

MASS SPECTROMETRIC ^{14}C AND U-Th MEASUREMENTS IN CORAL

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ABSTRACT. We discuss U-Th and ^{14}C measurements in coral. Samples with U-Th dates in excess of 50 ka BP were chosen for study. Some bulk samples from this group have measurable ^{14}C dates, which range from 30 ka to 43 ka BP. These can be explained by 0.5–2.5% contamination by modern carbon. This small amount of contamination can produce significant offsets in ^{14}C dates of coral samples older than ~10 ka. It may be undetectable in X-ray powder diffraction patterns. We describe a sample pretreatment that removes the modern carbon by selective dissolution and produces accurate ^{14}C dates.

INTRODUCTION

Mass spectrometric determinations of uranium and thorium (U-Th) isotope abundances now permit precise dating of coral in the time range of 50 yr to about 500 ka BP (Edwards *et al.* 1987). Ages of coral determined by the U-Th method are not affected by factors that produce secular variations in ^{14}C . Thus, U-Th dating can provide an independent time scale to which radiocarbon measurements can be compared. Bard *et al.* (1990a) have produced U-Th - ^{14}C calibration curves from Barbados, and, more recently, from Mururoa Atoll, French Polynesia (Bard *et al.* 1991). In Barbados, $\Delta^{14}\text{C}$ values were 400–500‰ higher than values calculated by ^{14}C decay equations, for the period 18–22 ka BP. The authors suggested that changes in the Earth's magnetic field during this period could account for these values.

Stuiver *et al.* (1991) discuss the relationship between the Barbados U-Th - ^{14}C calibration curve and a composite tree-ring and varve chronology. The composite chronology is based on macrofossil dates from Swiss lakes (Zbinden *et al.* 1989), a floating preboreal pine tree-ring chronology (Becker & Kromer 1986; Stuiver *et al.* 1991), and the Swedish varve chronology (Stuiver 1970, 1971). The Barbados U-Th - ^{14}C calibration curve differs by as much as 200‰ in the floating portion of the chronology, between 14 ka and 12.3 ka cal BP. The correspondence is much better however, from 11.5 ka cal BP to present (Becker, Kromer & Trimborn 1991).

The purpose of this work is to study background contributions for U-Th - ^{14}C measurements of coral. We identify potential problems in making ^{14}C measurements of coral, and demonstrate that sample contamination can be overcome by dissolving and discarding a portion of the coral prior to analysis. This technique has been employed by Bard *et al.* (1990b).

METHODS

Samples

We selected five samples for analysis (Table 1). Based on U-Th ages, all of the samples are older than 50 ka. Samples AFS-10 and AFS-12 are from the Rendezvous Hill Terrace on Christ Church Ridge, Barbados (Bender *et al.* 1979). They have been dated previously at 125.7 and 123.0 ka BP (Edwards *et al.* 1987). Samples KWA-Q-1, FRT-F-1 and SIAL-E-1 are from the Huon Peninsula, Papua, New Guinea (Chappell 1974; Bloom *et al.* 1974). All of the samples were well preserved, with corallites intact.

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TABLE 1. Sample Descriptions

Sample	Taxonomy	Locality
AFS-1	<i>Acropora palmata</i>	Christ Church Ridge, Barbados
AFS-12	<i>Acropora palmata</i>	Christ Church Ridge, Barbados
SIAL-E-1	<i>Montipora</i>	Huon Peninsula, Papua, New Guinea
FRT-F-1	<i>Porites lutea</i>	Huon Peninsula, Papua, New Guinea
KWA-Q-1	<i>Gardineroseris planulata</i>	Huon Peninsula, Papua, New Guinea

AMS Sample Preparation and Analysis

Bulk coral samples were prepared for AMS analysis in the following manner. About 15 mg of sample were placed in a vacuum line, and the system was evacuated. After pumping for 1 h, the sample was dissolved in 70% H₃PO₄. CO₂ produced by the reaction passed through two cold traps at -80°C (dry ice + alcohol) to remove water. The dried gas was reduced to graphite at 500°C over an iron catalyst. Details of the graphitization procedure are given in Slota *et al.* (1987).

