

[MK]

## Uranium-series evidence on diagenesis and hydrology in Pleistocene carbonates of Barbados, West Indies

Jay L. Banner<sup>a,b</sup>, G.J. Wasserburg<sup>a</sup>, James H. Chen<sup>a</sup> and John D. Humphrey<sup>c</sup>

<sup>a</sup> *The Lunatic Asylum of the Charles Arms Laboratory, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA*

<sup>b</sup> *Department of Geological Sciences, University of Texas, Austin, TX 78713-7909, USA \**

<sup>c</sup> *Programs in Geosciences, University of Texas at Dallas, Richardson, TX 75083-0688, USA*

Received December 12, 1990; revision accepted July 31, 1991

### ABSTRACT

Uranium-series isotope measurements were made by mass spectrometry on aragonite, dolomite and groundwater samples from Pleistocene coral-reef terraces on Barbados in order to evaluate the behavior of U-Th isotopes during water-rock interaction in carbonate systems. Well-preserved aragonitic corals from the Golden Grove terrace yield precise  $^{230}\text{Th}$  ages of  $219 \pm 3$  and  $224 \pm 6$  ky, and have high and variable initial  $\delta^{234}\text{U}$  relative to values for modern seawater. These high  $\delta^{234}\text{U}$  values are common to Pleistocene carbonates from many localities and indicate that the U-series has not followed closed-system behavior since the time of deposition. Pervasively dolomitized samples from the Golden Grove terrace have significantly lower  $\delta^{234}\text{U}$  than the unreplaced aragonite, and  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  (activity ratios) in excess of values for secular equilibrium. Groundwaters sampled from 125–460 ky old portions of the Pleistocene carbonate aquifer have  $\delta^{234}\text{U}$  values close to secular equilibrium, and low  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  of less than  $4 \times 10^{-3}$ . The pronounced differences in the U-Th isotope systematics between the aragonitic corals, dolomites and groundwaters reflect the enhanced mobility of U relative to Th during water-rock interaction. These results demonstrate that diagenesis can profoundly affect the U-Th isotopic composition of marine carbonates and therefore the accuracy of high-precision  $^{230}\text{Th}$  ages determined on such samples. However, diagenesis involving fluids such as the present-day groundwaters on Barbados or those which formed the dolomites cannot account for the elevated  $\delta^{234}\text{U}$  values of the corals. The mechanism by which apparently well-preserved corals become enriched in  $^{234}\text{U}$  remains to be identified. Low  $\delta^{234}\text{U}$  for the dolomites and the groundwaters records the transport of dissolved U from portions of the aquifer that are significantly older (e.g.,  $> 10^6$  yrs) than their present host carbonate rocks. The preservation of these distinct U-isotopic compositions during fluid migration through younger carbonates indicates that interaction between groundwaters and these carbonates, with accompanying  $^{234}\text{U}$  enrichment in the waters from dissolution or alpha-recoil, has been extremely limited.

### 1. Introduction

The development of a thermal-ionization mass spectrometric (TIMS) technique, which can give high-precision  $^{230}\text{Th}$  ages of deposition for unaltered Pleistocene and Holocene carbonates has refocused attention on mechanisms of sea-level and climate change [1–3]. The technique has also been used to calibrate the  $^{14}\text{C}$  geochronometer [4]. The level of precision shown by Edwards et al. [2] is  $\pm 1$  ky at 100 ky, and the potential exists for resolving sea-level highstands for much of the late

Pleistocene. The fundamental issues related to such precise data are syn- and post-depositional diagenetic changes to the concentrations of the pertinent U-series nuclides ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{230}\text{Th}$ ), which could shift the ages far outside of analytical error. Barbados is an excellent natural laboratory to study the processes of carbonate deposition, diagenesis, and hydrology, owing to a well-defined pattern of coral-reef terrace ages, a favorable climate for the preservation of aragonitic corals over a large portion of the Pleistocene, and an active meteoric hydrologic system. In addition, the island provides a setting in which to examine these processes that is removed from the complexities of a continental environment. Previous studies on

\* Address for correspondence

Barbados have focussed on delineating hydrologic and diagenetic zones [5–9] and on dating carbonate deposition using alpha-counting techniques [10,11]. Recent advances in determining depositional ages for corals from Barbados and other localities have come from the application of TIMS [2,4,12–15]. Our study is centered on the U-series analysis of present-day groundwaters, which may be analogous to those involved in diagenesis during the Pleistocene, and a suite of both well-preserved and pervasively altered Pleistocene carbonates. The results have bearing on the use of  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  disequilibrium as a geochronometer in carbonate systems, and on tracing the sources of dissolved radionuclides in carbonate aquifers.

## 2. Geologic setting and methodology

Barbados is located 150 km east of the Lesser Antilles magmatic arc. The island's position atop the Barbados Ridge accretionary prism has resulted in continual tectonic uplift throughout its history [16]. Shallow-water carbonate sedimentation was initiated over 600 ky ago, in the form of fringing coral reefs and associated facies that are thought to have developed during sea-level highstands [17,11]. The combination of highstand reef growth and tectonic uplift has resulted in the development of late Pleistocene reef terraces whose age and stair-step topography decrease toward the island's perimeter. This Pleistocene Coral Cap is underlain by folded Tertiary deep-sea sediments (Fig. 1). Groundwater flow in the Coral Cap is controlled by three main factors: (1) orographic effects on rainfall, which occurs primarily in the central elevated portion of the island that is composed of older Pleistocene coral reefs [18], (2) a permeability contrast between the porous and permeable Coral Cap and underlying Tertiary sediments, which form an aquitard below the Coral Cap, and (3) the topography of the aquitard. Meteoric groundwaters are recharged by flow and seepage through the vadose zone and transmitted by gravity flow along the base of the Coral Cap toward the coast [19].

