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Annual cycles of U/Ca in coral skeletons and U/Ca thermometry

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Abstract—We have discovered annual variations in the $^{238}U/^{40}Ca$ ratio of *Porites* coral skeletons. Measurements were made using thermal ionization mass spectrometric techniques, yielding precisions of $\pm 2‰$ (2σ) for $^{238}U/^{40}Ca$ and $\pm 1‰$ (2σ) for $^{88}Sr/^{40}Ca$. Coralline aragonite subsamples weighed ~2 mg, enabling sub-millimeter sampling resolution corresponding to ~monthly temporal resolution. The annual nature of the cycles was confirmed by comparison with annual banding observable in X-radiographs. For two modern and one fossil sample, the amplitude of the U/Ca variation ranges from 6 to 23%, well outside of analytical error. As annual U/Ca cycles appear to be a general feature of primary coralline aragonite, the preservation of such features will be important in identifying unaltered coral for U-series dating studies. U/Ca variations mimic and are in phase with annual variations in $^{88}Sr/^{40}Ca$. For a given fractional shift in Sr/Ca, the fractional shift in U/Ca is about 6 times larger. For the two modern corals, $^{238}U/^{40}Ca$ is strongly anticorrelated with measured temperature, suggesting that $^{238}U/^{40}Ca$ has potential as a paleothermometer. If temperature is the only significant control on coralline $^{238}U/^{40}Ca$, we reach the following conclusions from analyses of fossil samples: a Vanuatu sample, which grew halfway through the last deglaciation, gives U/Ca temperatures 4 to 5°C below modern values. U/Ca thermometry applied to published data for Barbados corals indicates that (1) temperature generally correlates with sea level, (2) glacial temperatures (stages 2 and 4) were 4 to 6°C lower than interglacial temperatures (stages 7a, 5e, and 1), and (3) temperatures rose from glacial to interglacial values early in the last deglaciation. Thermometry applied to Papua New Guinea corals indicates that (1) temperatures were 5 to 6°C lower than interglacial temperatures from ~13 to ~10 Ky BP, then rose to present values ~9 Ky BP, (2) the temperature depression between ~13 and ~10 Ky BP is consistent with low temperatures observed in Vanuatu during the same time interval, and (3) the Papua New Guinea deglacial temperature history differs from that of Barbados. The results generally support estimates of tropical temperatures obtained from Sr/Ca thermometry and snow line elevation data, but disagree with those based on foram transfer functions. A thermodynamic model suggests that coralline $^{238}U/^{40}Ca$ may also be sensitive to marine carbonate ion concentration, raising the possibility that some of the observed glacial-interglacial $^{238}U/^{40}Ca$ variation may result from glacial-interglacial carbonate ion changes. However, the key experiments that might establish a coralline $^{238}U/^{40}Ca$-carbonate ion relationship have yet to be performed.

INTRODUCTION

Variations in trace and minor element contents of coral skeletons have been used to monitor a wide range of environmental parameters and processes, such as sea surface temperature (Beck et al., 1992; de Villiers et al., 1994; Guilderson et al., 1994), upwelling intensity (Shen et al., 1987; Lea et al., 1989), wind direction and intensity (Shen et al., 1992), and diagenesis (Mesollela et al., 1969; Bloom et al., 1974; Cross and Cross, 1983). Among the trace metals, uranium is particularly important because ^{238}U is the parent isotope, and ^{234}U is an intermediate daughter in the ^{238}U series, a decay chain upon which ^{230}Th dating of corals is based. ^{230}Th dating, in turn, provides the basis for much of our knowledge of late Quaternary chronology, including the starting point for marine $\delta^{18}O$ chronologies (see Imbrie et al., 1984), late Quaternary sea levels (Gallup et al., 1994), and calibration of much of the radiocarbon timescale (Bard et al., 1990a, 1993; Edwards et al., 1993). Thus, the mechanism(s) whereby uranium is incorporated into coral skeletons, reactions, and environmental conditions that control the uranium content in corals, crystallographic site(s) occupied by uranium in corals, and the susceptibility of coralline uranium to diagenetic remobilization are all important issues that have a bearing on our knowledge of late Quaternary chronology.

In part for these reasons and in part because ^{230}Th dates themselves require measurement of uranium, there is a tremendous amount of data on uranium concentrations of corals (see, e.g., Barnes et al., 1956; Tatsumoto and Goldberg, 1959; Veeh and Turekian, 1968; Schroeder et al., 1970; Thompson and Livingston, 1970; Gvirtzman et al., 1973; Amiel et al., 1973; Swart and Hubbard, 1982; Cross and Cross, 1983; Edwards et al., 1987a,b, 1993; Bard et al., 1990a,b). These data indicate that the uranium content of hermatypic corals ranges between 1.5 and 4.0 ppm. This range is similar to that of inorganically precipitated marine aragonite (Tatsumoto and Goldberg, 1959), but orders of magnitude higher than values for molluscan aragonite (Broecker, 1963; Edwards et al., 1987b). Thus, the mechanism of uranium incorporation into coralline aragonite appears to be similar to that of inorganic

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aragonite, but quite different from that of molluscan aragonite, where biochemical processes seem to exclude uranium to a large degree.

Beyond this generalization, surprisingly little is known about uranium incorporation into corals. Swart (1980) and Swart and Hubbard (1982) have performed experiments that constrain possible chemical reactions involved in uranium incorporation into corals. There is also some indication that uranium concentration is, in part, dependent on species (Cross and Cross, 1983). The search for variations in uranium content within a given skeleton has, up until now, produced ambiguous results. As early as 1970, Schroeder et al. (1970) reported that uranium is not uniformly distributed in a given coral. Their data, obtained by fission track analysis, showed higher uranium concentrations in bands, a few tens of microns thick, along the edges of skeletal cavities. For a single sample, they also reported zonal variations in uranium concentration subparallel to growth surfaces, an early observation upon which we will build. They suggested that growth rate changes may have controlled the zonal changes, a mechanism that may be a factor, given the results that we will present. On the other hand, Gvirtzman (1973) concluded, again with fission track analysis, that differences between the uranium concentration of thecal and septal coralline aragonite could not be resolved, nor did they observe uranium concentration differences on transverse versus longitudinal sections through corals. Using the same method, Swart and Hubbard (1982) analyzed seventy-one thin sections of recently live coral skeletons and saw no evidence for zonal uranium distribution.

In this study we re-examine the possibility of zonal variability in uranium concentration subparallel to growth surfaces. We wished to determine if there were spatial patterns in the uranium concentration of primary coralline aragonite that could be used as fingerprints to identify unaltered material for ^{230}Th dating studies. If we observed seasonal variation in uranium concentration, we wished to examine the relationship of this variation to environmental variables, most notably temperature. The Sr/Ca ratio in coralline aragonite has been shown to be an indicator of sea surface temperature (Smith et al., 1979; Beck et al., 1992; de Villiers et al., 1994), and we wished to examine the possibility that the U/Ca ratio would serve as an additional proxy for sea surface temperature. From a technical standpoint, we determined uranium concentrations by thermal ionization mass spectrometric (TIMS) methods. The earlier studies of uranium distribution in corals used fission track methods, which have excellent spatial resolution, but much lower analytical precision than TIMS methods. The key advantage of TIMS methods over fission track methods is the ability to resolve much smaller variations in uranium concentration (0.2 vs. 10%). Uranium concentrations of corals were first determined by TIMS methods by Schubert and Szabo (1978). Since then, similar measurements have been made by a number of laboratories (see Edwards et al., 1987a,b; Bard et al., 1990a,b; Ludwig et al., 1991; Gray et al., 1992; Edwards et al., 1993; Henderson et al., 1993; McCulloch and Mortimer, 1994). However, the focus of all previous TIMS work has been U-series dating, which requires relatively large samples (>100 mg) so that the rare isotopes of uranium and thorium can be measured with sufficient precision. The relatively large samples integrate large spatial domains and information on spatial variability is lost. In this study we measure only the higher abundance uranium isotopes, ^{238}U and ^{235}U, allowing us to reduce sample size to 2–3 mg, while maintaining a measurement precision of better than $\pm 0.2\%$ (2σ). Using these techniques we can obtain high analytical precision in uranium determinations as well as high spatial resolution.

Our strategy in examining intraskeletal uranium variability is as follows. We chose to work on a common coral genus, *Porites*. We started by analyzing modern samples collected near temperature recording stations, then analyzed a fossil sample that grew during the last deglaciation. In addition to uranium and calcium, we measured strontium in all samples. We subsampled corals along transects perpendicular to growth surfaces, at intervals representing half a month to a month of skeletal growth. We show that corals have seasonal changes in U/Ca that are well outside of analytical error (see also Shen and Dunbar, 1995). We also show that U/Ca anticorrelates strongly with temperature, raising the potential for U/Ca thermometry. However, we also show that at least one other factor besides temperature also effects U/Ca. For the modern samples, we related changes in U/Ca to changes in measured temperature, as well as changes in Sr/Ca, a proxy for temperature (Smith et al., 1979; Beck et al., 1992; de Villiers et al., 1994; Guilderson et al., 1994). We then used these relationships to interpret the U/Ca and Sr/Ca data for a fossil sample. Finally, we apply our U/Ca-temperature relationships to the large body of published TIMS measurements of uranium concentration in corals.

SAMPLES

A modern *Porites lobata* coral was collected live near Amedee Lighthouse, Noumea, New Caledonia, and a modern *Porites solida* coral was collected live near Papeete, Tahiti. These samples are described in Beck et al. (1992), where Sr/Ca measurements for both samples, and δ^{18}O measurements for the New Caledonia sample can be found. Both sites are located near daily temperature recording stations. In addition, daily salinity measurements have been made at the New Caledonia site, and show that temporal variations in salinity (that could plausibly change seawater elemental or isotopic composition) are very small. The salinity at the site averages about 35.8‰. Values for salinity averaged over two-week intervals do not deviate from the average by more than about 0.5‰.

One fossil *Porites* sample was collected by drilling into a deglacial reef on the southern extreme of Espiritu Santo Island, Vanuatu. Sr/Ca data for this sample can also be found in Beck et al. (1992). This sample has a ^{230}Th age of 10,344 ± 42 years (S. C. Gray pers. commun), indicating that it grew about halfway through deglaciation, during the second melt water pulse after the Younger Dryas (see Edwards et al., 1993).

All three samples were slabbed. X-radiographs were prepared for growth-band analysis. Corals were then subsampled on transects perpendicular to coral growth banding. Subsamples were obtained by scoring each slab parallel to the banding with a thin diamond saw blade, then breaking off subsamples with a spatula. Samples are continuous except for material lost in the saw cut and as indicated in the tables and figures. The width of the material lost to the saw blade cut is typically 0.15 mm. Subsamples weighed 2 to 3 mg and were about 1 mm thick. For the New Caledonia and Vanuatu samples, this represents an approximately monthly growth interval. For the Tahiti sample, this represents approximately a half-month growth interval.

EXPERIMENTAL PROCEDURES

I. Chemical Procedures

Subsamples were dissolved by adding 2 N HNO_3. The solution was then heated for about 1 h, and divided into two aliquots, one for

Table 1. Sr and Ca measurements on the Tahiti Secondary Standard.

run number	μmoles ^{40}Ca/g Standard	2σ fractional error (‰)	nmoles ^{88}Sr/g Standard	2σ fractional error (‰)	^{88}Sr/^{40}Ca ratio (x10^{-3})	2σ fractional error (‰)
1	2.0338±6	0.3	15.365±9	0.6	7.5545±39	0.5
2	2.0371±10	0.5	15.382±4	0.2	7.5509±45	0.6
3	2.0336±10	0.5	15.360±20	1.3	7.5532±126	1.7
4	2.0345±10	0.5	15.378±7	0.5	7.5585±56	0.7
5	2.0321±12	0.6	15.345±10	0.7	7.5513±69	0.9
6	2.0353±23	1.1	15.363±13	0.8	7.5483±69	0.9
7	2.0350±6	0.3	15.362±8	0.5	7.5487±45	0.6
mean of 7 runs and 2σ error of the population	2.0345±32	1.6	15.365±25	1.6	7.5522±71	0.9

strontium and calcium analysis, the other for uranium analysis. The Sr-Ca aliquot was spiked with a triple ^{42}Ca-^{44}Ca-^{84}Sr. The spike has a ^{42}Ca/^{44}Ca ratio ~1 and a ^{42}Ca/^{84}Sr ratio of ~200. The spike was added so that ^{40}Ca/^{42}Ca was ~20 and ^{88}Sr/^{84}Sr was ~30 in the mixture. The spiked solution was evaporated to dryness, and a portion of the residue corresponding to about 20 μg of Ca and 400 ng of Sr was loaded on a zone-refined rhenium filament in 0.1 N HNO_3. Strontium and calcium isotopes were then measured using the double rhenium filament method as described below. Thus, both strontium and calcium are measured using the same filament, without prior chemical separation.

