

Seawater ($^{234}\text{U}/^{238}\text{U}$) during the last 800 thousand years

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Abstract

Constraining the history of seawater ($^{234}\text{U}/^{238}\text{U}$) is important because this ratio is used to assess the validity of U/Th ages, and because it provides information about the past rate of physical weathering on the continents. This study makes use of U-rich slope sediments from the Bahamas in an attempt to reconstruct seawater ($^{234}\text{U}/^{238}\text{U}$) for the last 800 kyr. For the last 360 kyr, U/Th dating of these sediments provides ages and initial ($^{234}\text{U}/^{238}\text{U}$) values. Sixty-seven samples, largely from marine highstands, have initial ($^{234}\text{U}/^{238}\text{U}$) which scatter somewhat about the modern seawater value (~ 1.145) but neither this scatter nor the average value increases with age of sample. These data contrast with published coral data and suggest that seawater ($^{234}\text{U}/^{238}\text{U}$) has remained within 15% of the modern value for the last 360 kyr. This confirms the rejection of coral U/Th ages where the initial ($^{234}\text{U}/^{238}\text{U}$) is significantly different from modern seawater. Data from older highstands, dated with $\delta^{18}\text{O}$ stratigraphy or by the presence of the Brunhes/Matuyama (B/M) reversal at 780 kyr, allow seawater ($^{234}\text{U}/^{238}\text{U}$) to be assessed prior to the range of the ^{230}Th chronometer. Unfortunately, diagenetic scatter in the data between the B/M reversal and 360 kyr is rather large, probably relating to low U concentrations for these samples. But there is no indication of a trend in seawater ($^{234}\text{U}/^{238}\text{U}$) with age. High U samples from close to the B/M reversal show less diagenetic scatter and an initial ($^{234}\text{U}/^{238}\text{U}$) that averages 1.102. This lower value can be explained by lower seawater ($^{234}\text{U}/^{238}\text{U}$) at the time of the B/M reversal, or by progressive loss of ^{234}U from the sediment by α -recoil. A simple box model is presented to illustrate the response of seawater ($^{234}\text{U}/^{238}\text{U}$) to variations in riverine input, such as might be caused by changes in continental weathering. Comparison of the Bahamas ($^{234}\text{U}/^{238}\text{U}$) data with model results indicates that riverine ($^{234}\text{U}/^{238}\text{U}$) has not varied by more than 65% for any 100 kyr period during the last 360 kyr. It also indicates that the ratio of physical to chemical weathering on the continents has not been higher than at present for any extended period during the last 800 kyr. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: U-238/U-234; sea water; Th/U; Bahamas; weathering

1. Introduction

Seawater ($^{234}\text{U}/^{238}\text{U}$) is higher than secular equilibrium [1,2]. This reflects the process of

α -recoil during decay of ^{238}U which leads to high ($^{234}\text{U}/^{238}\text{U}$) in river waters [3], and to a flux of ^{234}U into the oceans from marine sediment pore-waters [4]. These inputs keep seawater ($^{234}\text{U}/^{238}\text{U}$) high and counteract the decay of excess ^{234}U in the oceans which constantly attempts to return it to a secular equilibrium value of 1.0. Changes in the input of excess ^{234}U to the oceans will be reflected by changes in the ($^{234}\text{U}/^{238}\text{U}$) of

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seawater. Constraining such variation in past seawater ($^{234}\text{U}/^{238}\text{U}$) is of value both for Pleistocene chronology and to provide information about past continental weathering.