Carbonate samples were obtained from the Golden Grove terrace in the East Point Shelf area (Fig. 1). This terrace lies between terraces previously dated at 194 and 460 ky [11], and has been

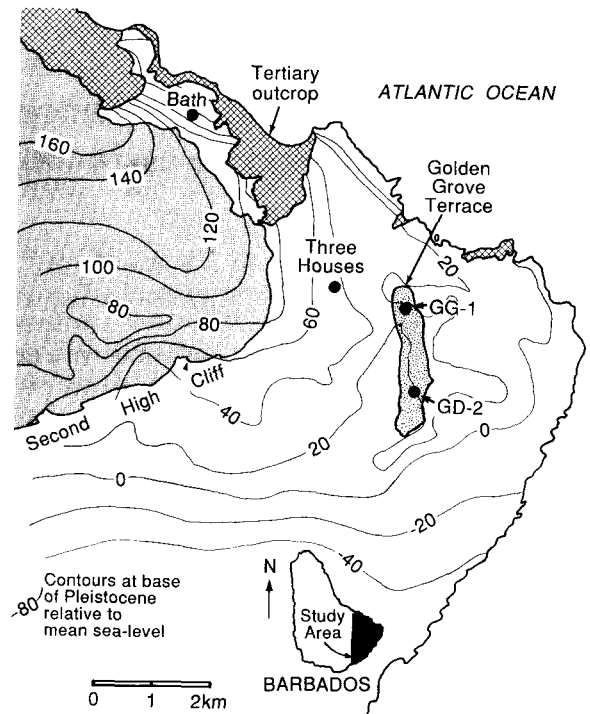


Fig. 1. East Point Shelf area of Barbados. Golden Grove (stippled area) is one of a series of Pleistocene coral-reef terraces that comprise the Coral Cap (or Coral Rock Formation) and overlie the Tertiary Oceanic and Scotland Formations. Coral-reef terraces that are located in the shaded area above Second High Cliff and toward the center of the island are older than 460 ky [11]. Contours (in meters) mark base of Pleistocene and top of Tertiary. Paths of groundwater transmission in the Coral Cap are dictated by the topography of this surface [19]. Carbonate samples were recovered from the Golden Grove terrace from outcrop locality GG-1 and from borehole GD-2. Groundwaters were sampled from springs in the Coral Cap at the Bath and Three Houses localities. Rendezvous Hill groundwater sample (Table 1) is from water well in Rendezvous Hill terrace (not shown here) on southern Barbados. Inset shows location of East Point Shelf area on Barbados.

correlated with either  $\delta^{18}\text{O}$  stage 7.3 (216 ky) or stage 7.5 (238 ky) [8]. Although diagenesis has extensively altered original marine components to dolomite and calcite at the Golden Grove terrace, recent coring here has recovered well-preserved coral specimens. Two specimens of *Acropora palmata* from reef-crest facies in borehole GD-2 (Fig. 1, samples 2–3-3 and 2–5-7 in Table 1) were chosen for study based on their mineralogy (> 99% aragonite), lack of visible cathodoluminescence, and the trace element and stable isotope criteria

TABLE 1  
Uranium and thorium isotopic and geochemical data for Barbados carbonates and groundwaters

Sample	$^{238}\text{U}^a$ ( $\mu\text{g/g}$ )	$\delta^{234}\text{U}(0)^b$ [ $\delta^{234}\text{U}(T)$ ] (%)	$^{232}\text{Th}$ (ng/g)	$^{230}\text{Th}$ (pg/g)	$(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$	$^{230}\text{Th}$ age <sup>c</sup> (ky)	$^{232}\text{Th}/^{238}\text{U}$ ( $\times 10^5$ )	$\delta\text{D}^d$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Ca ( $\times 10^{-3}$ )	Mg	Sr
<i>Aragonite</i>													
2-5-7	3.28 ± 5	137 ± 4 [255 ± 6]	0.110 ± 1	54.25 ± 9	1.016 ± 2	219 ± 3	3.46	-	-2.80	-0.15	386	620	8700
2-3-3	3.04 ± 5	123 ± 6 [232 ± 8]	0.398 ± 9	49.96 ± 10	1.008 ± 5	224 ± 6	30.3	-	-3.19	-0.53	390	700	8400
<i>Dolomite</i>													
1.18	7.92 ± 4	37 ± 7	61.5 ± 12	139 ± 2	1.080 ± 16	-	797	-	2.40	-17.26	249	104,000	890
86-1	0.825 ± 2	35 ± 7	0.928 ± 9	14.4 ± 8	1.068 ± 6	-	115	-	3.06	-9.06	238	105,000	690
<i>Groundwater</i>													
Three Houses	0.001040 ± 3	2 ± 5	1.50(±0.02) $\times 10^{-4}$	4.2(±2.5) $\times 10^{-5}$	0.0024 ± 15	-	14.8	-17.7	-3.10	-	0.0790	10.7	0.98
Replicate	0.001050 ± 2	3 ± 7	-	-	-	-	-	-	-	-	-	-	-
Bath	0.000767 ± 4	-2 ± 6	5.94(±0.06) $\times 10^{-4}$	3.9(±0.6) $\times 10^{-5}$	0.0031 ± 15	-	79.4	-17.2	-3.14	-	0.0769	8.69	0.62
Rendez. Hill	0.00688 ± 4	14 ± 4	-	-	-	-	-	-16.1	-3.03	-	0.0766	35.4	12.3
Seawater <sup>e</sup>	0.00314 to 0.00326	140 to 150	0.92 $\times 10^{-4}$ to 1.45 $\times 10^{-4}$	1 $\times 10^{-5}$ to 0.3 $\times 10^{-5}$	1 $\times 10^{-5}$ to 4 $\times 10^{-5}$	-	2.9 to 4.6	0	0	-	0.415	1280	8
<i>Continental groundwaters<sup>f</sup></i>													
	5 $\times 10^{-5}$ to 20 $\times 10^{-5}$	1 $\times 10^{-3}$ to 1.5 $\times 10^4$	1 $\times 10^{-4}$ to 0.3	1 $\times 10^{-5}$ to 26 $\times 10^{-5}$	0.005 to 0.068	-	140 to 9630	-108 to -45	-14.6 to -6.5	-	0.335 to 1.53	141 to 472	8.1 to 40.8

