## San Jose State University SJSU ScholarWorks

#### Master's Theses

Master's Theses and Graduate Research

1999

# Growth rate and potential climate record from a rhodolith using C AMS

Brian Robert Frantz San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd\_theses

#### **Recommended** Citation

Frantz, Brian Robert, "Growth rate and potential climate record from a rhodolith using C AMS" (1999). *Master's Theses*. 1811. DOI: https://doi.org/10.31979/etd.kd98-sxxj https://scholarworks.sjsu.edu/etd\_theses/1811

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

#### **INFORMATION TO USERS**

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.



A Bell & Howell Information Company 300 North Zeeb Road, Ann Arbor MI 48106-1346 USA 313/761-4700 800/521-0600

Growth Rate and Potential Climate Record From a Rhodolith Using <sup>14</sup>C AMS

A Thesis Presented to The Faculty of Moss Landing Marine Laboratories, San Jose State University

> In Partial Fulfillment of the Requirements for the Degree Masters of Science

> > By

Brian Robert Frantz May 1999

UMI Microform 1394523 Copyright 1999, by UMI Company. All rights reserved.

This microform edition is protected against unauthorized copying under Title 17, United States Code.

## UMI

300 North Zeeb Road Ann Arbor, MI 48103

© 1999

Brian Robert Frantz

ALL RIGHTS RESERVED

## APPROVED FOR MOSS LANDING MARINE LABORATORIES

#### SAN JOSE STATE UNIVERSITY

Monnety H. Coale

Dr. Kenneth Coale

Dr. Michael Foster

Dr. Ken Johnson

Kasy,a March

Dr. Michaele Kashgarian

APPROVED FOR THE UNIVERSITY

William Fish

#### ABSTRACT

#### Growth Rate and Potential Climate Record From a Rhodolith Using <sup>14</sup>C AMS

By Brian R. Frantz

Rhodoliths, calcareous red algae, create large and diverse habitats worldwide. Although these plants are ecologically important, little is known about their growth rate. The growth rate for an individual rhodolith, *Lithothamnium crassiusculum*, from the southern Gulf of California was determined through <sup>14</sup>C analysis using Accelerator Mass Spectrometry (AMS). Growth rate was determined by locating an increase in radiocarbon within the carbonate matrix due to cold war atmospheric nuclear weapons testing and comparing it to the radiocarbon record of a coral (*Porites panamensis*) with known growth rate. The comparison of radiocarbon from this coral with the radiocarbon record of the rhodolith indicates a growth rate of a 0.6 mm/yr. The  $\Delta^{14}$ C record suggests <sup>14</sup>C analysis may identify large past climatic events. The ability to determine past climate changes through AMS <sup>14</sup>C analysis of rhodoliths would increase the geographic range of available climate records from the tropics to the entire global ocean.

#### ACKNOWLEDGEMENTS

I would like to thank Dr. John Southon, Dr. Michaele Kashgarian, Dr. Tom Brown, and Dr. Tom Guilderson at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory for providing laboratory facilities and expert advice for the <sup>14</sup>C analysis, Dr. Howie Spero at the University of California, Davis for providing the Mass Spectrometer and laboratory facilities for the <sup>18</sup>O analysis, H. Reyes Bonilla and R. Riosmena-Rodriguez from the Universidad Autonoma de Baja California Sur (UCABS) for providing collection permits and assistance in collecting the coral and rhodolith analyzed in this study, and my graduate advisors Dr. Kenneth Coale, Dr. Mike Foster, Dr. Ken Johnson from Moss Landing Marine Laboratories and Dr. Michaele Kashgarian from Lawrence Livermore National Laboratory for advice in both the analysis and presentation of data.

## Table of Contents

Introduction	1
Methods	5
Results	10
Growth Rate Determination	11
Discussion	13
Figures	19
References	23
Appendix A	26

#### INTRODUCTION

Rhodoliths occupy large areas of the world's oceans, dominating diverse and ecologically important communities (Bosence 1983. Foster et al. 1997). However little is known about the rate at which these communities develop, their rate of recovery after natural or anthropogenic disturbances, their contribution to carbonate sediments, or their effects on the global carbon budget. Because some rhodoliths apparently grow slowly and are long lived they may also provide information on past oceanic conditions. These plants deposit carbonate as they grow which contains an isotopic record reflecting environmental conditions. In their 1983 study of coral, Druffel and Suess found that the amount of <sup>14</sup>C deposited as a part of the total carbon in carbonate organisms is proportional to the <sup>14</sup>C of the ocean water surrounding the organism, and that ocean water <sup>14</sup>C varies with water mass. This type of variation is also found in the carbonate of rhodoliths and can potentially be used as a record of past climates in older living rhodoliths.

Rhodoliths are found in many locations and environments around the world ranging from polar deep water to tropical shallows (Bosence 1983) (Fig. 1). The subtropical region of the Gulf of California where the rhodolith *Lithothamnium crassiusculum* (Foslie) L. R. Mason, the main focus of this study, was collected has a variety of rhodolith habitats ranging from 1-25 m deep beds in tidal channels to shallow, rocky habitats with mild surf (Foster et al. 1997). Rhodolith beds in these habitats can occur over many square kilometers and can cover 100% of the subtidal habitat (Foster et al. 1997). Rhodoliths provide habitat for organisms that would not otherwise be present, especially other macroalgae, crustaceans, sea stars, anemones, and molluscs. These organisms also comprise extensive fossil beds throughout the terrestrial portions of Baja California (Steller and Foster 1995; Foster et al. 1997).

Examination with a dissecting microscope showed growth patterns in the rhodolith, Lithothamnium crassiusculum, that were similar to other nongeniculate coralline red algae as described in Woelkerling (1988). The rhodolith had a vegetative thallus consisting of individual protuberances (branches) of monomerous filaments that produce a radial organization (Woelkerling 1988). The outer (exposed) surface of the plant consists of epithallial cells that convert to monomerous filaments as the plant continues to grow, creating new layers of epithallial cells on its outer surface. In L. *crassiusculum*, all but the tips of branches appear to have determinant growth; branch width from the rhodolith center to outer surface remains constant at 0.5-1.0 cm while the branch elongates. Calcification of the coralline red algae occurs at the formation of the monomerous filaments, leaving the conceptacles as the only remaining organic structure within the plant (Woelkerling 1988) and providing a carbonate growth axis which can be analyzed for changing <sup>14</sup>C over the life span of the plant. The manner in which the thallus develops is well known, but the rate at which the carbonate matrix develops is poorly understood. Several laboratory and *in situ* studies have been conducted to determine this rate of development, but these studies were only able to provide data from

a limited portion of the plant's life due to slow growth of rhodoliths (e.g. Adey and McKibbin 1970; Adey and Vassar 1975; Potin et al. 1990).

