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HIGH PRECISION THORIUM-230 DATING OF CORALS USING THERMAL IONIZATION MASS SPECTROMETRY: APPLICATIONS TO PALEOSEISMOLOGY

by

R. Lawrence Edwards[1], F. W. Taylor[2], J. H. Chen[1] and G. J. Wasserburg[1]

[1] The Lunatic Asylum of the Charles Arms Laboratory, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125

[2] Institute for Geophysics, University of Texas at Austin, Austin, Texas 78759

ABSTRACT

The recent development of mass spectrometric methods for determining ^{230}Th abundances reduces the analytical error in ^{230}Th ages of corals. Errors of ±3 yrs (2σ) for a 17 yr old coral, ±5 yrs at 180 yrs, ±44 yrs at 8,294 yrs, and ±1.1 ky at 123.1 ky (1 ky = 1,000 yrs) were obtained using these techniques. Within the error of the measurements, ^{230}Th ages agree with ages determined by counting of annual growth bands. These measurements indicate that the maximum amount of ^{230}Th incorporated into a coral skeleton during growth is equivalent to the amount of ^{230}Th generated by radioactive decay in <6 yrs. Using these techniques, we have dated two emerged corals from north Malekula Island and two from northwest Santo Island, Vanuatu. By analogy to partially emerged corals that were killed by coseismic uplift on Santo in 1973 (M_s = 7.5) and on Malekula in 1965 (M_s = 7.5), it appears that each pair of emerged corals was killed by an earlier coseismic uplift event. Pairs of emerged coral heads from each of the localities yield similar ^{230}Th ages. This demonstrates that each pair of corals died at the same time and is consistent with the idea that they were killed by the same event (presumed to be coseismic emergence). The ^{230}Th growth dates of the emerged corals (A.D. 1864±4 (2σ) and A.D. 1865±4 for Santo; A.D. 1729±3 and A.D. 1718±5 for Malekula) in conjunction with the dates of historical earthquakes yield recurrence intervals of 108 yrs for northwest Santo Island and 236 yrs for north Malekula Island. If a slip-predictable model is used, average uplift rates over the past few centuries are similar to uplift rates averaged over the past 6,126 yrs. It may be possible to extend this approach back in time and to other localities because coral features that represent paleoseismic events are preserved in the geologic record and we have the ability to recognize these features in the field. However, the difficulties in recognizing and sampling corals that represent paleoseismic uplifts become increasingly greater with increasing age.

INTRODUCTION

We have recently developed high precision mass spectrometric techniques to measure ^{230}Th and ^{234}U abundances in small amounts of coral (Edwards and others, 1987a, b). Use of these techniques reduces the analytical error in a ^{230}Th age, decreases the sample size required for an analysis, and increases the time range over which useful ages can be determined. The purpose of this note is to review the systematics and assumptions used in ^{230}Th dating, to summarize the recent technical improvements in ^{230}Th measurements, and to examine situations where use of these techniques will have immediate impact in paleoseismologic studies.

SYSTEMATICS

^{230}Th dating of corals is based on the decay of ^{238}U through a series of intermediate daughters:

$$^{238}U \xrightarrow[6.446\times10^{9}\ yr]{} {}^{234}U \xrightarrow[352.7\times10^{3}\ yr]{} {}^{230}Th \xrightarrow[108.8\times10^{3}\ yr]{} {}^{206}Pb,$$

where the numbers below the arrows are mean lives and only the pertinent intermediate daughters are shown. The differential equations for radioactive production and decay can be solved for time as a function of the measured $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios if: (1) the initial $^{230}Th/^{238}U$ ratio, when the coral grew, is assumed to be zero, and (2) corals are assumed to be closed systems with respect to U and Th. The solutions are:

$$[^{230}Th/^{238}U]_{act} - 1 = [(\delta^{234}U(0)/1000)(\lambda_{230}/(\lambda_{230}-\lambda_{234}))](1-e^{(\lambda_{234}-\lambda_{230})T}) - e^{-\lambda_{230}T} \quad (1)$$

