การหาอายุเปลือกหอยทะเลจากจังหวัดสงขลาด้วยคาร์บอนรังสี
Radiocarbon Dating of Marine Shell from Songkla Province

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บทคัดย่อ

การหาอายุวัตถุด้วยเทคนิคคาร์บอน-14 นิยมใช้อย่างแพร่หลายในงานด้านโบราณคดีศึกษา วัตถุที่ใช้ศึกษา ได้แก่ ไม้ ถ่าน กระดูก เครื่องปั้นดินเผา และเปลือกหอยโบราณ อย่างไรก็ตาม การหาอายุเครื่องปั้นดินเผา พบว่าอาจให้ผลที่ผิดพลาดได้ เนื่องจากดินที่ใช้ในการปั้นมีส่วนผสมของคาร์บอนจำนวนน้อยมาก ทำให้อายุที่วิเคราะห์ได้สูงกว่าปีที่ปั้นจริง เพราะเป็นค่าอายุของดินที่ใช้ปั้น การหาอายุของเปลือกหอยทะเลด้วยคาร์บอน-14 สามารถประยุกต์ใช้ในงานศึกษาการตั้งถิ่นฐานของมนุษย์และเส้นชายฝั่งทะเลก่อนยุคปัจจุบัน ในงานวิจัยนี้ ศึกษาความน่าเชื่อถือได้ของการใช้เทคนิคคาร์บอน-14 หาอายุเปลือกหอยโบราณ พร้อมนำเสนอข้อมูลเบื้องต้นเปลือกหอยทะเลที่ใช้ในงานวิจัยนี้เป็นเปลือกหอยแครง (*Anadara granosa*) ขุดพบที่จังหวัดสงขลา ผลการวิจัยพบว่า เปลือกหอยจำนวน 7 ตัวอย่างให้ค่าอายุตั้งแต่ 510 – 6950 ปี และมี 2 ตัวอย่างแสดงค่าอายุของยุคปัจจุบัน ในขณะที่ผลวิเคราะห์ของตัวอย่างไม้ มีค่าอายุเท่ากับ 3300 ปี ข้อเสนอแนะจากงานวิจัยนี้ คือ ควรใช้ตัวอย่างที่ขุดพบในพื้นที่ ระดับความลึกเดียวกัน มีจำนวนมากพอและต่างชนิดกัน เพื่อยืนยันความถูกต้องของผลการวิเคราะห์ นอกจากนี้ตัวอย่างที่ใช้วิเคราะห์ควรคัดเลือกตัวอย่างที่เหมาะสม เพื่อลดความผิดพลาดที่อาจเกิดจากการหาอายุด้วยคาร์บอน-14

คำสำคัญ : การหาอายุด้วยคาร์บอนรังสี การหาอายุด้วยคาร์บอน-14 เปลือกหอยทะเล จังหวัดสงขลา

Abstract

The ^{14}C dating technique is widely used in archaeological studies. Typical materials for radiocarbon dating include wood, charcoal, bone, earthenware and fossil shells. However, dates of earthenware may possess error because the clay materials contain a small amount of carbon and they provide older ages corresponding to original clay formation. The use of marine shells for ^{14}C dating can be applied to study of chronology settlement and to search former shorelines with a reliable results. This paper considers the reliability of radiocarbon dates of marine shells and presents the preliminary ^{14}C dating results of marine shells (*Anadara granosa*) excavated from Songkla province. Seven shell specimens revealed sequence dating between 510 and 6950 years. Two marine shells indicated recent past while the wood specimen obtained 3300 years. It is suggest that analysis of several and various specimens excavated within a stratum should be confirmed the results. In addition, selecting appropriate specimens can be minimized the ^{14}C dating error.