The uranium measurements are modifications of those described by Chen and Wasserburg (1981), Chen et al. (1986), and Edwards et al. (1987a, 1993). The uranium aliquot was spiked with a double ^{233}U-^{236}U spike, with ^{233}U/^{236}U ~ 1. Spike was added so that ^{238}U/^{233}U was ~10 in the mixture. In order to insure sample-spike equilibration, the mixture was dried, fumed with one drop of concentrated $HClO_4$, and dried. It was then dissolved in 2 N HCl, and 15 μg of iron, in chloride solution, was added. The uranium was coprecipitated with iron by the addition of ammonium hydroxide. The mixture was centrifuged and the supernate discarded. The residue was then rinsed twice with distilled water, dissolved in concentrated HNO_3, dried, and re-dissolved in concentrated HNO_3 twice, dried, and dissolved in 0.1 N HNO_3. The solution was loaded on a zone-refined rhenium filament with colloidal graphite (Chen and Wasserburg, 1981). Uranium isotopes were measured using the single-filament method. The main modifications of the chemical procedure are (1) a large reduction in the amount of iron added and (2) loading of the sample without separation of the uranium from the iron by ion exchange. This greatly simplifies chemical procedures and reduces analytical blank. The analytical blank is less than 2 pg and is negligible.

II. Thermal Ionization Mass Spectrometric Procedures

All isotope measurements were carried out on the Minnesota Isotope Laboratory's Finnigan MAT 262-RPQ mass spectrometer. Strontium and calcium were measured using static Faraday collection. Initially, a current of 0.6 amperes was passed through the evaporation filament and a current of 2.2 amperes was passed through the ionization filament. This corresponds to a temperature of 1200 to 1250°C. $^{39}K^+$ current was monitored until it fell to values of less than 1×10^{-14} amperes. The evaporation filament current was then turned up to 1.2 amperes, and the ionization filament turned down to 1.5 amperes, corresponding to a temperature of 1000 to 1100°C. $^{39}K^+$ was again monitored until it fell to less than 1×10^{-14} amperes. The evaporation filament was then turned down to 0.6 amperes, and the ionization filament up to 2.2 to 2.5 amperes, corresponding to a temperature of 1250 to 1350°C. At these conditions, the $^{40}Ca^+$ beam intensity is 1×10^{-11} to 4×10^{-11} amperes. Before measuring calcium isotopes, mass 39 was again monitored to verify that $^{39}K^+$ was less than 1×10^{-14} amperes. Data for ^{40}Ca, ^{42}Ca, ^{43}Ca, and ^{44}Ca were acquired in static mode. In the course of a run, about fifty sets of ratios, each determined with a 4 s integration time, were measured. Ratios were grouped into blocks of ten. For a given ratio, the average for the block was normalized for instrumental fractionation using the "exponential law" (see Russell et al., 1978), with natural ^{42}Ca/^{44}Ca = 0.31221 (Russell et al., 1978) and spike ^{42}Ca/^{44}Ca consistent with the Russell et al. (1978) normalization, determined as discussed below. For each block, a ^{40}Ca concentration is calculated. The ^{40}Ca concentrations for all the blocks in a run are then averaged and 2σ of the mean of the block concentrations is taken as the internal error for the run. Internal errors for the Ca concentration are typically less than ±1‰ (2σ; see Table 1, see below for a discussion of external errors).

After the calcium run, the ionization filament current was increased to 2.4 to 2.6 amperes, while the evaporation filament current was maintained at 0.6 amperes. At these conditions, the filament temperature ranges from 1300 to 1400°C. The $^{88}Sr^+$ ion current is typically 0.6 to 1.0×10^{-11} amperes. ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr are then measured in static mode. About fifty sets of ratios are collected, each determined with a 4 s integration time. Strontium data are reduced in a similar fashion to the calcium data, normalizing to ^{86}Sr/^{88}Sr = 0.1194 (Nier, 1938). using the "exponential law." Internal errors for the strontium concentration are also typically less than 1‰ (2σ; see Table 1; see below for a discussion of external errors). Replicate analyses of Sr/Ca agree within internal errors (Table 2).

We periodically test our Sr/Ca measurements for reproducibility by measuring Sr/Ca in the Tahiti Standard (see Section III; Table 1). As with the samples, the internal error for measurements of the Sr/Ca ratio are generally ±1‰ or less. The seven Sr/Ca measurements of the Tahiti Standard all agree within internal errors. In most, but not all cases, the measurements of calcium concentration in the Tahiti Standard agree within errors. The same is true for strontium concentration measurements. The external error is somewhat higher than the internal error for both strontium and calcium concentrations measurements; however, for measurements of the Sr/Ca ratio, the external error is similar to the internal error. This indicates that there are small but detectable errors in weighing the standard and spike solutions, which, for measurements of the Sr/Ca ratio, are eliminated by our use of a mixed Sr-Ca spike.

The uranium runs were also carried on the Finnigan MAT 262-RPQ mass spectrometer, but using the electron multiplier (prior to the static quadrupole second stage) in pulse counting mode. Data are acquired by peak-jumping in the sequence ^{233}U-^{235}U-^{236}U-^{238}U and about fifty sets of ratios were measured at filament temperature ranging from about 1650 to 1750°C. Instrumental fractionation was corrected using the ^{233}U-^{236}U double spike, and the "Habfast Law" (Habfast, 1983). Internal errors in U concentration are typically 2 permil (2σ). Replicate analyses of U/Ca either agree within internal error or disagree slightly. The slight disagreements are most likely due to weighing errors associated with spiking and aliquoting.

III. Spikes and Standards

A gravimetric calcium standard was prepared by weighing and dissolving a piece of Iceland Spar. We assumed that the calcite was

Table 2. Data for U, Sr and Ca isotope ratios, calculated U/Ca and Sr/Ca temperatures and sea-surface temperatures. The 2σ errors in the last significant figures are in parentheses.

Location	Distance* (cm)	^{88}Sr/^{40}Ca ($\times10^{-3}$) (molar)	^{238}U/^{40}Ca ($\times10^{-6}$) (molar)	T(°C)§ ^{88}Sr/^{40}Ca	T(°C)‡ ^{238}U/^{40}Ca	SST¶ (°C)
Amedee Lighthous Noumea, New Caledonia	4.00	7.751 (9)	1.2283 (16)	22.3	21.6	20.9
	4.10	7.777 (11)	1.2204 (18)	21.8	21.8	21.4
	4.15	—	—	—	—	21.6
	4.20	7.729 (10)	1.2138 (13)	22.7	21.9	22.0
	4.30	7.722 (8)	1.2589 (23)	22.9	20.9	22.9
	4.50	—	1.1579 (43)	—	23.1	25.4
	4.62	—	—	—	—	24.4
	4.75	7.724 (5)	1.2131 (15)	22.8	21.9	23.8
	4.85	7.727 (11)	1.2027 (19)	22.7	22.1	23.1
	4.92	7.775 (6)	1.2500 (18)	21.8	21.1	23.2
	5.00	7.779 (5)	1.2718 (14)	21.8	20.7	22.8
	5.08	7.820 (6)	1.2771 (18)	21.0	20.5	21.7
	5.15	—	1.3041 (88)	—	20.0	20.1
	5.22	7.846 (9)	1.2799 (13)	20.5	20.5	20.3
	5.31	—	—	—	—	20.8
	5.39	—	—	—	—	22.0
	5.47	7.801 (9)	1.2636 (44)	21.4	20.8	23.0
	5.54	7.753 (10)	1.2207 (9)	22.3	21.8	23.6
	5.60	—	—	—	—	24.5
	5.75	7.664 (7)	1.1428 (22)	23.9	23.4	26.1
	5.81	7.596 (9)	1.0856 (16)	25.2	24.7	26.3
	5.90	7.642 (8)	1.1456 (13)	24.3	23.4	24.7
	6.00	7.616 (4)	1.1604 (40)	24.9	23.1	23.2
	6.10	7.607 (3)	1.1385 (13)	25.0	23.5	22.6
	6.20	7.717 (3)	1.1999 (14)	22.9	22.2	21.3
	6.28	7.804 (12)	1.2505 (15)	21.3	21.1	20.4
	6.34	7.854 (6)	1.2782 (17)	20.4	20.5	20.1
	6.40	7.796 (12)	1.2362(19)	21.5	21.4	20.6
	6.50	7.699 (9)	1.1801(12)	23.3	22.6	22.0
	↳					
	6.70	7.669 (6)	1.1509 (31)	23.8	23.3	22.3
	6.80	7.763 (10)	1.2881 (19)	22.1	20.3	21.6
	6.90	7.789 (13)	1.3284 (18)	21.6	19.4	21.1
	7.00	7.835 (10)	1.3100 (17)	20.7	19.8	21.3
	7.10	7.825 (13)	1.2504 (22)	20.9	21.1	21.7
	7.18	7.718 (5)	1.1757 (14)	22.9	22.7	22.9
	7.25	7.658 (9)	1.1484 (22)	24.1	23.3	23.8
	7.32	—	—	—	—	24.5
	7.41	7.661 (6)	1.1413 (16)	24.0	23.5	25.3
	7.48	7.677 (9)	1.1550 (15)	23.7	23.2	24.9
	7.58	7.745 (11)	1.1744 (23)	22.4	22.8	24.1
	7.62	7.714(5)	1.2363 (32)	23.0	21.4	23.7
	7.70A	7.750 (9)	1.2065 (18)	22.3	22.1	23.8
	7.70B	7.759 (5)	1.2140 (20)	22.2	21.9	23.8
	7.80	—	—	—	—	22.0
	7.88	7.877 (6)	1.2922 (10)	19.9	20.2	20.4
	7.94	—	—	—	—	21.1
	8.00	7.845 (10)	1.2578 (21)	20.5	21.0	21.8
	8.10	7.787 (4)	1.1909 (12)	21.6	22.4	23.0
	8.19	7.653 (9)	1.1102 (14)	24.2	24.1	24.3
	8.26	7.611 (6)	1.0833 (12)	24.9	24.7	25.7
	8.32A	7.613 (13)	1.0910 (13)	24.9	24.5	25.7
	8.32B	7.626 (9)	1.0925 (14)	24.7	24.5	25.7
	8.40	7.629 (9)	1.1001 (13)	24.6	24.3	25.6
	8.49	7.616 (16)	1.0767 (25)	24.8	24.9	25.6
	8.55	7.603 (4)	1.0706 (15)	25.1	25.0	25.7
	8.63	7.649 (7)	1.0983 (17)	24.2	24.4	24.5
	8.70	7.700 (8)	1.1389 (12)	23.3	23.5	23.9
	8.80	—	—	—	—	23.3
	8.89	7.856 (11)	1.2874 (20)	20.3	20.3	20.6
Papeete, Tahiti	0.40	—	—	—	—	26.7
	0.48	7.511 (4)	0.9153 (8)	26.8	28.3	27.3
	0.58A	7.488 (8)	0.8970 (9)	27.3	28.7	28.1
	0.58B	7.482 (9)	0.8961 (11)	27.4	28.7	28.1
	0.67	—	—	—	—	28.4
	0.72	—	—	—	—	28.9
	0.80	7.407 (6)	0.8833 (11)	28.8	29.0	28.8
	0.90	7.423 (7)	0.8959 (11)	28.5	28.7	28.4
	0.98	7.484 (22)	0.9247 (19)	27.3	28.1	28.2
	1.05	7.467 (6)	0.9160 (10)	27.6	28.3	27.8
	1.13	—	—	—	—	27.6
	1.22	7.497 (3)	0.9384 (16)	27.1	27.8	27.2
	Sol. order†					
Espiritu Santo Island, Vanuatu	1	7.848 (4)	1.2132 (20)	20.5	21.9	
	2	7.838 (6)	1.2003 (14)	20.7	22.2	
	3	—	—	—	—	
	4	7.792 (6)	1.1668 (41)	21.5	22.9	
	5	7.776 (7)	1.1609 (17)	21.8	23.0	
	6	7.759 (3)	1.1646 (14)	22.1	23.0	
	7	7.850 (4)	1.2063 (19)	20.4	22.1	
	8	—	—	—	—	
	9	7.946 (8)	1.2655 (17)	18.6	20.8	
	10	7.933 (6)	1.2649 (15)	18.9	20.8	
	11	7.897 (8)	1.2673 (14)	19.5	20.8	
	12	7.939 (8)	1.2754 (20)	18.8	20.6	
	13	7.908 (4)	1.2479 (16)	19.4	21.2	
	14	7.851 (10)	1.2223 (18)	20.4	21.7	
	15	7.796 (8)	1.2041 (20)	21.5	22.1	
	16A	—	1.1979 (19)	—	22.2	
	16B	7.768 (10)	1.1926 (27)	22.0	22.4	
	17	7.767 (11)	1.1690 (19)	22.0	22.9	
	18	7.800 (5)	1.1929 (19)	21.4	22.4	
	19	7.787 (5)	1.1978 (18)	21.6	22.2	
	20	7.850 (5)	1.2362 (24)	20.4	21.4	
	21	7.895 (7)	1.2706 (21)	19.6	20.7	
	22	7.916 (3)	1.2757 (17)	19.2	20.6	
	23	7.855 (4)	1.2286 (17)	20.4	21.6	
	24	7.861 (13)	1.2397 (35)	20.2	21.3	
	25	7.864 (6)	1.2482 (13)	20.2	21.2	
	26	7.841 (7)	1.2465 (19)	20.6	21.2	
	27	7.830 (5)	1.2420 (13)	20.8	21.3	
	28	7.756 (5)	1.2214 (15)	22.2	21.7	
	29	7.752 (6)	1.1880 (17)	22.3	22.5	
	30	7.762 (8)	1.1960 (18)	22.1	22.3	

* Numbers indicate the distance down axis from the surface of coral to the middle of the subsample. † Numbers indicate subsample order down axis from the top of coral, each sample size was about 1 mm thick. Letters A and B indicate duplicate analyses of different aliquots of the same solution. § The ^{88}Sr/^{40}Ca temperatures were calculated from the Eqn. 5 (see text). ‡ The ^{238}U/^{40}Ca temperatures were calculated from the equation 4 (see text). ¶ The SSTs were calculated as described in the Fig. 3 and 4 captions. ↳ Discontinuity in record due to ~ 0.4 cm parallel offset in sampling transect. — Analysis of subsample or aliquot was not made.

stoichiometric and corrected for solid solution using inductively coupled plasma–mass spectrometric (ICP–MS) analyses of minor and trace elements in the resulting solution. We prepared a secondary calcium and strontium standard (Tahiti Standard) by dissolving a large quantity of modern coralline aragonite, collected off of Tahiti. At regular intervals, we spike and run the Tahiti Standard to check the precision of our measurements of Sr/Ca, strontium concentration, and calcium concentration (see Table 1 and the discussion above).