Substrates forming from seawater, most notably corals, capture the ($^{234}\text{U}/^{238}\text{U}$) of seawater. Decay of excess ^{234}U after their formation provides a potential chronometer for these samples for about the last 1 Ma [4]. This chronometer requires knowledge of the U isotope ratio at the time of formation (i.e. the seawater ratio). In practice, although this chronometer has found some uses [5], few substrates appear to be sufficiently reliable recorders of ($^{234}\text{U}/^{238}\text{U}$) to provide robust age information. In unreliable substrates, the ($^{234}\text{U}/^{238}\text{U}$) ratio is used, rather than directly for dating, as a check for closure of the U-series system to assess the quality of U/Th ages [6,7]. This has become standard practice during U/Th dating of corals. Although corals of Holocene age exhibit initial ($^{234}\text{U}/^{238}\text{U}$) similar to modern seawater, many older corals do not, instead having values which are more scattered and generally higher (Fig. 1). Where such samples have initial ($^{234}\text{U}/^{238}\text{U}$) which differs from the modern seawater value they are considered to provide unreliable U/Th ages, e.g. [8,9]. This rejection approach makes the inherent assumption that seawater ($^{234}\text{U}/^{238}\text{U}$) has remained constant. Assessing the history of seawater ($^{234}\text{U}/^{238}\text{U}$) would allow this assumption to be tested, and the rejection criteria for coral U/Th ages to be refined.

As seawater ($^{234}\text{U}/^{238}\text{U}$) is held above secular equilibrium by river input, the history of seawater ($^{234}\text{U}/^{238}\text{U}$) also provides information about past riverine fluxes and hence about past continental weathering. The controls on riverine ($^{234}\text{U}/^{238}\text{U}$) are not completely understood but clearly relate to the rate of weathering, and are probably controlled predominately by the rate of physical weathering relative to chemical weathering [10]. This reflects the fact that physical weathering (i.e. mechanical breakdown of rocks) exposes fresh surfaces – a process which both releases ^{234}U in damaged crystallographic sites and increases surface area from which ^{234}U recoil can occur. Seawater ($^{234}\text{U}/^{238}\text{U}$) therefore offers po-

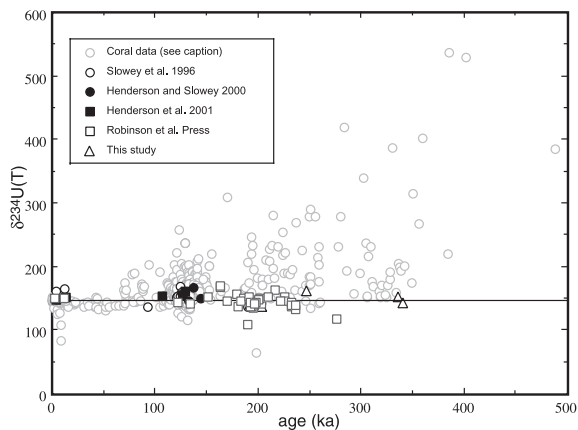


Fig. 1. $\delta^{234}\text{U}(T)$ data plotted against age for corals and U/Th-dated bulk Bahamas sediment. Coral data are a collation of 554 points from [6–9,11,27,34–55]. The Bahamas data are from this study (Table 1), or are from [13,14,19,20]. Errors are within symbol size except for some of the oldest coral samples. $\delta^{234}\text{U}(T) = \delta^{234}\text{U}_{\text{measured}} \cdot e^{\lambda^{234}t}$, where $\delta^{234}\text{U}_{\text{measured}}$ is the deviation of ($^{234}\text{U}/^{238}\text{U}$) from secular equilibrium in permil and t is the age of the sample. The horizontal line represents the modern seawater value. The first TIMS measurement of modern seawater placed it at $144 \pm 4\%$ using an old value for the ^{234}U half-life [1]. Subsequent analysis of marine carbonates suggested that seawater was at the higher end of this range at $\sim 148\%$ [9], again using an old half-life. The updated value of the ^{234}U half-life [25] causes this value to be recalculated to $\sim 145\%$. In this study, the modern seawater value is taken as $\sim 145\%$ and the new half-lives used throughout.

tential to assess changes in physical weathering of the continents during the Pleistocene.