Keywords : Radiocarbon dating, ^{14}C dating, marine shell, Songkla province

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Introduction

Radiocarbon dating has been widely used in the multidisciplinary studies throughout the world since its discovery by W. F. Libby sixty years ago. The studied fields include climate change, oceanic circulation, archaeology, hydrology and many aspects of Earth sciences. The Earth's environment has been changed by climatic variations and human activities in the past few centuries. Studies of these changes require a precise and accurate chronological frame work, to which radiocarbon dating can contribute. The technique provides one of the most reliable and well-established means of dating the Holocean and late Pleistocene. Hua (2009)

Aquatic mollusks occupy a wide variety of environments, from marine to brackish to fresh-water, and tropical to arctic, and they exhibit a wide variety of preferences for different bottom conditions; many live in clean sand, others are mud dwellers, still others prefer to attach themselves to rocks exposed at low tide. Marine shells consist mainly of either calcite or aragonite which serves well for radiocarbon dating.

The most often used fraction in radiocarbon dating is the calcium carbonate, which is the inorganic fraction of the shell, and it is the largest percentage fraction. The use of marine shells for ^{14}C dating can be applied to study of chronology settlement and to search former shorelines with a reliable results. Pigati, J. S. Rech, J.A. & Nekola, J.C. (2010)

This study presents the preliminary results and reliability of radiocarbon dating of marine fossil shells (Anadara granosa) and wood specimen excavated from two sites of Songkla province where each site was 3 meters depth. Direct absorption 14C dating by liquid scintillation counting of 14CO2 absorbed into an alkaline liquid was performed in this study .Vita-Finzi & Leaney (2006)

Materials and Methods

Principle

Carbon has three natural isotopes: ^{12}C, ^{13}C and ^{14}C or radiocarbon. ^{14}C is produced continuously in the atmosphere and is oxidized to produce $^{14}CO_2$, which is dispersed rapidly throughout the atmosphere. The ^{14}C is transferred to other carbon reservoirs: the biosphere and oceans via photosynthesis and air-sea exchange of CO_2, respectively. Living organisms take up ^{14}C through the food chain and via metabolic processes. This provides a supply of ^{14}C that compensates for the decay of the existing ^{14}C in the organism, establishing equilibrium between the ^{14}C concentration in living organisms and that of the atmosphere. When an organism dies, this supply is cut off and the ^{14}C concentration of the organism starts to decrease by radioactive decay at a rate given by the radiocarbon half-life. This rate is independent of other physical and environmental factors. Any organism containing carbon and that once lived in equilibrium with atmospheric radiocarbon can be dated by the radiocarbon method.

Radiocarbon ages are reported in years before present (BP) where present is conventionally defined as AD 1950, a hypothetical value is conventionally set at 100 percent Modern Carbon (PMC). To simplify the calculation of radiocarbon ages, atmospheric ^{14}C concentration is assumed to be constant through time, with the implication that all living terrestrial materials have an initial ^{14}C concentration of fraction modern carbon equal 1. Hua (2009) and Pigati, J. S. Rech, J.A. & Nekola, J.C. (2010)

The measured ^{14}C activity and the ^{14}C age of the material are related by the familiar decay equation

$$A = A_0 e^{-\lambda t}$$

Where A and A_0 are the measured and initial ^{14}C activities of the material, respectively, λ is the decay constant and t is the time elapsed since the death of the organism.

Conventional radiocarbon ages assume that the atmospheric ^{14}C is invariant through time (i.e., $A_0 = 1$).

Sampling

Two set of samples were used in this work. The analyzed samples were collected in 2011 and 2012 from two locations of Songkla province as show in Figure 1. However, each sample set obtained from the same

stratum depth of 3 meters and all marine shells were cockle (*Anadara granosa*). The collected locations were in a restrictd area that corresponds to a well defined archaeological context.