Data on age and growth of rhodoliths will provide insight into the life histories of an ecologically important organism. The banding present due to changes in the carbonate density across the growth axis does not currently provide any information on age or growth because the plant lays down what appears to be multiple bands per year and the rate and timing of this development is unknown. Furthermore, other methods of dating such as <sup>210</sup>Pb:<sup>226</sup>Ra disequilibrium are not possible because the calcite matrix of these organisms will incorporate authigenic <sup>210</sup>Pb into the carbonate matrix. In addition some post formational migration of <sup>226</sup>Ra daughter products is known to occur. These characteristics of calcite deposition may cause <sup>210</sup>Pb:<sup>226</sup>Ra dating to produce potentially inaccurate ages.

Radiocarbon can be used as a tool to determine details about the lives of carbonate depositing organisms such as calcareous algae. <sup>14</sup>C is naturally produced by the interaction of cosmic rays with atoms in the upper atmosphere (Broecker and Peng 1982). Although conventional <sup>14</sup>C dating methods are not applicable in the study of growth (because <sup>14</sup>C half is > 5000 years) environmental changes in activity can provide bench marks in chronology which can be used to asses growth rate. Changes in atmospheric production of <sup>14</sup>C are reflected in the surface ocean as atmospheric CO<sub>2</sub> exchanges with the surface ocean. These changes can be observed by analyzing the <sup>14</sup>C of the CaCO<sub>3</sub> of the calcareous organisms (e.g. Druffel 1987). Anthropogenic effects cause fluctuating atmospheric <sup>14</sup>C concentrations that produce distinct time markers within biogenic

carbonate and these time markers allow information about the growth history of carbonate organisms such as rhodoliths to be determined.

Anthropogenic activities have contributed to the dilution of or addition to naturally produced atmospheric <sup>14</sup>C since 1850, the beginning of the industrial revolution. The burning of fossil fuels has increased the levels of <sup>12</sup>C, diluting natural levels of <sup>14</sup>C, while atmospheric nuclear weapons testing in the late 1950's and early 1960's increased the atmospheric levels of <sup>14</sup>C from 0 ‰ to over 900 ‰ resulting in an almost instantaneous spike of <sup>14</sup>C in the atmosphere which peaked in the early 1960's (Druffel and Suess 1983). This "bomb spike" raised levels of <sup>14</sup>C in surface ocean waters as early as 1958 when <sup>14</sup>C from nuclear weapons tests began to exchange with oceanic surface water in the Northern Hemisphere (Druffel 1987).

Bomb <sup>14</sup>C from the atmosphere has mixed into the surface waters in most of the world's oceans over the last 40 years, changing <sup>14</sup>C levels from pre-bomb levels of approximately -50‰ to over 200‰ after the weapons testing (Ostlund and Niskin 1970). The changes in atmospheric <sup>14</sup>C recorded by carbonate organisms can thus be used as distinct time markers over the organism's life span. In this paper, the discovery of anthropogenic time markers created by changes in atmospheric <sup>14</sup>C, along with differences in <sup>14</sup>C between the water masses in which the red calcareous alga, *Lithothamnium crassiusculum*, grows, were used in conjunction with <sup>14</sup>C measurements and <sup>18</sup>O measurements from a coral located in close proximity to develop a growth rate for the plant. <sup>14</sup>C measurements from the rhodolith were compared to <sup>14</sup>C measurements

from the coral based on previous research showing banded corals are good recorders of changing radiocarbon levels in the surface ocean of the Pacific (Druffel 1987).

In this paper the growth rate of *Lithothamnium crassiusculum* will be determined using accelerator mass spectrometry (AMS) analysis of <sup>14</sup>C along a transect across the carbonate thallus to provide insight into the development and life history of these calcium carbonate accreting plants. The potential to develop a record of past climatic changes was also explored.

#### METHODS

To characterize changes in isotopic levels a total of two hundred and six samples were analyzed from an individual coral head, *Porites panamensis* Verill, and an individual rhodolith, *Lithothamnium crassiusculum*, from the Gulf of California directly west of La Paz, Baja California Sur. All samples for isotopic analyses were taken along a radial transect of the growth axis in the CaCO<sub>3</sub> matrix of both organisms. Isotopic analysis for <sup>14</sup>C was performed on both the rhodolith and coral samples, and <sup>18</sup>O analysis were performed on the coral. <sup>18</sup>O measurements were made using stable isotope mass spectrometry and <sup>14</sup>C measurements were made using accelerator mass spectrometry.

## CORAL ANALYSIS

The <sup>18</sup>O analysis was performed to identify seasonal cycles of sea surface temperature changes and data were used to identify an annual growth rate of the coral (Weber and Woodhead 1972). These annual cycles of temperature cause changes in <sup>18</sup>O concentration in the surface ocean. The determination of the annual temperature cycles through <sup>18</sup>O analysis allowed for the determination of a growth rate for the coral, *Porites* 

*panamensis*, which was collected in June, 1997 using SCUBA from Bahia San Gabriel, Isla Espiritu Santo, east of La Paz, Baja California Sur (B.C.S.) (Fig. 1). The coral measured 32 cm in diameter and was located 50 meters from shore in a protected lagoon at a depth of 3 m.

In order to identify sub-annual changes of <sup>18</sup>O eighty-three samples were taken from the coral head sampling every 2.3 mm using a 350  $\mu$ m burr driven by a hand held DREMEL<sup>TM</sup> tool. Approximately 10-50  $\mu$ g of carbonate material was removed from the carbonate matrix of the coral growth axis. Each sample was loaded into a sample boat and placed into the stable isotope mass spectrometer. Samples were dissolved in phosphoric acid under the control of the mass spectrometer auto sampler and the CO<sub>2</sub> gas released from the carbonate material was analyzed for <sup>18</sup>O content. <sup>18</sup>O values are reported in standard delta notation in units of ‰ normalized to Pee Dee Belemite shown in equation 1.1(Hoefs 1980).

1.1 
$$\delta^{18}O = [({}^{18}O/{}^{16}O)sample - ({}^{18}O/{}^{16}O)standard] * 1000$$
$$({}^{18}O/{}^{16}O)standard$$

To characterize changes in <sup>14</sup>C over the life span of the coral a total of fortythree samples were taken for <sup>14</sup>C analysis. The first sample was taken at the outer most edge of the living surface and the last sample was taken at the most interior point of the coral head (approximately at the attachment point). Samples were taken every 5 mm using a hand held DREMEL<sup>TM</sup> tool with an attached grinding bit. Approximately 10 mg of CaCO<sub>3</sub> was removed at each sample position and weighed into an individual Vaccutainer<sup>TM</sup> blood vial. Each Vaccutainer<sup>TM</sup> was then evacuated and 1 mL of 85% phosphoric acid was injected into each vial using a 10 mL Hamilton<sup>TM</sup> syringe and 26 gauge needle in order to dissolve the CaCO<sub>3</sub>. The sample vials were then placed on a heating block at 95° C to aid the dissolution of CaCO<sub>3</sub>. CO<sub>2</sub> gas from the dissolved carbonate was released through a sample port into an evacuated graphite reduction line via a 26-gauge needle. Each gas sample is then combined with a cobalt catalyst and two times the volume of CO<sub>2</sub> gas in hydrogen gas, and heated to a temperature of 570° C for seven hours (Vogel et al. 1987; Vogel et al. 1984). The cobalt catalyst drives the formation of carbon graphite with a byproduct of H<sub>2</sub>O (CO<sub>2</sub>+2H<sub>2</sub>→C+2H<sub>2</sub>O). The water is removed from the reaction using a dry-ice/isopropyl cold trap, leaving graphite on the catalyst that is then compressed into aluminum AMS targets and analyzed for <sup>14</sup>C using AMS.

