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DETERMINATION OF THE CORAL AGE FROM KERATON BUTON FORT, BAUBAU CITY, BASED ON ^{14}C ACTIVITIES USING LIQUID SCINTILLATION COUNTING METHOD

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ABSTRACT

DETERMINATION OF THE CORAL AGE FROM KERATON BUTON FORT, BAUBAU CITY BASED ON ^{14}C ACTIVITIES USING LIQUID SCINTILLATION COUNTING METHOD.

Determination of the age of the corals that make up Keraton Buton Fort based on ^{14}C activity using the LSC (Liquid Scintillation Counting) method has been carried out. The coral samples analyzed were the corals that made up the fort taken from the gate of Keraton Buton Fort and a coral sample from the beach of Makassar Island Baubau, as modern coral. Sample preparation was carried out physically and chemically using a mixture of NaOH with 30% H_2O_2 , followed by a mixture of HClO_4 with 30% H_2O_2 , and finally with 5% HCl solution to produce a clean and whiter-looking sample with a weight reduction of 10.5% - 15.8%. The carbonate of coral samples was separated as CO_2 by reaction with 10% HCl and absorption by KOH 1 N solution as K_2CO_3 . The total carbon in the two fort coral sample and modern coral was 0.129, 0.132, and 0.129 grams, respectively, and was obtained through the titration method. The specific activity of ^{14}C in the samples was 13.95 DPM/gC and 14.38 DPM/gC in both fort coral samples, and 15.48 DPM/gC in modern coral. The age of the coral samples of Keraton Buton Fort calculated from the ^{14}C specific activity data was between 817 ± 0.123 and 565 ± 0.105 years, which is older than the ages of the Keraton Buton Fort according to the historical reviews.

Keywords: ^{14}C specific activities, carbon dating, liquid scintillation counting, coral, Keraton Buton Fort.

INTRODUCTION

The Keraton Buton Fort, located in the city of Baubau, Southeast Sulawesi, is a cultural site, a famous tourist attraction, and has received much attention. The fort was built by the Sultanate of Buton around the 16th – 17th centuries with a maritime pattern and is one of the largest remains, which is known as the widest and longest fort in the world [1]. One of the maritime features of the Buton Sultanate that stood out was the fort's construction material: coral. The length of the fort is 2,740 meters with a thickness of between 1 and 2 meters and a height of between 2 and 8 meters [2]. The rocks used to construct the Keraton Buton Fort are thought to have been taken from the surrounding islands.

The coral, as a construction material for the Keraton Buton Fort, was taken from dead coral reefs. Coral, which is a coral reef structure with the main constituent of calcium carbonate (CaCO_3), is formed by colonies of millions of CaCO_3 -producing polyps as hard limestone structures. The formation of these structures involves biosystem processes and carbon dioxide balance in marine and atmospheric waters [3],[4],[5]. As the main component of coral, the content of CaCO_3 is more than 98% [6].

The presence of ^{14}C in corals is maintained through the balance of the coral reef carbon biosystem with water and CO_2 in the atmosphere. Radioisotope ^{14}C in the atmosphere comes from the interaction of cosmic radiation with nitrogen and the results of nuclear testing with oxygen, forming carbon oxides, especially $^{14}\text{CO}_2$. Atmospheric carbon dioxide is absorbed by seawater as carbonate ions, which coral polyps convert into a CaCO_3 framework, which contains ^{14}C . The amount of ^{14}C in the body of living coral is always the same because, in addition to income, there is also continuous expenditure and decay, but after the coral die, the metabolic process stops so that the amount of ^{14}C continues to decrease exponentially with time [7], which is associated with the death of coral reefs.

The age of carbon-based materials such as coral can be determined by the radiocarbon dating method, which is based on calculating the ^{14}C activity remaining in a carbon sample. This activity value is then converted into age after being compared with modern reference standards [8] or ^{14}C activity

in live coral. One of the methods for counting very low radioactivity, such as ^{14}C , is liquid scintillation counting [9],[10],[11], with a very low background radiation (*low background counter*), and the counting efficiency reaches up to 99.99% [12].

In this research, we have determined the ages of the corals that make up the Keraton Buton Fort in Southeast Sulawesi. Age determination was based on data from measurements of the specific radioactivity in ^{14}C from fort coral samples and live coral samples using the liquid scintillation counting method.

METHODOLOGY

1. Materials

The materials used are rock samples from the Keraton Buton Fort and coral reefs (live corals) from the sea waters of Makassar Baubau Island, HCl pa, KOH pa, NaOH pa, HClO_4 pa, H_2O_2 30%, AgNO_3 pa, *silica gel*, *Methyl Orange* (MO), N_2 gas (UHP), *Aqualight scintillator*, filter paper, aluminum foil, distilled water, plastic samples and gloves.