Figure 1 Illustrate of Songkla Province

Pretreatment and analysis

Before samples were processed for dating; they were cleaned from soil and dust by brushes, and washed with 18.2 mΩ distilled (hereafter "ultrapure") water. The cleaned samples were immersed for a few minutes in 10% HCl to remove the superficial calcite layer which may contain contamination, then rinsed with ultrapure water in order to remove adhere solution and dried at 100°C. The dried samples were crushed and ground into 150 μm powder for analysis. The shell powders were treated following the ASTM D6866-12 method. ASTM (2003)

Shell aragonite of 50 grams was converted to CO_2 by acid hydrolysis using concentrated HCl under vacuum. The generated CO_2 was incorporated as a carbamate in a mixture of absorber and cocktail, Carbosorb E and Permafluor V, respectively. The relative proportion of Carbosorb to Permafluor (C+P) was 1:1 ratio. A batch of prepared C+P samples, standard and background were counted in the Liquid Scintillation Counter (Quantulus™ 1220). Each sample was counted for 50 minutes and the whole counting procedure was performed for 20 cycles. The results were evaluated statistically and the standard deviations were calculated.

Table 1 ^{14}C dates of shells and wood from Songkla

Sample code	Type	PMC	^{14}C Age years BP
Site 1			
MS 1	Marine shell	53.79 ± 3.13	3360 ± 450
MS 2	Marine shell	47.74 ± 3.02	5940 ± 520
MS 3	Marine shell	53.44 ± 3.11	5030 ± 480
MS 4	Marine shell	45.85 ± 3.02	6260 ± 550
Site 2			
MS 5	Marine shell	77.89 ± 2.88	2010 ± 300
MS 6	Marine shell	82.75 ± 2.89	1520 ± 280
MS 7	Marine shell	83.03 ± 3.03	1490 ± 300
MS 8	Marine shell	112.70 ± 3.64	Modern Carbon
MS 9	Marine shell	99.97 ± 4.73	Modern Carbon
WD	Wood	71.42 ± 3.16	2700 ± 360

The reproducibility test of replicated sample maintained the results within the error bars defined by the counting statistics.

Results and Discussion

Radiocarbon dates of marine cockle shells and wood specimen are listed in Table 1.

Ten ^{14}C dates suggest that the sites were occupied between about 6260 and 1490 Years B.P. Radiocarbon dates of marine fossil shells and wood specimen are shown in Figure 2.

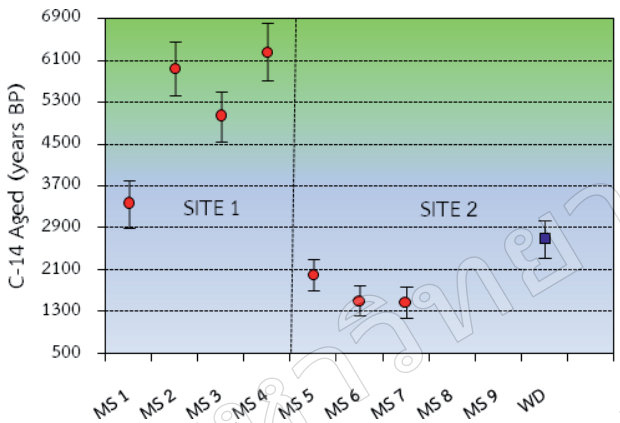

Figure 2 Comparison of radiocarbon dates of marine shells from site 1 with those of site 2

Two sets of shell specimen dates were consistent within each set. Marine shell specimens from site 1 were shown to be considerably older than specimens from site 2. It should be noted that site 1 has no dateable material in stratigraphic association to check its validity. Radiocarbon dates of shells from site 1 and site 2 ranged from 6260 to 3360 years B.P. (6950 to 3870 years) and 2010 to 1490 years B.P (2480 to 2990 years), respectively. The only one wood specimen excavated from site 2 indicated the same magnitude value with marine shells. However, among the ^{14}C dates obtained for the site 2, two marine shells indicated modern carbon or recent past (less than 200 years). It recommend that analysis of several and various specimens excavated within a stratum should be confirmed and clarified the results.

