3. U-Th DATING AND DIAGENESIS OF PLEISTOCENE HIGHSTAND SEDIMENTS FROM THE BAHAMAS SLOPE¹

Gideon M. Henderson,² Rebecca H. Rendle,³ Niall C. Slowey,⁴ John J.G. Reijmer³

ABSTRACT

We have performed U-Th isotope analyses on pure aragonite samples from the upper sections of Leg 166 cores to assign each aragonite-rich sediment package to the correct sea-level highstand. The uppermost sediment package from each of the four sites investigated (Sites 1003, 1005, 1006, and 1007) yielded a Holocene U-Th age. Sediment packages from deeper in the cores have suffered diagenesis. This diagenesis consists of significant U loss (up to 40%) in the site nearest the platform (Site 1005), slight U gain in sites further from the platform, and continuous loss of pure 234U caused by alpha recoil at all sites. The difference in diagenesis between the sites can be explained by the different fluid-flow histories they have experienced. Site 1005 is sufficiently close to the platform to have probably experienced a change in flow direction whenever the banks have flooded or become exposed. Other sites have probably experienced continuous flow into the sediment. Although diagenesis prevents assignment of accurate ages, it is sufficiently systematic that it can be corrected for and each aragonite-rich package assigned to a unique highstand interval. Site 1005 has sediment packages from highstands associated with marine isotope Stages 1, 5, 7, 9, and 11. Site 1006 is similar, except that the Stage 7 highstand is missing, at least in Hole 1006A. Site 1003 has sediment only from Stage 1 and 11 highstands within the U-Th age range. And Site 1007 has sediment only from the stage 1 highstand. This information will allow the construction of better age models for these sites. No high-aragonite sediments are seen for Stage 3 or Substages 5a and 5c. Unless rather unusual erosion has occurred, this indicates that the banks did not flood during these periods. If true, this would require the sea level for Substages 5a and 5c to have remained at least ≈ 10 m lower than today.

INTRODUCTION

Good age control is essential to make full use of the sedimentological and paleoceanographic information preserved in marine slope sediments such as those recovered from the Bahamas during Leg 166. In such slope environments, however, sedimentation rates are highly responsive to sea-level change, which makes the development of age models difficult. During highstands, the flooded banks produce large amounts of aragonite, which forms high-sedimentation-rate aragoniterich packages of sediment on the slopes (Heath and Mullins, 1984; Neumann and Land, 1975; Wilber et al., 1990; Droxler and Schlager, 1985, Glaser and Droxler, 1991). During lowstands, aragonite production is dramatically reduced and sedimentation rates on the slopes are significantly slower (e.g., Kier and Pilkey, 1971; Droxler et al., 1983; Boardman et al., 1986). This changing sedimentation rate makes linear extrapolation between biostratigraphic marker horizons of only limited use.

On the other hand, the changeable sediment composition can be an aid to developing age models. Aragonite-rich sediment packages can simply be counted off from the top of the core and matched with the known sequence of sea-level highstands. But two major problems exist with this approach. The first is that it's necessary to know the sea-level height required to produce a distinct sediment package. For instance, do the highstand events of marine isotope Substages 5a, 5c, and 5e result in discrete sediment packages? Or is all of Stage 5 recorded as one event? Or does only Substage 5e cause sufficient flooding of the banks to produce an aragonite-rich sediment package? The second problem is that a low-aragonite interval in the core may represent more than a single lowstand, possibly including a hiatus of sedimentation or a period of sediment erosion due to down-slope or lateral transport.

In the Pleistocene portions of the Leg 166 cores, recognition of biostratigraphic reference markers such as the first occurrence of *Emiliania huxleyi* is made difficult by the large dilution of pelagic material by bank-derived sediment. Biostratigraphic age control is therefore not sufficiently good to unambiguously assign ages to sediment packages and independent dating is required. C-14 can be used to test whether the uppermost sediment packet is Holocene, but other dating tools are required to assess the age of older sediment packages.

In this study, we make use of the high U content of the aragonite that makes up much of the highstand sediment on the Bahamas slopes (Slowey et al., 1996). This enables us to pursue U/Th techniques to derive age information for the Leg 166 cores. We have used recently developed techniques for U/Th dating of aragonite-rich sediments (Slowey et al., 1996; G.M. Henderson, N.C. Slowey, and M.Q. Fleisher, unpubl. data) to investigate key sediment horizons from four of the five sites of the northerly Leg 166 transect. These U/Th ages enable refinement of the Pleistocene age model for each of the cores. In addition, these data contribute to our understanding of sediment diagenesis and fluid flow in the Bahamas banks and provide clues about sea-level history.

SAMPLES AND SAMPLE TREATMENT

Eighteen samples were selected from highstand aragonite-rich sediment packages from Sites 1003, 1005, 1006, and 1007 (Table 1; Fig. 1). In general, samples were taken from successive sediment packages down to a depth assessed to be marine isotope Stage 11 in preliminary age models (Eberli, Swart, Malone, et al., 1997). Stage 11, at \approx 400 ka, occurs just over 5 half-lives of ²³⁰Th ago and, therefore, represents the approximate limit of the U/Th approach in closed-system samples.

¹Swart, P.K., Eberli, G.P., Malone, M.J., and Sarg, J.F. (Eds.), 2000. *Proc. ODP, Sci. Results*, 166: College Station TX (Ocean Drilling Program).

²Lamont-Doherty Earth Observatory of Columbia University, Route 9W, Palisades NY 10964, USA. (Present address: Department of Earth Sciences, Oxford University, Parks Road, Oxford, OX1 3PR, England, gideonh@earth.ox.ac.uk)

³GEOMAR Research Centre for Marine Geosciences, Christian-Albrechts-Universitat zu Kiel, Wischhofstrasse 1-3, Gebaude 4, D-24148 Kiel, Federal Republic of Germany.