Our gravimetric strontium standard is National Institute of Science and Technology (NIST) Standard Reference Material (SRM) 987, a strontium carbonate prepared and dissolved as recommended by NIST. Our gravimetric uranium standard is New Brunswick Laboratories SRM 112a, a uranium metal prepared and dissolved as recommended by New Brunswick Laboratories.

The ^{42}Ca-^{44}Ca-^{84}Sr triple spike was prepared by dissolving two calcium carbonate powders, one enriched in ^{42}Ca, the other enriched in ^{44}Ca, both obtained from Oak Ridge National Laboratory (ORNL). The solutions were mixed so that ^{42}Ca/^{44}Ca $\sim$ 1. This solution was then mixed with a solution prepared by dissolving an ^{84}Sr-rich carbonate, also obtained from ORNL. The ^{84}Sr concentration of the spike was determined by measuring mixtures of spike and our gravimetric strontium standard. The ^{40}Ca/^{43}Ca ratio of the Tahiti Standard was measured, using the ^{42}Ca/^{44}Ca value of Russell et al. (1978) for normalization. The fractionation-corrected ^{42}Ca/^{44}Ca ratio of the spike was then determined by measuring mixtures of spike and Tahiti Standard, using ^{40}Ca/^{43}Ca to normalize for instrumental fractionation. The concentration of ^{42}Ca in the spike could then be determined by measuring mixtures of spike and Iceland Spar Standard. We used our measured ^{42}Ca/^{44}Ca value for the spike and the Russell et al. (1978) ^{42}Ca/^{44}Ca value for the standard solution, to normalize for instrumental fractionation. Thus, for all of our calcium runs, the normalization is ultimately based upon the Russell et al. (1978) ^{42}Ca/^{44}Ca value.

The ^{233}U-^{236}U double spike was prepared by dissolving two uranium oxide powders, one rich in ^{233}U, one rich in ^{236}U, both obtained from ORNL. The solutions were mixed so that ^{233}U/^{236}U $\sim$ 1. The fractionation-normalized ^{233}U/^{236}U value for the spike was determined by measuring mixtures of spike and NBL SRM U500, and using the U500 ^{235}U/^{238}U value for normalization. The concentration of ^{233}U in the spike was determined by measuring mixtures of spike and gravimetric uranium standard (NBL 112a), using the spike ^{233}U/^{236}U ratio for normalization.

RESULTS

The ^{238}U/^{40}Ca and ^{88}Sr/^{40}Ca ratios for all of the subsamples collected from three different localities are presented in Table 2 and Figs. 1 and 2. All three samples have cyclical variations in ^{238}U/^{40}Ca, which are well in excess of ($\sim$100 times) analytical error (Fig. 1). The amplitude ranges from 23% (highest value divided by lowest value minus 1 times 100%) for the New Caledonia sample to about 6% for the Tahiti samples, and the total range in ^{238}U/^{40}Ca for the three samples is 50%. Comparison with X-radiographs demonstrates that the ^{238}U/^{40}Ca cycles are annual. The ^{238}U/^{40}Ca values correlate strongly with the ^{88}Sr/^{40}Ca values, although there is scatter about a best fit line, which is outside of analytical error (Fig. 2). For a given ^{238}U/^{40}Ca value, the fossil subsamples are offset to slightly higher ^{88}Sr/^{40}Ca values or slightly lower ^{238}U/^{40}Ca values compared to the modern New Caledonia subsamples. For a given fractional shift in ^{88}Sr/^{40}Ca, the fractional shift in ^{238}U/^{40}Ca is about 6 times larger. Annual cycles of ^{238}U/^{40}Ca mimic and are in phase with the ^{88}Sr/^{40}Ca cycles, although, in detail one observes differences in the shapes of the curves (Fig. 1), which are outside of analytical error.

Given the known strong anticorrelation between ^{88}Sr/^{40}Ca and temperature (Smith et al., 1979; Beck et al., 1992; de Villiers et al., 1994) and the strong correlation between ^{88}Sr/^{40}Ca and ^{238}U/^{40}Ca observed here, one would expect a strong anticorrelation between ^{238}U/^{40}Ca and temperature. That is indeed the case for the two modern samples for which we have temperature data (Figs. 3, 4).

DISCUSSION

Identification of Primary Coralline Aragonite

The two aspects of our data that will be important in paleoceanographic and paleoclimatological research are (1) the observation that corals have annual cycles in U/Ca and (2) the correlation between U/Ca and temperature. The first observation will aid in ^{230}Th dating studies, where identification of unaltered coralline aragonite, which records accurate ages is a problem. As noted in the introduction, ^{230}Th dating of corals forms the basis for much of our knowledge of the chronology of late Quaternary paleoclimatic events and for the calibration of a large portion of the radiocarbon timescale. Thus, any information that has a bearing on the accuracy of key ^{230}Th dates is important. Our data and that of Shen and Dunbar (1995) show that annual cycles in U/Ca are a general feature of primary coralline aragonite. Therefore, any sample that does not have these cycles is quite likely altered, and a poor candidate for ^{230}Th dating. Although other elements are known to exhibit seasonal variations in coralline aragonite, for this application uranium is particularly important because it is the ultimate parent of ^{230}Th. Furthermore, the amplitude of the observed variations is large enough so that this sort of sample screening could be performed by ICP–MS (see Shen and Dunbar, 1995), which would facilitate sample throughput.

Thermometry, the Relationship Between U/Ca and Temperature

The second observation may be important for reconstructing past sea surface temperatures. We can quantify the correlation between temperature and ^{238}U/^{40}Ca in a number of ways. A basic issue is the functional form of the equation relating temperature to ^{238}U/^{40}Ca. A thermodynamicist might argue for a linear relationship between inverse absolute temperature and the logarithm of ^{238}U/^{40}Ca. At this stage, we have chosen not to use this functional form because (1) there is no clear indication in the data (Fig. 4) for deviations from a linear temperature vs. U/Ca relationship, (2) the difference between a linear fit and an inverse absolute temperature vs. logarithm of U/Ca fit is small because of the limited temperature range of applicability, and (3) we do not know whether the variations in U/Ca are the result of equilibrium thermodynamic or kinetic processes or both. Instead we have chosen an empirical approach and fit lines to the temperature-^{238}U/^{40}Ca points. The equation of a best-fit line through all of the temperature-^{238}U/^{40}Ca points (points for both the New Caledonia and the Tahiti samples, Fig. 4) is

$$T\,(^\circ\mathrm{C}) = 45.0 - 18.4 \times 10^6 \times (^{238}\mathrm{U}/^{40}\mathrm{Ca})_{\mathrm{molar}}. \quad (1)$$

We can also regress the data points for New Caledonia and Tahiti separately (Fig. 4), yielding

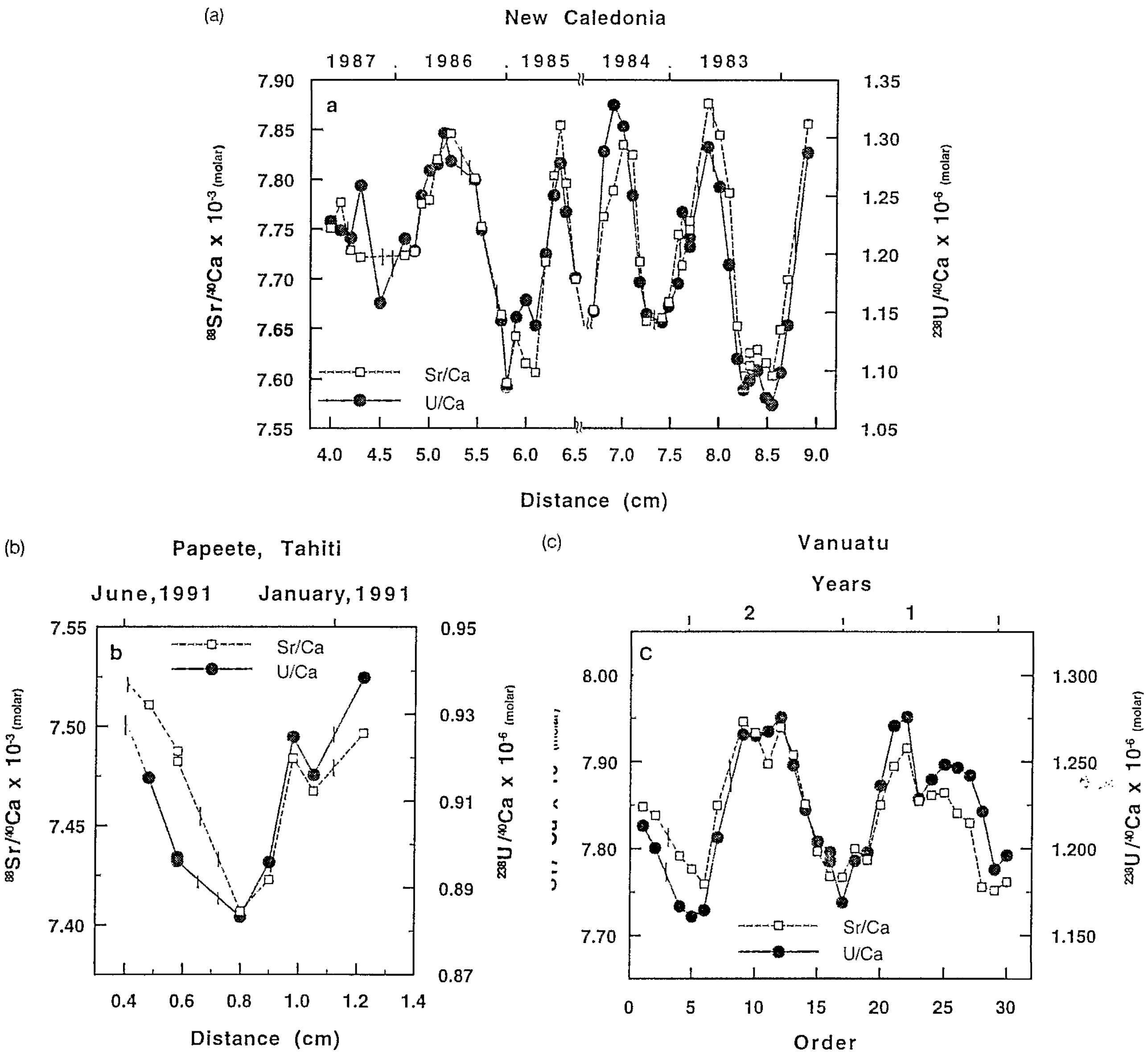

FIG. 1. Comparison between variations in ^{238}U/^{40}Ca (filled circles) and ^{88}Sr/^{40}Ca (open squares) ratios of *Porites* coral skeletons collected from three different localities in the south Pacific Ocean: (a) a modern coral collected near a temperature and salinity recording station at Amedee Lighthouse, Noumea, New Caledonia, (b) a modern coral collected near temperature recording station near Papeete, Tahiti, (c) a fossil coral drilled from a paleoreef on the island of Espiritu Santo Island, Vanuatu. The Vanuatu coral has a ^{230}Th age of 10,344 ± 42 (S. C. Gray, pers. commun.). The variations are annual based on comparison with annual growth bands. The symbol, ≈, is a discontinuity in the record due to a 0.4 cm parallel offset in the sampling transect. The symbol, |, represents the position of a subsample for which a particular analysis was not made.

for New Caledonia:

$$T(^\circ\mathrm{C}) = 48.8 - 21.5 \times 10^{6} \times (^{238}\mathrm{U}/^{40}\mathrm{Ca})_{\mathrm{molar}}, \quad (2)$$

for Tahiti:

$$T(^\circ\mathrm{C}) = 49.2 - 23.3 \times 10^{6} \times (^{238}\mathrm{U}/^{40}\mathrm{Ca})_{\mathrm{molar}}. \quad (3)$$

All three lines have similar slopes and intercepts, indicating that the correlation between temperature and U/Ca is similar at both localities. The fractional change in U/Ca per degree Celsius from the three lines ranges from 4.5 to 5.6%/°C. This is about 6 times the fractional change in Sr/Ca per degree Celsius. One potential advantage of U/Ca over Sr/Ca thermometry is the lower analytical precision required to obtain a given precision in temperature. U/Ca thermometry may therefore be possible with lower precision higher throughput techniques such as ICP-MS (see Shen and Dunbar, 1995). Our data suggests that temperature plays a major role in controlling U/Ca in corals and that U/Ca thermometry is a viable possibility.