and

$$\delta^{234}U(T) = \delta^{234}U(0)e^{\lambda_{234}T}. \quad (2)$$

Equation 1 (modified from Kaufman and Broecker, 1965) is used to calculate the ^{230}Th age. T is the age; the λ's are decay constants; $[^{230}Th/^{238}U]_{act}$ is the measured $^{230}Th/^{238}U$ atomic ratio times $\lambda_{230}/\lambda_{238}$; and $\delta^{234}U$ is the fractional enrichment of the $^{234}U/^{238}U$ ratio (at any given time) relative to the $^{234}U/^{238}U$ ratio at secular equilibrium in parts per thousand:

$$\delta^{234}U = [(^{234}U/^{238}U)(\lambda_{234}/\lambda_{238})-1](1000). \quad (3)$$

The value of $\delta^{234}U$ changes with time. The relationship between the present value $[\delta^{234}U(0)]$ and the initial value when the coral grew $[\delta^{234}U(T)]$ is given by equation 2. Equation 2 provides an independent test of the closed system assumption used in solving the radioactive decay equations. The initial uranium isotopic composition can be calculated using the age, T (from eq. 1) and the measured uranium isotopic composition. If the isotopic composition of uranium in seawater does not change with time, then differences between the calculated $\delta^{234}U(T)$ of the fossil coral and the present $\delta^{234}U$ value of seawater (Chen and others, 1986) would indicate open system behavior.

MEASUREMENT OF ^{230}Th AND ^{234}U BY THERMAL IONIZATION MASS SPECTROMETRY

^{230}Th ages of corals were first measured by Barnes and others (1956) using α-spectrometry to determine the $^{230}Th/^{238}U$ ratios. Thurber and others (1965) and Broecker and Thurber (1965) measured $^{234}U/^{238}U$ ratios as well as $^{230}Th/^{238}U$ ratios (again by α-spectrometry) and calculated ^{230}Th ages taking into account the fact that the $^{234}U/^{238}U$ ratio in seawater differs from the value at secular equilibrium (Thurber, 1962). Improvements in detector systems increased the resolution of α-spectra (see Rosholt, 1984) and obviated some of the problems associated with α-counting measurements, but major improvements in the precision of ^{230}Th, ^{234}U and ^{238}U measurements (by α-spectrometry) have not been made since the pioneering work of Broecker and coworkers. This is because the precision of a measurement is limited by the number of atoms (or α-particles) that can be detected during a measurement. By α-spectrometry, only decaying particles can be detected. ^{230}Th has a mean life of ~ 10^5 yrs, so for a laboratory counting time of one week, only one out of 10^7 ^{230}Th atoms in a sample can be detected. In mass spectrometric measurements, ions are detected, and the precision of a measurement is limited by the fraction of ^{230}Th atoms that one can ionize. We have obtained ionization efficiencies of one out of 10^3 (Edwards and others, 1987a) for Th. For the same size sample, 10^4 times more atoms of ^{230}Th can be detected by mass spectrometric determination than by α-counting methods. Based solely on counting statistics, a ^{230}Th measurement by mass spectrometry should be about 10^2 times more precise than a ^{230}Th measurement (on the same size sample) by α-counting. Both methods of measurement have other sources of error (Harmon and others, 1979; Rosholt, 1984; Edwards and others, 1987a). Table 1 compares the methods and shows that, for a 120,000 yr old (120 ky) sample, the error in age is about an order of magnitude smaller and the sample size around fifty times smaller for mass spectrometric measurements.

TABLE 1.-- Comparison between mass spectrometric and α-counting methods for measuring ^{230}Th and ^{234}U in a ~ 120 ky old coral

Method	Coral sample size	Number of ions or alpha particles measured/run		2σ uncertainty[1]		
		^{230}Th	^{234}U	$^{230}Th/^{238}U$	$^{234}U/^{238}U$	Age(ky)
Mass spectrometry	200 mg	5×10^6	2×10^6	±2°/₀₀	±5°/₀₀	±1
α-counting	10 g	3×10^3	5×10^3	±40°/₀₀	±30°/₀₀	±10

[1] The α-counting uncertainties are taken from Harmon and others (1979) and are based on counting statistics. °/₀₀ indicates parts per thousand.