⁴Department of Oceanography, Texas A&M University, College Station TX 77843, USA.

Table 1. Sediments analyzed for U and Th isotopes in this study.

Core, section, interval (cm)	Position	Water depth (m)	Depth (mbsf)	Sample identifier
166-1003A- 2H-1, 122-124 2H-6, 82-84 3H-2, 112-114 4H-1, 55-56 5H-1, 122-124 5H-5, 2-4	24°32.75′N, 79°15.64′W	483	8.22 14.40 19.12 26.55 36.72 41.52	3-1 3-2 3-3 3-4 3-5 3-6
166-1005A- 2H-6, 116-118 4H-1W, 4-6 5H-2W, 4-6 7H-1W, 84-8 8H-6W, 123-125 13X-2W, 44-46	24°33.77′N, 79°14.14′W	351	11.16 16.04 27.04 45.34 60.33 93.14	5-1 5-2 5-3 5-4 5-5 5-6
166-1006A- 1H-1, 135-137 1H-4, 55-57 2H-4, 135-137 2H-6, 135-137	24°23.99′N, 79°27.55′W	658	1.35 5.05 12.95 15.95	6-1 6-2 6-3 6-4
166-1007A- 1H-1, 22-24	24°30.26'N, 79°19.34'W	650	0.22	7-1
166-1007B- 1H-2, 92-94	24°30.26'N, 79°19.34'W	659	2.42	7-2

Note: Sample identifiers listed in the final column are used throughout the text and figures of this paper.

Existing U/Th work has been most successful with coral samples (Bard et al., 1990; Broecker et al., 1968; Edwards et al., 1987). Corals are an ideal material for U/Th dating as they contain almost no detrital material and incorporate essentially no initial Th on growth, thus yielding initial (230Th/238U) ratios of zero (where parentheses signify an activity ratio). The increase of this ratio toward secular equilibrium therefore provides a measure of the coral's age, provided it has remained a closed system. The aragonite-rich sediments of the Bahamas have U concentrations similar to those of corals but, while their initial (230Th/238U) ratios are low, they are not zero (Slowey et al., 1996; G.M. Henderson, N.C. Slowey, and M.Q. Fleisher, unpubl. data). This is because of the presence of small amounts of detrital material in the sediment and the presence of Th scavenged from the water column. These sources of Th add both 232Th and 230Th to the sediment and can, therefore, be recognized from the pure 230Th produced from U decay. However, detrital and scavenged Th have different ²³²Th/²³⁰Th ratios from one another, so if the ²³²Th is to be used to correct for a nonzero initial (230Th/238U), either the relative proportion of detrital versus scavenged Th must be assessed or one of these sources of Th must be eliminated prior to analysis.

In this study, we eliminate the detrital fraction from the sediments prior to analysis. Sediment is first sieved to acquire a 63- to 250- μ m fraction. Removal of the <63- μ m fraction eliminates clay minerals, which are the majority of the detrital fraction. Removal of the >250- μ m fraction reduces the number of foraminifers and pteropods that may be filled with clay minerals and that have low U concentrations (Henderson and O'Nions, 1995). Bulk sediment samples of 6–10 g yielded 0.7–3.0 g of 63- to 250- μ m material after sieving.



Figure 1. Fine-fraction (<63 µm) aragonite-percent curves for Sites 1003, 1005, 1006, and 1007 (from Rendle et al., Chap. 6, this volume). Sites are arranged schematically with increasing distance from the platform to the left. Details of site position and water depth are included in Table 1. Horizons in the cores sampled for this study are indicated by the arrows and sample identifiers (Table 1). Further details of the setting and sedimentology of these sites can be found in the Leg 166 *Initial Reports* volume (Eberli, Swart, Malone, et al., 1997).

Each 63- to 250-µm sample then undergoes density separation to give a >2.8 g/cm³ fraction. This stage concentrates the aragonite, which is the only major mineral constituent of these sediments with a density >2.8 g/cm³. This stage also removes any silicate minerals surviving the sieving stage, including most clays, quartz, and opal. The 63- to 250-µm fractions were placed in 10 mL of sodium polytungstate solution (SPT) with a density of 2.80 (\pm 0.01) g/cm³ and centrifuged for 10 min. The dense fraction in the bottom of the centrifuge tubes was frozen with liquid nitrogen and the light fraction poured off. Further density separations were conducted on this light material to yield a high-Mg calcite (HMC) and low-Mg calcite (LMC) fraction, but these samples have not been analyzed for this study. Thorough washing of all SPT-treated samples with multiple water rinses is required to fully remove the heavy liquid. Effective removal can be checked by X-ray diffraction (XRD) analysis because dried SPT causes many spurious peaks throughout the XRD spectrum. Heavy-liquid separation yielded between 0.09 and 1.9 g of >2.8 g/cm³, 63- to 250-µm material.

In addition to cleaning the samples of any detrital Th, the sieving and heavy-liquid procedures decrease the importance of scavenged Th because the coarse grain size decreases the surface area to volume ratio. The removal of low-U grains and the concentration of high-U aragonite also increases the U content of the analyzed sample to a maximum. A final reason for these pretreatment steps is that the coarser grain size should make the effect of alpha recoil less significant.

The composition of representative final >2.8 g/cm³ 63- to 250-µm separates was assessed by XRD (Fig. 2; Table 2). Aragonite percentages of significantly less than 100 in bulk sediment were increased to within error of 100% in each case. These final 63- to 250-µm aragonite fractions are expected to consist predominantly of small pieces of bank-derived algae such as *Halimeda* and also appear to include a high U organic material, probably as a coating (Henderson et al., 1999).

