g} \quad (1.5)$$

Therefore, the highest age of the sample which this device can detect is determined as the following equation:

$$T=\frac{T_{1/2}}{Ln2}.Ln[\frac{A_o}{A_{min}}] = (5730/\ln2).\ln(13.56/0.083) = 41740 \text{ years BP} \quad (1.6)$$

Hence, the highest threshold age for sample in this circumstance is about 41740 years BP. This value is

slightly lower than previous studies by other authors [5]. In our opinion, this may be due to the aging of the instrumentation, but it is still sufficient to measure the selected samples.

Based on the experimental data in Table 2, determine the radioactivity of ^{14}C in 1 gC of 15 samples according to the formula:

$$A_s = A_{st}\frac{n_s/m_s}{n_{st}/m_{st}} \quad (1.7)$$

A_s and A_{st} are respectively the radioactivity of the tested samples and the standard samples (dpm/gC); m_s and m_{st} are the masses of the tested sample and standard samples (g); n_s and n_{st} are background corrected counting rate of the tested and standard samples.

4. Results and discussion

The results of the ^{14}C radioactivity of the samples are given in Column 5, Table 2. Table 2 also shows the Fraction factors ($\delta^{13}C$) of the samples according to each of the given elements as suggested by Aitken [2] and Nguyen Quang Mien [7]. Using the formula (1.3) to calculate the age of the samples, the results are given in column 7 of Table 2.

Table 2: Measurements and age profiles of the samples

No.	Samples	m_s(g)	n_s(cpm)	Radioactivity of ^{14}C (dpm/gC)	$\delta^{13}C$ (‰)	Results (years BP)
1	M1	2.233	7.07± 0.11	4.71± 0.07	-25	8750 ± 125
2	M2	2.237	13.57± 0.24	9.03± 0.16	-20	3280 ± 145
3	M3	2.251	12.28± 0.38	8.12± 0.25	-16	4090 ± 260
4	M4	2.236	12.55± 0.22	8.35± 0.14	-16	3860 ± 145
5	M5	2.229	12.57± 0.19	8.39± 0.13	-16	3820 ± 125
6	M6	2.232	10.48± 0.22	6.98± 0.15	0	5060 ± 175
7	M7	2.235	9.33± 0.22	6.21± 0.14	0	6030 ± 195
8	M8	2.232	9.51± 0.18	6.34± 0.12	0	5860 ± 160
9	M9	2.231	11.02± 0.12	7.35± 0.08	0	4640 ± 95
10	M10	2.236	8.25± 0.23	5.49± 0.15	0	7050 ± 230
11	M11	2.228	3.71± 0.09	2.48± 0.06	-16	13920 ± 210
12	M12	2.235	2.48± 0.19	1.65± 0.12	-16	17280 ± 645
13	M13	2.232	7.48± 0.11	4.99± 0.07	-16	8120 ± 115
14	M14	2.101	1.76± 0.06	1.25± 0.04	-16	19600 ± 250
15	M15	2.232	4.64± 0.08	3.10± 0.05	-16	12070 ± 138
	OX1	2.650	34.77± 0.15	19.36 ± 0.09		
	BKG	2.650	0.690± 0.010			

Remarks about the sediment environment through the measurement of ^{14}C age

The results of the ^{14}C age obtained in the table are quite consistent with some of the results of the age analysis by other methods in the area. Therefore, in conjunction with the geological survey materials in the same area, we have some remarks as follows:

In the vicinity of Pleistocene to present, the studied area is strongly influenced by tides and waves, with different system of sand dikes of different height and low. For instance, the sediment layer about 3,800 years ago in LKBT2 has a depth of 22.6-22.7 m whereas in LKBT3 the depth is only 5.0 m; 13.5 m. The composition of the material reflecting the sediment environment in this area is the coastal marshes with the vegetation growing widely with saline submerged species such as mangrove, mangrove, yellow fish....

Comparison the above ages with the ^{14}C datings in the drilling hole BT2 (Figure 2), which measured in Nagoya University (Table 3), we can see that the ^{14}C dating data taken by Laboratory in Institute of Archaeology, are quite consistent with the ^{14}C data taken by Laboratory in Japan.

Table 3: The ^{14}C datings in the drilling hole BT2 [11]

No	Items	Material	Depth (m)	Description sediment	Age (year BP)
1	S1	Shell	-10.20	Sedimentary component consists of fine sands and humic silt and mollusk, shells…	3660 ± 80
2	S2	Shell	-15.40	Sedimentary component consists of fine sands and humic silt and mollusk, shells…	4550 ± 90
3	S3	Shell	-32,54	Sedimentary component consists of plastic clay and humic silt and mollusk, shells…	5210 ± 90
4	S4	Shell	-35,10	Sedimentary component consists of plastic clay and humic silt and shells, mollusk…	5320 ± 80
5	S5	Wood	-60,87	Sedimentary component consists of plastic clay and plant fragments and mollusk…	11340 ± 115

On the basis of the results of the ^{14}C and the field data of the three drilling-holes, researchers are able to draw a line on the Pleistocene-Holocene boundary in the following areas: On the one hand, LKBT1-The Pleistocene-Holocene boundary is defined closer to the ground than to a depth of about 28 m and has an age around 12200 ± 110 years BP. On the other hand, at Pleistocene-Holocene boundary LKBT3, the Pleistocene-Holocene boundary is defined from about 57.5 m - 54.5 m with time from 11700 to 10130 ± 110 years BP. Hence, a general assessment of the Pleistocene - Holocene boundary is of 11700 years ago.

5. Conclusion

The paper presents methods for measuring age based on ^{14}C isotope by benzene synthesis and beta radioactivity on the liquid scintillation analyzer, Tri-carb-2770 TR/SL For a 100-minute measurement, the number of repetitions of 20 are in used to determine the device's threshold to be at the detection level of 0.083 dpm/gC, which corresponds to the maximum age detected by this instrument as 41740 BP. There were 15 sedimentary samples from the three boreholes at the coastal estuary (in Ben Tre province) were determined radiocarbon ages. The obtained results have contributed to the study of the sediment environment in the Lower Mekong Delta and

determine the Pleistocene-Holocene boundary in the area equals around 11700 years ago.

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