Table 2 shows samples that were dated by ^{14}C, counting of coral growth bands, ^{230}Th (α-counting) and ^{230}Th (mass spectrometric). The errors in the mass spectrometric ages, based on analytical errors, range from ±3 yrs (2σ) for a coral that is 17 yrs old to ±1.1 ky for samples that are around 120 ky old. Assuming typical analytical errors, we calculate that, for a 500 ky old sample, the error in age due to analytical uncertainty would be ±50 ky (2σ). Samples CWS-A, CWS-A-1d and TAN-E-1g were collected when the surface of the coral head was still alive, and their ages were determined from the counting of annual growth bands. For all three samples, the ^{230}Th ages and growth band ages agree within the error of the measurements (fig. 1). The ^{230}Th ages were calculated assuming that the initial amount of ^{230}Th incorporated into the coral skeleton was zero. The agreement between the ^{230}Th ages and the growth band ages indicates that this assumption is valid, within errors. For CWS-A, the ^{230}Th age is three yrs older than the mean growth band age and the 2σ error is ±3 yrs, so the maximum amount of initial ^{230}Th incorporated into the skeleton is equivalent to the amount of ^{230}Th produced by radioactive decay in 6 yrs.

TABLE 2.-- Coral ages determined by different methods or techniques[1]

Sample[2]	^{14}C[3] (conventional) (yrs)	^{14}C[4] (corrected) (yrs)	Growth Bands (yrs)	^{238}U-^{234}U-^{230}Th[5] (α-counting) (ky)	^{238}U-^{234}U-^{230}Th[6] (mass spectrometric)
CWS-A	---	---	13-15	---	17±3 yrs
CWS-A-1d	---	---	49-51	---	54±5 yrs
TAN-E-1g	270±120	30-70, 180-270, or 300-500	176-182	---	180±5 yrs
CWS-F-1	980±120	780-1010	---	---	845±8 yrs
CH-8	8990±120	~10,000	---	---	8294±44 yrs
AFS-12 A	---	---	---	129±9	122.1±1.1 ky
B					122.7±1.3 ky
C					124.5±1.3 ky
E-T-2 A	---	---	---	141±16	129.9±1.1 ky
B					129.2±1.1 ky

1 Ages refer to the ages in 1986. Reported errors are 2σ. For ^{14}C and α-counting, the errors are based on counting statistics. Errors in mass spectrometric ages are based on the standard deviation of the mean of 60-300 isotope ratios measured in the course of a mass spectrometric run.

2 For AFS-12, A and B are different fractions of the same powder; C is a different fragment of coral. For E-T-2, A and B are different fragments of coral.

3 ^{14}C ages are as reported by Taylor and others (1985) in radiocarbon years; the mean life of 8033 yrs was used; no corrections have been made for natural fractionation of carbon isotopes, the difference between ^{14}C/C in surface water and the atmosphere, or differences in initial ^{14}C/C.

4 ^{14}C ages have been corrected by us to dendroyears using the curves of Stuiver (1982) for TAN-E-1g and CWS-F-1 and for CH-8, assuming a ^{14}C/C initial ratio from Klein and others (1982) for tree rings ~ 8,000 yrs old. No corrections have been made for natural fractionation of carbon isotopes or the difference between ^{14}C/C in the surface water and the atmosphere.

5 Ages from T.-L. Ku (written commun., 1986) except for E-T-2 which is from Bloom and others (1978).

6 From Edwards and others (1987b) and R. L. Edwards (unpub. data).

For TAN-E-1g and CWS-F-1, the ^{230}Th age and ^{14}C age agree within the analytical errors (table 2). For TAN, however, the ^{14}C age has three ranges that span several centuries. This is because of changes in the initial ^{14}C/C ratio in the atmosphere with time. For CH-8, the ^{14}C and ^{230}Th ages do not agree. The reasons for this are unclear and the discrepancy emphasizes the importance of more detailed studies comparing ^{14}C and ^{230}Th ages.