Previous works Pigati, J. S. Rech, J.A. & Nekola, J.C. (2010) and Bezerra, F.H.R. Vita-Finzi, C. & Filho, F.P.L. (2000) concluded that marine shells from open ocean environments or near upwelling zone are not likely to provide the reliable radiocarbon ages. For reliable ^{14}C dating, the pool of carbon atoms measured during the ^{14}C dating process must consist only of carbon atoms that originally resided in the shell. Thus, following burial shells must resist the addition or exchange of ^{14}C atoms with the open environment. Specimens in this study were collected in non-upwelling zone and in burial environment. Therefore, radiocarbon ages in this study are considered to be reliability results.

Radiocarbon dating of marine shell may possess error due to contamination through carbonate exchange with material of unknown age which appeared in calcite layer. Pretreatment with 10% HCl before radiocarbon assay is suggested as a precaution against this. Unaltered aragonite shells, cleaned as indicated in the pretreatment section may be dated with reasonable confidence. Preece, R.C. *et al*., (1983) and Rick, T.C. Vellanoweth, R.L. & Erlandson, J. M. (2005) However, dating error can be minimized by selecting ecologically appropriate specimens or by comparison of analyzes of several fossil specimens within a stratum.

Typical material for radiocarbon dating includes wood, charcoal, bones earthenware and fossil shell. However, dates of earthenware may possess error because the clay materials contain a small amount of carbon and they provide older ages corresponding to original clay formation. Yoshida, K. *et al*., (2004) With recent refinements in shell dating, dating of marine shells can be more accurate than dating earthenware.

Conclusion

This study analyzed the radiocarbon dating of the aragonite shells of cockles (*Anadara granosa*) in Songkla province. The preliminary results suggest the reliability radiocarbon dating values and the great potential for

paleo studies. In this study, direct absorption ^{14}C dating method was performed. As the method requires the CO_2 through the absorbing mixture, acidification of carbonates provides the simplest gas source. Thus the ideal material is organic carbonate such as marine shells, corals and barnacles.

Marine shell has been used in multidisciplinary studies due to their abundance and their utility in ^{14}C dating. In many coastal sites marine shells are the only readily available biogenic materials for radiocarbon measurements. However, the specimen should be pretreated as a precaution against contamination in order to verify that only shell aragonite remained prior to ^{14}C analysis. In addition, dates from marine shells in area near upwelling zones may possess error, because deep ocean water is depleted in radiocarbon compared to surface water. Through careful sample selection, use of well preserved or burial specimens, proper pretreatment (i.e., acid etching), use of established reservoir corrections and calibration curves, and the dating of multiple samples from a site, the reliability result should be achieved.

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References

ASTM (2003). "Standard Test Methods for Determining the Biobased Content of Solid, Liquid and Gaseous Samples Using Radiocarbon Analysis" *ASTM International, West Conhohocken, PA DOI 10,1520/D6866-12*.

Bezerra, F.H.R. Vita-Finzi, C. & Filho, F.P.L. (2000). *Revista brasileira de Geociencias, 30*, 211-213.

Hua, Q. (2009). *Quaternary Geochronology, 4*, 378-390.

Pigati, J. S. Rech, J.A. & Nekola, J.C. (2010). *Quaternary Geochronology, 5*, 519-532.

Preece, R.C. Burleigh, R. Kerney, M.P. & Jarzembowski E.A. (1983). *J. Of Archaeological Science, 10*, 249-257.

Rick, T.C. Vellanoweth, R.L. & Erlandson, J. M. (2005). *J. Archaeological Science, 32*, 1641-1648.

Vita-Finzi, C. & Leaney, F. (2006). *Quaternary Science Review, 25*, 1073-1079.

Yoshida, K. Ohmichi, J. Kinose, M. Ijima, H. Oono, A. Abe, N. Miyazaki, Y. & Matsuzaki H., (2004). *Nucl. Inst. And Meth. In Phys. Res., B 223-224*, 716-722.