Partial dissolution experiments were made on AFS-12 and FRT-F-1. In these experiments, a single piece of coral was dissolved progressively, and gas subsamples were collected at 5–10 vol% intervals. For AFS-12, 2 g of sample were used. For FRT-F-1, 0.2 g were used. The gas pressure produced during the dissolution was monitored with a capacitance manometer.

To calculate ¹⁴C ages, (¹⁴C/¹³C) ratios in the samples and standards were measured and the “fraction modern,” F, was determined (Linick *et al.* 1986). F is defined as

$$F = (^{14}\text{C}/^{13}\text{C})_{\text{S}} / (^{14}\text{C}/^{13}\text{C})_{\text{STD}} \quad (1)$$

where (¹⁴C/¹³C)_S is the sample ratio, normalized to δ¹³C = -25‰, and (¹⁴C/¹³C)_{STD} is the calculated standard ratio at 1950, determined from measurements of NBS oxalic acid standards, also normalized to δ¹³C = -25‰ (Donahue, Linick & Jull 1990). The age of the sample is computed with the equation

$$\text{Radiocarbon Age} = -\tau \ln F \quad (2)$$

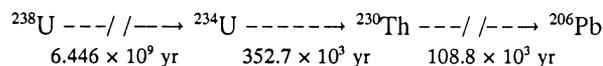
where τ is the Libby mean life (5568/ln 2 = 8033 yr). For old samples, limits to F are calculated from the equation

$$F_{\text{limit}} \leq \{(F_{\text{measured}})^2 + (2\Delta f)^2\}^{1/2} \quad (3)$$

where Δf is the uncertainty in the system background. Details of the calculation, including a discussion of background, are given in Donahue, Linick and Jull (1990) and Donahue, Jull, and Toolin (1990).

U-Th Systematics, Sample Preparation and Analysis

U-Th dates are based on the decay sequence:



where the numbers below the arrows represent mean lives. The daughter isotope, ²³⁰Th, is produced within the coral, from the decay of ²³⁴U. We assume that the initial amount of ²³⁰Th incorporated into a coral skeleton is zero. This assumption has been verified by ²³⁰Th measurements on very young coral (Edwards, Taylor & Wasserburg 1988). Using this assumption, and the laws governing

radioactive production and decay, one calculates the following equation (modified from Kaufman & Broecker 1965)

$$1 - [^{230}\text{Th}/^{238}\text{U}]_{\text{act}} = e^{-\lambda_{230}T} - \left(\frac{\delta^{234}\text{U}(\text{O})}{1000}\right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}}\right) (1 - e^{(\lambda_{234} - \lambda_{230})T}) \quad (4)$$

where T is the age of the sample, the λ s are the appropriate decay constants, $\delta^{234}\text{U}(\text{O})$ is a reformulation of the measured $^{234}\text{U}/^{238}\text{U}$ ratio in the sample, and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ is a function of the measured $^{230}\text{Th}/^{238}\text{U}$ ratio in the sample.

The principles of U-Th dating have been known for many years. However, the approach has been limited by the inability to measure $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ precisely. The development of mass spectrometric methods for measuring these nuclides allows us to obtain U-Th ages as precise as or more precise than ^{14}C ages (Edwards *et al.* 1987; Edwards, Chen & Wasserburg 1987).

Mass spectrometric measurement of U-Th isotopes in sample KWA-Q-1 were performed at the Minnesota Isotope Laboratory. This is a new facility that focuses on mass spectrometric measurement of uranium series nuclides. The procedures for chemical separation and mass spectrometric measurement of U-Th isotopes are variants of those detailed in Chen, Edwards and Wasserburg (1986), and Edwards, Chen and Wasserburg (1987). The measurements in the Minnesota laboratory are somewhat more precise and significantly more sensitive than those outlined in the above references. The improvements result largely from the use of a Finnigan 262 mass spectrometer with ion-counting capabilities and a baffled flight tube.

Sample preparation involved several steps. The sample was dissolved and spiked with a ^{229}Th tracer and a mixed ^{233}U - ^{236}U tracer. Iron hydroxide precipitation and ion exchange techniques were used to separate purified U-Th fractions. Each fraction was dried onto a zone-refined rhenium filament. The filaments were loaded into the Finnigan 262 mass spectrometer, and the U-Th isotopes measured. The $^{230}\text{Th}/^{238}\text{U}$ ratio was calculated using standard isotope dilution equations. To avoid contamination, the whole procedure was performed under clean-room conditions.