<sup>a</sup> All errors are  $2\sigma_m$  and correspond to last digits shown. These errors do not incorporate those in  $\lambda$  values.  $\lambda_{230} = 9.195 \times 10^{-6} \text{ y}^{-1}$ ;  $\lambda_{234} = 2.835 \times 10^{-6} \text{ y}^{-1}$ ;  $\lambda_{238} = 1.551 \times 10^{-10} \text{ y}^{-1}$ ; as compiled in [2]. 1 mg =  $10^{-6}$  g; 1 ng =  $10^{-9}$  g; 1 pg =  $10^{-12}$  g.

<sup>b</sup>  $\delta^{234}\text{U}(0) = \{[(^{234}\text{U}/^{238}\text{U})_s / (^{234}\text{U}/^{238}\text{U})_{\text{eq}}] - 1\} \times 10^3$ , where  $s$  and  $\text{eq}$  denote measured value for sample and value for secular equilibrium, respectively.  $(^{234}\text{U}/^{238}\text{U})_{\text{eq}} = \lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$ .  $\delta^{234}\text{U}(T) = \delta^{234}\text{U}(0)e^{\lambda_{234}T}$ ; NBS standard SRM 960 gives  $\delta^{234}\text{U}(0) = -40 \pm 6$ .

<sup>c</sup> Ages calculated using:  $1 - (^{230}\text{Th}/^{238}\text{U})_{\text{ACT}} = e^{-\lambda_{230}T} - (\delta^{234}\text{U}(0)/1000) \times [\lambda_{230}/(\lambda_{230} - \lambda_{234})] \times (1 - e^{(\lambda_{234} - \lambda_{230})T})$ .

<sup>d</sup> Isotope data expressed as follows:  $\delta\text{D}$  relative to SMOW;  $\delta^{18}\text{O}$  relative to PDB for carbonates and SMOW for waters;  $\delta^{13}\text{C}$  relative to PDB. Elemental data expressed in ppm.

<sup>e</sup> Seawater values from compilations in [1,2,32].

<sup>f</sup> Range for groundwaters from central Missouri from [2,32].

discussed below. Nearly pure (99%) dolomites were sampled from forereef deposits at locality GG-1 and consist of a *Montastrea cavernosa* coral (sample 86-1) and an algal-foram-coral packstone (sample 1.18). Unfiltered groundwater samples from the Coral Cap were obtained from natural springs at the Bath and Three Houses localities in the East Point Shelf area (Fig. 1), and from a water well in the Rendezvous Hill terrace on southern Barbados. The springs are located between terraces that have been dated at 220 ky (this study) and 460 ky [11]. The Rendezvous Hill well penetrates the water table at a depth of 43–45 m (near locality AFS described in [10]), which is close to the subsurface contact between 125 and 180 ky old reef terraces [20]. Major and trace element and stable isotope analyses were conducted using standard ICP and mass-spectrometric procedures. U-Th isotopic analyses were conducted following previously detailed TIMS proce-

dures [1,2,21]. For fission-track analyses, carbonates were irradiated in the TRIGA reactor at Texas A&M University.

### 3. Results

Data are given in Table 1. The aragonitic *A. palmata* coral specimens have Sr concentrations and  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values within the range for Holocene and living counterparts from Barbados and other localities [20,22,23]. These corals have 3 ppm  $^{238}\text{U}$  and extremely low  $^{232}\text{Th}$  concentrations, which is typical of modern *A. palmata* specimens [2]. They also have present-day  $\delta^{234}\text{U}(0)$  values of 137‰ and 123‰. Assuming that (1) the U-Th isotope systematics in these well-preserved corals have not been affected by diagenesis, and (2) initial  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}} = 0$ , depositional ages and initial U-isotopic compositions may be calculated using the equations given in Table 1. Using the