ANALYTICAL DETAILS

Pure aragonite samples of 0.09 to 1.0 g were spiked with a ²²⁹Th-²³⁶U mixed spike to give an expected ²³⁶U/²³⁵U ratio of \approx 5 and ²²⁹Th/ ²³⁰Th ratio of 2 to 40 depending on sediment age. Samples were then covered with distilled water and dissolved by drop-wise addition of 7.5M HNO₃. U and Th were separated using techniques described before (e.g. Edwards et al., 1987). After co-precipitating with Fe, they were loaded on 2 mL of 1 x 8 anion-exchange resin in 7.5M HNO₃, washed with 7.5M HNO₃, the Th eluted with 12M HCl, and the U with 0.01M HCl. Both the U and Th separates were cleaned further using 100 µL of 1 x 8 anion-exchange resin. Thorium separates were loaded in 7.5M HNO₃, washed with 7.5M HNO₃, and eluted with 1M HNO₃. U separates were loaded in a 90% acetone-10% 6M HCl mix, washed with the same mixture, and eluted with 1M HCl. Chemical yields for the entire procedure were ~80% for both U and Th.

U and Th were analyzed as the metal by thermal ionization mass spectrometry using a VG 54-30 mass spectrometer (Edwards et al., 1987). Thorium-229, ²³⁰Th, and ²³²Th were measured by single-collector peak switching using the daly ion-counting system. Uranium-234, ²³⁵U, and ²³⁶U were also measured by ion counting, but ²³⁶U was additionally monitored in a faraday cup during the daly-²³⁴U collection step, and ²³⁸U monitored in the same faraday during the daly-²³⁶U collection step. This enables in-run assessment of the daly/faraday gain and measurement of the ²³⁸U/²³⁵U to correct the analyses for mass fractionation.

Uranium was measured at ≈ 200 counts per second of 234 U and 200 ratios were taken for each sample. Thorium runs were more variable depending on the sample size but at least 80 ratios were collected for each sample. Machine performance was assessed during the collec-

tion of this data by repeated measurement of the U-500 standard, which yielded an average ${}^{235}\text{U}/{}^{234}\text{U}$ of 95.79 ± 0.35 (2 SD; *N* = 16), within error of the certified value of 95.95 (Garner et al., 1971). Two total-procedure blanks (from dissolution to analysis) were measured as 68 and 22 pg ${}^{238}\text{U}$ and 77 and 55 pg ${}^{232}\text{Th}$.

RESULTS

Uranium concentrations for the samples are uniformly high, ranging from 2.6 to 4.4 ppm (Table 3). Thorium-232 concentrations range from 23 to 98 ppb and are sufficiently low that corrections for scavenged Th remain reasonably small. The uppermost sample from each core has $\delta^{234}U(0)$ values close to the modern seawater value of ≈ 149 (Stirling et al., 1995). Deeper samples from Sites 1005 and 1006 show a general decrease in $\delta^{234}U(0)$ with depth, while samples from Site 1007 and particularly Site 1003 show more scatter and are close to the secular equilibrium value of zero. Three samples from Site 1003 have $\delta^{234}U(0)$ of less than zero.

Measured (230 Th/ 238 U) ratios are low for the uppermost sample in each core (0.1–0.3). With the exception of Sample 6-2 with a ratio of ~0.7, all other samples have (230 Th/ 238 U) greater than 0.97. For samples from Sites 1003, 1006, and 1007, the values are generally close to 1.0, but for deep samples from Site 1005, (230 Th/ 238 U) values are all significantly greater than 1.0, ranging to 1.2.

Raw U-Th ages calculated from this data are shown in Table 3, together with ages corrected for initial ²³⁰Th scavenged from seawater by assuming a ²³²Th/²³⁰Th atom ratio for seawater of 12,000 \pm 6,000. This range of values easily incorporates observed values of the ²³²Th/²³⁰Th ratio for seawater from close to the Bahamas (Hoff et al., in press) and also fits with initial ²³²Th/²³⁰Th ratios calculated from modern Bahamas sediment (Slowey et al., 1996). The uncertainty in the value of the ratio used to make this correction introduces error to the final corrected age, which in most cases is larger than the analytical uncertainty.

Corrected ages for the uppermost sample from each site are <25 ka and yield $\delta^{234}U(T)$ values close to modern seawater. Sample 6-2 gives an age of 109 ka and also yields a $\delta^{234}U(T)$ close to modern seawater. All other samples either do not yield ages, or return ages that are older than 280 ka with $\delta^{234}U(T)$ values very different from modern seawater.

DISCUSSION

Diagenetic Alteration of Sediments

U Loss and Gain

The majority of samples analyzed in this study have clearly undergone some form of diagenesis which has perturbed their U-Th systematics. This is most clearly demonstrated by $(^{230}\text{Th}/^{238}\text{U})$ values in excess of secular equilibrium, and is also shown by the anomalous $\delta^{234}\text{U}(\text{T})$ values of many samples.

The high (²³⁰Th/²³⁸U) values of Site 1005 indicate that either U loss or ²³⁰Th gain has occurred. Thorium is generally a highly immobile element, so U loss is the more likely case. Future discussion here will make the assumption that U loss has occurred, rather than ²³⁰Th gain, but if the situation were reversed much of the interpretation would stand unaltered.