All samples analyzed for <sup>14</sup>C content using AMS were measured along with standards and <sup>14</sup>C-free materials. Background levels of radiocarbon were identified using a <sup>14</sup>C free material from the Third International Radiocarbon Comparison (tiri-calcite; Gulliksen and Scott 1995). Oxalic Acid-1, the primary standard reflecting more contemporary levels of radiocarbon (Stuiver and Polach 1977), was also used.

 $\Delta^{14}$ C values that reflect <sup>14</sup>C/total C ratios were calculated from <sup>14</sup>C/<sup>13</sup>C ratios determined through AMS analysis for each sample.  $\Delta^{14}$ C is calculated through equation 2.1 (Stuiver and Polach 1977).  $\Delta^{14}$ C the ‰ deviation of <sup>14</sup>C activity from 19<sup>th</sup> century

wood used to report <sup>14</sup>C measurements and results for AMS (Stuiver and Polach 1977). The reporting of <sup>14</sup>C measurements as  $\Delta^{14}$ C corrects for both the fractionation of the heavier isotope from vital effects during uptake and the change of <sup>14</sup>C due to isotopic decay within standard materials (Stuiver and Polach 1977). <sup>14</sup>C/<sup>13</sup>C AMS ratios are related to the term A<sub>sn</sub>/A<sub>on</sub> in Stuiver and Polach (1977) by equation 2.2 (Brown 1994).

2.1 
$$\Delta^{14} C = \begin{bmatrix} A_{sn} \\ A_{on} e^{\lambda(y-1950)} & -1 \end{bmatrix} 1000 \%$$

$$2.2 \quad \frac{A_{sn}}{A_{on}} = \frac{1}{0.95} \left[ \frac{1 + (-25/1000)}{1 + (-19/1000)} \right]^2 \left[ \frac{1 + (-19/1000)}{1 + (\delta 13C/1000)} \right] \frac{(14/13)_{sample}}{(14/13)_{standard}}$$

In equation 2.1,  $A_{sn}/A_{on}$  is the activity of the unknown sample normalized to a  $\delta^{13}$ C of -25 and age corrected for the decay of the standard OX-1 since 1950 divided by the activity of the standard normalized to a  $\delta^{13}$ C of -19 and a correction of 0.95 so OX-1 will reflect 1890 wood radiocarbon levels.  $\lambda$ =1/8267 yr and y= year of measurement. This corrects for the decay of the primary standard OX-1 since 1950 to the time of measurement. Equation 2.2, (1/0.95) is one over the internationally accepted radiocarbon dating reference (95% the activity in, 1950), NBS oxalic acid (Stuiver and Polach 1977),

 $[1+(-25/1000)/1+(-19/1000)]^2$  is the conversion of the unknown sample to a  $\delta^{13}$ C of -25 and the conversion of the standard (oxalic acid-1)  $\delta^{13}$ C to -19, and

 $[1+(-19/1000)/1+(\delta 13C/1000)]$  is the standard with a  $\delta^{13}$ C value of -19 over the unknown sample  $\Delta^{14}$ C values reported in this paper do not include correction for decay of sample  $^{14}$ C between the time of carbonate deposition to the time of analysis. The absence of this correction has no affect on the data analysis.

#### **RHODOLITH ANALYSIS**

A rhodolith, *Lithothamnium crassiusculum*, with a radius of approximately 5 cm was collected in October, 1994 off the coast of La Paz, B.C.S. in approximately 4 m of water using SCUBA (Fig. 1). The rhodolith was on a rocky substrate exposed to open ocean conditions of the Gulf of California.

To determine <sup>14</sup>C changes along the growth axis of the rhodolith a total of 79 <sup>14</sup>C measurements were performed using AMS on three separate branches of a single rhodolith. Samples from the first two branches measured were analyzed in pilot studies to identify the presence of pre and post bomb <sup>14</sup>C and to ensure data reproducibility. The third branch was sampled every 1 mm to characterize annual <sup>14</sup>C changes over the plant's entire growth period. The latter sampling produced 52 samples taken along a transect from the most interior portion of the rhodolith (at the origin of growth) to the most exterior portion of the branch (living surface of the plant). Ten mg of CaCO<sub>3</sub> were removed from each position sampled using a 350  $\mu$ m burr attached to a hand held DREMEL<sup>TM</sup> tool. The powdered carbonate material was processed in the same manner as the carbonate material removed from the coral samples analyzed for <sup>14</sup>C.

#### RESULTS

#### CORAL $\delta^{18}O$

The  $\delta^{18}$ O measurements from the coral reflect annual variations in sea surface temperature over the entire growth span (Weber and Woodhead 1972). The temperature change determined through  $\delta^{18}$ O analysis in the coral ( $\approx 6^{\circ}$  C) agree with direct temperature measurements made by IGOSS at 110.5W 24.5N ( $\approx 10^{\circ}$  C), off the east coast of La Paz, B.C.S (Fig. 2). Although the range of  $\delta^{18}$ O measurements from the coral reflect the annual fluctuation of sea surface temperature off the coast of La Paz, a clear record of annual cycles was not present (Fig. 2). This irregular record probably reflects the fact that the coral was growing in close proximity to shore within a protected lagoon and may have been influenced by terrestrial effects as well as being far from open ocean conditions. Because a consistent annual record was not present, four cycles were identified within the coral CaCO<sub>3</sub> record and assumed to represent annual cycles of <sup>18</sup>O (Fig. 2). The four cycles used to determine annual growth occurred over distances of 11.5 mm, 13.5 mm, 13.5 mm, and 13.5 mm of deposited carbonate (Fig. 2). CORAL  $\Delta^{14}C$ 

The  $\Delta^{14}$ C analysis indicated a radiocarbon peak of 42 ‰ within the coral at 100 mm beneath the surface (Fig. 3a). The  $\Delta^{14}$ C plateaued between 55 mm and 200 mm below the living surface. The  $\Delta^{14}$ C values of the plateau, ranging from 0‰ to 42 ‰, identify the peak as being a post-bomb increase of <sup>14</sup>C. The 5 mm sampling interval resulted in a  $\Delta^{14}$ C record that displayed <sup>14</sup>C changes on a sub-annual level.