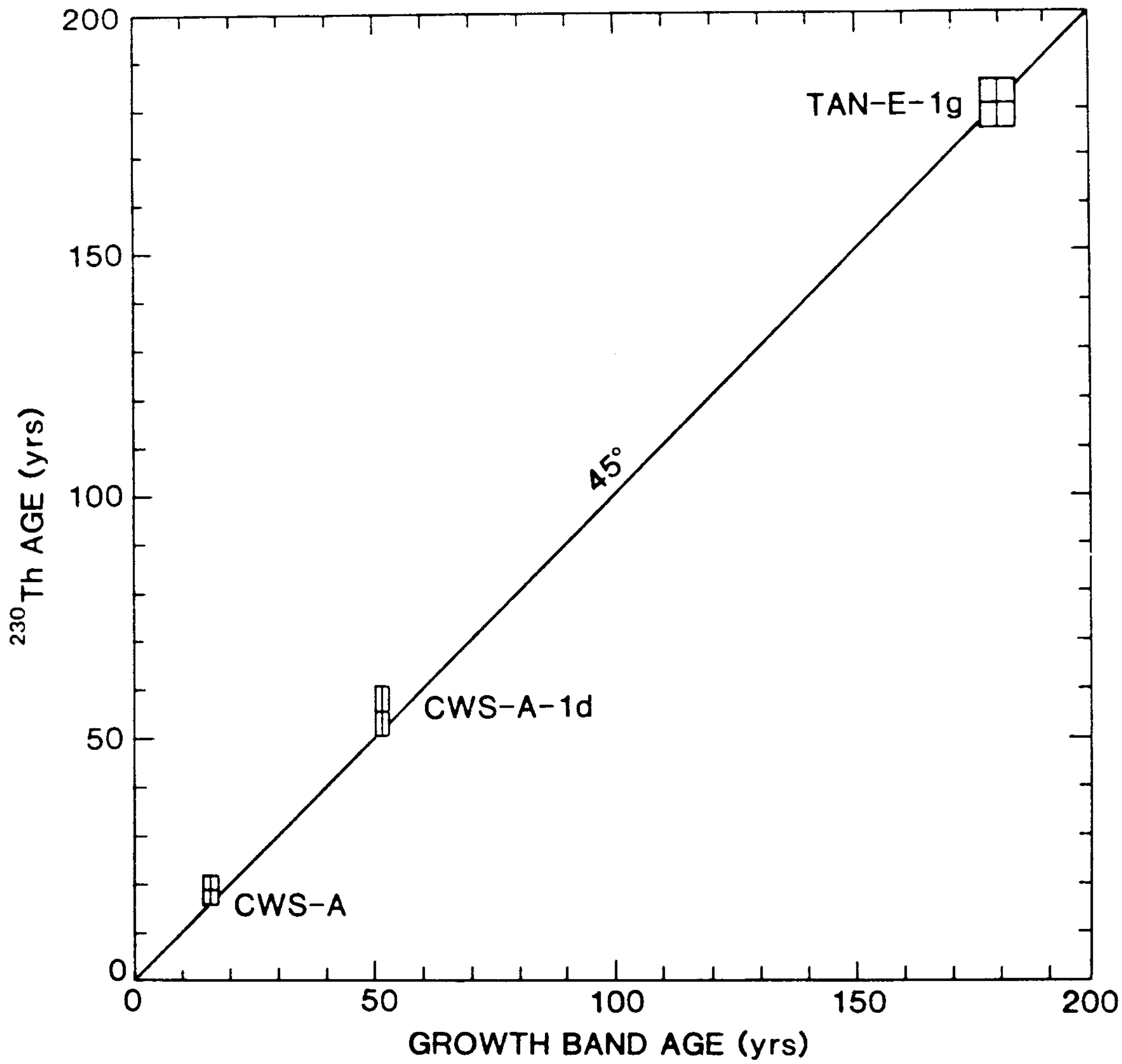

FIGURE 1.--^{230}Th age versus age determined by counting of annual growth bands. The error in the ^{230}Th age is 2σ and is based on analytical errors. The error in the growth band age is the range of ages in the sample which was analyzed. Boxes indicate the error limits of the age determinations.