Loss of U makes the apparent age too great and therefore increases the δ^{234} U(T). This loss can be investigated by constructing curves on a δ^{234} U(T)-vs.-age diagram for each sample (Henderson et al., 1993) (Fig. 3). The position of the curve is controlled by the measured δ^{234} U(0) value and samples move toward the bottom left as U is returned to the age calculation to correct for U lost from the sample. Because U loss is unlikely to cause a significant isotopic fraction-



Figure 2. XRD scans for Sample 3-5, measured using Co K α radiation ($\lambda = 1.7903$). The upper panel shows the bulk sediment. The lower panel shows a separate from this sediment, which has a grain size of 63- to 250- μ m and a density of >2.8 g/cm³. Gray bands represent the expected position of calcite peaks. Prominent peaks are seen at these angles for the bulk sediment but are nearly completely absent from the separate, demonstrating that the separation protocol effectively concentrates aragonite (see Table 2).

ation, the true age of each sample is expected to lie somewhere on a curve derived in this way.

Similar curves can be constructed for some of the samples from Sites 1003 and 1006, but here U addition seems to have occurred rather than U loss (Fig. 3). In this case, the possibility exists of adding U with an isotopic composition different from the sediment; however, the amount of U addition required for these samples is sufficiently small that, unless the isotopic ratio of the added U is extreme, it is not expected to cause samples to deviate significantly from the curves shown in Figure 3.

The percentage of U lost or gained can be calculated for each sample (although this is somewhat dependent on the diagenetic model, discussed below [see "Diagenetic Models" section]). Sample 5-2 requires a U loss of some $\approx 40\%$, while other Site 1005 samples require

progressively less U loss downcore to a value of only $\approx 5\%$ for Sample 5-6 (Fig. 3). Much smaller amounts of U addition are required for the Site 1003 and 1006 samples, with the only significant additions being $\approx 2\%$ for Sample 6-3 and $\approx 3\%$ for Sample 6-4. Note that these percentages are calculated assuming that all loss or gain occurred recently. Total U addition would need to be higher if some of it occurred in the past.

Diagenetic Models

There are two diagenetic models with which to estimate true ages for these samples. First, if straightforward gain or loss of U occurred, then the intersect between the curves and the seawater value of δ^{234} U (\approx 149) would provide the true age. This approach, however, yields ages that are unreasonable given that these high-aragonite samples are expected to come from a sea-level highstand. In particular, Sample 5-4 would yield an age of \approx 270 ka and Samples 5-6 and 6–3 ages close to 560 ka—both times of sea-level lowstands (Fig. 3).

The second diagenetic model assumes that, in addition to the gain or loss of U, α -recoil of ²³⁴U causes a continuous loss of pure ²³⁴U from these U-rich samples. If the samples are assumed to come from a highstand interval, then the intersection of the curves in Figure 3 with highstands (shown as gray bands) enables an assessment of the ²³⁴U loss and of the possible age. Such intersections for all nine samples in Figure 3 define a linear trend toward decreasing $\delta^{234}U(T)$ with

 Table 2. Representative XRD analyses for three samples that demonstrate the effectiveness of the aragonite concentration protocol.

Sample	Sediment type	Depth (mbsf)	LMC (%)	HMC (%)	ARAG (%)
3-2	Bulk sediment	14.40	6.5	0.9	92.6
	Fine fraction (<63 µm)	14.40	6.4	0.7	92.8
	63- to 250-µm aragonite separate	14.40	–1.1	-1.5	102.6
3-5	Bulk sediment	36.72	18.9	5.5	75.5
	Fine fraction (<63 μm)	36.72	29.6	5.4	65.0
	63- to 250-μm aragonite separate	36.72	-0.6	–0.8	101.4
6-2	Fine fraction (<63 µm)	5.05	6.7	7.0	86.3
	63- to 250-µm aragonite separate	5.05	-1.3	-2.0	103.3

Notes: LMC = low-Mg calcite, HMC = high-Mg calcite, ARAG = aragonite. Percentages were calculated using peak areas and standards of known composition (Fig. 2). 63- to 250-µm aragonite separates have undergone the sieving and heavy liquid protocols described in the text. age of sample (shown by the bold dashed arrow). This trend is as expected for continuous loss of 234 U, and the fact that all samples fall on the same trend lends support to the idea that α -recoil is systematically effecting these samples.

Such α -recoil is probably an internal reorganization within the sediment. Measurements presented in this paper are on U-rich separates from the bulk sediment. This U-rich material is expected to lose more ²³⁴U by α -recoil than it gains from the U-poor fraction of the sediment. The surprise is that α -recoil can be so significant for 63- to 250-µm grain size separates as the recoil distance is short compared to this grain radius. A possible explanation is that U-rich organics on the grain surface play an important role in α -recoil exchanges between grains.

Whatever the process, there is clear empirical evidence that α -recoil is occurring for these samples and for similar samples from elsewhere in the Bahamas. For instance, deep samples from Site 1003 have $\delta^{234}U(0)$ less than zero, indicating that they have preferentially lost ^{234}U . Measurements from the Little Bahama Bank show that aragonite in slope sediments is prone to loss of ^{234}U (G.M. Henderson, N.C. Slowey, and M.Q. Fleisher, unpubl. data). The rate of ^{234}U loss can be calculated from the deep Site 1003 samples and is similar to that required to explain the α -recoil trend shown in Figure 3.

In general, the clear linear trend toward low $\delta^{234}U(T)$ (Fig. 3), together with independent evidence for the importance of α -recoil, suggests that a diagenetic model involving both U loss/gain and continuous ²³⁴U loss by recoil is reasonable for these sediments.