Two studies have previously attempted to constrain the history of seawater ($^{234}\text{U}/^{238}\text{U}$) [11,12]. Both these studies were limited to highstand periods of the last 250 ka and both concluded that seawater ($^{234}\text{U}/^{238}\text{U}$) was close to its modern value at those times. In the present study, I test and extend that work by assessing seawater ($^{234}\text{U}/^{238}\text{U}$) during highstands for the last 800 kyr. U-rich aragonite sediments found on the slopes of the Bahamas have proved suitable for U/Th dating [13,14] and offer diagenetic advantages over corals because they have never been subaerially exposed. They allow reconstruction of seawater ($^{234}\text{U}/^{238}\text{U}$), especially during periods of sealevel highstand when they have a high sedimentation rate and high U content. Lower sedimentation rates during periods of sealevel lowstand make

Table 1
TIMS U and Th concentration and isotope data for Leg 166 samples

	U conc. (ppm)	$\delta^{234}\text{U}$ measured	$(^{230}\text{Th}/^{232}\text{Th})$	$(^{230}\text{Th}/^{238}\text{U})$ measured	Raw age (ka)	$(^{230}\text{Th}/^{238}\text{U})$ corrected	Corrected age (ka)	$\delta^{234}\text{U}$ final
1005A 4H-1W 4–6 cm	9.783 ± 0.022	76.4 ± 2.5	307.9 ± 0.5	0.965 ± 0.004	231.3 ± 2.7	0.961 ± 0.004	228 ± 3	146 ± 3
1006A 2H-4 135–137 cm	9.633 ± 0.021	54.4 ± 3.4	308.4 ± 1.1	1.027 ± 0.009	344.1 ± 21.7	1.025 ± 0.009	341 ± 22	142 ± 9
1006A 2H-6 135–137 cm	3.592 ± 0.003	54.1 ± 2.8	36.3 ± 0.2	1.049 ± 0.010	410.2 ± 48.9	1.043 ± 0.010	387 ± 50	161 ± 26
1008A 3H-1 12–14 cm	7.956 ± 0.008	76.2 ± 3.1	247.9 ± 1.2	0.931 ± 0.007	207.6 ± 4.1	0.926 ± 0.008	204 ± 4	136 ± 4
1008A 4H-5 62–64 cm	8.624 ± 0.007	56.7 ± 2.4	269.6 ± 3.9	1.037 ± 0.022	359.9 ± 73.7	1.035 ± 0.022	356 ± 74	155 ± 36
1009A 8H-2 140–150 cm	5.039 ± 0.010	81.6 ± 7.0	341.5 ± 4.5	0.915 ± 0.011	194.2 ± 6.4	0.910 ± 0.011	192 ± 7	140 ± 8
1009A 9H-5 109–111 cm	6.750 ± 0.009	79.8 ± 4.8	281.5 ± 2.4	0.991 ± 0.014	250.5 ± 13.2	0.987 ± 0.014	247 ± 13	161 ± 8
1009A 11H-2 15–17 cm	8.029 ± 0.007	58.8 ± 3.5	358.7 ± 2.2	1.030 ± 0.008	338.8 ± 18.0	1.029 ± 0.008	336 ± 18	152 ± 9

Errors are 2σ and incorporate uncertainty on the mass spectrometric measurement, on weighing, and on the spike concentration. Round brackets around isotope ratios signify an activity ratio. Corrected $(^{230}\text{Th}/^{238}\text{U})$ and ages are corrected for initial ^{230}Th as described in the text. Note that the two samples with $\delta^{234}\text{U}(\text{T})$ errors $> 10\%$ are discounted from further discussion due to their poor precision.

these sediments less suited to the reconstruction of seawater ($^{234}\text{U}/^{238}\text{U}$) and prevents a test of the recent suggestion [15] that glacial–interglacial changes in seawater ($^{234}\text{U}/^{238}\text{U}$) may occur.

2. Approach and samples used

All data discussed in this study are from sediments draped on the slopes of the Bahamas Banks. Some literature data are from the leeward slope of the Little Bahamas Bank but most data, including all new data, are from the leeward slope of the Great Bahama Bank and were sampled during ODP Leg 166 [16]. This ODP leg drilled a total of seven sites in water depths between 200 m and 700 m. The carbonates recovered show regular cyclicity between rapidly accumulating aragonite-dominated sediment, formed during highstand periods when the banks are flooded, and calcite/aragonite sediments with lower accumulation rates formed when they are not [17]. These sediments form continuously from material swept from the banks by tides and storms [18]. They have U concentrations of up to 12 ppm [19] and the high sedimentation rate, coupled to the lack of detrital sources, leads to very low initial Th concentrations.