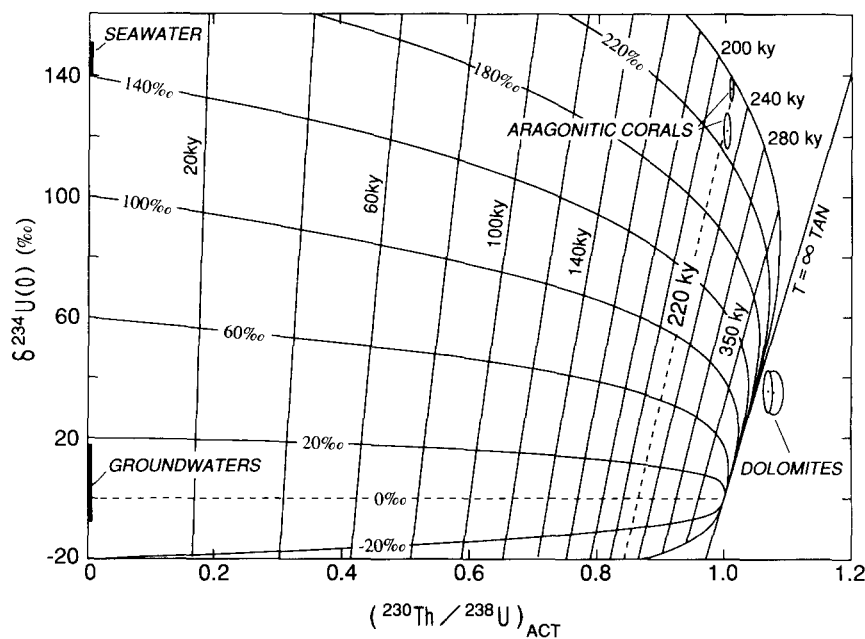


Fig. 2. Present-day U-isotopic composition,  $\delta^{234}\text{U}(0)$ , versus  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  in carbonates and groundwaters from Barbados and modern seawater. Contours are for initial U-isotopic composition,  $\delta^{234}\text{U}(T)$ , and time, in ky. Present-day U-Th isotopic compositions are plotted, and contours allow initial U-isotopic compositions and ages to be estimated by inspection. For closed-system behavior, time trajectories for a given  $\delta^{234}\text{U}(T)$  value start on the y-axis at  $T=0$  and end at  $T=\infty$  at the point  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}=1$ ,  $\delta^{234}\text{U}(0)=0$ . The  $T=\infty$  TAN line is tangent to all closed-system time trajectories at  $T=\infty$ . Contour construction detailed in [14] and [30]. Aragonitic corals give ages of 219 and 224 ky and high  $\delta^{234}\text{U}(T)$  relative to modern seawater values. The dolomites have low  $\delta^{234}\text{U}(0)$  and high  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  values in excess of secular equilibrium. They plot to the right of the  $T=\infty$  TAN line and therefore have not followed closed-system behavior. Errors in  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  for groundwater samples and seawater have been exaggerated for clarity. Data from Table 1.

$^{232}\text{Th}$  contents of the corals and the inference that  $^{230}\text{Th}$  and  $^{232}\text{Th}$  were initially incorporated into the corals in the same proportions as in seawater (as given in Table 1), we calculate the amount of  $^{230}\text{Th}$  incorporated during coral growth to correspond to less than 0.04% of the  $^{230}\text{Th}$  in each sample. This indicates that assumption (2) is reasonable. The ages of  $219 \pm 3$  and  $224 \pm 6$  ky for the Golden Grove corals are consistent with the correlation of this terrace with oxygen isotope stage 7.3 [8]. The analytical precision demonstrates the potential utility of the  $^{238}\text{U}$ - $^{230}\text{Th}$  geochronometer for testing models for climate change that require resolution of sea-level highstands occurring 20 ky apart in this age range. However,  $\delta^{234}\text{U}(\text{T})$  for the aragonitic corals of 255‰ and 232‰ are much higher than the narrow range of  $\delta^{234}\text{U} = 140\text{--}150\text{‰}$  for modern open-ocean water (Fig. 2, Table 1). With regard to assumption (1) and the discussion below, variations in  $\delta^{234}\text{U}(\text{T})$  for marine carbonates must reflect diagenetic alteration or secular changes in the U-isotopic composition of seawater.

Fission-track analysis reveals a uniform distribution of U in both aragonitic and dolomitized coral samples, whereas the dolomitized packstone sample, which has a very high U content of 8 ppm (Table 1), contains a heterogeneous distribution of U. There are significantly higher U concentrations in skeletons of coralline red algae relative to the foram, coral and mud components of this pervasively dolomitized sample. In contrast to the wide range in U contents, the dolomites have a narrow range of  $\delta^{234}\text{U}(0) = 35\text{--}37\text{‰}$ , which is far lower than values for the aragonite samples. The dolomites have higher  $^{232}\text{Th}/^{238}\text{U}$  than seawater, the aragonitic corals and the groundwaters (Table 1). Dolomite ( $^{230}\text{Th}/^{238}\text{U}$ )<sub>ACT</sub> values are in excess of values for secular equilibrium (Fig. 2). This shows that these samples have not followed closed-system behavior. Using the measured  $\delta^{234}\text{U}(0)$  values of the dolomites, the  $^{238}\text{U}$ - $^{234}\text{U}$  age relationship (Table 1), and  $\delta^{234}\text{U}(\text{T}) = 150\text{‰}$ , apparent ages of 490 to 510 ky are calculated for the dolomites. The Golden Grove carbonates were sampled from a conformable facies, stratigraphic and petrographic sequence [8,24] that indicates that the dolomites post-date deposition of the aragonitic corals and therefore are younger than  $\sim 220$  ky. This discrepancy in ages and the high