Differences Between Sites

The diagenetic model favored above requires significant U *loss* from Site 1005 samples but slight addition of U to samples from Sites 1003 and 1006. The difference between the sites may be explained by their distance from the platform and the different fluid-flow history that they have, therefore, experienced.

Data collected during Leg 166 (Eberli, Swart, Malone, et al., 1997) suggest that fluid flow through the slopes of the Bahamas has two modes, depending on whether the banks are flooded or not (Henderson et al., 1999). This is illustrated in Figure 4 and is most clearly seen from the chlorinity data. At Site 1005, pore-water Cl concentrations show a clear inversion at depth because of lowstand circulation (Fig. 4, upper panel) and a flushed zone of seawater values above reflecting highstand circulation (Fig. 4, lower panel).

Table 3. U-Th concentrations and isotope ratios for Leg 166 samples, together with age information derived from them.

Sample identifier	²³⁸ U (ppm)	²³² Th (ppb)	²³² Th/ ²³⁰ Th	$\delta^{234}U(0)$	(²³⁰ Th/ ²³⁸ U)	Raw age (ka)	Scavenging corrected age (ka)	$\delta^{234} U(T)$	MIS stage
3-1 3-2 3-3 3-4 3-5	$\begin{array}{c} 4.080 \pm 0.006 \\ 3.636 \pm 0.002 \\ 3.857 \pm 0.002 \\ 3.324 \pm 0.002 \\ 3.274 \pm 0.001 \end{array}$	$\begin{array}{c} 40.18 \pm 0.22 \\ 29.90 \pm 0.06 \\ 23.63 \pm 0.09 \\ 42.15 \pm 0.09 \\ 28.59 \pm 0.05 \end{array}$	$6271 \pm 81 496 \pm 2 377 \pm 2 790 \pm 4 530 \pm 2$	$144.0 \pm 4.9 \\ 28.6 \pm 2.1 \\ -12.7 \pm 3.1 \\ -19.6 \pm 2.9 \\ 9.2 \pm 2.0$	$\begin{array}{c} 0.095 \pm 0.002 \\ 1.010 \pm 0.002 \\ 0.997 \pm 0.004 \\ 0.980 \pm 0.002 \\ 1.003 \pm 0.002 \end{array}$	9.5 ± 0.2 387.9 ± 11.5 505.9 ± 27.5	5 ± 6 383 ± 13 497 ± 28	146.0 ± 5.7 84.5 ± 6.2 37.6 ± 7.5	1 >11 >11 >11 >11 >11
3-6 5-1 5-2 5-3 5-4 5-5	3.890 ± 0.002 4.197 ± 0.003 4.395 ± 0.003 3.409 ± 0.002 3.704 ± 0.003 3.468 ± 0.003	$37.85 \pm 0.10 54.20 \pm 0.49 31.97 \pm 0.15 44.24 \pm 0.19 57.62 \pm 0.20 39.21 \pm 0.43$	$592 \pm 2 6557 \pm 286 405 \pm 2 722 \pm 3 793 \pm 3 634 \pm 9$	-4.7 ± 2.7 148.2 ± 2.9 113.7 ± 3.0 68.7 ± 3.4 79.7 ± 3.9 45.0 ± 3.0	$1.005 \pm 0.003 \\ 0.120 \pm 0.038 \\ 1.093 \pm 0.005 \\ 1.096 \pm 0.006 \\ 1.198 \pm 0.004 \\ 1.078 \pm 0.020$	12.0 ± 0.5 325.1 ± 11.5	6 ± 8 322 ± 12	150.7 ± 4.5 282.9 ± 8.2	1 5 7 7 9
5-6 6-1 6-2 6-3 6-4 7-1 7-2	$\begin{array}{c} 3.628 \pm 0.003 \\ 4.016 \pm 0.004 \\ 4.092 \pm 0.003 \\ 3.962 \pm 0.003 \\ 2.870 \pm 0.002 \\ 3.643 \pm 0.004 \\ 2.625 \pm 0.002 \end{array}$	77.49 ± 0.63 97.86 ± 0.25 43.31 ± 0.10 34.85 ± 0.10 31.38 ± 0.08 43.68 ± 0.13 42.10 ± 0.20	$1230 \pm 11 \\8281 \pm 101 \\879 \pm 4 \\543 \pm 3 \\678 \pm 3 \\2643 \pm 17 \\1012 \pm 7$	$\begin{array}{c} 30.7 \pm 3.2 \\ 146.1 \pm 2.9 \\ 109.5 \pm 2.3 \\ 42.6 \pm 2.3 \\ 31.0 \pm 2.2 \\ 136.8 \pm 3.5 \\ -2.3 \pm 3.4 \end{array}$	$\begin{array}{c} 1.061 \pm 0.015 \\ 0.179 \pm 0.003 \\ 0.734 \pm 0.002 \\ 0.986 \pm 0.003 \\ 0.985 \pm 0.003 \\ 0.276 \pm 0.007 \\ 0.970 \pm 0.007 \end{array}$	18.4 ± 0.3 114.7 ± 0.8 296.0 ± 5.9 318.4 ± 6.8 30.1 ± 0.3 394.6 ± 34.2	7 ± 14 110 ± 6 291 ± 8 312 ± 10 24 ± 7 385 ± 36	149.1 ± 6.6 149.4 ± 4.2 97.3 ± 5.5 75.2 ± 5.5 146.6 ± 4.9 -6.9 ± 10.0	11 1 5 9 11 1 >11

Notes: All errors are 2 s.e. and are propagated to include weighing error, blank uncertainty, and in-run statistical error from the analyses. $\delta^{234}U(0) = [(^{234}U)^{238}U) - 1]/1000$, where parentheses signify an activity ratio. Raw age is calculated directly from the data in the previous two columns. Scavenging corrected age = the age corrected for initial 230 Th by assuming that all 232 Th is scavenged from seawater at a 232 Th/ 230 Th ratio of 12,000 ± 6,000. Only those ages listed in bold give $\delta^{234}U(1)$ values that indicate little or no diagenesis; other samples have suffered diagenesis and the ages are therefore not correct. $\delta^{234}U(1)$, which equals $\delta^{234}U(0) e^{\lambda 234 T}$, is an expression of the initial $\delta^{234}U$. MIS stage = the marine oxygen isotope stage during which the sample is thought to have formed based on the diagenetic model discussed in the text and in Figure 3.