## RHODOLITH $\Delta^{14}$ C

In all three rhodolith branches analyzed <sup>14</sup>C displayed pre- and post-bomb carbon levels of the surface ocean from the Gulf of California (Fig. 3b). Pre-bomb levels (less than -60 ‰) extended from 1 mm to 30 mm from the origin of growth. An abrupt increase of <sup>14</sup>C to +40 ‰ due to the atmospheric weapons testing was observed between 31 mm and 40 mm, and post-bomb levels from 40 mm to (surface). Samples from 28 mm, 45mm, and 51 mm (from the origin of growth) were analyzed two times to insure the reliability of low  $\Delta^{14}$ C values, and gave the same results.

#### **GROWTH RATE DETERMINATION**

The growth rate of the rhodolith was determined by using  $\Delta^{14}C$  data to characterize the <sup>14</sup>C increase due to nuclear weapons testing. The time the atmospheric increase of <sup>14</sup>C began to exchange with the surface ocean has been determined through  $\Delta^{14}C$  analysis of corals to have occurred between 1958 and 1966 (Druffel and Suess 1983). The abrupt increase of <sup>14</sup>C due nuclear weapons testing begins at 31 mm from the origin of growth in the rhodolith. If the increase in  $\Delta^{14}C$  observed in the rhodolith is assumed to have occurred during this same time span (1958-66) and a collection date of 1994 is known, a growth rate of  $0.6 \pm 0.1$  mm/yr is calculated by dividing the distance of carbonate deposition by time. This would suggest that the atmospheric bomb <sup>14</sup>C began exchanging with the surface waters of the Gulf of California almost instantaneously which allowed it to be used to determine growth and age of calcareous organisms in the Gulf.

The growth rate determined by analysis of the<sup>14</sup>C increase due to nuclear weapons testing was confirmed by matching radiocarbon measurements and known dates based on the  $\delta^{18}$ O determined growth from the coral to the  $\Delta^{14}$ C record of the rhodolith. The average growth during the four temperature induced  $\delta^{18}$ O cycles that were identifiable in the coral record was 13 mm/yr. Although the coral record was not consistent, the four cycles identified in the  $\delta^{18}$ O record approximately reflect actual SST measurements and are assumed to be representative of an annual cycles. This growth rate was then applied to the  $\Delta^{14}$ C record produced from the same coral sample. The time of occurrence and duration of the  $\Delta^{14}$ C peak were determined based on collection date (1997), the location of the  $\Delta^{14}$ C peak within the coral (55 mm-200 mm below the living surface), and a 13 mm/yr growth rate. The  $\Delta^{14}$ C peak was thus identified, as a post-bomb peak that occurred between 1982 and 1992 (Fig 3a). This ten year period of the  $\Delta^{14}$ C record from the coral was used to establish a time scale for the  $\Delta^{14}C$  record produced from the rhodolith instead of the rapid increase of <sup>14</sup>C due to nuclear weapons testing because the coral contained no pre-bomb data due to its young age. The  $\delta^{18}$ O and  $\Delta^{14}$ C data from the coral provided sufficient information to determine an age model for the coral that could be applied to the rhodolith.

The  $\Delta^{14}$ C peak identified in the coral record is consistent with a post-bomb plateau of <sup>14</sup>C in the rhodolith. This peak was identified in the  $\Delta^{14}$ C record produced from the rhodolith between 45 mm and 51 mm from the origin of growth (Fig. 3b). The postbomb increase of <sup>14</sup>C observed in the coral was fitted to the post-bomb <sup>14</sup>C increase in the rhodolith based on the decrease from 20 ‰ to below 0 ‰ on the interior edge (oldest portion) of the peak in both the coral and the rhodolith records. Both  $\Delta^{14}$ C records also display rises to above 30 ‰ and then declines to approximately 0 ‰ at the most recent portions of the organisms (Fig. 4). The  $\Delta^{14}$ C peak in both the coral and the rhodolith were correlated with a coefficient of R=0.623 (using AnalySeries<sup>TM</sup> 1.0a7, 1996 statistical mapping program), indicating a high probability of properly identifying the same  $\Delta^{14}$ C peak in two separate  $\Delta^{14}$ C records.

The growth rate of the rhodolith was confirmed using the time of occurrence of a  $\Delta^{14}$ C peak identified in both the rhodolith and in the coral. The duration of the peak was then compared to the total carbonate growth in the rhodolith that occurred during the  $\Delta^{14}$ C peak (10 years and 6 mm) and a growth rate determined by dividing the two,  $0.6 \pm 0.1$  mm/yr. This agrees well with the growth rate determined by identifying a known time for the rapid increase of bomb <sup>14</sup>C. The error (~15 %) was assigned based on three sampling uncertainties: (1) the sample interval overlapped the average growth per year in the rhodolith, (2) the  $\delta^{18}$ O variation was not clearly resolved for every year of the coral, and (3) the application of the coral  $\delta^{18}$ O based growth rate to the coral  $\Delta^{14}$ C record.

#### DISCUSSION

The rhodolith axial growth rate combined with the total length of the rhodolith branch gives an age of approximately 86 years. The largest individual so far found at the collection site was approximately 12 cm in diameter indicating a maximum age of approximately 100 years. The growth rate is in close agreement with independent measurements of the field growth of plants tagged with Alizarin red (0.63 mm/yr; M.

Georgina-Rivera personal communication) as well as growth rates for other nongeniculate coraline algae from several laboratory and field experiments. Adey and McKibbin (1970) determined a maximum growth rate under ideal conditions for Lithothamnion corallioides (Crouan et Crouan) to be 1.9  $\mu$ /day which, if sustained year round, would give a growth rate of 0.69 mm/yr. Potin et al (1990) found L. corallioides increased at 12%/year, which also agrees well with growth rate for L. crassiusculum, determined through AMS. Adey and Vassar (1975) showed growth rates for a variety of rhodoliths and encrusting corallines to range from 0.3-4 mm/yr. Although these experiments were conducted on a variety of species they show that the growth rate for L. crassiusculum determined in this study fits within a range determined from several independent studies. Two additional studies have determined rhodolith growth rates using <sup>14</sup>C AMS between 0.01-0.09 mm/yr with the majority at 0.03 mm/yr (Reid and MacIntyre 1988; Littler et al. 1991). These low growth rates are inconsistent with this study, and may reflect differences in interpretation. These investigators used an age determined for the sample by <sup>14</sup>C analysis and then divided the distance of carbonate deposition by the radiocarbon age to get a growth rate. <sup>14</sup>C in oceanic water, in contrast to the atmosphere, is affected by the reservoir age of the water which will cause radiocarbon dates from the ocean to appear older than they actually are (Stuiver and Braziunas 1993). This reservoir age must be accounted for if actual dates are to be applied to an organism through <sup>14</sup>C analysis, otherwise, older ages will be incorrectly assigned to the organism. The growth rate in this study used <sup>14</sup>C as an oceanic tracer, not as a determinant of age.

Several locations within the  $\Delta^{14}$ C record of the rhodolith potentially provide additional evidence in support of the determined growth rate, but also may provide information about past climatic events and their rates of occurrence. Three depressions within the rhodolith  $\Delta^{14}$ C record were identified as potentially being caused by El Niño Southern Oscillation (ENSO) events in 1957, 1982, and 1992 (Fig. 3 b).