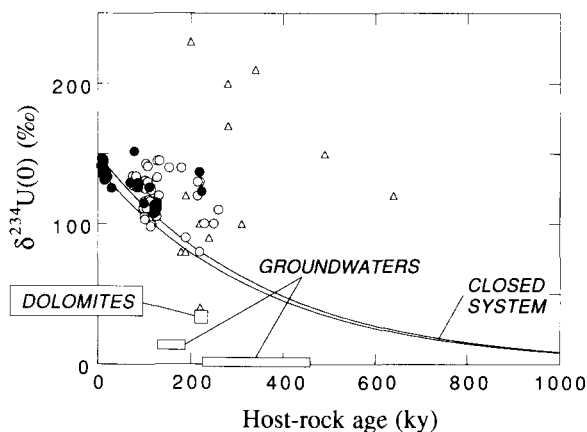


Fig. 3.  $\delta^{234}\text{U}(0)$  versus host-rock age for aragonitic corals, dolomites and groundwaters from Barbados. For corals, host-rock ages are either coral  $^{230}\text{Th}$  ages by TIMS (dots, data from [2,4,12,13] and this study) or alpha-counting (circles, data from [11,31]), or corrected coral U-He ages (triangles, data from [11]). For dolomite and groundwater samples,  $\delta^{234}\text{U}(0)$  values are from this study, and host-rock ages are constrained using coral ages, as discussed in text. Closed-system curves represent evolution of marine carbonate samples having  $\delta^{234}\text{U}$  between 140 and 150‰ at the time of their formation. Typical analytical uncertainty for  $\delta^{234}\text{U}$  by TIMS is  $\pm 5\text{--}7\text{‰}$ , based on within-run statistics, and less than  $\pm 2\text{‰}$ , based on the mean deviation of replicates from these studies.

( $^{230}\text{Th}/^{238}\text{U}$ )<sub>ACT</sub> of the dolomites may be reasonably explained by open-system behavior during diagenesis involving exchange of U and Th between the dolomites and diagenetic fluids, as discussed below.

The Barbados groundwaters have  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values that are characteristic of tropical meteoric precipitation [25]. The spring waters from the East Point Shelf area (Fig. 1) have  $\delta^{234}\text{U}(0) \sim 0\text{‰}$ , which is the value for  $^{238}\text{U}$ - $^{234}\text{U}$  secular equilibrium. The Rendezvous Hill groundwater also has a low  $\delta^{234}\text{U}(0)$  value of 14‰. These values are in contrast to the extremely high  $\delta^{234}\text{U}$  values common to many continental groundwaters (Table 1), although values near zero are also found (c.f. [26]). High groundwater  $\delta^{234}\text{U}$  values are attributed to alpha-recoil processes [27].  $\delta^{234}\text{U}$  values in the Barbados waters are also significantly lower than values for the carbonate rocks that comprise the portion of the aquifer in the Coral Cap through which the waters are presently migrating (Fig. 3). Groundwater U/Ca ratios ( $10^{-5}$  to  $10^{-4}$ ) are higher than values for seawater and aragonitic

corals ( $8 \times 10^{-6}$ ). Meteoric waters may attain high U/Ca ratios through the aragonite to calcite ( $U/Ca < 8 \times 10^{-6}$ ) conversion, or through an increase in fluid  $P_{CO_2}$  levels, which will enhance the solubility of the  $UO_2^{2+}$  ion [28]. Uranium may also be contributed to the dissolved U budget of the groundwaters during recharge through fertilized soil zones, as has been determined for Sr, Mg and Ca in Barbados groundwaters [6,19]. Determining the U and Th contributions to Barbados groundwaters from soil zones requires further study. The  $^{230}Th$  concentrations,  $(^{230}Th/^{238}U)_{ACT}$  values, and  $^{232}Th/^{238}U$  ratios in the Barbados groundwaters are higher than seawater values and lower than most values for continental groundwaters, based on the few studies to date (Table 1). As a significant fraction of  $^{230}Th$  in natural waters can be associated with particulates, the results for unfiltered samples may be taken as maximum values for dissolved Th concentrations. The low  $(^{230}Th/^{238}U)_{ACT}$  values in the waters relative to the carbonates that comprise the aquifer reflect the control on dissolved Th levels by sorption processes [21].

#### 4. Discussion

The results of this study show clear distinctions between fossil aragonitic corals, replacement dolomites, meteoric groundwaters, and seawater on the  $\delta^{234}U(0) - (^{230}Th/^{238}U)_{ACT}$  diagram (Fig. 2). The mineralogic, petrographic, trace element, and C-O isotopic data on the fossil corals from Golden Grove indicate that these samples have experienced very little alteration since their formation from seawater. However, the variably elevated  $\delta^{234}U(T)$  values in the corals relative to modern seawater indicate that the U-Th isotopic system in the aragonitic coral skeletons has not remained closed since the time of deposition from seawater, and as such may affect the accuracy of the  $^{230}Th$  age determinations. Late Pleistocene corals and mollusks from Barbados and other localities have similar  $^{234}U$  enrichments [2,4,11–15,29,30]. These data have been explained by diagenetic alteration by fluids with high  $\delta^{234}U$  values, as are found in groundwaters from continental environments. Alternatively, the coral  $\delta^{234}U(T)$  values may reflect changes in the U-isotope composition of seawater during the Pleistocene. However, the wide range in

$\delta^{234}U(T)$  values for samples from the same stratigraphic interval (this study, [2,14]) must reflect post-depositional alteration in some samples. The petrographic, mineralogic and geochemical criteria applied to the characterization of coral diagenetic histories apparently are not as sensitive to alteration as U-Th isotopes. A rigorous basis for estimating the effect of open-system behavior on  $^{230}Th$  ages of corals has yet to be established, and requires knowledge of the time of U-Th exchange. The addition of  $^{234}U$  to marine carbonates by diagenetic processes shortly after deposition may have a negligible effect on  $^{230}Th$  age determinations, while more recent  $^{234}U$  additions can have a significant effect [14,31]. Our results for the Barbados dolomites and groundwaters are consistent with an aquifer system in which U is mobilized during the dissolution of relatively old carbonates with low  $\delta^{234}U(0)$ . If alpha-recoil processes are operating in such an aquifer system, the effects on U-isotopic compositions of porewaters are overwhelmed by the dissolution process. It is clear that alteration of aragonitic corals by diagenetic fluids represented by the present-day groundwaters or the dolomite-forming waters cannot account for the elevated  $\delta^{234}U(T)$  values common to many Pleistocene marine carbonates from non-continental settings. These high  $\delta^{234}U$  values may result from relatively early processes of marine diagenesis. The source of the uranium with high  $\delta^{234}U$  and the timing of its diagenetic addition to the aragonitic fossil corals are key issues in the application of the  $^{238}U - ^{230}Th$  geochronometer to marine carbonates that have yet to be resolved.