Figure 3. δ^{234} U(T) vs. age plot for nine of the samples from this study that are thought to have undergone U loss or gain. Filled symbols represent the measured values and are off the figure for Site 1005 samples. Curves are labelled with sample identifiers and are derived by progressively subtracting/adding U from/to the measured (²³⁰Th/²³⁸U) ratio. The lower panel shows an approximation of sea-level constructed by scaling the marine–oxygen isotope curve (Imbrie et al., 1984) so that the most recent deglaciation corresponds to 120 m of sea-level rise. Because the oxygen isotope curve also contains a temperature component, this is not an accurate indicator of past sea level but it is useful to highlight the times in the past at which sea level has come close to its present-day value. These periods are indicated by gray shading and marine-isotope-stage numbers on the lower panel, and gray bars on the upper panel. Because the samples are known to have formed during sea-level highstands, the intersection of the sample curves with highstand intervals enables each sample to be corrected for U loss or gain and assigned to a highstand event (see text for full discussion). All five samples from Site 1005 showed loss of U, with the uppermost sample having lost the most (percentage loss is shown after the sample identifier). The remaining four samples showed slight U gain. The intersections between the curves and high-stand events define a broad trend toward lower δ^{234} U(T) with increasing age as indicated by the dashed arrow. This is due to alpha recoil of 234 U from the U-rich aragonite material analyzed here. Of the nine samples not on this figure, four yielded Holocene ages and five were sufficiently old that no useful age information could be gleaned from the U-Th system.

Close to the banks the direction of fluid flow, therefore, probably changes from outward flow caused by fresh-water compensation during low sea level to inward, thermally driven flow when the banks are flooded. Site 1005 sediments, therefore, experience long periods (\approx 90 k.y.) of outward flow of nonoxygenated pore water while the banks are exposed, followed by a shorter periods (\approx 10 k.y.) of downward flow of oxygenated seawater during peak interglacials (Fig. 3).

In contrast, sites situated farther from the platform have always experienced inflow of seawater. In these sites, U-rich organic material in the sediment is remineralized relatively quickly by the continuous inflow of oxygenated water. But at Site 1005, U-rich organic material may survive for considerable periods while producing radiogenic ²³⁰Th before oxidation during a highstand event. For instance, after ≈115 ka, sediments from Site 1005 were probably bathed in nonoxy-



Figure 4. Cartoon to illustrate probable change in fluid-flow regime between lowstand and highstand periods. During lowstands, the banks are exposed setting up freshwater flow through the upper portions of the platform while thermally driven flow continues farther offshore. During highstands, the banks are flooded, shutting off the freshwater flow and allowing venting of the thermal flow at the bank top. Note that Site 1005, close to the platform, experiences flow which is out of the banks during lowstands and into the banks during highstands. Other sites experience continual inward flow, although the rate of flow probably varies. This scenario provides a good explanation for the chlorinity data collected aboard ship (Eberli, Swart, Malone, et al., 1997) as well as for the data presented in this paper.

genated pore waters while producing radiogenic ²³⁰Th. Then, at ~10 ka, the banks flooded, flow reversed, oxidation of organic material began, and U was removed while leaving behind the immobile ²³⁰Th, thus yielding apparent ages that are too old. This scenario is supported by the fact that the percentage of U loss required to explain the measured U-Th ages of the sediment decrease downcore for Site 1005. This is the result of deeper sediment packages experiencing multiple phases of U loss at previous sea-level highstands.

The small amount of U addition experienced by the samples from Sites 1003 and 1006 is probably explained by the downward advection of pore waters from oxidizing conditions to reducing conditions. As U is insoluble when reduced, the process of fluid flow moves small amounts of U downcore to precipitate in the more reducing conditions at depth.

The differences in fluid-flow regime experienced by the sediments of this study produce U diagenesis sufficiently complex that precise age information cannot be calculated for these samples. Nevertheless, there appears to be a coherent diagenetic explanation of the data such that each sample can be assigned to a single highstand event, enabling the production of age models for these cores.

Ages of Sediment Packages

Samples have been assigned to particular highstand events on the basis of their measured U-Th compositions and the consideration of diagenesis above. The sequence of highstands preserved at each site is now discussed briefly, working from the basin toward the platform edge.

Site 1006

This site has marine oxygen isotope Stages 1, 5, 9, and 11 but is missing Stage 7. This has been ascribed to a coring gap in Hole 1006A; the same coring gap does not exist in Hole 1006B (Kroon et al., Chap. 2, this volume). Sedimentation has, therefore, occurred and been preserved for each of the major highstand events back to Stage 11 for this basin site.

Site 1007

The uppermost sample in this core yields a U-Th age which is older than Holocene (24 ka). This probably reflects mixing of small amounts of older material upward in the core as this sample was taken from the transition from high- to low-aragonite-content sediment. The second sample in this core is too old to date by U/Th methods. This site has, therefore, suffered either a significant hiatus or considerable sediment erosion so that the highstands associated with Stages 5, 7, 9, 11, and possibly others are missing. This conclusion confirms the initial interpretation of the Western Seismic Line and the observations made by the Leg 166 shipboard party, both of which indicate a significant hiatus near the top of Site 1007 (Eberli, Swart, Malone, et al., 1997).