However, when one considers the U/Ca-temperature relationship in detail (Fig. 4), one realizes that at least one other variable must contribute to changes in U/Ca. The two re-

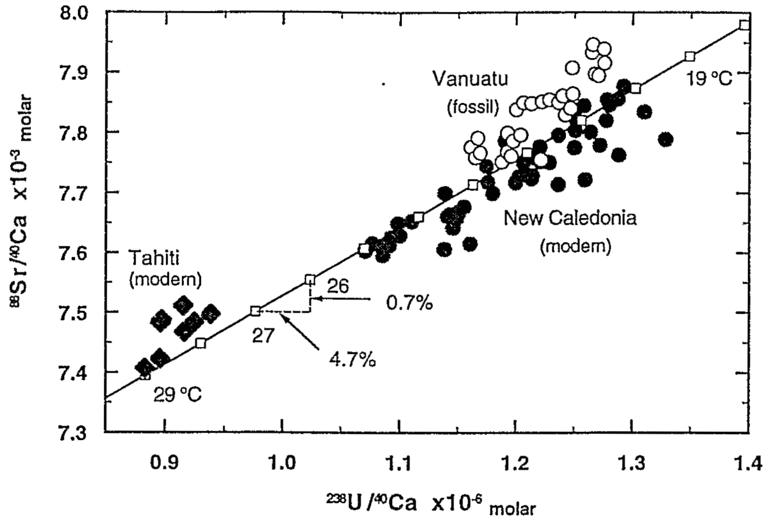

FIG. 2. A plot of ^{88}Sr/^{40}Ca vs. ^{238}U/^{40}Ca for subsamples of three corals from different localities: Noumea, New Caledonia (filled circles), Papeete, Tahiti (filled diamonds), and Espiritu Santo Island, Vanuatu (open circles). For each sample taken individually and for all subsamples taken as a whole, Sr/Ca and U/Ca correlate strongly. As Sr/Ca is known to correlate with temperature (Smith et al., 1979; Beck et al., 1992), this suggests that U/Ca also correlates with temperature. The relationship of both isotope ratios to temperatures is depicted by the points (open boxes) on the line. The line and the boxes were calculated from Eqns. 4 and 5 (see text). The percentages 4.7 and 0.7 are the fractional shifts in ^{238}U/^{40}Ca and ^{88}Sr/^{40}Ca per °C at 26.5.

gressions for individual samples (Eqns. 2, 3) are subparallel, but have different intercepts and the regression through all points (Eqn. 1) has a shallower slope than the other lines (Eqns. 2, 3). Equation 1 gives mean annual U/Ca temperatures that agree very well with measured mean annual temperatures at both sites; however, the seasonal amplitude in the U/Ca temperatures of Eqn. 1 is smaller than the measured amplitude at both sites. In contrast, Eqns. 2 and 3 recover seasonal amplitudes at both sites, but only recover the mean annual temperature at the site for which the regression was made. We do not believe that this discrepancy is the result of averaging U/Ca values for material that precipitated over extended periods of time. In the case of the New Caledonia sample, the subsample thickness was about 1 mm, equivalent to a temporal interval of a month. This is the interval over which our temperature measurements were averaged. In the case of the Tahiti sample, the subsample thickness was about 0.6 mm, equivalent to a temporal interval of half a month, the interval over which we averaged the temperature measurements. At any one time, calcification occurs over some depth interval. If this interval is large, one could average U/Ca values for material that precipitated over a significant time interval even if sample thickness is small. However, inspection of the surface of the both the New Caledonia and Tahiti samples indicates that the depth interval over which significant precipitation occurs is less than 1 mm. The surface topography is well under 1 mm and there does not appear to be significant thickening of skeletal parts below about 0.5 mm. Thus, skeletal averaging does not appear to be the source of the discrepancy. Therefore, some other variable besides temperature affects U/Ca. This factor could either offset U/Ca values to different amounts at the two localities or could change seasonally and affect the amplitude of the U/Ca ratios. The simpler of the two possibilities is a variable that differs between the two localities, causing a mean annual offset in U/Ca. Assuming this is the case, our best estimate for a generally applicable U/Ca-temperature relationship for *Porites* corals is

$$T\,(^\circ\mathrm{C}) = 48.0 - 21.5 \times 10^6 \times (^{238}\mathrm{U}/^{40}\mathrm{Ca})_{\mathrm{molar}}. \qquad (4)$$

This equation uses the slope of Eqn. 2 (which is similar to but better constrained than the slope of Eqn. 3) but uses an intercept that is intermediate between the two. Equation 4 gives amplitudes in U/Ca temperature that are similar to the amplitudes in measured temperature at both sites (Figs. 5, 6), but mean annual U/Ca temperatures that are offset by 0.5 to 1°C from the measured mean annual temperatures at New Caledonia and Tahiti. Presumably this offset results from the unknown addition factor(s) that also affects U/Ca. Plausible choices for this factor include coral species, extension rate, coral physiology, salinity, pH, and total CO_2 (see below). Note that the extension rate for the Tahiti sample ($\sim$1.4 cm/y) is larger than for the New Caledonia sample ($\sim$1.1 cm/y, horizontal scales in Fig. 1).

Thermometry, The Relationship Between U/Ca and Sr/Ca

We can also examine the relationship between U/Ca and temperature by comparing U/Ca and Sr/Ca (Fig. 2) because Sr/Ca is known to be a proxy for temperature (Smith et al., 1979; Beck et al., 1992; de Villiers et al., 1994; McCulloch et al., 1994). The strong correlation between Sr/Ca and U/Ca for all three samples again suggests that U/Ca is largely controlled by temperature. While Sr/Ca and U/Ca correlate strongly, the scatter about a best-fit line of data for the modern subsamples is outside of analytical error. The largest deviations of the modern subsamples from a best-fit line are $\sim$4.8% for U/Ca or $\sim$0.7% for Sr/Ca. These deviations are

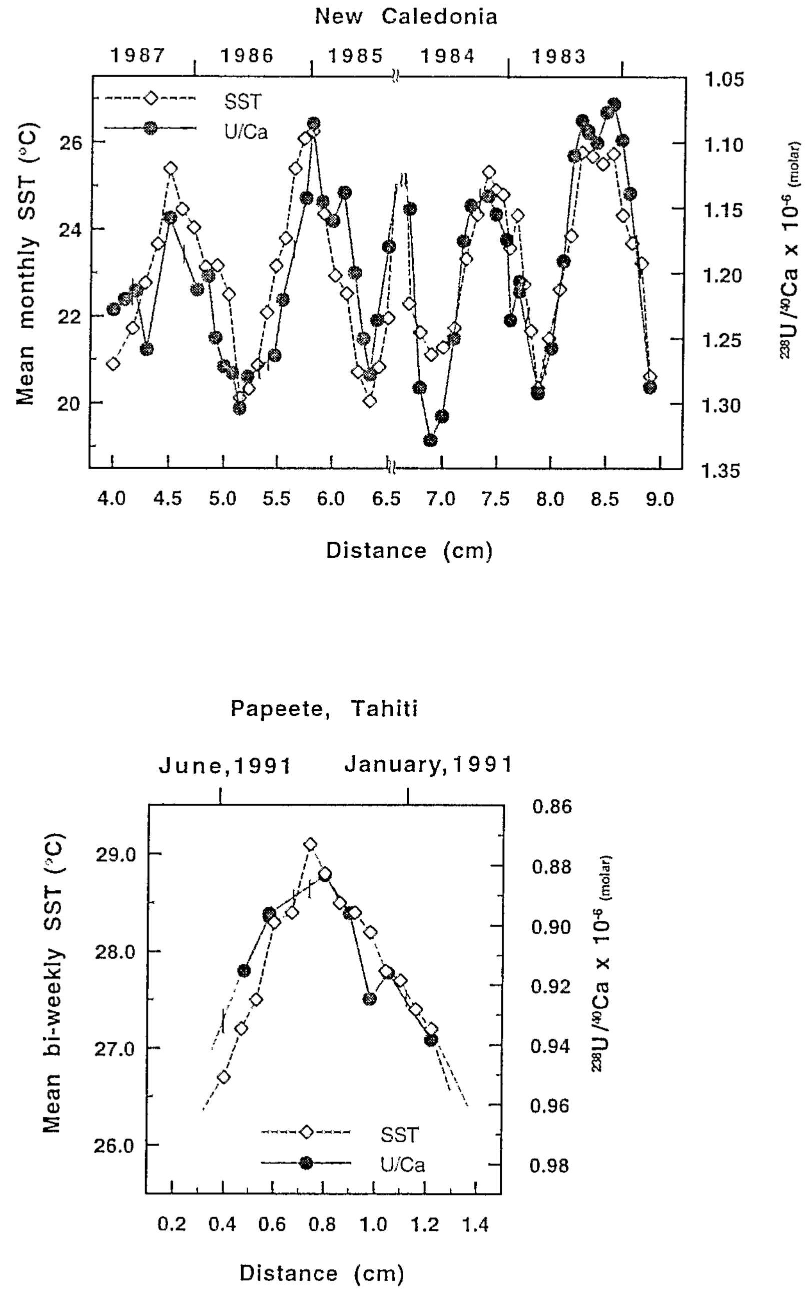

FIG. 3. Comparison between variations in ^{238}U/^{40}Ca ratio and sea-surface temperature (SST) for both modern coral samples. The abscissa are linear in distance along the growth axis. Times were assigned to particular distances based on density banding visible in X-radiographs. The distance corresponding to the maximum ^{238}U/^{40}Ca value for a particular growth band was assigned to the minimum value in mean monthly SST for a particular year for the New Caledonia coral. The distance corresponding to the minimum ^{238}U/^{40}Ca value was then assigned to the maximum SST. Distances were assigned to the other temperatures by linear interpolation between distances for the maximum and minimum temperature. For the Tahiti coral, the distance corresponding to the each temperature value was assigned based on knowledge of the time of sample collection and assuming a constant growth rate determined from annual bands. The symbols, ≈ and |, are described in the Figure 1 caption.

equivalent to ~1°C (using the Eqn. 5 Sr/Ca vs. temperature relationship (see Beck et al., 1992) and the Eqn. 4 U/Ca vs. temperature relationship), indicating that either the U/Ca or Sr/Ca thermometer or some combination of both can have inaccuracies of at least this magnitude. The Sr/Ca-U/Ca points for the fossil Vanuatu sample are slightly offset from those of the modern New Caledonia sample. This may be due to small but resolvable changes in the seawater U/Ca ratio (6%) over the last 10,000 years (see Russell, 1994, for a discussion of this possibility). It may also be due to the addition factor, discussed above, which affects coral U/Ca.

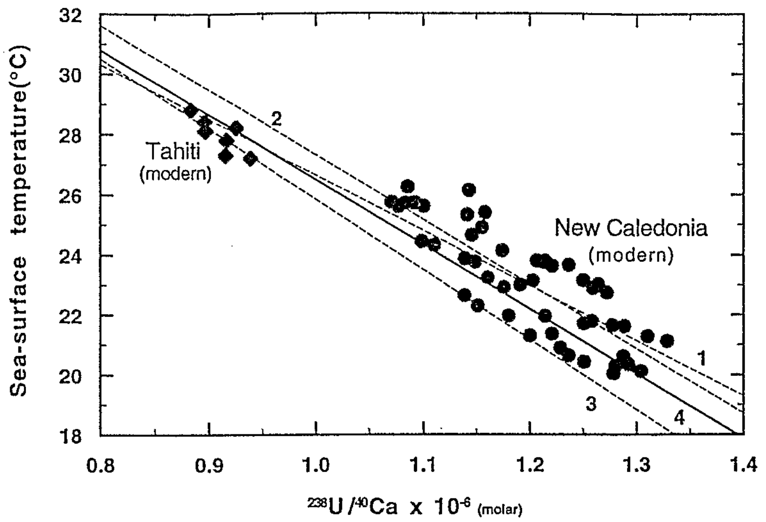

FIG. 4. Sea-surface temperature vs. $^{238}U/^{40}Ca$ ratio for both modern coral samples. Temperatures were assigned to each $^{238}U/^{40}Ca$ value by linear interpolation of monthly or half-monthly temperatures in Fig. 3. As surmised from Figs. 1 to 3, U/Ca correlates strongly with temperature. Best-fit line 1 is fit through all of the temperature-$^{238}U/^{40}Ca$ points (Eqn. 1 in text). Best-fit lines 2 and 3 are fit to New Caledonia and Tahiti data points, respectively (see Eqns. 2 and 3 in text). Line 4 uses the slope of line 2 and an intercept that is intermediate between lines 2 and 3. Line 4 is our best estimate of a generally applicable U/Ca-temperature relationship for *Porites* (see Eqn. 4 in text).