X-Ray Diffraction Analysis

X-ray powder diffraction patterns were taken for all of the samples. These were measured with a Siemens D-500 diffractometer using $\text{CuK}\alpha$ radiation (40 kV, 30 mA) and a scintillation counter. The samples were measured at a scan rate of $2^\circ 2\theta \text{ min}^{-1}$. The detection limit for these measurements is a function of the peak to background ratio and the number of counts collected under the peak of interest (Klug & Alexander 1974). For our analyses, the detection limit was about 2% of the total sample.

RESULTS AND DISCUSSION

Modern Contamination in Old Coral

Bulk Samples. Table 2 lists results of bulk sample ^{14}C measurements. Based on U-Th dates, all of the samples measured in this study are >50 ka old. Thus, they should have F values corresponding to F_{limit} (Eq. 3), at the background level of our laboratory. This is true only for AFS-10. The other samples contain the equivalent of 0.5 to 2.5 pMC.

Living coral produces aragonite, which is unstable at near-surface temperatures and pressures (Jamieson 1953) and is more soluble than calcite (Chave *et al.* 1962). Modern carbon could be introduced during recrystallization of the coral, or from the addition of modern calcite as over-

TABLE 2. Calculated Bulk Sample Results

Sample	Fraction modern (F)	¹⁴ C age (1 σ) (yr BP)	U-Th age (2 σ) (yr BP)
AFS-10	$\leq .0024$	$\geq 48,500$	$125,700 \pm 1200^*$
AFS-12	$.0240 \pm .0013$	$30,000 \pm 400$	$123,000 \pm 1000^*$
SIAL-E-1	$.0046 \pm .0011$	$43,200 \pm 1900$	$\sim 60,000^{**}$
FRT-F-1	$.0093 \pm .0011$	$37,600 \pm 1000$	$\sim 60,000^{**}$
KWA-Q-1	$.0085 \pm .0011$	$38,300 \pm 1100$	$57,010 \pm 110$

*AFS-12 is the weighted mean of AFS-12A, AFS-12B and AFS-12C (Edwards *et al.* 1987)

**Terrace IV (Bloom *et al.* 1974)

growths on the coral framework. Matthews (1968) has shown that the diagenesis of coral from Barbados depends on kinetic factors and climate. Relatively dry regions, such as the Christ Church area, favor aragonite preservation. In contrast, coral from the relatively wet east-central portion of Barbados is largely recrystallized to calcite.

X-ray powder diffraction techniques are useful for monitoring calcite crystallization. Calcite has a strong X-ray peak at $29.4^\circ 2\theta$. This peak is absent in the spectra of AFS-10, which is uncontaminated, and is conspicuous in the spectra of the contaminated samples, AFS-12, SIAL-E-1 and FRT-F-1. However, the peak is not observed in the pattern for KWA-Q-1, which contains the equivalent of about 1 pMC. If this modern carbon is introduced by 2% or less calcite crystallization, then it may be undetectable with the X-ray method.

Contamination on the order of 2% can be significant. Table 3 shows the effect of contaminating a coral with 2 pMC. For the purposes of the calculation, we assume that the carbon is introduced as calcite that precipitates on the sample. Apparent ages are computed at 10, 20, 30 and 40 ka BP. The effect is measurable for young samples (<10 ka), and becomes more significant with increasing age. Also shown in Table 3 is the effect on the U-Th age. We assume that the modern material contains no ²³⁰Th, so that the addition of modern calcite only dilutes the sample. The effect on the U-Th age is much smaller than the effect for ¹⁴C.

TABLE 3. Calculated Effect of 2% Modern Contamination in Corals of Different Ages*

Actual age (yr BP)	Apparent ¹⁴ C age (yr BP)	Apparent U-Th age (yr BP)
10,000	9612	9790
20,000	18,395	19,560
30,000	25,201	29,307
40,000	29,092	39,027

*The calculations were made on the basis of Equations 1–4. We assume that calcite crystallizes on the surface of the aragonite. $F = 1$ for the calcite and it contains no ²³⁰Th. We assume $\delta^{234}\text{U}(T) = 150$ for the original coral.