The low  $\delta^{234}U(0)$  values in the Barbados groundwaters indicate the derivation of dissolved U in the waters from aquifer rocks that are close to secular equilibrium with respect to  $^{238}U - ^{234}U$ . A model involving the derivation of dissolved U in the waters from marine carbonates requires that these carbonates are older than  $10^6$  yrs and have remained closed to  $^{238}U - ^{234}U$  exchange (e.g., Fig. 3). Nearly all aragonitic samples from Barbados studied to date have  $\delta^{234}U(0)$  greater than 80‰ and  $\delta^{234}U(T)$  in excess of seawater values (Fig. 3). If these  $\delta^{234}U$  values are representative of the reactive portion of the aquifer through which the waters migrate,  $\delta^{234}U$  in groundwaters in this system would be reset to these high values during

the dissolution of small amounts of aragonite, equivalent to molar rock:water ratios of approximately  $10^{-4}$  [21]. Similar arguments apply to calcite and dolomite in the aquifer, which also have  $\delta^{234}\text{U}$  values higher than those of the groundwaters (this study, [30]). It can be concluded that the Barbados groundwaters have (1) derived their dissolved U from significantly older sediments than the portion of the aquifer through which they are presently migrating, (2) experienced negligible input of  $^{234}\text{U}$  from a recoil processes, and (3) experienced extremely limited extent of interaction with their present host rocks. Note that the implications for a relatively old source of U in the groundwaters applies to waters sampled from both older (220–460 ky) and younger (125–180 ky) portions of this carbonate aquifer (Fig. 3). Fluid–rock interaction in this system may be limited by thermodynamic or kinetic barriers imposed by (1) the saturation state of the waters with respect to the minerals in the aquifer, acquired during initial recharge through older updip carbonates, (2) flow along pathways that have been mineralogically equilibrated during previous diagenetic episodes, and (3) high flow rates in the aquifer [e.g., 5,8,19,32]. For water–rock interaction occurring at a very low rock:water ratio of  $<10^{-4}$ , a shift in the water's  $\delta^{234}\text{U}(0)$  value from 0 to 30‰ would be detectable in a system comprising groundwater with  $\delta^{234}\text{U}(0)$  near 0‰ and carbonate rocks with  $\delta^{234}\text{U}(0)$  of 80–200‰ (Fig. 3). Such a shift is not observed in the Barbados groundwaters, constraining the extent of interaction that these waters have experienced. The high precision of the U-isotopic measurements and the large differences in the U concentrations in the groundwaters and the carbonates make this isotopic system a sensitive indicator of water–rock exchange processes, both in terms of estimating the extent of water–rock exchange and tracing the sources of dissolved constituents in the waters.

The low  $\delta^{234}\text{U}(0)$  values of the dolomites relative to their marine carbonate precursors indicate a relatively old source of U, similar to that proposed for the groundwaters. Because dolomites are susceptible to recrystallization, this U-isotopic signature could have been acquired during or subsequent to the initial dolomitization process. A meteoric groundwater source of U for the

dolomites is consistent with low  $\delta^{234}\text{U}(0)$  and  $\delta^{13}\text{C}$  values in the latter, whereby low  $\delta^{13}\text{C}$  values are derived during vadose recharge through organic-rich soil zones (e.g., [8]), and low  $\delta^{234}\text{U}(0)$  values are derived from relatively old carbonates in the recharge area. Mass balance calculations indicate that at low degrees of interaction with a limestone, a groundwater's  $\delta^{234}\text{U}(0)$  value can be extensively reset toward that of the limestone, while the water's  $\delta^{13}\text{C}$  value will be significantly less altered during the same interaction process. We note that U in groundwaters from carbonate aquifers may not be derived entirely from reactions with carbonate minerals, and that studies of U-series isotope distributions in soil zones are required to further our understanding of the migration of these radionuclides in carbonate aquifers.

The apparent ages of 490–510 ky calculated earlier from  $\delta^{234}\text{U}(0)$  values for the dolomites may instead reflect the age of the reactive portion of the carbonate aquifer from which the dolomitizing (or dolomite-recrystallizing) waters acquired their dissolved U. These ages are minimum ages, considering that (1) only partial exchange of U may have occurred between the dolomite-precursor sediment (high  $\delta^{234}\text{U}$ ) and these waters (low  $\delta^{234}\text{U}$ ), in which case the dolomites would record higher  $\delta^{234}\text{U}$  values than the fluid from which they formed; and (2) the majority of Barbados carbonates have elevated  $\delta^{234}\text{U}(0)$  and  $\delta^{234}\text{U}(T)$  compared with values for closed-system evolution, in which case a given fluid  $\delta^{234}\text{U}$  value inferred for the dolomites corresponds to an older carbonate source of dissolved U (Fig. 3). Diagenetic low-Mg calcite with low  $\delta^{234}\text{U}(0)$  values relative to marine aragonite from the same limestone samples from western Barbados [31] may also be explained by the precipitation of calcite from fluids which have incorporated U from a relatively old source. Such old sources of U for the Barbados groundwaters, dolomites and calcites include older portions of the Pleistocene aquifer in the central part of the island, the underlying Tertiary aquitard, and allochthonous components of soil zones [32]. Preliminary Sr isotope analyses indicate a predominantly Pleistocene versus Tertiary source for Sr in the groundwaters and dolomites (Banner, in prep.).