In addition to U/Ca temperature and measured temperature, we have also plotted Sr/Ca temperature as a function of distance along the growth axis (time) in Figs. 5 and 6. $^{88}Sr/^{40}Ca$ temperatures are calculated from the following equation:

$$T\,(^\circ C) = 168.1 - 18.81 \times 10^3 \times (^{88}Sr/^{40}Ca)_{molar}. \quad (5)$$

This equation is based on the data of Beck et al. (1992). There was an error in the value for the intercept in Eqn. 1 of Beck et al. (1992; see *Science* **264**, 891, 1994). Equation 5 has the correct intercept and has been further modified for minor changes in standardization and so that the dependent variable is the measured quantity, $^{88}Sr/^{40}Ca$, as opposed to the derived quantity, Sr/Ca. As shown by Beck et al. (1992), Sr/Ca temperatures are very similar to the measured temperatures for the Tahiti and New Caledonia samples. Thus, our discussion

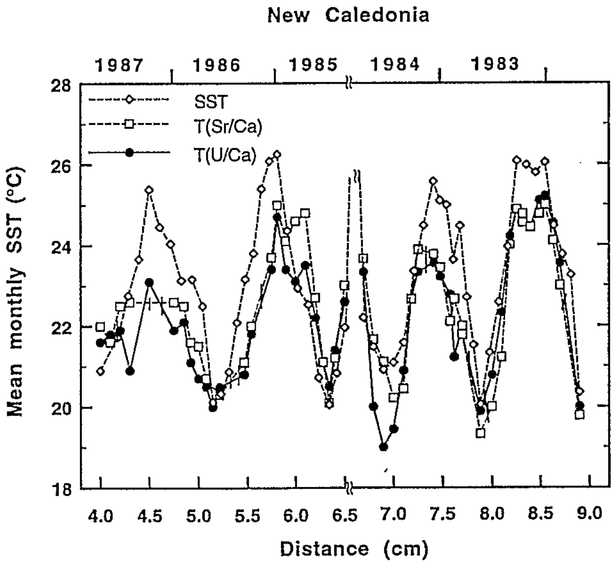

FIG. 5. Comparison among measured SST (open diamonds) from the temperature-salinity recording station at Amedee Lighthouse, Noumea, New Caledonia, $^{238}U/^{40}Ca$ temperatures (solid circles, calculated from Eqn. 4) and $^{88}Sr/^{40}Ca$ temperatures (open boxes, calculated from Eqn. 5) recorded in a *Porites lobata* coral collected near the station. The symbols, ≈ and |, are described in the Fig. 1 caption.

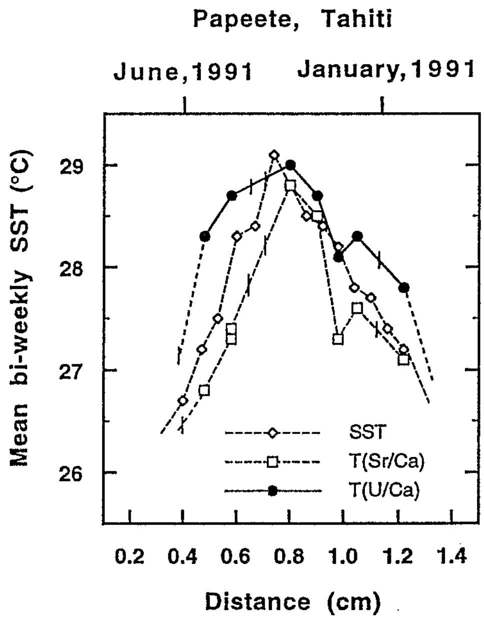

FIG. 6. Comparison among measured SST (open diamonds) from the temperature recording station at Papeete, Tahiti, $^{238}U/^{40}Ca$ temperatures (solid circles, calculated from Eqn. 4) and $^{88}Sr/^{40}Ca$ temperatures (open boxes, calculated from Eqn. 5) recorded in a *Porites solida* coral collected near the station. The symbol, |, is described in the Fig. 1 caption.

of the relationship between temperature and U/Ca temperature applies equally well to the relationship between Sr/Ca temperature and U/Ca temperature.

Sr/Ca temperatures (Eqn. 5) and U/Ca temperatures (Eqn. 4) for the fossil Vanuatu sample are plotted as a function of distance along the growth axis (Fig. 7). Both sets of temperatures give similar amplitudes. There is a small offset in mean annual temperature, which may result from a slight temporal change in marine U/Ca or may be due to our unknown additional factor affecting U/Ca. However, both thermometers give mean annual temperatures that are 4 to 5°C lower than present value for Vanuatu (26.5°C), and seasonal amplitudes that are larger than the present amplitude (3°C). Thus, the U/Ca temperatures support the idea that temperatures during deglaciation in the western Pacific were 4 to 5°C lower than present (see discussion of paleotemperatures below). Beck et al. (1992) reached the same conclusion based on Sr/Ca analysis of the same sample.

Thermometry, Theoretical Considerations

To this point, our discussion of U/Ca thermometry has focused on purely empirical considerations. Development of a model within which to view our observations will, out of necessity, require simplifying assumptions. We make the following assumptions. The system is in partial thermodynamic equilibrium. The aqueous marine uranium species (UO_2^{2+}, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$) and the aqueous species involved in carbonate reactions (CO_3^{2-}, HCO_3^-, $H_2CO_3^*$, OH^-, H^+, H_2O, Ca^{2+}) are all in thermodynamic equilibrium with respect to each other and with the uranium component of coralline aragonite. Total dissolved uranium and Ca^{2+} are constant at modern values, and total CO_2, temperature, and pH are controlled externally. Uranium substitutes as UO_2^{2+} into the ninefold Ca^{2+} site in aragonite. We do not assume thermodynamic equilibrium between the aqueous species and aragonite.

Some of the assumptions require additional discussion. The lack of thermodynamic equilibrium between aragonite and the aqueous species is reasonable as the tropical surface ocean is known to be out of equilibrium with aragonite. The assumption of thermodynamic equilibrium between the uranium component in aragonite and the aqueous species may not be valid but is made out of necessity, a point upon which we elaborate below. A fairly strong argument can be made for the substitution of uranium as uranyl into the Ca^{2+} site in coralline aragonite. In seawater, uranium is always speciated as uranyl or uranyl complexed to (a) carbonate anion(s). Uranyl has the same valence as calcium. The uranyl ion is linear and has a half-length of 3.15 Å along the linear axis (De Voto, 1978) and a radius of 1.35 Å perpendicular to this axis (De Voto, 1978), whereas Ca^{2+} has an ionic radius of 1.18 Å (Dickson, 1990). Although the uranyl ion is a different shape than the calcium ion and is generally larger, it is plausible that it substitutes for calcium for a number of reasons. Uranium partitions preferentially into aragonite over calcite (see Meece and Benninger, 1993). Preference of uranyl for the large irregular calcium site in aragonite over the small regular calcium site in calcite is a reasonable explanation for this. Furthermore (although not isostructural with aragonite), a naturally occurring orthorhombic uranyl carbonate is known (rutherfordine, UO_2CO_3; Marckwald, 1906). Thus, the assumption of uranyl substitution for calcium in coralline aragonite is reasonable.

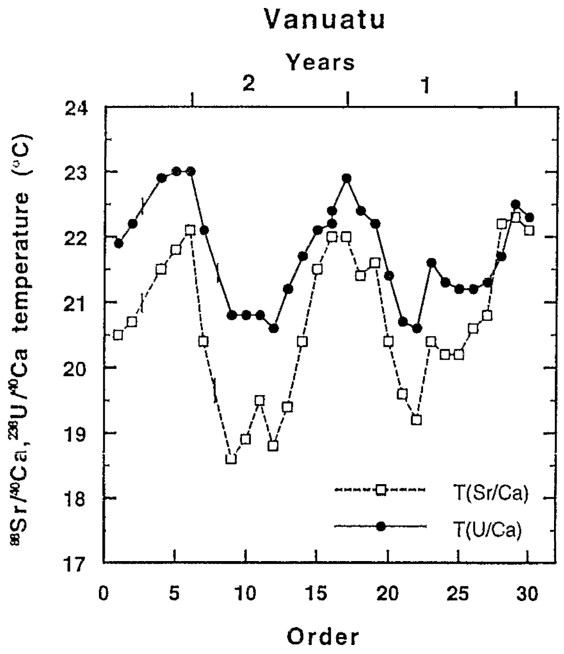

FIG. 7. Plot of $^{238}U/^{40}Ca$ (solid circles) and $^{88}Sr/^{40}Ca$ (open boxes) derived temperatures from Eqns. 4 and 5 as a function of subsample order along the growth axis for the Vanuatu fossil sample. Distances along the growth axis are unavailable for this sample; however, ten subsamples correspond to about 1 cm. The symbol, |, is described in the Fig. 1 caption. This coral has a ^{230}Th age of 10,344 ± 42 years (S. C. Gray, pers. commun.). It shows that both $^{234}U/^{40}Ca$ and $^{88}Sr/^{40}Ca$ temperatures have similar amplitudes, and give mean annual temperatures that are 4 to 5°C lower than the present value for Vanuatu (26.5°C; Beck et al., 1992). The small offset in mean annual $^{238}U/^{40}Ca$ and $^{88}Sr/^{40}Ca$ temperatures may result from a slight temporal change in marine U/Ca or may be due to our unknown additional factor affecting U/Ca (see discussion in text). The fact that the offset is small indicates that either coralline U/Ca is not sensitive to differences in the concentrations of the aqueous carbonate species in ambient seawater or that the difference in aqueous carbonate ion concentration between the Vanuatu and New Caledonia situation is small.

Given these assumptions, the substitution of uranium into coralline aragonite is governed by the following exchange reaction:

$$UO_{2\,(\mathrm{seawater})}^{2+} + CaCO_{3\,(\mathrm{aragonite})} = UO_2CO_{3\,(\mathrm{aragonite})} + Ca_{(\mathrm{seawater})}^{2+}. \quad (6)$$

We can solve for the UO_2CO_3 content of aragonite if we know the UO_2CO_3 activity in aragonite and assume ideal solution of UO_2CO_3 in aragonite. The UO_2CO_3 activity can be calculated if we know the equilibrium constant of Eqn. 6 as a function of temperature and the activities of the three other components in the exchange reaction. Thermodynamic data for the equilibrium constant is given in the appendix. Most notably, we have substituted rutherfordine thermodynamic data for the unknown uranyl carbonate endmember in solid solution with aragonite. Given the known seawater Ca^{2+} concentration, the calculation of Ca^{2+} activity is straight forward (see appendix). The activity of aragonite is assumed to be unity as (for the present purposes) coralline aragonite is essentially pure. Calculation of the activity of uranyl ion is more complicated because of the four uranyl species in seawater. We have assumed that total dissolved uranium is constant, but how that uranium is apportioned into the various aqueous species is governed by the following equations (Langmuir, 1978):

$$UO_{2\,(seawater)}^{2+} + CO_{3\,(seawater)}^{2-} = UO_2CO_{3\,(seawater)}^{0}; \tag{7}$$

$$UO_2CO_{3\,(seawater)}^{0} + CO_{3\,(seawater)}^{2-} = UO_2(CO_3)_{2\,(seawater)}^{2-}; \tag{8}$$

$$UO_2(CO_3)_{2\,(seawater)}^{2-} + CO_{3\,(seawater)}^{2-} = UO_2(CO_3)_{3\,(seawater)}^{4-}. \tag{9}$$

We can solve for the activities of the aqueous uranium species given total uranium content (see appendix), activity-composition relationships for the uranyl species (see appendix), the equilibrium constants for the three reactions (see appendix), and the CO_3^{2-} activity. The CO_3^{2-} activity is controlled by well-known carbonate equilibria (see Garrels and Christ, 1965, and appendix) and varies as a function of pH, temperature, and total CO_2.

Thus, we can calculate the CO_3^{2-} activity as a function of pH, temperature, and total CO_2, then solve for the activity of uranyl ion using the equilibrium constants for Eqns. 7 to 9 (see appendix) and the stipulation that total dissolved uranium is constant at the modern value (see appendix). Finally we can solve for the activity (and amount) of uranyl carbonate in aragonite, using the equilibrium constant for Eqn. 6 and the activities of the other components in Eqn. 6.

Calculated U/Ca ratios of coralline aragonite, as a function of temperature, pH, and total CO_2, are shown in Fig. 8. While any such model has a number of sources of error, there are lessons to be learned from the results. First, the model reproduces the observed inverse relationship between temperature and U/Ca. Of interest is the fact that, for the model calculation, much of the U/Ca temperature dependence results from temperature dependent changes in the equilibrium constants for reactions among the aqueous species, not from temperature dependent changes in the equilibrium constant for the exchange reaction. Second, the model suggests that U/Ca should be very sensitive to pH and total CO_2 changes.