Three large depressions in the  $\Delta^{14}$ C record of the rhodolith are consistent with the change in oceanic currents at the entrance of the Gulf of California during ENSO events (Bray and Robles 1991). The first large  $\Delta^{14}$ C depression at the base of the bomb spike is thought to be the result of a large El Niño event that occurred in 1957 and the two postbomb depressions are the result of two large El Niño events occurring in 1982 and 1992 (NOAA-CIRES). The normal source water for the southern Gulf of California is a 500 m deep layer which originates from tropical surface and subsurface water in the North Equatorial Current (Bray and Robles 1991; Baumgartner and Christensen 1985). During ENSO events the source water switches from the tropical North Equatorial Current to the California Current and Pacific deep-water. These El Niño events appear to be displayed as depletions in the rhodolith  $\Delta^{14}$ C record at 1957, 1982 and 1992. The <sup>14</sup>C depletions are due to lower levels of radiocarbon in the California Current that is mixed with upwelled Pacific deep and intermediate water at the mouth of the Gulf of California in comparison with tropical surface water (Bray and Robles 1991; Goodfriend and Flessa 1997). This signal also appears in data sets produced from shells collected in both the California Current and the North Equatorial Current (Ingram and Southon 1997; Stuiver et al. 1986).

Given this association of <sup>14</sup>C with water mass, rhodoliths and long-lived nongeniculate corallines in general have the potential to be used as recorders of past climate conditions. This long life span along with wide distribution of rhodoliths could provide additional data for global climate models over a wider latitudinal range than corals. The ability to provide long histories of ocean climate conditions from a wide range of the world's oceans could help to understand how global climate has changed in the past, and could indicate potential changes in the future. The data presented above suggests that rhodoliths may be able to provide some of these much-needed data.

Along with their importance ecologically and as potential indicators of past climates determined through growth rate analysis, rhodoliths may also be an important component of global carbon sequestration. As the rhodolith deposits CaCO<sub>3</sub> it removes dissolved inorganic carbon from the ocean. The relationship between calcium carbonate formation and carbon sequestration, however, is not as straight forward as would be expected. Where as one might predict the reaction:

3.1 
$$Ca^{2+} + CO_3^2 \leftrightarrow CaCO_3 (s)$$

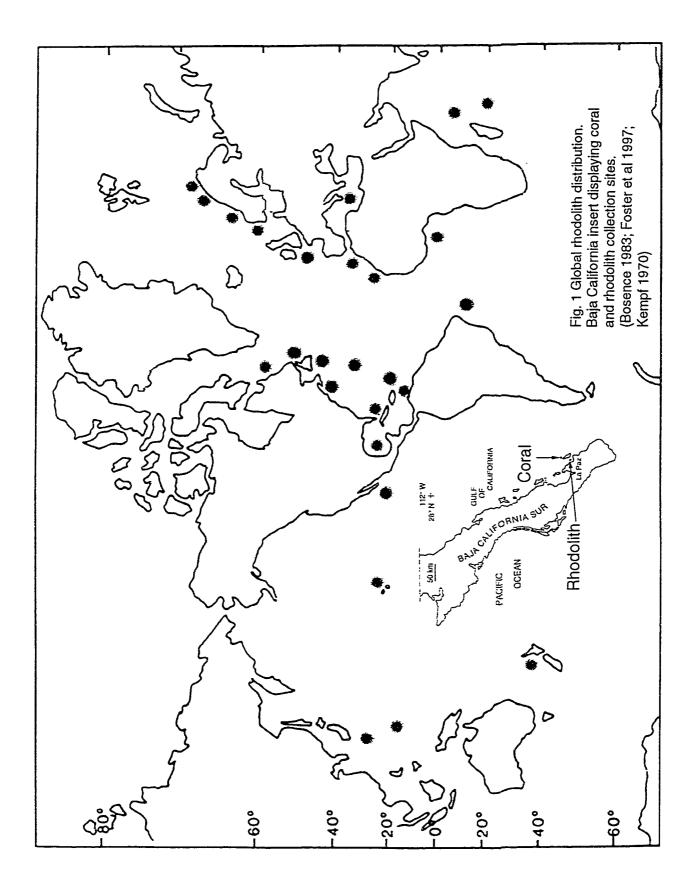
to describe this process, this is a common misconception. In fact the reaction described by Broecker and Peng (1982) is as follows:

3.2 
$$Ca^{2+} + 2(HCO_3) \leftrightarrow CaCO_3 (s) + H_2O + CO_2 (aq)$$

in which one molecule of  $CO_2$  is released for every molecule of  $CaCO_3$  precipitated. In this way the role of rhodolith growth has a double impact on carbon cycling. With rhodolith growth predominately occurring in shallow water the  $CO_2$  produced is rapidly released to the atmosphere. Furthermore, shallow deposition of calcium carbonate renders these deposits sensitive to environmental change such that redissolution of these formations could consume large quantities of CO<sub>2</sub>.

The presence of rhodolith beds world wide as well as extensive fossil rhodolith beds suggests rhodoliths may be an important part of the global carbon cycle (Foster et al. 1997). Conservative estimates of total area covered by rhodoliths (70,500 km<sup>2</sup>) from the Brazilian shelf (Kempf 1970) and the Gulf of California (Foster et al. 1997) were used to estimate total carbon sequestered by rhodoliths in these areas. A radius of 2.5 cm was used for an average rhodolith and 100% cover of rhodoliths on the bottom was assumed. With a growth rate of 0.6 mm/yr the change of volume per year would be dv/dt = 4.8cm<sup>3</sup>/yr/rhodolith. Assuming the carbonate matrix is calcite with a density of 2.71 g/cc along with a rhodolith porosity of 20% (estimated by visual inspection of an individual plant) gives an increase of 10.5 g of CaCO<sub>3</sub>/year/rhodolith. With CaCO<sub>3</sub> = 100 g/mol, each rhodolith deposits 0.1 mol C/yr/rhodolith, or 1.25 g C/yr/rhodolith sequestered. Assuming 100% cover in the estimated areas gives a total of 5 X  $10^8$  rhodoliths/km<sup>2</sup> and a total of 6.4 X  $10^8$  g C/yr/km<sup>2</sup>. Applying this to the estimated area of two rhodolith populations (70,500 km<sup>2</sup>), a total of 4.5 X  $10^{-2}$  GT C/yr would be sequestered. In consideration of equation 3.2, however, an equivalent amount of carbon would be released to the atmosphere as CO<sub>2</sub>. This estimate would increase perhaps by a factor of 10 if extrapolated globally. Some have estimated total terrestrial carbon uptake to equal <0.5 GT carbon (Sarmiento and Sundquist 1992). Thus, rhodoliths may be quite important to the global carbon cycle.