Site 1003

This site is also missing several highstand events, a fact hinted at by the abrupt change in δ^{18} O between the uppermost sediment package and deeper packages, indicating a change in sediment diagenesis (Rendle et al., Chap. 6, this volume). Stage 11 has been preserved at this site, but Stages 5, 7, and 9 are missing. The four deeper sediment packages measured in this study are older than the U/Th limit of ~450 ka.

Site 1005

This site, closest to the platform, appears to have a complete sequence of the major highstands, yielding ages from Stages 1, 5, 7, 9, and 11. The relative spacing of these ages is somewhat problematic, however. Stage 5 is very close to Stage 1, possibly suggesting sediment erosion of much of the Stage-5 sediment. Stage 7 features two distinct aragonite peaks separated by some distance. This might be explained if each package was from a different substage of Stage 7, but the U-Th dating presented here cannot distinguish these events.

The Magnitude of Sea-Level Rises

Samples analyzed in this study were selected from horizons in the cores with the highest aragonite content. Such high aragonite contents are only produced when the banks are flooded and large areas of shallow water become available for aragonite production. None of these peak aragonite intervals has been dated as Stage 3, or as Substage 5a or 5c. It is possible that the absence of high-aragonite sediment of these ages reflects erosion of any such material originally deposited. Erosion of sediment is, after all, indicated by missing highstands in the sediments of three of the four sites investigated here. It is, however, more difficult to allow for removal of such sediment from Site 1006, which is situated on horizontal sea floor, some way from the platform. The lack of erosion from this site is supported by the complete sequence of major highstands recovered there.

Site 1006 features a rather monotonic decrease in aragonite concentration upward from the Substage 5e aragonite peak (Fig. 1). There is nothing approaching a return to the high values seen in Substage 5e. This pattern is similar to that reported for a core from the Tongue of the Ocean by Droxler et al. (1983). The lack of a return to high aragonite values in Substages 5c and 5a suggests that the banks were not flooded during these intervals.

The position of sea level during Substage 5c and particularly 5a has been the subject of significant controversy. Estimates based on U-Th dated corals have placed it anywhere from +2 m to -19 m compared to today's sea level (see Ludwig et al., 1996, for summary). Estimates from δ^{18} O and Mg/Ca measurements from deep-sea cores put Substage 5a sea level significantly lower (\approx -60 m) (Dwyer et al., 1995). The banks in the vicinity of the Leg 166 Sites range from 6 to 10 m in water depth, and the Bahamas are tectonically reasonably stable. The lack of a return to high aragonite fractions in Bahamas sediments during these periods suggests that the banks were not flooded and that sea level therefore did not come within \approx 10 m of the modern value. At this stage, such a conclusion is not robust due to the possibility of erosion of important sections of the few cores studied. How-

ever, if continuing work on Bahamas slope sediments fails to provide evidence for high-aragonite sedimentation during Substages 5a and 5c, it will increasingly suggest that sea level during these periods was lower than today.

CONCLUSIONS

Sieving and heavy-liquid treatment has enabled us to produce a pure aragonite separate from the mixed-carbonate bulk sediment of the Bahamas slopes and to remove detrital material. This solves the problems of initial Th for these samples and allows use of U-Th techniques to learn about their age.

Sediments recovered during Leg 166 have suffered diagenesis that has altered their U-Th systematics. This diagenesis varies from site to site, probably reflecting the different fluid-flow regimes experienced at various distances from the platform. Samples from Site 1005 have experienced U loss while those from Sites 1006 and 1003 have experienced U gain. Samples from all sites have also suffered continuous loss of pure ²³⁴U due to α-recoil. Correcting sample ages for both U loss/gain and for ²³⁴U loss does not allow precise ages to be assigned, but does enable each aragonite-rich sediment package to be matched with the sea-level highstand that formed it. Site 1005 has a complete sequence of highstands, equivalent to marine oxygen isotope Stages 1, 5, 7, 9, and 11. Hole 1006A is missing only the Stage 7 highstand (but this is present in Hole 1006B). Site 1003 has only the Stage 1 and Stage 11 highstands and is missing all those in between. Site 1007 still has sediment from the present day highstand but features sediments older than the U-Th age range immediately beneath that.

No aragonite-rich sediment packages are identified for Stage 3, or Substages 5a and 5c, even in the basin-located Site 1006. Unless somewhat unusual erosion has occurred, this suggests that the banks were not flooded during these periods and that sea level was therefore at least \sim 10 m lower than today.

ACKNOWLEDGEMENTS

The Leg 166 shipboard party are thanked for collecting these samples. In particular, Peter Swart and Gregor Eberli are thanked for their role as Co-chiefs and for discussion. Discussion of Site 1006 age models with Dirk Kroon is gratefully acknowledged. Roseanne Schwartz is thanked for lab support. Harry Elderfield and Andre Droxler are thanked for constructive reviews. Research was funded by the German Science Foundation (DFG Re1051/4-1, 4–2, 4–3 to R.R. and J.R.). Geomar Research Institute in Kiel and the Geology and Geophysics Department at Edinburgh University are thanked for providing laboratory facilities. The Core Repository in Bremen is thanked for providing additional samples.