The model leaves us with an apparent paradox. There is one piece of evidence that suggests that the concentrations of the aqueous carbonate species do not have a large effect on coralline U/Ca. The modern New Caledonia sample grew at a time (1980s) when atmospheric CO_2 levels were well above preindustrial values. The Vanuatu sample grew about halfway through deglaciation, when atmospheric CO_2 levels were well below preindustrial values. Thus, one would expect that the concentrations of the aqueous carbonate species would be different in the fossil Vanuatu vs. modern New Caledonia cases. In fact, if one assumes constant pH, and uses CO_2 partial pressure instead of total CO_2 as an external variable, the model predicts a factor of two difference in coralline U/Ca for the two scenarios. Such a difference should be obvious in the U/Ca values of the two samples. Because we have analyzed the subsamples for Sr/Ca as well as U/Ca, we can subtract off the component of U/Ca variation that results from temperature change, subject to the assumption that Sr/Ca is only sensitive to temperature. If the concentrations of the aqueous carbonate species do not affect U/Ca, the Vanuatu points should plot on the same line as the New Caledonia points in Fig. 2. There is a slight offset between the sets of points. However, the magnitude of the offset is small compared to that predicted by our model. Thus, either the aqueous carbonate ion concentrations in the New Caledonia and fossil Vanuatu situations are similar or coralline U/Ca is not controlled appreciably by aqueous carbonate ion concentration.

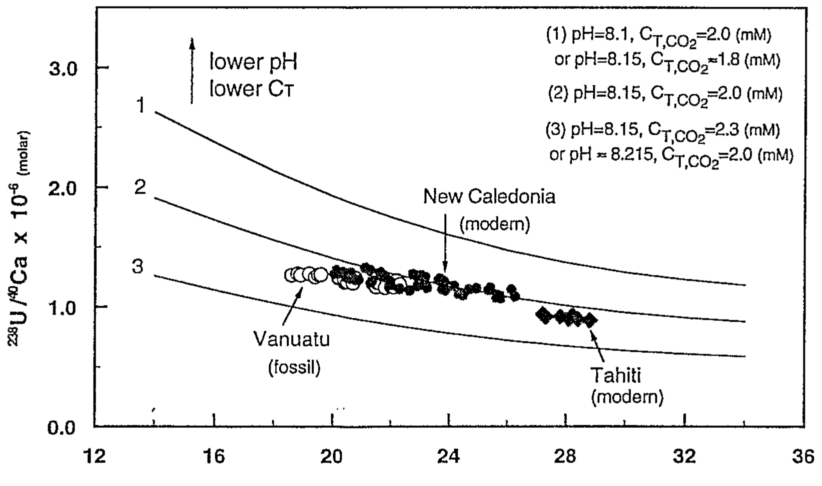

FIG. 8. Plot of calculated $^{238}U/^{40}Ca$ ratio of coralline aragonite as a function of temperature, pH, and total CO_2 (from our model, see text and appendix). Lines 1, 2, and 3 show calculated U/Ca-temperature relationships at different pH and total CO_2 values. Filled circles and diamonds are $^{238}U/^{40}Ca$ and measured SST values for the New Caledonia and Tahiti sites. Open circles are $^{238}U/^{40}Ca$ ratios and $^{88}Sr/^{40}Ca$ temperatures for the fossil Vanuatu coral. This model reproduces the observed inverse relationship between temperature and U/Ca. It also suggests that U/Ca should be very sensitive to pH and total CO_2 changes, a possibility that merits further research.

In addition to our Vanuatu sample, there is another set of samples for which we can compare Sr/Ca and U/Ca values: the Barbados deglacial sequence for which TIMS uranium concentrations were measured (Bard et al., 1990a,b) in order to obtain ^{230}Th ages, and Sr/Ca values were measured as a proxy for temperature (Guilderson et al., 1994). As deglaciation proceeds, both U/Ca (calculated from uranium concentration) and Sr/Ca generally decrease, consistent with increasing temperature. However, the shapes of the Sr/Ca and U/Ca curves differ somewhat, particularly 15 to 12 thousand years ago. In that interval, U/Ca values appear to be anomolously low (Figs. 9, 10) compared to Sr/Ca values (Guilderson et al., 1994). These low values could plausibly reflect anomolously low aqueous carbonate ion concentrations. However, it is not clear whether the uranium and Sr/Ca measurements in this interval were made on the same samples. In some cases, they clearly are not, as the interval contains seven uranium analyses but only four Sr/Ca analyses. Given the uncertainties in the dataset, we choose to interpret past U/Ca variations in terms of temperature, but the possibility of a coralline U/Ca-aqueous carbonate connection remains open. We encourage further research into this possibility.

However, if we follow the line of reasoning that corralline U/Ca is not a function of ambient aqueous carbonate ion concentration, we run into an apparent paradox. Our model is able to reproducė the observed inverse U/Ca-temperature relationship only because it takes into account the changes in concentration of the aqueous carbonate species as a function of temperature. To explain this paradox, we propose that during calcification corals produce microenvironments in which the concentrations of the aqueous carbonate species are controlled or buffered in some fashion, and therefore different

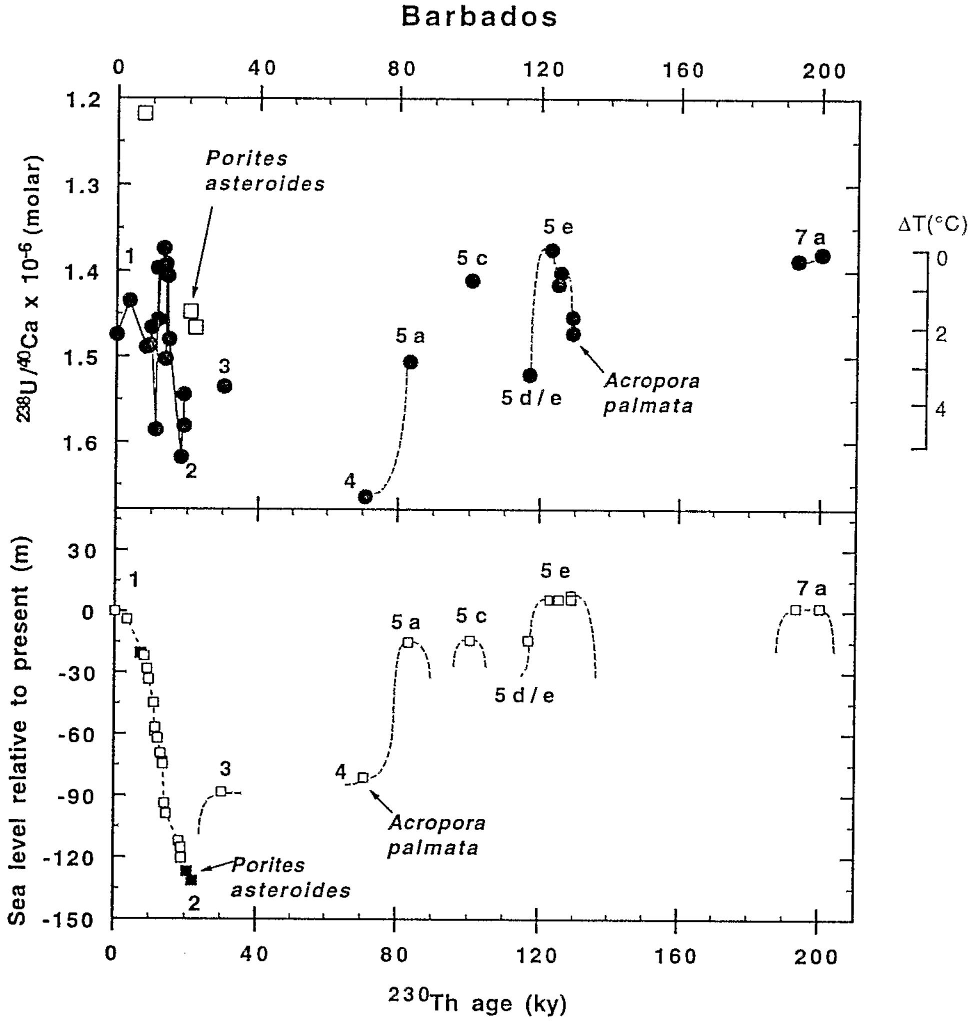

FIG. 9. (a) Plot of ^{238}U/^{40}Ca for *Acropora palmata* (filled circles) and *Porites asteroides* (open boxes) vs. ^{230}Th age. (b) Sea level based on *Acropora palmata* (open boxes) and *Porites asteroides* (filled boxes) vs. ^{230}Th age. Oxygen isotope stages are labelled 1 to 7a. Temperature bars are calculated from Eqn. 4. All data are from Barbados corals and are taken from Edwards (1988), Bard et al. (1990a,b), and Gallup et al. (1994). U/Ca varies systematically with sea level, with high U/Ca values coinciding with low sea level and low U/Ca coinciding with high sea level. If the U/Ca change is interpreted in terms of changing temperature, the net glacial-interglacial change in temperature at Barbados is 4 to 6°C. The offset in U/Ca values for *Porites* and contemporaneous *Acropora* corals indicates the U/Ca is, in part, controlled by species.

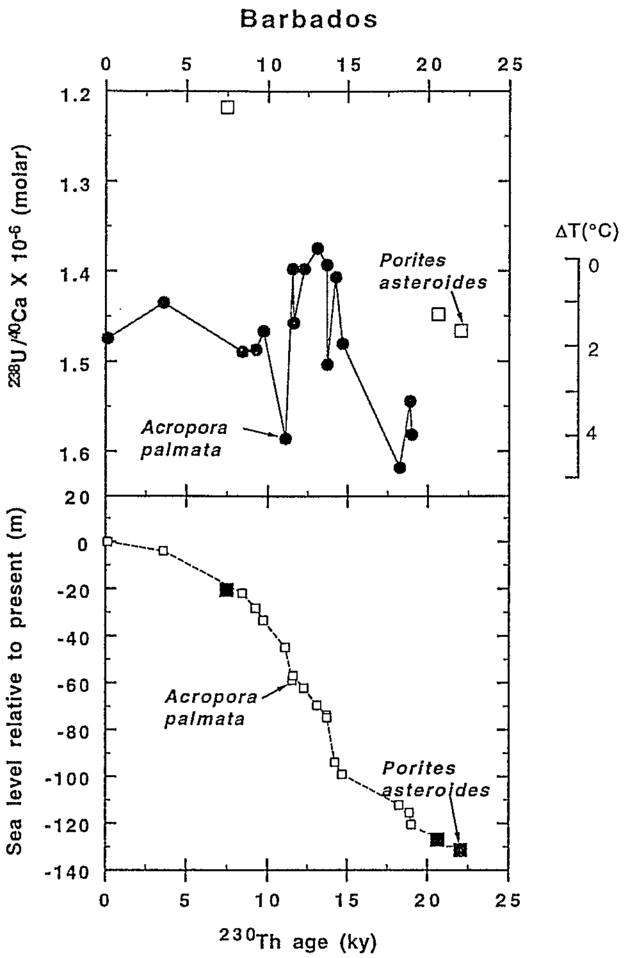

FIG. 10. The last 25 Ky of the Barbados *Acropora palmata* (filled circles) and *Porites asteroides* (open boxes) $^{238}U/^{40}Ca$ and sea level records are shown detail. The temperature bar is calculated from Eqn. 4. The difference between the glacial (stage 2) and interglacial (stage 1) $^{238}U/^{40}Ca$ temperature is 3 to 4°C. Temperature rises rapidly during the initial stage of deglaciation (18 to 15 Ky BP), reaching values that are comparable or even higher than interglacial values. While sea level continues to rise, temperatures remain generally high between 15 to 11 Ky BP, then (except for one very low temperature point at 11 Ky BP) drop slightly to modern values. During deglaciation, $^{238}U/^{40}Ca$ temperature does not change linearly with sea level.

than the concentrations in ambient seawater. If ambient temperature changes, the temperature in this microenvironment changes in concert, causing shifts in the proportions of the aqueous carbonate species, subject to the controls of the buffering reaction(s). These shifts, then, affect the concentrations of the aqueous uranyl and uranyl carbonate species, which in turn affect the U/Ca ratio in the precipitating coralline aragonite. In support of this idea, we argue that corals must have some such chemical control over the aqueous carbonate species in order to precipitate aragonite in the first place. The exact buffering reactions or mechanism may vary from species to species, perhaps explaining the U/Ca species dependence discussed below.

The main limitation of our model is the assumption of equilibrium between the aqueous species and the uranium component of the coralline aragonite. However, even if this assumption is wrong, it does not necessarily negate some of the basic model results. Kinetic control of uranyl incorporation into coralline aragonite is certainly a possibility and perhaps likely. It is not difficult to imagine differences in rates at which various uranyl-containing ions and Ca^{+2} reach sites of calcification. Nor is it difficult to imagine differences in the rates at which these ions are incorporated into coralline aragonite. As such rates would be a function of temperature, U/Ca ratios could be controlled by kinetic processes and still be sensitive to temperature. Furthermore, as indicated by our model, the proportions of the various uranyl-containing ions are a function of temperature. Therefore, if the rates at which the various uranyl-containing ions and Ca^{+2} reach sites of calcification or the rates at which they are incorporated into coralline aragonite differ, then coralline U/Ca would be a function of temperature. Thus, regardless of whether the incorporation of uranium into coralline aragonite is a kinetically controlled process or an equilibrium thermodynamic process, aspects of the model are valid.