The high ( $^{230}\text{Th}/^{238}\text{U}$ )ACT and  $^{232}\text{Th}/^{238}\text{U}$

ratios in the dolomites relative to seawater, the corals and the groundwaters (Table 1) are a likely result of the low mobility of Th relative to U in aqueous systems [e.g., 34]. During carbonate dissolution-precipitation reactions, nearly all dissolved Th may be scavenged from solution onto newly formed mineral surfaces, while most of the U which is not partitioned into the lattice of the precipitating carbonate may remain in solution during the same process. An increase in  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  during replacement and recrystallization, such as in the examples outlined here, will significantly affect  $^{230}\text{Th}$  age determinations on both depositional and diagenetic carbonates.

## 5. Conclusions

The results of our study demonstrate major U-Th isotope distinctions among Pleistocene aragonitic corals, replacive dolomites, meteoric groundwaters and seawater. Precise age determinations of  $\pm 1-3\%$  can be obtained on 220 ky old marine carbonates by mass spectrometry. However, the variably elevated initial  $\delta^{234}\text{U}$  values of aragonitic corals from Barbados and other non-continental settings, relative to values for modern seawater, indicate that the U-Th isotope system has not remained closed since the time of their growth. Barbados dolomites have significantly lower  $\delta^{234}\text{U}$  and higher  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  and  $^{232}\text{Th}/^{238}\text{U}$  than their  $\text{CaCO}_3$  precursors, and groundwaters have extremely low  $\delta^{234}\text{U}$  and  $(^{230}\text{Th}/^{238}\text{U})_{\text{ACT}}$  values compared with their carbonate host rocks. These results demonstrate that the U-Th isotope systematics of marine carbonates can be significantly altered during diagenesis, and are consistent with the high mobility of U relative to Th in aqueous systems. However, diagenetic processes involving the present-day groundwaters or the dolomite-forming fluids cannot account for the high  $^{234}\text{U}$  contents of many fossil corals from non-continental environments. Early diagenetic processes involving marine porewaters may result in these high  $\delta^{234}\text{U}(\text{T})$  values.

Low  $\delta^{234}\text{U}$  for the dolomites and the groundwaters compared with values for their 125-460 ky old host rocks reflect the derivation of dissolved U from much older sediments, with negligible input

of  $^{234}\text{U}$  from alpha-recoil. For example,  $\delta^{234}\text{U}(0)$  values in the groundwaters are near values for secular equilibrium. This requires a source of U that is older than  $10^6$  yrs. These distinct U-isotopic compositions, which are imparted to the water during early stages of fluid-rock interaction, are maintained during transport through younger portions of the aquifer and indicate that fluid-rock interaction has been extremely limited during groundwater migration. It is clear from this preliminary study that precise U-series measurements can provide insight into the processes and pathways of fluid-rock interaction in Quaternary carbonate systems.

## Acknowledgements

We wish to thank L. Barker, M. Denham and S. Thieben for technical assistance in the field and laboratory. Constructive comments were provided by two anonymous reviewers. We also thank H. Cander, R. Stoessel and D. Papanastassiou for helpful scientific discussion. This research was supported by grants from the donors to the Petroleum Research Fund of the American Chemical Society (21213-AC2 and 22483-G8), the Department of Energy (DE-FG03-88ER13851), the National Science Foundation (EAR-8720376), Texaco, Inc., and the Geology Foundation of the University of Texas. This is contribution 710.

## References

- 1 J.H. Chen, R.L. Edwards and G.J. Wasserburg,  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{232}\text{Th}$  in seawater, *Earth Planet. Sci. Lett.* 80, 241-251, 1986.
- 2 R.L. Edwards, J.H. Chen and G.J. Wasserburg,  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$ - $^{232}\text{Th}$  systematics and the precise measurement of time over the past 500,000 years, *Earth Planet. Sci. Lett.* 81, 175-192, 1987.
- 3 I.J. Winograd, T.B. Coplen, K.R. Ludwig, B.J. Szabo, A.C. Riggs and K.M. Revesz, Continuous 500,000-year climatic record from Great Basin vein calcite: 1. The  $\delta^{18}\text{O}$  time series, *Geol. Soc. Am. Abstr. Programs* 22, A209, 1990.
- 4 E. Bard, B. Hamelin, R.G. Fairbanks and A. Zindler, Calibration of the  $^{14}\text{C}$  timescale over the past 30,000 years using mass spectrometric U-Th ages from Barbados corals, *Nature* 245, 405-410, 1990.
- 5 R.K. Matthews, Carbonate diagenesis: Equilibration of sedimentary mineralogy to the subaerial environment: Coral cap of Barbados, West Indies, *J. Sediment. Petrol.* 38, 1110-1119, 1968.