Selective Dissolution Experiments. Selective dissolution experiments were carried out for AFS-12 and FRT-F-1. These were designed to remove successive layers of aragonite by dissolution. For FRT-F-1, a ¹⁴C age was computed for successive fractions, sampled at *ca.* 6% intervals, up to 50%. For AFS-12, the first and last 10% were sampled. Results are given in Table 4 and Figure 1. In both samples, the initial fraction dissolved contained a large proportion of ¹⁴C, which decreased with successive fractions. In FRT-F-1, 53% of the bulk ¹⁴C was contained in the first 11.7%

TABLE 4. Results of Selective Dissolution Experiments

% Dissolved	Fraction modern (F)	Age (yr BP)
<i>FRT-F-1</i>		
0-5.6	.0721 ± .0017	21,100 ± 200
5.6-11.7	.0147 ± .0007	33,700 ± 400
11.7-17.4	.0059 ± .0011	41,200 ± 1500
17.4-23.1	.0055 ± .0011	41,100 ± 1500
23.1-28.9	.0060 ± .0011	41,800 ± 1700
28.9-35.2	.0090 ± .0012	37,800 ± 2100
35.2-40.5	≤.0035	≥45,400
40.5-46.8	≤.0026	≥47,800
<i>AFS-12</i>		
0-10	.2000 ± .0024	12,900 ± 100
90-100	≤.0028	≥47,200

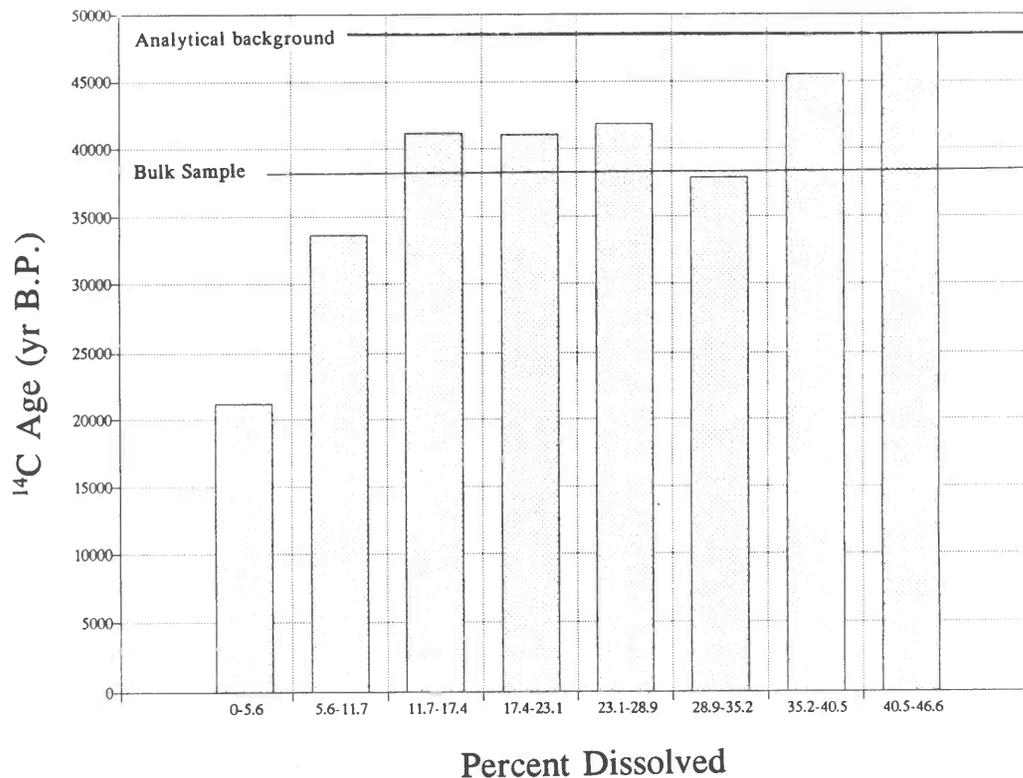


Fig. 1. Measured ¹⁴C ages of subsamples from FRT-F-1. Ages were calculated with Equations 1-3. Each fraction represents a portion of the sample that was selectively dissolved from a single piece of coral. Bulk sample has a ¹⁴C age of 37,600 ± 1000 BP. U-Th age is ~60,000 BP (Table 2).

removed by dissolution. In AFS-12, *ca.* 80% of the bulk ^{14}C was contained in the first 10%. In excess of 40% of sample FRT-F-1 had to be dissolved and discarded in order to measure an accurate date.