Calculation of initial ($^{234}\text{U}/^{238}\text{U}$) requires knowledge of the age of the sample in order to correct for decay of excess ^{234}U within the sample

since formation. In this study, ages are assessed in three ways: by U/Th chronology; by $\delta^{18}\text{O}$ stratigraphy; and/or by the presence of the Brunhes/Matuyama (B/M) reversal. In the first category are a total of 61 bulk sediment samples with U/Th dates and ($^{234}\text{U}/^{238}\text{U}$) analyses. Fifty-five of these are from the literature [13,14,19,20] and the remaining eight are from this study (Fig. 1, Table 1).

In the Bahamas setting some cores have existing stratigraphies based on $\delta^{18}\text{O}$ and carbonate mineralogy. These allow age models to be constructed to well beyond the limits of the ^{230}Th chronometer. At Site 1006, $\delta^{18}\text{O}$ and aragonite percent measurements have enabled marine isotope stages (MIS) to be identified back to at least MIS 37 [21]. The accuracy of the upper portion of this stratigraphy is confirmed by the presence of the B/M reversal in MIS 19 [22]. Continuous deep-ocean sediment records also place this event in MIS 19 at an age of 780 ka [23]. Twenty samples were selected from this core from intervals with particularly high aragonite content (Fig. 2, Table 2).

Other cores from Leg 166 have less continuous stratigraphies [24] so $\delta^{18}\text{O}$ cannot be used to produce reliable age models, but the B/M reversal has been identified at three sites (Site 1003, Site 1004, and Site 1006) [16]. Because this reversal has a well-constrained age, ($^{234}\text{U}/^{238}\text{U}$) measurements from samples close to it can be age-corrected.

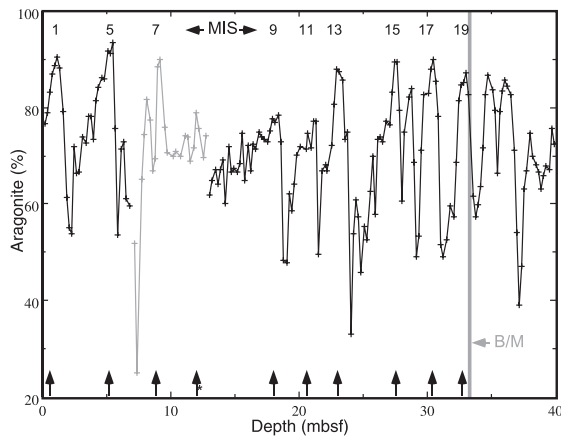


Fig. 2. Aragonite stratigraphy for ODP Site 1006 after Kroon et al. [21]. Data in black are from the A hole while those in gray are from the B hole and were analyzed to fill a break in the A hole stratigraphy. The depth scale is the depth in the composite stratigraphy of Kroon et al. [21]. Marine isotope stages are marked at the top of the figure and are confirmed by the presence of the B/M reversal within MIS 19 [22]. Arrows at the base of the figure indicate the depths of samples measured in this study, with two samples separated by 10 cm taken at each arrow (Table 2). Ages for these samples are assigned following the $\delta^{18}\text{O}$ age model of Bassinot et al. [23] (see Table 2). The two samples taken from ~ 12 m depth and marked with an asterisk were re-assigned from MIS 7.3 to MIS 11 on the basis of their U and Th isotope data.

Fourteen such samples were selected for the purposes of this study (Table 2).