Samples AFS-12 and E-T-2 are beyond the range of ^{14}C dating. The mass spectrometric ages agree with the α-counting ages but the errors for the mass spectrometric determinations are about an order of magnitude smaller. Replicate analyses of different fragments of AFS-12 and E-T-2 agree within analytical error. This indicates not only analytical reproducibility but also shows that different fragments of the same hand specimen could not have been altered to different degrees.

In summary, errors in ^{230}Th ages of corals due to analytical uncertainty are significantly lower when analysis is done by mass spectrometry instead of α-spectrometry. The error in mass spectrometric ^{230}Th ages are also lower than the errors in ^{14}C ages (due to analytical uncertainty). Mass spectrometric ^{230}Th ages have 2σ errors of ±3 yrs for a 17 yr old coral, ±5 yrs at 180 yrs, ±44 yrs at 8,294 yrs, ±1.1 ky at 123.1 ky, and an estimated error of ±50 ky at 500 ky. The sample size for the corals younger than 10 ky is ~ 3 g and for the 123.1 ky old sample, ~ 250 mg. For corals that grew during the past two centuries, ^{230}Th ages agree with ages determined from counting of growth bands. These measurements place an upper limit on the amount of initial ^{230}Th incorporated during coral growth (equivalent to the amount generated by radioactive decay in <6 yrs). This shows that the assumption that initial ^{230}Th is zero is valid. Future studies will address the validity of the assumption that corals can be chosen which have been closed with respect to U and Th exchange. The strongest evidence that diagenetic alteration is not a problem is the agreement between analyses of different fragments of the same sample (AFS-12 and E-T-2). This shows that different parts of the same hand specimen could not have been altered to different degrees.

APPLICATIONS IN PALEOSEISMOLOGY

Corals grow close to the sea surface. Therefore, the elevations and ages of fossil corals record changes in sea level with time. Apparent changes in sea level are caused by tectonic uplift (or subsidence), isostatic readjustments, and glacio-eustatic fluctuations in sea level. To the extent that eustatic and isostatic fluctuations in sea level (and apparent sea level) can be subtracted off, corals provide a record of tectonic movement. This approach has been used in a number of localities to determine uplift and subsidence rates averaged over ~ 10^5 yrs (see, for example, Moore and Fornari, 1984; Mesolella and others, 1969; Bloom, 1980).

There are two ways in which mass spectrometric ^{230}Th measurements will extend this approach. The first takes advantage of the ability to measure small samples. Reef-forming corals generally grow in the tropics. However, solitary corals grow in marine environments worldwide. Fossil solitary corals are only found in small masses in marine terraces. Therefore, dating by α-counting methods has only been possible in a few localities. Dating by mass spectrometric methods should extend this approach.

The second way takes advantage of the ability to date young corals (last several thousand years) very precisely. It may be possible to date corals which were killed by coseismic uplift and thereby date earthquakes. The ability to do this depends not only on the ability to date corals precisely, but also on the ability to identify fossil corals that were killed by coseismic uplift. The rest of this note will describe our results on samples from a specific locality where F. W. Taylor (unpub. data) found fossil corals presumed to have been killed by coseismic uplift.

Taylor and others (1987) examined partially emerged coral heads from Vanuatu. The tops of these coral heads were above sea level and were dead. The portions of the heads below sea level were still alive. The time of emergence and death of the upper part of a coral head could be determined by counting annual growth bands starting with the living portion of the coral. Using this approach, Taylor and others (1987) showed that the times of coral emergence correlated with the times of major earthquakes on northwest Santo Island (1973, $M_S = 7.5$) and north Malekula Island (1965, $M_S = 7.5$). The amount of emergence was 0.6 m on northwest Santo in 1973 and 0.8 m at the north Malekula locality in 1965.