Figure 2 shows a thin section of FRT-F-1, before and after dissolving *ca.* 30% of the sample. A feature common to all of the coral species studied is the large surface area available for reaction. The large proportion of ^{14}C collected in the first stages of dissolution is consistent with surface exchange involving a modern ^{14}C reservoir, through dissolution/recrystallization, or with modern calcite crystallization on the surface of the coral. This is consistent with the findings of Chappell and Polach (1972), who described recrystallization effects in corals from New Guinea. They found that 11 of 13 corals analyzed were contaminated with modern carbon. Petrographic textures demon-

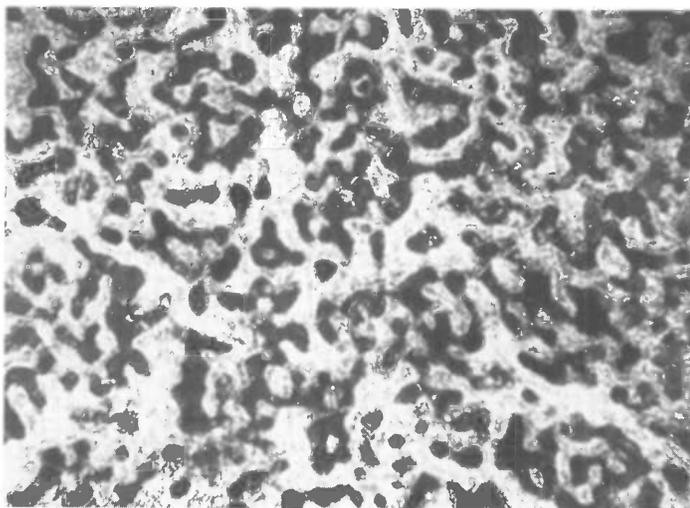


Fig. 2A. Thin section of FRT-F-1 before dissolution.

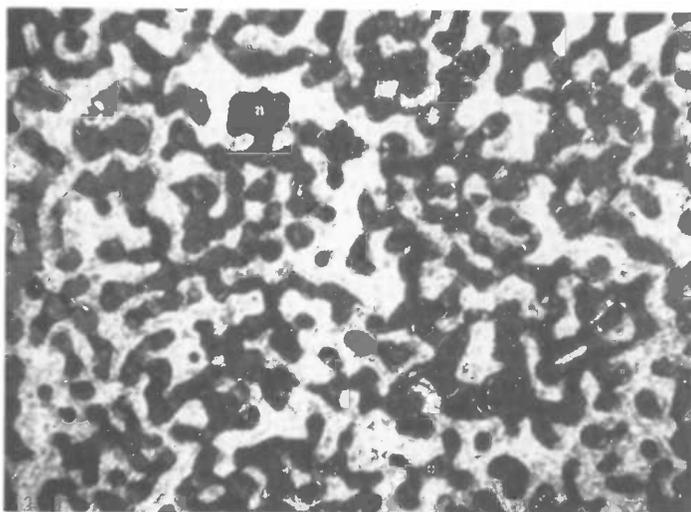


Fig. 2B. Thin section of FRT-F-1 after 30% dissolution. Both photographs were taken under plain polarized light. White portion is coral, black is pore space. Scale is 1:20.

strated two modes of recrystallization: inversion and sparry calcite crystallization. The authors suggested that calcite recrystallization was the likely path for modern carbon exchange and that inversion was probably a closed system process.

CONCLUSIONS

Combined ^{14}C and U-Th dating of coral requires special attention to sample pretreatment. We have shown that ^{14}C dates of coral are sensitive to small amounts of contamination by modern carbon, especially for samples that are >10 ka BP. To determine accurate ^{14}C ages, samples should be selectively dissolved prior to analysis.

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