3. Analytical methods

For each of the 42 samples reported here (Tables 1 and 2), approximately 1 g of bulk sediment was weighed, spiked with a mixed ^{236}U – ^{229}Th spike [13] and dissolved slowly by drop-wise addition of nitric acid. After dissolution of all carbonate material, the strength of the acid was increased to > 5 N and the sample dried at 180°C . This procedure ensured dissolution of organic material in the samples, and ensured that Th did not re-adhere to residual particulate material. Such residual particulate material was always a very minor portion of the sediment ($< 2\%$) and was removed by high-speed centrifuging prior to chemical separation of U and Th by ion ex-

change. The eight samples listed in Table 1 were analyzed by thermal ionization mass spectrometry (TIMS) following the approach outlined in [13]. The remaining 34 samples (Table 2) were analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using a Nu instrument. Full details of the MC-ICP-MS work are given in Robinson et al. [19]. This technique is considerably faster than TIMS for the measurement of U and Th isotopes while providing U isotope precision as good as the best TIMS analyses, and Th isotope precision better than can be achieved by TIMS. Long-term repeatability for ($^{234}\text{U}/^{238}\text{U}$) is 1.3‰ (2 S.D. $n=39$) and of the ($^{230}\text{Th}/^{232}\text{Th}$) is better than 1‰. This high level of precision is important for this study, particularly for the older samples, because the deviation of ($^{234}\text{U}/^{238}\text{U}$) from secular equilibrium become increasingly small as the sample ages and is only $\sim 10\%$ for samples 780 kyr old. The accuracy of the analyses has been tested by measurement of the CRM-145 standard (also known variously as NBS U-960 or CRM 112a) relative to HU-1, a uraninite standard which is widely thought to have ^{234}U in secular equilibrium with ^{238}U [25,26]. The measured offset of CRM-145 from secular equilibrium is $-36.6 (\pm 1.7)$ which is in agreement with recent TIMS analyses of this offset [25,27]. Half-lives used in this study are 245.250 kyr for ^{234}U and 75.690 kyr for ^{230}Th [25].

4. Results

Uranium concentrations for the 42 samples range from 2.6 to 10.6 ppm (Tables 1 and 2), appreciably higher than most marine sediments and higher than corals. For the purposes of discussion, the samples will be subdivided into three groups: those with ages of less than 360 ka ($n=16$), those from Site 1006 with stratigraphic ages greater than 360 ka ($n=12$), and those taken from close to the B/M reversal ($n=14$). Samples in the first group have an average U concentration of 6.3 ppm; those in the second average 4.8 ppm; and samples from close to the B/M have the highest concentrations, averaging 8.3 ppm. The

variability in U concentration reflects factors such as sedimentation rate, aragonite content, and organic content of the sediment. In general it is high closer to the banks and in the middle of highstand periods where the sedimentation rate is at a maximum and dissolution of U-rich organic material at a minimum.

For all samples the ($^{230}\text{Th}/^{232}\text{Th}$) ranges from 15 to 360 (where round brackets signify activity ratio). These values contrast with typical upper continental crust which has a value of ~ 0.5 (assuming secular equilibrium with 13.5 ppm Th and 2.4 ppm U). This difference indicates that detritus contributes a maximum of between 0.1 and 3.7% of the total U for these samples (Table 2). These values are upper limits because some of the ^{232}Th is probably derived by scavenging from seawater. The ($^{230}\text{Th}/^{232}\text{Th}$) ratios therefore indicate that the vast majority of U in these samples is derived directly from seawater.

Measured ($^{230}\text{Th}/^{232}\text{Th}$) can also be used to correct measured ($^{230}\text{Th}/^{234}\text{U}$) for the presence of small amounts of initial ^{230}Th . This is done here by assuming that initial ($^{230}\text{Th}/^{232}\text{Th}$) equals 9.3 ± 4.7 , equivalent to a 50/50 mix of local seawater Th and detrital Th. This initial Th correction is important for deriving accurate U/Th ages for these samples [19], but does not make a significant difference to the initial uranium isotope ratios – the main discussion point of this paper.