2. Equipment

The tools used are a series of CO_2 absorption devices, Hidex 300 SL LSC counters, scintillator *vials*, *hotplates*, staves, mortars, gloves, baskets, ovens, chisels, hammers, GPS, sonicators, and tools commonly used in laboratory.

3. Research procedure

Sampling

Sampling of the Keraton Buton Fort for research purposes has obtained a permit from the South Sulawesi Cultural Heritage Preservation Center, Number: 0974/F7.1/PG.02.00/2022. Samples were taken at two locations, the main gate of the fort or Lanto gate, at coordinates 5°28'23" South Latitude and 122°36'06" East Longitude, and Bariya gate at the back of the fort, at coordinates 5°28'37" S and 122°36'10" E. In addition, live corals were collected from sea waters off the coast of Makassar Baubau Island at coordinates 5°26'08" S and 122°37'26" E. Fort coral samples were taken sufficiently by removing them using a chisel and hammer from the edge of the building while live corals were taken directly at the bottom of the waters and then all samples were put in separate plastic bags and labeling.

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Sample preparation

Coral sample preparation includes washing and carbonate extraction. Washing of coral samples followed the procedure [13]. Coral samples were washed using flowing water and rinsed with distilled water to remove moss and other impurities. Chemical washing was carried out by a mixture (1:1) of 30% H_2O_2 and 1 N NaOH for 10 minutes, then in a mixture of (1:1) 30% H_2O_2 and 1% HClO_4 , sonicated for 2 minutes. The last process in

chemical washing is soaking in 5% HCl. Next, the samples were rinsed with distilled water, then dried in an oven at 105 °C. The dried samples were crushed to a fine powder. The crushed coral samples were weighed as much as 5 g and then put into a three-neck flask, previously the flask was saturated with N_2 gas. Next, 10% HCl was added until the sample finished reacting, then the N_2 gas was flowed into a series of CO_2 extraction equipment, which can be seen in Figure 1.

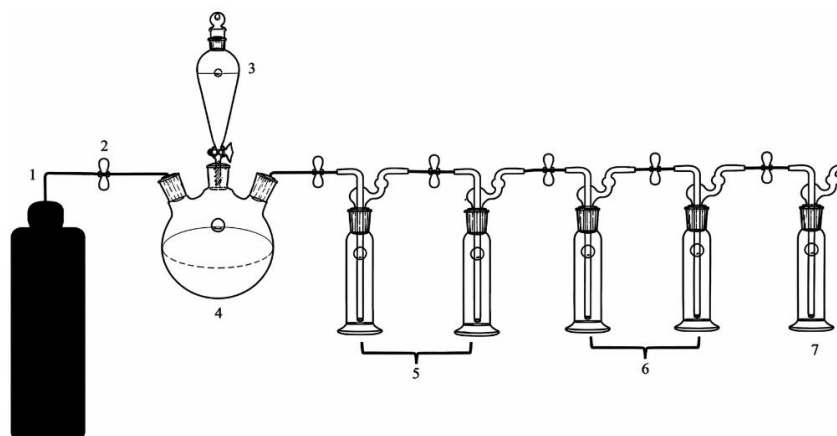


Figure 1. Carbonate extraction equipment set. (1) N_2 gas cylinder, (2) valve, (3) separating funnel, (4) three-neck flask, (5) AgNO_3 impinger, (6) silica gel impinger, (7) 1 N KOH solution impinger. (Source: FMIPA UNHAS Radiation Chemistry Laboratory).

The result of the CO_2 gas is flowed through a series of extraction equipment through several *impingers*, each of which contains filter paper that has been moistened with AgNO_3 and *silica gel*. The gas sample is accommodated in an absorption column containing 1 N KOH as an absorbent. The flow of N_2 gas was stopped, and the results obtained in the absorption column were then used to determine ^{14}C activity and determine the total carbon in the sample solution [14].

Determination of total carbon

The sample solution, as K_2CO_3 , was pipetted as much as 5 mL into a 250 mL Erlenmeyer flask, and then MO indicator was added and then titrated with 0.5 M HCl until the color changed from yellow to pink. The procedure for determining total carbon in coral samples was carried out in triplicate [13].

Determination of ^{14}C activity in samples

The ^{14}C activity in the samples was measured using LSC Hidex 300 SL. 8 mL of the extracted sample solution was mixed with

12 mL of the scintillator in a 20 mL vial, chopped, and shaken until homogeneous. The sample solution was chopped for 5-240 minutes to get the optimum counting time. The same procedure was carried out for *background enumeration* [14][15].