The use of AMS to analyze changing levels of <sup>14</sup>C over the growth axis of the rhodolith, *Lithothamnium crassiusculum*, has given several insights into the life history of the organism as well as its ecological importance. Changes in atmospheric <sup>14</sup>C due to nuclear weapons testing allowed the determination of a growth rate of  $0.6 \pm 0.1$  mm/yr. Along with the determination of a growth rate estimates of total carbon sequestration were produce. <sup>14</sup>C also gave insight into the potential use of rhodoliths and other calcareous algae as recorders of past climates. These factors suggest that rhodoliths not only play an important role in the present oceanic environment, but they may also provide data about how past environments have changed which in turn may give information on how the environment will change in the future.



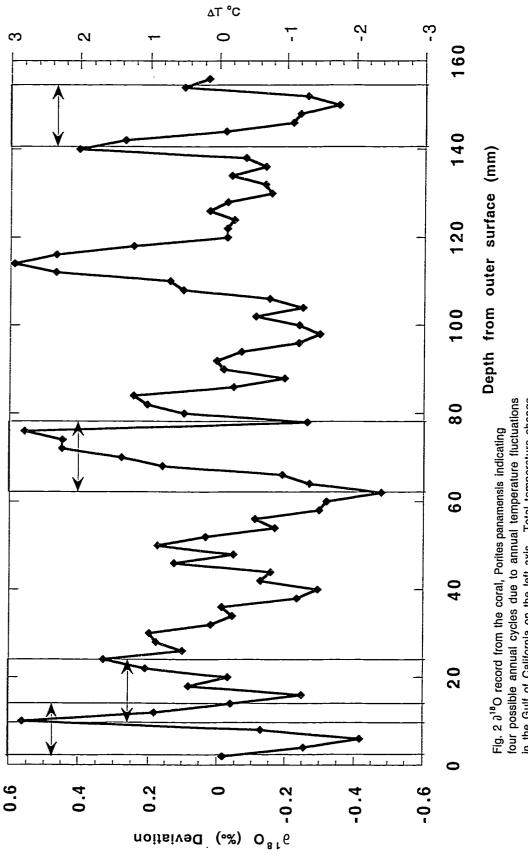


Fig. 2  $\partial^{18}$ O record from the coral, Porites panamensis indicating four possible annual cycles due to annual temperature fluctuations in the Gulf of California on the left axis. Total temperature change is indicated on right axis. Arrows and boxes denote annual cycles, Graph is the deviations from the best fit linear regression line for the data.

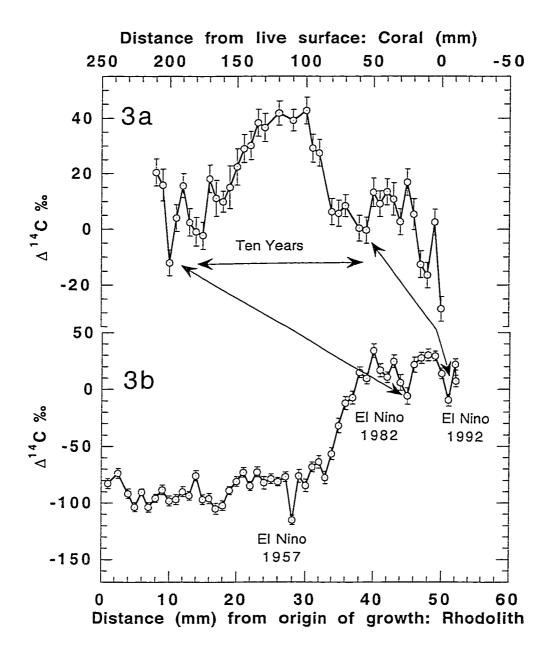
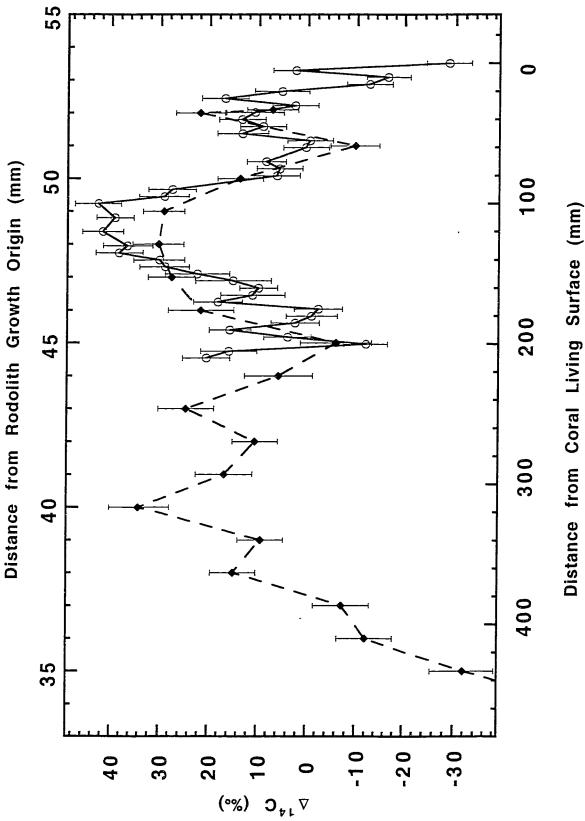


Fig. 3  $\Delta^{14}$ C histories for a coral and a rhodolith collected near La Paz. (a) Coral collected in 1997. (b) Rhodolith collected in 1994. Errors are derived from AMS measurement counting statistics



#### REFERENCES

- Adey, W. H. and D. L. McKibbin. 1970. Studies on the Maerl Species *Phymatolithon Calcareum* (Pallas) nov. comb. and *Lithothamnium corralloides* Crouan in The Ria de Virgo.Botanica Marina. 13: 100-106
- Adey, W. H. and M. Vassar. 1975. Colonization, Succession and Growth Rates of Tropical Crustose Coralline Algae (Rhodophyta, Cryptonemiales). Phycologia. 14: 55-69
- Baumgartner, T. R. and N. Christensen, Jr. 1985. Coupling of the Gulf of California to Large-scale Interannual Climatic Variability. Journal of Marine Research. 43: 825-848.
- Bosence, D.W.J. 1983. The Occurrence and Ecology of Recent Rhodoliths-A Review. p225-242. *In* Tadeusz, M. P. [eds]. Coated Grains. Springer-Verlag. Berlin Heidelberg.
- Bray, N.A. and J. M. Robles.1991. Physical Oceanography of the Gulf of California, p511-553. In Simoneit, B.R.T. &J.P. Dauphin [eds.], The Gulf of California and Peninsular Province of the Californias. Am. Assoc. Petr. Geol. Mem. 47.
- Broecker, W. S. and T.-H. Peng. 1982. Tracers in the Sea. Lamont-Doherty Geological Observatory.
- Brown, T. A. 1994 Radiocarbon Dating of Pollen by Accelerator Mass Spectrometry. Doctoral dissertation. University of Washington.
- Druffel, E.R.M. 1987. Bomb Radiocarbon in the Pacific: Annual and Seasonal Timescale Variations. Journal of Marine Research. 45: 667-698.
- Druffel, E.R.M. and H. E. Suess. 1983. On the Radiocarbon Record in banded Corals: Exchange Parameters and Net Transport of <sup>14</sup>CO<sub>2</sub> Between Atmosphere and Surface Ocean. Journal of Geophysical Research. 88: 1271-1280.
- Foster, M.S., R. Riosmena-Rodriguez, D. L. Steller, Wm. J. Woelkerling. 1997. Living Rhodolith Beds in the Gulf of California and their Implications for Paleoenvironmental Interpretation. Geological Society of America, Special Paper 318: 127-139.
- Goodfriend, G.A. and K W. Flessa. 1997. Radiocarbon Reservoir Ages in the Gulf of California: Roles of Upwelling and Flow from the Colorado River. Radiocarbon. 39: 139-148.