For samples with ages assigned from $\delta^{18}\text{O}$ stratigraphy or from the presence of the B/M reversal, the age assignment and the diagenetic integrity can be assessed by comparing the corrected ($^{230}\text{Th}/^{234}\text{U}$) with that expected from closed-system decay. On this basis, two samples from Site 1006B which were initially ascribed to MIS 7.3 were reassigned to MIS 11 (shown with asterisks in Table 2 and Fig. 2). Both these samples have ($^{230}\text{Th}/^{234}\text{U}$) significantly higher than would be expected for MIS 7 and closer to that expected at MIS 11. Their $\delta^{234}\text{U}$ values also seem more appropriate for MIS 11. Because these samples were from the small section of Site 1006B core spliced into the main Site 1006A stratigraphy (Fig. 2), this incorrect initial assignment does not prejudice the age assignment of other Site 1006 samples. Samples with corrected ($^{230}\text{Th}/$

^{234}U) more than 3% from that expected by closed-system decay are considered to have been diagenetically altered and are not discussed further. Twenty-three of 34 samples have ($^{230}\text{Th}/^{234}\text{U}$) which pass this test and these are printed in bold in Table 2. The 3% cut-off is somewhat arbitrary, but allows for age uncertainty in the stratigraphic assignment, for analytical uncertainty, and for uncertainty on the correction for initial ^{230}Th . It was also chosen because it represents a reasonably distinct cut-off between samples which fall close to the expected values, and those that clearly deviate from it. The average deviation for accepted samples is only 0.8%, while that for rejected samples is 17%.

($^{234}\text{U}/^{238}\text{U}$) is expressed in the delta notation [28] where $\delta^{234}\text{U}$ is the deviation in permil of ($^{234}\text{U}/^{238}\text{U}$) from its secular equilibrium value of 1.000. Measured $\delta^{234}\text{U}$ is corrected for decay of excess ^{234}U since the time of sample formation to get the initial value – $\delta^{234}\text{U}(\text{T})$. For a closed system, this initial value will be the value for seawater at the time the sample formed.

Sixteen samples from this study have ages less than 360 ka. Two of these are rejected as they have ($^{230}\text{Th}/^{234}\text{U}$) which disagrees with their stratigraphic age (Table 2). Another two are rejected as they have very poorly constrained U/Th ages (Table 1). The remaining 12 samples augment 55 existing literature values from similar Bahamas sediment in this age range (Fig. 1). $\delta^{234}\text{U}(\text{T})$ for all 67 samples range from 108‰ to 169‰ and show no clear trend with age. The data exhibit more scatter about the modern seawater value than can be explained by analytical uncertainty alone, but this scatter does not increase with age of sample (Fig. 1). The lack of both a long-term trend and an increase in scatter with age contrasts with coral data.

Eight of the 12 samples from 1006 which are > 360 ka in age have acceptable ($^{230}\text{Th}/^{234}\text{U}$) values. $\delta^{234}\text{U}(\text{T})$ for these samples show more scatter than the younger samples and even samples taken from the same highstand disagree by up to 92‰. No clear trend to lower or higher values is observed in the > 360 ka data (Fig. 3). Nine of the 14 samples from close to the B/M pass the ($^{230}\text{Th}/^{234}\text{U}$) test, all have $\delta^{234}\text{U}(\text{T})$ lower than the mod-