The assumption of constant seawater U/Ca brings up a potential limitation of U/Ca thermometry. Accurate thermometry requires knowledge of the temporal variation in marine U/Ca. The marine residence time of calcium is 1.1 million years (Broecker and Peng, 1982) and that of uranium is about 300 thousand years (Ku et al., 1977). Thus, one would not expect large changes in the marine U/Ca ratio over the last few hundred thousand years. Uranium cycle models demonstrate that massive changes in rates of uranium input or output would be required to change marine uranium concentrations by even several percent over tens of thousands of years (Richter and Turekian, 1993; Russell, 1994). Some possibilities for massive uranium cycle changes (such as large glacial-interglacial changes in riverine uranium input) can be ruled out on the basis of uranium isotopic data (Edwards et al., 1993). In sum, there is no evidence for large changes in marine U/Ca on glacial-interglacial timescales and residence time considerations argue against such changes.

Paleotemperatures

At present the only empirical evidence for a correlation between U/Ca and an environmental variable is the inverse U/Ca vs. temperature relationship demonstrated here and by Shen and Dunbar (1995). We have determined that another factor must also affect U/Ca. There is also an intriguing difference between the deglacial U/Ca and Sr/Ca records on Barbados, which may be related to changes in aqueous carbonate ion concentration. However, given the empirical evidence and the arguments presented above, we choose at present to interpret data on fossil corals in terms of the known relationship between temperature and U/Ca.

A large number of high precision uranium concentrations of corals (measured by TIMS methods) are reported in the literature. U/Ca ratios can be calculated from the uranium concentrations to well within a percent. This dataset may contain important information on the temperature history of the tropics and subtropics. The dataset does, however, have limitations because all of the reported TIMS uranium measurements were determined in order to obtain ^{230}Th ages. Information such as the time of year over which the sample grew is not important for these studies and is generally not known. Fortunately, sample requirements (>0.2 g) for the dating studies are such that the samples should integrate a good portion of a year, if not more. Thus, the reported uranium concentrations are likely to be reasonable approximations of mean annual values. Samples for dating are generally screened for detectable calcite, an indicator of diagenetic alteration. However, such a test does not screen for marine aragonitic cement, which would not generally be a problem for dating studies, but which might shift U/Ca.

Whereas the published data have some limitations, they also have at least three major advantages. First, we know the ages of the samples. Second, we know the sea level height at the time each sample formed, so that we can compare temporal changes in U/Ca to global climate. Furthermore, in the process of measuring the ^{230}Th age, the ^{234}U/^{238}U ratio is also measured. TIMS measurements of ^{234}U/^{238}U are quite precise (±0.1 to $\pm0.7\%$, 2σ; see Chen et al., 1986; Edwards et al., 1987a,b, 1993) and the ^{234}U/^{238}U ratio is a sensitive indicator of diagenetic remobilization of uranium (see Banner et al., 1991; Bard et al., 1991; Hamelin et al., 1991; Gallup et al., 1994). Thus, we can use this ratio as a screen for samples that may have experienced diagenetic changes in U/Ca.

As temperatures may vary from site to site, we wished to examine uranium data by locality. As uranium content may vary from species to species (Cross and Cross, 1983), we examined the data by individual species where possible, by genus in some cases, and by family in others. The two most extensive datasets are from the west coast of Barbados and the northeast coast of the Huon Peninsula, Papua New Guinea.

We screened out those Barbados samples for which diagenetic shifts in uranium isotopic composition have been documented. Such shifts have been discussed in detail (Bender et al., 1979; Edwards et al., 1987a,b; Edwards, 1988; Banner et al., 1991; Hamelin et al., 1991; Bard et al., 1991; Richter and Turekian, 1993; Gallup et al., 1994). To screen the corals, we followed the criterion that Gallup et al. (1994) developed to screen Barbados corals for ^{230}Th dating: initial δ^{234}U values must be less than or equal to 158. Screening reduces the number of analyses of pre-25 Ky corals from hundreds to the twelve values plotted in Fig. 9. This includes samples that grew during the interglacial before last (correlated with oxygen isotope stage 7a; Gallup et al., 1994), the last interglacial (correlated with oxygen isotope stage 5e; Bard et al., 1990b; Gallup et al., 1994), a sample from the sea level regression after the last interglacial (transition between stages 5e and 5d; Gallup et al., 1994), one from the subsequent interstadial (stage 5c; Bard et al., 1990b), one from the next interstadial (stage 5a; Gallup et al., 1994), a sample that grew during glacial stage 4 (Bard et al., 1990b), and one from the following interstadial (stage 3; Bard et al., 1990a). Also plotted are the post-25 Ky samples, from the last glacial maximum (Bard et al., 1990a), the last deglaciation (Bard et al., 1990a), and the present interglacial (Edwards, 1988; Gallup et al., 1994). All but three analyses are of *Acropora palmata* corals, the remaining being analyses of *Porites asteroides* corals.

The two most striking aspects of the Barbados data are (1) the clear difference between the U/Ca ratios of *Porites* samples and contemporaneous *Acropora palmata* samples (Figs. 9 to 11), (2) the general inverse relationship between sea

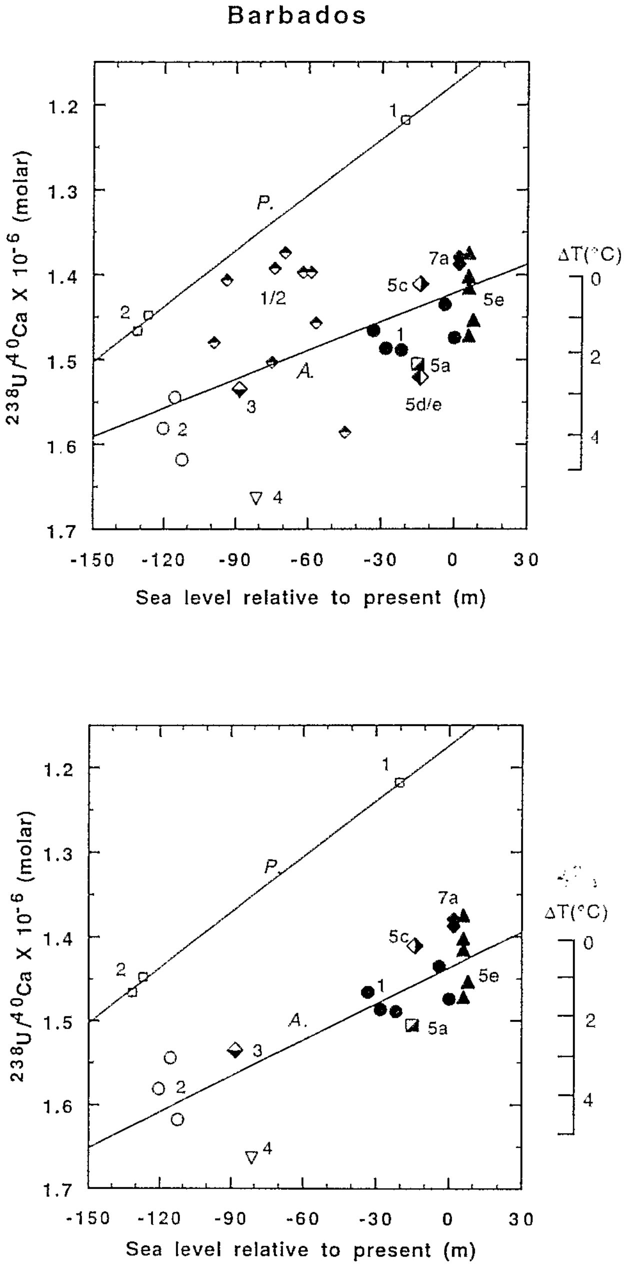

FIG. 11. Plot of ^{238}U/^{40}Ca ratio against sea level: (a) for all of the Barbados samples (taken from Edwards, 1988; Bard et al., 1990a,b; and Gallup et al., 1994) and (b) Barbados samples, except those that formed during transitions in global climate (1/2 and 5d/e samples). Open boxes represent *Porites asteroides* samples that formed during stage 1 and 2. Other symbols represent *Acropora palmata* samples that formed during various oxygen isotope stages, labeled as indicated from 1 to 7a. Best-fit lines are fit to *Acropora palmata* and *Porites asteroides* samples separately. Temperature bars are calculated from Eqn. 4. The best-fit lines suggest a glacial-interglacial change in Barbados temperature (corresponding to the full ~130 m change in sea level) of 4 and 5°C for the *Acropora* lines and 6°C for the *Porites* line. All three datasets show inverse correlations between U/Ca and sea level; however, the Fig. 11b *Acropora* correlation is stronger than the Fig. 11a correlation. This indicates that U/Ca and sea level are most strongly decoupled during transitions in global climate.

level and U/Ca among samples of the same species or genus (Figs. 9, 11). Regarding the first point, the U/Ca ratio of *Porites* samples is 10 to 25% lower than the U/Ca ratio of contemporaneous *Acropora* samples (Fig. 9). This indicates that U/Ca in corals is, in part, controlled by species.

The general relationship between the Barbados *Acropora palmata* U/Ca ratios and sea level can be summarized as follows (Fig. 9). The U/Ca ratios for corals that grew during the three interglacial periods (7a, 5e, 1), an interstadial (5c), and a portion of the last deglaciation (1/2 boundary) are the lowest, ranging from 1.38 to 1.47. Intermediate values of 1.51 to 1.54 are recorded by a sample that records the sea level drop after the last interglacial period (5d/e), samples that grew during two interstadials (3, 5a), and samples that grew during the last deglaciation (1/2). The highest values of 1.54 to 1.66 are recorded by corals that grew during glacial stages 2 and 4 and during the last deglaciation (1/2). Thus, the U/Ca values generally vary inversely with sea level (Figs. 9, 11). If the U/Ca ratios are controlled solely by temperature, this implies that temperature correlates with sea level.

We drew a best-fit line through all of the Barbados *Acropora palmata* U/Ca-sea level data (Fig. 11). The slope of this line confirms the inverse relationship between sea level and U/Ca. We have not calibrated *Acropora* directly; however, we have established $\Delta(U/Ca)/\Delta T$ for *Porites* (the slope of Eqn. 4). If this relationship holds for *Acropora*, we can translate changes in *Acropora* U/Ca to changes in temperature (temperature bars in Figs. 9–12). By multiplying $\Delta(U/Ca)/\Delta T$ by the slope of the *Acropora* best-fit line in Fig. 11, we calculate a $\Delta T/\Delta$(sea level) value of 3.1°C per 100 m of sea level rise. This corresponds to a 4°C shift in temperature at Barbados for a full glacial-interglacial variation in sea level of ~130 m.

Although there is a general inverse relationship between U/Ca and sea level, there is a significant amount of scatter about a best-fit line (Fig. 11). The source of the scatter may be related to the limitations in the dataset (discussed above), factors besides temperature that may control U/Ca, short-term variability in sea surface temperature, or a truly nonlinear relationship between sea surface temperature and sea level. Nonlinearity is likely, considering that sea surface temperature can change over hours, where as continental ice sheets grow and melt over thousands of years. In Fig. 10 the last 25 Ky of the Barbados U/Ca record is shown in detail. The difference between the glacial U/Ca temperatures (the points around 18 Ky) and interglacial temperatures (the points younger than 5 Ky) is 3 to 4°C. However, U/Ca temperature does not change linearly with sea level during deglaciation. U/Ca temperature rises rapidly during the initial stages of deglaciation (18 to 15 Ky BP), reaching values that are comparable or even higher than interglacial values. While sea level continues to rise, U/Ca temperatures remain generally high between 15 and 11 Ky BP, then (except for one very low temperature point at 11 Ky BP) drop slightly to modern values. Whereas U/Ca temperatures for the present interglacial are higher than those of the last glacial maximum, U/Ca temperature and sea level are not proportional during deglaciation.

If we remove from Fig. 11a data from samples that grew during transitions in global climate (1/2 and 5d/e samples), the inverse relationship between sea level and U/Ca is stronger (Fig. 11b). Thus, it would appear that sea level and U/Ca tend to be decoupled most strongly during transitions in global climate. A best-fit line through the resulting data gives a glacial-interglacial change in Barbados temperature (corresponding to the full ~130 m change in sea level) of 5°C.

Barbados *Porites* U/Ca ratios (Bard et al., 1990a) are only available for the last glacial period (stage 2) and the present interglacial (stage 1). Although there are only three analyses, the U/Ca values are consistent with the *Acropora* data as they indicate an inverse relationship between sea level and U/Ca, and a correlation between sea level and apparent temperature. These samples give temperature differences between stage 2 and 1 of 6°C. Our estimates of glacial-interglacial changes in Barbados sea surface temperature of 4 to 6°C are consistent with other coral-based estimates from Barbados (residual $\delta^{18}O$ and Sr/Ca thermometry; Guilderson et al., 1994).