- Gulliksen, S and M. Scott . 1995. Report of the TIRI Workshop, Saturday 13 August 1994. Radiocarbon. 37: 820-821.
- Hoefs, J. 1980. Stable Isotope Geochemistry. Springer-Verlag, Berlin Heidelberg New York.
- IGOSS. Integrated Global Ocean Services System. Columbia University. http://iri.ldeo.columbia.edu/climate/monitoring/ipb/.
- Ingram, B. L. and J. R. Southon. 1997. Reservoir Ages in Eastern Pacific Coastal and Estuarine Waters. Radiocarbon 38: 573-582.
- Kempf, M. 1970. Notes on the Benthic Bionomy of the N-NE Brazilian Shelf. Marine Biology. 5: 213-224.
- Littler, M. M., D. S. Littler, M. D. Hanisak. 1991. Deep-water Rhodolith, Productivity, And Growth History at Sites of Formation and Subsequent Degradation. Journal of Experimental Marine Biology and Ecolology 150: 163-182.
- NOAA-CIRES. Climate diagnostic center, University of Colorado, Boulder. http://www.cdc.noaa.gov/ENSO/enso.mei\_index.html
- Ostlund, H. G and S. Niskin. 1970 Radiocarbon Profile in the North Pacific 1969 Geosecs Intercalibration Satation. Journal of Geophysical Research. 75: 7667.
- Potin, P., J. Y. Foc'h, C. Augris, J. Cabioch. 1990. Annual Growth Rate of the Calcareous Red Alga Lithothamnion corallioides (Corallinales, Rhodophyta) In the Bay of Brest, France. Hydrobiologia. 204/205: 263-267.
- Reid, R. P. and I. G. MacIntyre. 1988. Foraminiferal-Algal Nodules from the Eastern Caribbean: Growth History and Implications on the Value of Nodules as Paleoenvironmental Indicators. PALAIOS. 3: 424-435.
- Sarmiento, J. L. and E. T. Sundquist. 1992. Revised Budget for the Oceanic Uptake Of Antropogenic Carbon Dioxide. Nature. 356: 589-592
- Steller, D.L. and M. S. Foster. 1995. Environmental Factors Influencing Distribution and Morphology of Rhodoliths in Bahia Concepcion, B.C.S., Mexico. Journal of Experimental Marine Biology and Ecology. 194: 201-212.
- Stuiver, M. and T. F. Braziunas. 1993. Modeling Atmospheric <sup>14</sup>C Influences and <sup>14</sup>C Ages of Marine Samples to 10,000 BC. Radiocarbon. 35: 137-189.
- Stuiver, M., G. W. Pearson, T. Braziunas. 1986. Radiocarbon Age Calibration of Marine Samples Back to 9000 Cal Yr BP. Radiocarbon. 28: 980-1021

- Stuiver, M.H. and H. A.Polach. 1977. Discussion Reporting of 14C Data. Radiocarbon. 19:355-363.
- Vogel, J.S., D. E. Nelson, J. R. Southon. 1987. <sup>14</sup>C Background Levels in an Accelerator Mass Spectrometry System. Radiocarbon. 29: 323-333.
- Vogel, J.S., J.R.Southon., D. E. Nelson, T. A. Brown. 1984. Performance of Catalytically Condensed Carbon For Use In Accelerator Mass Spectrometry. Nuclear Instruments and Methods in Physics Research. B5: 289-293.
- Weber, J.N. and P. M. J. Woodhead. 1972. Temperature Dependence of Oxygen-18 Concentration in Reef Coral Carbonates. Journal of Geophysical Research. 77: 403-473.
- Woelkerling, W.J. 1988. The Coralline Red Algae: An Analysis of the Genera and Subfamilies of Nongeniculate Corallinaceae. Oxford University Press, London & Oxford.

### **APPENDIX** A

- 1a) δ<sup>18</sup>O (‰) isotope data from the coral *Porites panamensis*.
   Sample distance from live surface of the coral.
   Data from best fit linear regression displayed in Fig. 1.
   Change in Temperature displayed by the range of δ<sup>18</sup>O results.
- 2a) Δ<sup>14</sup>C (‰) data from the coral *Porites panamensis*.
   Sample ID.
   Sample distances from live surface of the coral.
- 3a) Δ<sup>14</sup>C (‰) data from the third rhodolith branch analyzed in *Lithothamnium crassiusculum*.
  Sample ID.
  Sample distance from the origin of growth.

#### Appendix 1a 2180 (‰) coral data

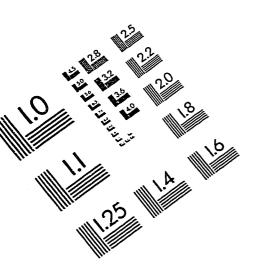
Depth from surface (mm)	ð180	Detrended	ΔT C	Depth from surface (mm)	ð180	Detrended	AT C
2.0	-4.14	-0.02	-0.08	80.0	-3.88	0.10	0.48
4.0	-3.89	-0.26	-1.28	82.0	-3.98	0.21	1.03
6.0	-3.72	-0.42	-2.08	84.0	-4.01	0.25	1.23
8.0	-4.00	-0.13	-0.63	86.0	-3.71	-0.04	-0.22
10.0	-4.68	0.56	2.81	88.0	-3.55	-0.20	-0.98
12.0	-4.29	0.18	0.91	90.0	-3.72	-0.02	-0.08
14.0	-4.06	-0.04	-0.19	92.0	-3.73	0.00	0.02
16.0	-3.84	-0.25	-1.24	94.0	-3.65	-0.07	-0.33
18.0	-4.16	0.08	0.40	96.0	-3.47	-0.24	-1.19
20.0	-4.04	-0.03	-0.15	98.0	-3.40	-0.30	-1.49
22.0	-4.27	0.21	1.05	100.0	-3.45	-0.24	-1.19
24.0	-4.38	0.33	1.65	102.0	-3.57	-0.11	-0.54
26.0	-4.14	0.10	0.50	104.0	-3.42	-0.25	-1.24
28.0	-4.21	0.18	0.89	106.0	-3.51	-0.15	-0.75
30.0	-4.22	0.20	0.99	108.0	-3.75	0.10	0.50
32.0	-4.03	0.02	0.09	110.0	-3.78	0.14	0.70
34.0	-3.96	-0.04	-0.21	112.0	-4.10	0.47	2.35
36.0	-3.98	-0.01	-0.07	114.0	-4.21	0.59	2.94
38.0	-3.75	-0.23	-1.17	116.0	-4.08	0.47	2.34
40.0	-3.68	-0.29	-1.47	118.0	-3.85	0.25	1.24
42.0	-3.84	-0.12	-0.62	120.0	-3.57	-0.02	-0.11
44.0	-3.80	-0.16	-0.78	122.0	-3.56	-0.02	-0.12
46.0	-4.07	0.12	0.62	124.0	-3.53	-0.04	-0.22
48.0	-3.89	-0.05	-0.23	126.0	-3.59	0.03	0.13
50.0	-4.10	0.17	0.87	128.0	-3.53	-0.02	-0.12
52.0	-3.95	0.03	0.17	130.0	-3.39	-0.15	-0.77
54.0	-3.74	-0.17	-0.84	132.0	-3.40	-0.14	-0.68
56.0	-3.79	-0.11	-0.54	134.0	-3.49	-0.04	-0.18
58.0	-3.59	-0.30	-1.49	136.0	-3.38	-0.14	-0.68
60.0	-3.56	-0.32	-1.59	138.0	-3.43	-0.08	-0.38
62.0	-3.39	-0.48	-2.40	140.0	-3.90	0.40	2.01
64.0	-3.59	-0.27	-1.35	142.0	-3.76	0.27	1.36
66.0	-3.66	-0.19	-0.95	144.0	-3.46	-0.02	-0.09
68.0	-4.00	0.16	0.80	146.0	-3.25	-0.22	-1.09
70.0	-4.11	0.28	1.39	148.0	-3.22	-0.24	-1.20
72.0	-4.27	0.45	2.24	150.0	-3.10	-0.35	-1.75
74.0	-4.26	0.45	2.24	152.0	-3.18	-0.26	-1.30
76.0	-4.36	0.56	2.79	154.0	-3.53	0.10	0.50
78.0	-3.53	-0.26	-1.31	156.0	-3.45	0.03	0.15