Table 2
MC-ICP-MS U and Th concentration and isotope data for Leg 166 samples

Depth (mbsf)	Arag. (%)	MIS	Age (ka)	U conc. (ppm)	$\delta^{234}\text{U}$ measured	$(^{230}\text{Th}/^{232}\text{Th})$	$(^{230}\text{Th}/^{234}\text{U})$ measured	$(^{230}\text{Th}/^{234}\text{U})$ corrected	Det. U (%)	$\delta^{234}\text{U}(\text{T})$
Site 1006 samples with ages based on $\delta^{18}\text{O}$ and aragonite stratigraphy										
1006A 1H-1 110–111 cm	90	1	11	3.627 ± 0.005	143.7 ± 1.3	16.02 ± 0.03	0.255 ± 0.001	0.121 ± 0.067	1.0	148 ± 4
1006A 1H-1 120–121 cm	90	1	11	3.609 ± 0.004	144.0 ± 1.3	15.71 ± 0.03	0.241 ± 0.000	0.112 ± 0.065	1.0	149 ± 4
1006A 1H-4 70–71 cm	91	5.5	132	4.674 ± 0.006	104.3 ± 1.3	61.48 ± 0.11	0.732 ± 0.001	0.699 ± 0.017	0.7	151 ± 5
1006A 1H-4 80–81 cm	91	5.5	132	4.769 ± 0.006	103.6 ± 1.3	57.50 ± 0.11	0.728 ± 0.001	0.693 ± 0.018	0.8	150 ± 5
1006B 2H-4 50–51 cm	88	7.1	207	2.614 ± 0.003	112.5 ± 1.3	146.39 ± 0.27	2.072 ± 0.004	2.053 ± 0.011	0.9	202 ± 6
1006B 2H-4 60–61 cm	88	7.1	207	6.290 ± 0.008	65.4 ± 1.3	23.39 ± 0.04	0.622 ± 0.001	0.585 ± 0.019	1.5	118 ± 4
1006A 2H-4 70–71 cm	77	9	339	7.597 ± 0.010	54.7 ± 1.3	336.77 ± 0.62	0.964 ± 0.002	0.963 ± 0.002	0.2	143 ± 4
1006A 2H-4 80–81 cm	77	9	339	7.427 ± 0.010	53.3 ± 1.3	333.64 ± 0.62	0.971 ± 0.002	0.970 ± 0.002	0.2	139 ± 4
1006B 2H-6 65–66 cm	76	11*	413	7.253 ± 0.009	42.7 ± 1.3	253.95 ± 0.47	0.976 ± 0.002	0.975 ± 0.002	0.2	137 ± 4
1006B 2H-6 75–76 cm	76	11*	413	7.723 ± 0.010	36.2 ± 1.3	311.70 ± 0.58	1.020 ± 0.002	1.019 ± 0.002	0.2	116 ± 4
1006A 2H-6 20–21 cm	75	11	413	3.598 ± 0.004	34.5 ± 1.3	27.57 ± 0.05	0.988 ± 0.002	0.980 ± 0.004	2.0	111 ± 3
1006A 2H-6 30–31 cm	75	11	413	3.044 ± 0.004	53.5 ± 1.3	25.89 ± 0.05	0.906 ± 0.002	0.899 ± 0.004	2.0	172 ± 5
1006A 3H-1 70–71 cm	87	13	492	7.633 ± 0.010	−2.0 ± 1.3	43.09 ± 0.08	1.000 ± 0.002	0.998 ± 0.002	1.3	−8 ± 1
1006A 3H-1 80–81 cm	87	13	492	5.083 ± 0.006	20.8 ± 1.3	40.00 ± 0.07	0.999 ± 0.002	0.996 ± 0.002	1.4	84 ± 3
1006A 3H-4 70–71 cm	90	15	580	3.607 ± 0.004	19.5 ± 1.3	36.68 ± 0.07	1.003 ± 0.002	1.001 ± 0.002	1.5	100 ± 3
1006A 3H-4 80–81 cm	90	15	580	3.605 ± 0.004	30.8 ± 1.3	40.82 ± 0.08	0.994 ± 0.002	0.993 ± 0.002	1.4	159 ± 5
1006A 3H-6 50–51 cm	90	17	692	3.455 ± 0.004	29.0 ± 1.3	15.15 ± 0.03	1.000 ± 0.002	0.999 ± 0.002	3.7	205 ± 6
1006A 3H-6 60–61 cm	90	17	692	4.024 ± 0.005	21.3 ± 1.3	26.67 ± 0.05	1.001 ± 0.002	1.000 ± 0.002	2.1	151 ± 5
1006A 4H-1 90–91 cm	85	19	783	4.129 ± 0.005	8.1 ± 1.3	32.92 ± 0.06	0.805 ± 0.002	0.805 ± 0.002	1.3	74 ± 2
1006A 4H-1 100–101 cm	85	19	783	4.120 ± 0.005	18.5 ± 1.3	19.99 ± 0.04	0.663 ± 0.001	0.663 ± 0.001	1.8	170 ± 5

Table 2 (continued)