REFERENCES

- Bard, E., Hamelin, B., Fairbanks, R.G., and Zindler, A., 1990. Calibration of the ¹⁴C time-scale over the past 30,000 years using mass spectrometric U-Th ages from Barbados corals. *Nature*, 345:405–410.
- Boardman, M.R., Neumann, A.C., Baker, P.A., Dulin, L.A., Kenter, R.J., Hunter, G.E., and Kiefer, K.B., 1986. Banktop responses to Quaternary fluctuations in sea level recorded in periplatform sediments. *Geology*, 14:28–31.
- Broecker, W.S., Thurber, D.L., Goddard, J., Ku, T.L., Matthews, R.K., and Mesollela, K.J., 1968. Milankovitch hypothesis supported by precise dating of coral reefs and deep sea sediments. *Science*, 159:297.
- Droxler, A.W., and Schlager, W., 1985. Glacial versus interglacial sedimentation rates and turbidite frequency in the Bahamas. *Geology*, 13:799–802.
- Droxler, A.W., Schlager, W., and Whallon, C.C., 1983. Quaternary aragonite cycles and oxygen-isotope record in Bahamian carbonate ooze. *Geology*, 11:235–239.

- Dwyer, G.S., Cronin, T.M., Baker, P.A., Raymo, M.E., Buzas, J.S., and Correge, T., 1995. North Atlantic deepwater temperature change during late Pliocene and Late Quaternary climatic cycles. *Science*, 270:1347–1351.
- Eberli, G.P., Swart, P.K., Malone, M.J., et al., 1997. Proc. ODP, Init. Repts., 166: College Station, TX (Ocean Drilling Program).
- Edwards, R.L., Chen, J.H., and Wasserburg, G.J., 1987. ²³⁸U-²³⁴U-²³⁰Th-²³²Th systematics and the precise measurement of time over the past 500,000 years. *Earth Planet Sci. Lett.*, 81:175–192.
- Garner, E.L., Machlan, L.A., and Shields, W.R., 1971. Uranium isotopic standard reference materials. NBS Spec. Publ., 260–27:144.
- Glaser, K.S., and Droxler, A.W., 1991. High production and highstand shedding from deeply submerged carbonate banks, northern Nicaragua Rise. *J. Sediment. Petrol.*, 61:128–142.
- Heath, K.C., and Mullins, H.T., 1984. Open-ocean, off-bank transport of fine-grained carbonate sediments in the Northern Bahamas. In Stow, D.A.V., and Piper, D.J.W. (Eds.), *Fine-grained Sediments: Deep-water Processes and Facies:* London (Blackwell Scientific), 199–208.
- Henderson, G.M., Cohen, A.S., and O'Nions, R.K., 1993. ²³⁴UJ²³⁸U ratios and ²³⁰Th ages for Hateruma Atoll corals: implications for coral diagenesis and seawater ²³⁴UJ²³⁸U ratios. *Earth Planet. Sci. Lett.*, 115:65–73.
- Henderson, G.M., and O'Nions, R.K., 1995. ²³⁴U/²³⁸U ratios in Quaternary planktonic foraminifera. *Geochim. Cosmochim. Acta*, 59:4685–4694.
- Henderson, G.M., Slowey, N.C., and Haddad, G.A., 1999. Fluid flow through carbonate platforms: constraints from ²³⁴U/²³⁸U and Cl⁻ in Bahamas pore-waters. *Earth Planet. Sci. Lett.*, 169:99–111.
- Hoff, J.A., Edwards, R.L., Buesseler, K.O., and Belastock, R.A., in press. TIMS measurements of ²³⁰Th and ²³²Th in liter-sized samples of seawater from the Northwest Atlantic Ocean. *Geochim. Cosmochim. Acta.*
- Imbrie, J., Hays, J.D., Martinson, D.G., McIntyre, A., Mix, A.C., Morley, J.J., Pisias, N.G., Prell, W.L., and Shackleton, N.J., 1984. The orbital theory of Pleistocene climate: support from a revised chronology of the

marine δ^{18} O record. *In* Berger, A., Imbrie, J., Hays, J., Kukla, G., and Saltzman, B. (Eds.), *Milankovitch and Climate* (Pt. 1), NATO ASI Ser. C, Math Phys. Sci., 126:269–305.

- Kier, J.S., and Pilkey, O.H., 1971. The influence of sea level changes on sediment carbonate mineralogy, Tongue of the Ocean, Bahamas. *Mar. Geol.*, 11:189–200.
- Ludwig, K.R., Muhs, D.R., Simmons, K.R., Halley, R.B., and Shinn, E.A., 1996. Sea-level records at ~80 ka from tectonically stable platforms: Florida and Bermuda. *Geology*, 24:211–214.
- Neumann, A.C., and Land, L.S., 1975. Lime mud deposition and calcareous algae in the Bight of Abaco, Bahamas: a budget. J. Sediment. Petrol., 45:763–786.
- Schlager, W., and Camber, O., 1986. Submarine slope angles, drowning unconformities, and self-erosion of limestone escarpments. *Geology*, 14:762–765.
- Slowey, N.C., Henderson, G.M., and Curry, W.B., 1996. Direct U-Th dating of marine sediments from the two most recent interglacial periods. *Nature*, 383:242–244.
- Stirling, C.H., Esat, T.M., McCulloch, M.T., and Lambeck, K., 1995. Highprecision U-series dating of corals from Western Australia and implications for the timing and duration of the last Interglacial. *Earth Planet. Sci. Lett.*, 135:115–130.
- Wilber, R.J., Milliman, J.D., and Halley, R.B., 1990. Accumulation of banktop sediment on the western slope of Great Bahama Bank: rapid progradation of a carbonate megabank. *Geology*, 18:970–974.

Date of initial receipt: 11 August 1998 Date of acceptance: 21 May 1999 Ms 166SR-106