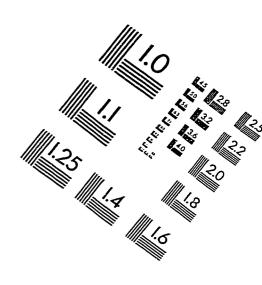
•

Sample ID	∆14C(‰)	±	Distance from Live surface
LPC-1	-28.63	4.45	0
LPC-2	2.53	4.67	5
LPC-3	-16.48	4.58	10
LPC-4	-12.6	4.79	15
LPC-5	5.32	5.53	20
LPC-6	16.89	4.73	25
LPC-7	2.63	4.67	30
LPC-8	10.83	5.84	35
LPC-9	13.4	4.68	40
LPC-10	9.16	4.65	45
LPC-11	13.28	5.16	50
LPC-12	-0.4	4.63	55
LPC-13	0.39	4.64	60
LPC-15	8.47	3.96	70
LPC-16	5.72	4.66	75
LPC-17	6.3	4.67	80
LPC-19	27.52	4.76	90
LPC-20	29.16	5.01	95
LPC-21	42.73	4.83	100
LPC-23	39.2	3.92	110
LPC-25	41.75	4.29	120
LPC-27	36.6	5.1	130
LPC-28	38.36	4.92	135
LPC-29	30.1	5.13	140
LPC-30	29.02	5	145
LPC-31	22.43	6.59	150
LPC-32	15.1	7.69	155
LPC-33	9.91	3.81	160
LPC-34	11.13	6.53	165
LPC-35	18.16	4.98	170
LPC-36	-2.26	4.88	175
LPC-37	-0.89	5.19	180
LPC-38	2.46	4.91	185
LPC-39	15.68	4.31	190
LPC-40	4	4.83	195
LPC-41	-12.05	4.61	200
LPC-42	15.89	5.74	205
LPC-43	20.51	4.82	210

•

Sample ID	∆14C (‰)	±	Distance from orign of growth (mm)
2R:1mm	-82.73	4.38	1
2R:2-3mm	-73.66	4.39	2.5
2R:4mm	-91.76	4.25	4
2R:5mm	-103.52	4.2	5
2R:6mm	-90.35	3	6
2R:7mm	-103.66	4.15	7
2R:8mm	-95.78	3.71	8
2R:9mm	-88.29	4.4	9
2R:10mm	-98.17	4.36	10
2R:11mm	-96.88	4.36	11
2R:12mm	-89.96	4.4	12
2R:13mm	-93.47	3.89	13
2R:14mm	-75.83	4.49	14
2R:15mm	-96.79	4.18	15
2R:16mm	-95.96	4.61	16
2R:17mm	-105.02	4.94	17
2R:18mm	-102.28	4.17	18
2R:19mm	-89.01	3.55	19
2R:20mm	-80.89	4.29	20
2R:21mm	-72.99	4.23	21
2R:22mm	-84.8	3.91	22
2R:23mm	-72.6	4.37	23
2R:24mm	-82.14	5.43	24
2R:25mm	-78.71	4.33	25
2R:26mm	-81.19	3.63	26
2R:27mm	-76.97	4.33	27
2R:28mm	-115.15	4.15	28
2R:29mm	-76.05	5.68	29
2R:30mm	-84.6	5.56	30
2R:31mm	-68.13	4.24	31
2R:32mm	-63.79	5.66	32
2R:33mm	-77.48	5.59	33
2R:34mm	-56.42	5.23	34
2R:35mm	-31.9	6.39	35
2R:36mm	-12.06	5.76	36
2R:37mm	-7.21	5.72	37
2R:38mm	14.89	4.63	38
2R:39mm	9.33	4.62	39
2R:40mm	34.07	6.11	40
2R:41mm	16.77	5.75	4 1
2R:42mm	10.48	4.6	42
2R:43mm	24.62	5.7	43
2R:44mm	5.78	6.95	44
2R:45mm	-5.92	7.26	45
2R:46mm	21.63	6.68	46
2R:47mm	27.58	4.7	47
2R:48mm	30.3	5.12	48
2R:49mm	29.26	4.19	49
2R:50mm	13.74	4.66	50
2R:51mm	-9.64	5.09	51
2R:52mm 2R:outside	21.93 7.24	4.98 5.2	52 53
	1.24	5.2	55





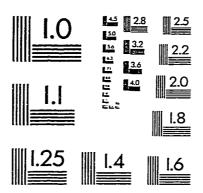
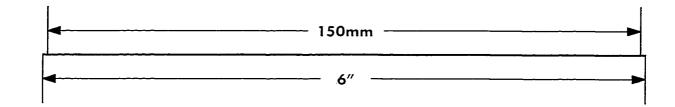
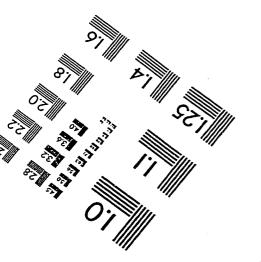


IMAGE EVALUATION TEST TARGET (QA-3)







© 1993, Applied Image, Inc., All Rights Reserved