In addition to the TIMS uranium analyses of Barbados corals, a significant number of analyses have also been reported for Huon Peninsula, Papua New Guinea, corals. Because of uncertainties about diagenetic remobilization of uranium for samples older than 25 Ky (see Stein et al., 1993), we only consider U/Ca values for samples younger than 25 Ky (Edwards et al., 1993). Those data cover the last half of deglaciation and are plotted in Fig. 12. Most analyses are on *Acropora* and *Montipora* samples. These samples give generally low U/Ca temperatures between 13 Ky and 9.6 Ky BP. One sample indicates a rapid rise in temperature between 9.6 and 8.7 Ky BP. The magnitude of this rise is about 6°C. The one *Porites* sample in the set has a U/Ca ratio that is about 27% lower than contemporaneous *Acropora* and *Montipora* U/Ca ratios, consistent in sense and generally consistent in magnitude with the U/Ca offset between Barbados *Acropora* and *Porites* samples. The one *Stylophora* sample has a U/Ca ratio that may be slightly lower than contemporaneous *Acropora* and *Montipora* U/Ca ratios.

There is a long-standing controversy (see Rind and Peteet, 1985) regarding tropical temperature estimates based on foram transfer functions (see CLIMAP, 1981) and those based on evidence for changes in snow line (see Rind and Peteet, 1985). CLIMAP last glacial maximum tropical sea surface temperatures are similar to modern values and imply that changes in tropical sea surface temperature on glacial-interglacial timescales are minimal. The snow line data suggest that glacial maximum tropical sea surface temperatures were on the order of 5°C lower than modern values. Coral Sr/Ca temperatures (Beck et al., 1992; Guilderson et al., 1994; Aharon et al., 1994) generally agree with the snow line estimates and disagree with the CLIMAP estimates. Taken as a whole, coralline U/Ca changes, when interpreted as reflecting temperature changes, paint a vastly different picture of tropical sea surface temperatures from the CLIMAP (1981) reconstructions, but one which is generally consistent with the snow line depression and coralline Sr/Ca estimates. The U/Ca data suggest that Barbados temperatures during the last three interglacial periods were similar to today's temperatures, that temperatures during interstadials have been slightly to greatly depressed from modern values, and that glacial temperatures (stages 2 and 4) were depressed 4 to 6°C below modern values. During the last deglaciation, U/Ca tempera-

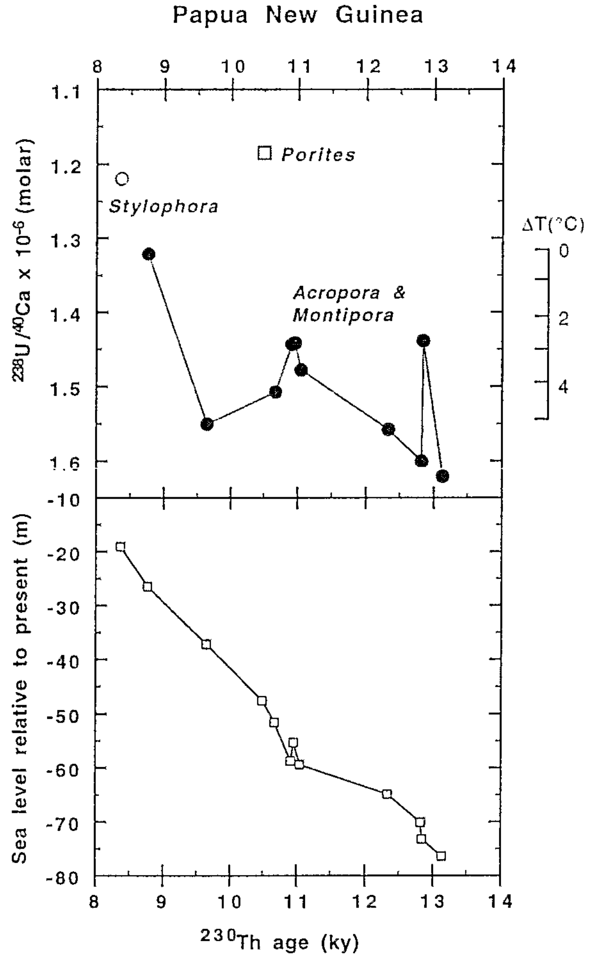

FIG. 12. ^{238}U/^{40}Ca values for Huon Peninsula, Papua New Guinea corals [*Acropora* and *Montipora* (filled circles), *Porites* (open box), and *Stylophora* (open circle)] vs. time (Edwards et al., 1993). This interval covers the last half of deglaciation. The temperature bar is calculated from Eqn. 4. ^{238}U/^{40}Ca temperatures are 5 to 6°C below present values between 13 Ky and 9.6 Ky BP and rise rapidly to modern values between 9.6 and 8.7 Ky BP. The low temperatures half way through deglaciation are consistent with low temperatures recorded by our Vanuatu sample at the same time. The Papua New Guinea, Vanuatu, and Barbados U/Ca temperatures are generally consistent with snow line depression data, as they document temperatures 4 to 6°C below modern values at various points in the glacial-interglacial cycle. In this respect, the U/Ca temperatures generally disagree with the estimates of tropical sea surface temperatures reported by CLIMAP (1981). Comparison of the Papua New Guinea and Barbados deglacial U/Ca records also indicates that the deglacial temperature histories in the two regions differ markedly.

tures at Barbados rose from glacial to interglacial values during the early portion of deglaciation. For Papua New Guinea, temperatures were 5 to 6°C lower than modern values halfway through deglaciation, rising to modern values about 9 Ky ago. Thus, in addition to documenting large temperature depressions during portions of the last interglacial-glacial-interglacial cycle, the U/Ca data suggest that during the last deglaciation longitudinal temperature gradients varied and were, in general, different from modern gradients.

CONCLUSIONS

We have used thermal ionization mass spectrometric techniques to measure ^{238}U/^{40}Ca and ^{88}Sr/^{40}Ca in coralline aragonite. Precisions of ±2‰ (2σ) on ^{238}U/^{40}Ca and ±1‰ (2σ) on ^{88}Sr/^{40}Ca are routinely attainable on samples of ~2 mg of coral, containing several nanograms of uranium. Both modern and fossil *Porites* coral skeletons have large annual cycles in ^{238}U/^{40}Ca (several to >20%). Because annual cycles in ^{238}U/^{40}Ca of coral skeleton appear to be general features of primary coralline aragonite, the preservation of such features will be important in identifying unaltered coral for U-series dating studies. Variations in ^{238}U/^{40}Ca mimic and are in phase with variations in ^{88}Sr/^{40}Ca. ^{238}U/^{40}Ca and ^{88}Sr/^{40}Ca correlate strongly in modern and fossil samples. For a given fractional shift in ^{88}Sr/^{40}Ca, the fractional shift in ^{238}U/^{40}Ca is 6 times larger. For modern samples, ^{238}U/^{40}Ca and ^{88}Sr/^{40}Ca are strongly anticorrelated with sea surface temperature. This suggests that annual variations in ^{238}U/^{40}Ca are largely controlled by temperature. There is some indication in the modern data for some other factor besides temperature, which may also affect U/Ca. Results of a model reproduce the observed inverse U/Ca vs. temperature relationship. The model also suggests that coralline U/Ca should be sensitive to pH and total CO_2. We encourage research into this possibility, which could plausibly be the source of a discrepancy between the deglacial Sr/Ca and U/Ca records from Barbados.

U/Ca thermometry of a Vanuatu sample, which grew halfway through the last deglaciation, gives temperatures 4 to 5°C lower than modern values, consistent with Sr/Ca thermometry on the same sample (Beck et al., 1992). U/Ca thermometry applied to published data for Barbados corals indicates that (1) temperature correlates with sea level, (2) glacial temperatures (stages 2 and 4) were 4 to 6°C lower than interglacial temperatures (stages 7a, 5e, and 1), and (3) temperatures rose from glacial to interglacial values early in the last deglaciation. Thermometry applied to published data on Papua New Guinea corals indicates that (1) temperatures were 5 to 6°C lower than interglacial temperatures from 13 to 9.6 Ky BP, then rose to present values by 8.7 Ky BP, and (2) the Papua New Guinea deglacial temperature history is quite different from that at Barbados. Taken as a whole, results from U/Ca thermometry generally support estimates of tropical temperatures obtained from Sr/Ca thermometry and snow line elevation data, but disagree with estimates based on foram transfer functions.

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APPENDIX—DATA USED FOR THE U/Ca MODEL

Concentration Data

$$[\mathrm{U}]_{\mathrm{T(seawater)}} = 3.2\ \mathrm{ppb}^{*}$$

$$[\mathrm{Ca}^{2+}]_{\mathrm{(seawater)}} = 410\ \mathrm{ppm}^{\dagger}$$

$$[\mathrm{Ca}^{2+}]_{\mathrm{(free)}} = 10^{-2.03}\ \mathrm{mole/L}^{\dagger}$$

$$[\mathrm{CO}_3^{2-}]_{\mathrm{(free)}} = 9\%\ [\mathrm{CO}_3^{2-}]_{\mathrm{(T)}}{}^{\ddagger}$$

$$C_{\mathrm{T}} = [\mathrm{H}_2\mathrm{CO}_3^{*}]_{\mathrm{(T)}} + [\mathrm{HCO}_3^{-}]_{\mathrm{(T)}} + [\mathrm{CO}_3^{2-}]_{\mathrm{(T)}}{}^{\dagger}$$

$$[\mathrm{U}]_{\mathrm{T(seawater)}} = [\mathrm{UO}_2^{2+}] + [\mathrm{UO}_2\mathrm{CO}_3^{0}] + [\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}] + [\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}]^{\S}$$

Activity Coefficients

$$\gamma_{\mathrm{Ca}^{2+}} = 0.28^{\ddagger} \quad \gamma_{\mathrm{CO}_3^{2-}} = 0.2^{\ddagger}$$

$$\mathrm{Log}\ \gamma = -Az^2\{(I)^{0.5}/[1 + (I)^{0.5}] - 0.3I\}$$

$$(A = 0.5,\ I = 0.7,\ \text{Davies Eq.}^{\dagger})$$

$$\gamma_{\mathrm{UO}_2^{2+}} = 0.323 \quad \gamma_{\mathrm{UO}_2\mathrm{CO}_3^{0}} = 1$$

$$\gamma_{\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}} = 0.323 \quad \gamma_{\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}} = 0.011$$

Activities of Relative Species

$$\alpha_{\mathrm{Ca}^{2+}} = \gamma_{\mathrm{Ca}^{2+}} \times [\mathrm{Ca}^{2+}]_{\mathrm{(free)}} = 10^{-2.583}\ \mathrm{mole/L}$$

$$\alpha_{\mathrm{CO}_3^{2-}} = \gamma_{\mathrm{CO}_3^{2-}} \times [\mathrm{CO}_3^{2-}]_{\mathrm{(free)}} = 0.2 \times 9\%\ [\mathrm{CO}_3^{2-}]_{\mathrm{(T)}}$$

$$\alpha_{\mathrm{UO}_2^{2+}} = \gamma_{\mathrm{UO}_2^{2+}} \times [\mathrm{UO}_2^{2+}]$$

$$\alpha_{\mathrm{UO}_2\mathrm{CO}_3^{0}} = \gamma_{\mathrm{UO}_2\mathrm{CO}_3^{0}} \times [\mathrm{UO}_2\mathrm{CO}_3^{0}]$$

$$\alpha_{\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}} = \gamma_{\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}} \times [\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}]$$

$$\alpha_{\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}} = \gamma_{\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}} \times [\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}]$$

Equilibrium Constant for Uranium Species in Seawater

$$K_6 = \frac{(\alpha_{\mathrm{UO}_2\mathrm{CO}_3}/\alpha_{\mathrm{CaCO}_3})_{\mathrm{(aragonite)}}}{(\alpha_{\mathrm{UO}_2^{2+}}/\alpha_{\mathrm{Ca}^{2+}})_{\mathrm{(seawater)}}} \qquad (6)$$

$$K_7 = \frac{\alpha_{\mathrm{UO}_2\mathrm{CO}_3^{0}}}{\alpha_{\mathrm{CO}_3^{2-}} \times \alpha_{\mathrm{UO}_2^{2+}}} \qquad (7)$$

$$K_8 = \frac{\alpha_{\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}}}{\alpha_{\mathrm{CO}_3^{2-}} \times \alpha_{\mathrm{UO}_2\mathrm{CO}_3^{0}}} \qquad (8)$$

$$K_9 = \frac{\alpha_{\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}}}{\alpha_{\mathrm{CO}_3^{2-}} \times \alpha_{\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}}} \qquad (9)$$

Thermochemical Data for Uranium and Non-Uranium Minerals and Aqueous Species at 25°C and 1 atm Total Pressure.[†§]

	ΔH_f° (Kcal/mol)	ΔG_f° (Kcal/mol)
UO_2^{2+}	−243.5	−227.7
$\mathrm{UO}_2\mathrm{CO}_3^{0}$	−404.5	−367.6
$\mathrm{UO}_2(\mathrm{CO}_3)_2^{2-}$	−563.7	−503.2
$\mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}$	−737.8	−635.4
$\mathrm{UO}_2\mathrm{CO}_{3\,(\mathrm{C})}$	−403.9	−373.6
$\mathrm{CaCO}_{3\,(\mathrm{aragonite})}$	−288.56	−269.55
CO_3^{2-}	−161.84	−126.17
Ca^{2+}	−129.74	−132.30

Equilibrium constant for standard carbonate equilibrium taken from Skirrow (1975).

[*] Chen et al. (1986).

[†] Stumm and Morgan (1981).

[‡] Garrels and Thompson (1962).

[§] Langmuir (1978).