At both localities, there are also completely emerged coral heads whose heights are 1.8 m above the highest living corals at northwest Santo and 1.3 m above the highest living corals on north Malekula. By analogy to the corals killed by coseismic uplift in 1965 and 1973, we considered the completely emerged corals also to have been killed by coseismic uplifts at earlier times. If this is true, then the ages of emerged coral heads at a given locality should be the same. We have dated the tops of two coral heads from each of the localities by ^{230}Th methods (table 3). At the northwest Santo locality, the growth dates of the two heads agree within analytical error (A.D. 1864±4, 1866±4), and at north Malekula, the dates of the two heads are similar to each other (A.D. 1729±3, 1718±4). The slight difference in growth date for the north Malekula locality is outside of analytical error and may be due to erosion of the outer (younger) part of the MAG coral head.

TABLE 3.-- ^{230}Th ages of emerged corals.

Sample	Island	Height[1] (m)	Date of growth (from ^{230}Th)[2] (yrs A.D.)
CWS-C	N.W. Santo	1.8	1866 ± 4
CWS-D-1[3]	N.W. Santo	1.8	1864 ± 4
CWS-D-2[3]	N.W. Santo	1.8	1868 ± 9
MAF	N. Malekula	1.3	1729 ± 3
MAG	N. Malekula	1.3	1718 ± 5

[1] Above the highest living corals at the same locality (F. W. Taylor, unpub. data).
[2] Determined by subtracting the ^{230}Th age from the date of analysis; dates are rounded to January 1 of the indicated year; reported errors are 2σ of the mean (R. L. Edwards, unpub. data).
[3] CWS-D-1 and CWS-D-2 are replicate analyses of the same coral.

The general agreement between growth dates of corals at a given locality is consistent with the idea that the heads were killed by coseismic uplift. The difference in growth dates between the north Malekula and northwest Santo corals indicates that they were killed by different events. The seismic recurrence interval at northwest Santo is (1973-1865) 108 yrs; the amount of uplift at this locality for the 1973 event was 0.6 m and for the 1865 event, 1.2 m. The uplift rate calculated by dividing 0.6 m by 108 yrs (slip-predictable model; see Shimazaki and Nakata, 1980) is 5.6 mm/y. The average uplift rate for the latter part of the Holocene can be estimated by dividing the height of coral collected near the top of the Holocene terrace by its age. For northwest Santo, the average uplift rate over the past 6,126 yrs is 4.2 mm/y (see Taylor and others, 1987). Similarly, the seismic recurrence interval at north Malekula is (1965-1729) 236 yrs; the amount of uplift at this locality in 1965 was 0.8 m and in 1729, 0.5 m. The average uplift rate between 1729 and 1965 was 3.0 mm/y (slip-predictable), and the average rate over the last 6,126 yrs was 2.7 mm/y (Taylor and others, 1987). The similarity between short-term and long-term uplift rates at each locality suggests that, if a slip-predictable model is appropriate, uplift rates have been relatively constant throughout the Holocene and the total Holocene uplift can be accounted for by events similar to the 1965 and 1973 events.

In summary, the error in ^{230}Th ages (based on analytical errors) for corals ranges from ±3 yrs for a 17 yr old coral to ±1.1 ky for a 123.1 ky old coral. The correlation between growth band age and ^{230}Th age for living corals shows that initial ^{230}Th is less than the amount of ^{230}Th produced by radioactive decay in 6 yrs. Because of the precision with which the ages of corals can be measured, studies of paleoseismicity may be designed to use dating of corals for time control. The major problems are associated with the preservation of corals in the geologic record which represent paleoseismic events, the identification of such features in the field, and the determination of the depth at which the corals grew. In this note, we have described one instance where we believe identification of such a feature was possible.

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