Calculation of the age of coral samples

The age of the coral sample was calculated based on a comparison of the specific activity of modern ^{14}C or the specific activity of ^{14}C in live coral (A_{S_0}) to the specific activity of the coral sample (A_{S_t}). Specific activity is ^{14}C activity in each gram of the total carbon sample. The calculation of sample age follows the radiocarbon decay rate equation:

$$t = \frac{t_{1/2}}{0,693} \ln \frac{A_0}{A_t} \quad (1)$$

with A_t is radioactivity of the ^{14}C isotope in coral samples (A_{S_t}), A_0 is radioactivity of the ^{14}C isotope in modern corals (A_{S_0}), $t_{1/2}$ is half-life (5730 ± 40 years), and t is age of coral sample.

RESULTS AND DISCUSSION

Sampling

Coral was taken from three locations. These locations include: the main gate or Lanto Gate (GL) (Figure 2a) and the Bariya Gate (GB) (Figure 2b), both being fort rocks within the Keraton Buton fort. The third sample is live coral or coral reef (CH) (Figure 2c), which was taken from the sea waters of Makassar Island, Baubau. The three coral samples are physically shown in Figure 2.

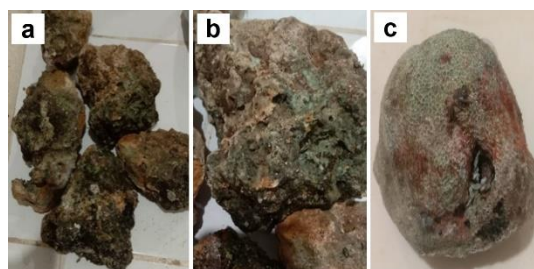
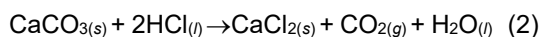


Figure 2. Coral samples: (a) Lanto Gate (GL) and (b) Bariya Gate (GB) Keraton Buton Fort, well as (c) live coral (CH) (Source: Documentation personal).

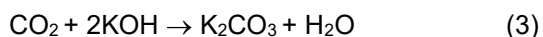
Sample Preparation

Sample washing was carried out physically and chemically. The washing aims to remove physically attached impurities and chemically bound impurities due to natural processes, both organic and inorganic impurities in the form of minerals. After drying, the coral samples looked cleaner and whiter with a weight reduction of 10.5 - 15.8%.

The carbon in the coral samples in the form of CaCO_3 was extracted as CO_2 , which was the result of the reaction between the carbonate material and hydrochloric acid. The reaction occurs quickly. The reaction that occurs between calcium carbonate and hydrochloric acid is as follows:



In the absorption column, CO_2 gas is absorbed in the KOH solution. The absorption process is a reaction between KOH and CO_2 gas to produce carbonate compounds, according to the reaction:



The weight of the coral sample needed to saturate the KOH solution with CO_2 as K_2CO_3

is about 30 g, as shown in Figure 3, both fort coral samples (GL and GB) and live coral samples (CH).

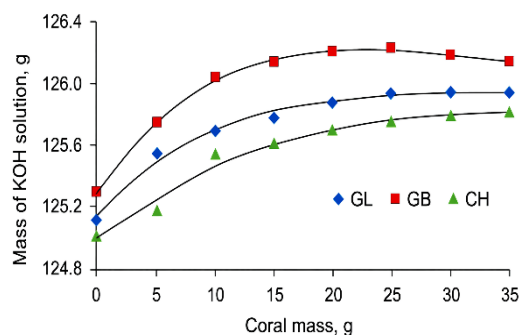


Figure 3. Trend of change in mass of KOH absorbent solution with increasing mass of extracted coral samples.

Total carbon

Total carbon was carried out by titration method using 0.5 M HCl and *methyl orange* (MO) indicator until the color changed from yellow to pink. The total carbon was 0.129 g in the GL coral sample, and 0.132 g in the GB coral sample, and 0.129 g in the CH coral sample. Calculation of the total carbon in the coral sample is then used to obtain the specific activity value of ^{14}C contained in the sample.

Enumeration ^{14}C

^{14}C activity of the coral samples was carried out in 2 stages: the stage of determining the optimum time of enumeration and the stage of determining the average of enumeration at the optimum time. The output of ^{14}C activity enumeration with LSC Hidex 300 SL is in the form of DPM (Disintegration Per Minute).

The ^{14}C activity count data in the measurement time series is shown in Figure 4. Based on these data, it is known that the optimum time for counting is reached at 90 - 120 minutes. The value of the counting gradually decreases until the 90 minutes and actually persists at 120 minutes. The instability of this counting can be caused by the quenching effect and the stability of the sample solution phase, which affects the number of photons produced in the beta interaction process with the scintillator.