- 6 W.H. Harris and R.K. Matthews, Subaerial diagenesis of carbonate sediments: Efficiency of the solution–reprecipitation process, *Science* 160, 77–79, 1968.
- 7 J.R. Allan and R.K. Matthews, Isotopic signatures associated with early meteoric diagenesis, *Sedimentology* 29, 797–817, 1982.
- 8 J.D. Humphrey, Late Pleistocene mixing-zone dolomitization, southeastern Barbados, West Indies, *Sedimentology* 35, 327–348, 1988.
- 9 N.P. James, Holocene and Pleistocene calcareous crust (caliche) profiles: criteria for subaerial exposure, *J. Sediment. Petrol.* 42, 817–836, 1972.
- 10 K.J. Mesolella, R.K. Matthews, W.S. Broecker and D.L. Thurber, The astronomical theory of climatic change: Barbados data, *J. Geol.* 77, 250–274, 1969.
- 11 M.L. Bender, R.G. Fairbanks, F.W. Taylor, R.K. Matthews, J.G. Goddard and W.S. Broecker, Uranium-series dating of the Pleistocene reef tracts of Barbados, West Indies, *Geol. Soc. Am. Bull.* 90, 577–594, 1979.
- 12 R.L. Edwards, J.H. Chen, T.L. Ku and G.J. Wasserburg, Precise timing of the last interglacial period from mass spectrometric determination of thorium-230 in corals, *Science* 236, 1547–1553, 1987.
- 13 E. Bard, B. Hamelin and R.G. Fairbanks, U-Th ages obtained by mass spectrometry in corals from Barbados: sea level during the past 130,000 years, *Nature* 346, 456–458, 1990.
- 14 J.H. Chen, H.A. Curran, B. White and G.J. Wasserburg, Precise chronology of the last inter-glacial period:  $^{234}\text{U}$ - $^{230}\text{Th}$  data from fossil coral reefs in the Bahamas, *Geol. Soc. Am. Bull.* 103, 82–97, 1991.
- 15 M. Stein, G.J. Wasserburg, K. Lajoie and J.H. Chen,  $^{230}\text{Th}$ -ages of solitary corals along the California coast by mass spectrometry, *Geochim. Cosmochim. Acta*, in press.
- 16 R. Torrini, Jr., R.C. Speed and G.S. Mattioli, Tectonic relationships between forearc-basin strata and the accretionary complex at Bath, Barbados, *Geol. Soc. Am. Bull.* 96, 861–874, 1985.
- 17 K.J. Mesolella, The uplifted reefs of Barbados: Physical stratigraphy, facies relationships, and absolute chronology, Ph.D. Dissert., Brown Univ., 1968.
- 18 W.R. Rouse, The moisture balance of Barbados and its influence on sugar cane yield, M.Sc. Thesis, McGill Univ., 1962.
- 19 W.H. Harris, Groundwater–carbonate–rock chemical interactions, Barbados, W.I., Ph.D. Dissert., Brown Univ., 1971.
- 20 R.G. Fairbanks and R.K. Matthews, The marine oxygen isotope record in Pleistocene coral, Barbados, West Indies, *Quat. Res.* 10, 181–196, 1978.
- 21 J.L. Banner, G.J. Wasserburg, J.C. Chen and C.H. Moore,  $^{234}\text{U}$ - $^{238}\text{U}$ - $^{230}\text{Th}$ - $^{232}\text{Th}$  systematics in saline groundwaters from central Missouri, *Earth Planet. Sci. Lett.* 101, 296–312.
- 22 D.J.J. Kinsman, Interpretation of  $\text{Sr}^{2+}$  concentrations in carbonate minerals and rocks, *J. Sediment. Petrol.* 39, 486–508, 1969.
- 23 L.S. Land, The carbon and oxygen isotopic chemistry of surficial Holocene shallow marine carbonate sediment and Quaternary limestone and dolomite, in: *Handbook of Environmental and Isotope Geochemistry*, Vol. 3, P. Fritz and J.Ch. Fontes, eds., pp. 191–217, 1989.
- 24 J.D. Humphrey and T.N. Kimbell, Sedimentology and sequence stratigraphy of late Pleistocene carbonates of southeastern Barbados, West Indies, *Am. Assoc. Pet. Geol. Bull.* 74, 1671–1684, 1990.
- 25 H. Craig, Isotopic variations in meteoric waters, *Science* 133, 1702–1703, 1961.
- 26 J.R. Osmond and J.B. Cowart, Ground water, in: *Uranium Series Disequilibrium: Applications to Environmental Problems*, M. Ivanovich and R.S. Harmon, eds., pp. 202–242, Clarendon, Oxford, 1982.
- 27 K. Kigoshi, Alpha-recoil thorium-234: dissolution into water and the uranium-234/uranium-238 disequilibrium in nature, *Science* 173, 47–48, 1971.
- 28 D. Langmuir, Uranium solution-mineral equilibria at low temperature with applications to sedimentary ore deposits, *Geochim. Cosmochim. Acta* 42, 547–569, 1978.
- 29 H.H. Veeh and W.C. Burnett, Carbonate and phosphate sediments, in: *Uranium Series Disequilibrium: Applications to Environmental Problems*, M. Ivanovich and R.S. Harmon, eds., pp. 459–480, Clarendon, Oxford, 1982.
- 30 R.L. Edwards, High-precision thorium-230 ages of corals and the timing of sea-level fluctuations in the late Quaternary, Ph.D. Dissert., California Inst. Technol., 1988.
- 31 T.L. Ku, M. Ivanovich and S. Luo, U-series dating of last interglacial high sea stands: Barbados revisited, *Quat. Res.* 33, 129–147, 1990.
- 32 J.L. Banner, G.J. Wasserburg, P.F. Dobson, A.B. Carpenter and C.H. Moore, Trace element and isotopic constraints on the origin and evolution of saline groundwaters from central Missouri, *Geochim. Cosmochim. Acta* 53, 383–398, 1989.
- 33 D.R. Muhs, R.C. Crittenden, J.N. Rosholt, C.A. Bush and K.C. Stewart, Genesis of marine terrace soils, Barbados, West Indies: evidence from mineralogy and geochemistry, *Earth Surf. Processes Landforms* 12, 605–618, 1987.
- 34 D. Langmuir and J.S. Herman, The mobility of thorium in natural waters at low temperatures, *Geochim. Cosmochim. Acta* 44, 1753–1766, 1980.