The optimum time for counting the activities of ^{14}C , which was achieved for the three sample solutions, was 120 minutes. The enumeration was then repeated 10 times

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at the optimum time to obtain an average activity value of ¹⁴C, which was closer to the absolute value. ¹⁴C activity data from repeat enumeration at the optimum time can be seen in Table 1.

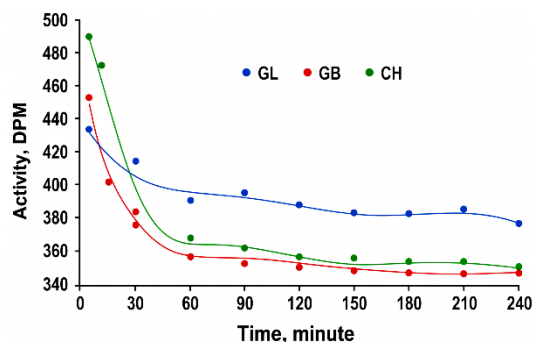


Figure 4. Trend of changes in ¹⁴C activity of coral samples with increasing enumeration time.

Table 1. Data on the results of the enumeration of ¹⁴C activity in the sample at the optimum time.

No	Activity (DPM)		
	GL	GB	CH
1	379	374	366
2	373	374	377
3	374	373	377
4	372	376	373
5	375	371	374
6	371	371	374
7	369	368	371
8	371	374	371
9	370	372	373
10	370	372	370
Average	372.4	372.5	372.6

The average of ¹⁴C activity in GI 372.4 DPM and natural GB 372 DPM samples as well as in CH 372.6 DPM coral samples. The average activity data is then used to determine the specific activity of coral samples corrected for *background activity*. The *background* used is marble which is given the same treatment as the sample. Marble includes *dead carbon* which is a material that is considered not to give radioactive activity. The average activity of the *background count* was 370.6 DPM for 120 minutes of enumeration with 10 repetitions. The data on the results of the *background counts* are used as a correction factor for the chopped coral samples when determining the specific activity of ¹⁴C.

Determination of specific activities ¹⁴C

The specific ¹⁴C activity of coral samples was determined based on a comparison between the ¹⁴C activity in the sample in DPM units corrected by the *background count* to the total carbon content of the sample. The specific activity of ¹⁴C in the three coral samples is as shown in Table 2.

Table 2. ¹⁴C Specific Activity Data of Coral Samples.

No	Sample	Total C (g)	¹⁴ C Specific Activity (DPM/gC)
1	GL	0.129	13.95
2	GB	0.132	14.38
3	CH	0.129	15.48

The data in Table 2 shows that the specific activity of ¹⁴C of dead coral samples (GL and GB) is relatively lower than that of live coral (CH) with an activity of 15.48 DPM/gC as modern carbon. The specific carbon activity of modern corals is not much different from that of terrestrial plants, an average of 15.3 dpm/gC [8] and the results of measurements of modern corals from the Spermonde Islands [16]. When the corals are still alive, the process of forming the coral CaCO₃ framework from seawater carbonate is still ongoing, which is in equilibrium with CO₂ in the atmosphere layer containing the ¹⁴C (¹⁴CO₂) fraction, while in dead coral samples, the process has stopped since the beginning of their death until their death. This relative activity became the basis for determining the ages of the two coral samples from the Keraton Buton Fort of Baubau City.

Determination The Age of Coral Samples

The age of each GL and GB fort coral sample was determined based on a relative comparison of the specific activity of ¹⁴C each with the specific activity of ¹⁴C of live coral CH as modern carbon according to Equation (1). The age of the GL coral samples is around 817 ± 0.123 years, while the GB corals are around 565 ± 0.105 years old. The age of the coral is older than the age of the Baubau Keraton fort, according to the history of its construction, which began during the reign of Sultan Buton IV, Sultan La Eaglei, whose title is *Dayanu Ikhsanuddin* (1578-1631M), was then completed during the reign of Sultan Buton VI, Sultan La Buke whosetitle is *Gafur*

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Wadudu (1632-1645 AD) [2]. This is reasonable because the main construction materials for the fort came from coral reefs that had died hundreds of years before and became rocks or rocks as loose reefs or coral mountains on the islands around the fort.

CONCLUSIONS

The age of the coral samples that make up the Keraton Buton Fort in Southeast Sulawesi ranged from 817 ± 0.123 to 565 ± 0.105 years based on the results of the ^{14}C radiocarbon method. The age of the fort coral is hundreds of years older than the fort based on its construction period in the history of the Buton sultanate.

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