Depth (mbsf)	Arag. (%)	MIS	Age (ka)	U conc. (ppm)	$\delta^{234}\text{U}$ measured	$(^{230}\text{Th}/^{232}\text{Th})$	$(^{230}\text{Th}/^{234}\text{U})$ measured	$(^{230}\text{Th}/^{234}\text{U})$ corrected	Det. U (%)	$\delta^{234}\text{U(T)}$
Site 1003 and 1004 samples from close to the B/M reversal										
1003A 9H-3 10–11 cm		B/M	780	8.485 ± 0.011	9.6 ± 1.3	245.50 ± 0.17	0.995 ± 0.002	0.995 ± 0.002	0.2	87 ± 2
1003A 9H-3 20–21 cm		B/M	780	7.932 ± 0.010	8.5 ± 1.3	262.06 ± 0.18	0.963 ± 0.002	0.963 ± 0.002	0.2	77 ± 2
1003A 9H-3 25–26 cm		B/M	780	8.278 ± 0.017	7.2 ± 1.3	240.43 ± 0.17	1.027 ± 0.002	1.027 ± 0.002	0.1	65 ± 2
1003A 9H-3 45–46 cm		B/M	780	9.264 ± 0.012	13.9 ± 1.3	258.37 ± 0.18	0.987 ± 0.002	0.987 ± 0.002	0.3	126 ± 2
1003B 9H-5 15–16 cm		B/M	780	8.514 ± 0.010	7.8 ± 1.3	242.50 ± 0.17	0.960 ± 0.002	0.960 ± 0.002	0.2	71 ± 2
1003B 9H-5 35–36 cm		B/M	780	7.643 ± 0.009	10.9 ± 1.3	218.21 ± 0.15	0.987 ± 0.002	0.987 ± 0.002	0.0	99 ± 2
1003B 9H-5 55–56 cm		B/M	780	7.070 ± 0.009	11.1 ± 1.3	203.24 ± 0.14	0.992 ± 0.002	0.992 ± 0.002	0.2	101 ± 2
1003B 9H-5 74–75 cm		B/M	780	7.173 ± 0.009	8.4 ± 1.3	200.52 ± 0.14	0.976 ± 0.002	0.976 ± 0.002	0.2	76 ± 2
1003B 9H-5 95–96 cm		B/M	780	7.310 ± 0.009	−0.2 ± 1.3	353.00 ± 0.24	1.603 ± 0.003	1.603 ± 0.003	0.2	−2 ± 1
1004A 9H-5 5–6 cm		B/M	780	7.402 ± 0.009	12.4 ± 1.3	251.82 ± 0.17	0.990 ± 0.002	0.990 ± 0.002	0.3	112 ± 2
1004A 9H-5 25–26 cm		B/M	780	8.370 ± 0.010	12.4 ± 1.3	233.46 ± 0.16	0.991 ± 0.002	0.991 ± 0.002	0.2	113 ± 2
1004A 9H-5 45–46 cm		B/M	780	9.831 ± 0.012	15.3 ± 1.3	329.97 ± 0.23	0.976 ± 0.002	0.976 ± 0.002	0.2	139 ± 2
1004A 9H-5 65–66 cm		B/M	780	10.636 ± 0.034	19.3 ± 1.3	279.83 ± 0.19	0.615 ± 0.001	0.615 ± 0.001	0.2	175 ± 3
1004A 9H-4 135–136 cm		B/M	780	7.968 ± 0.010	15.2 ± 1.3	291.08 ± 0.20	0.968 ± 0.002	0.968 ± 0.002	0.2	138 ± 2

Core depths are taken from the ODP Init. Rep. [16]. Aragonite percentages are for the closest sample from the study of Kroon et al. [21]. MIS generally follow that study as well, although the two Site 1006B samples marked with asterisks were reassigned from MIS 7 to MIS 11 based on their $(^{230}\text{Th}/^{234}\text{U})$. U and Th isotope measurements are described in Section 3. Errors are 2σ and incorporate uncertainty on the mass spectrometric measurement, on weighing, and on the spike concentration. Det. U is the maximum percentage of U in each sample derived from detritus (see Section 4). The $\delta^{234}\text{U(T)}$ is age-corrected using the stratigraphic ages shown in the Age column. Age uncertainty of 10 kyr is assumed for those ages based on MIS picks, and of 5 kyr is assumed for those samples close to the B/M reversal. This error is propagated into the quoted $\delta^{234}\text{U(T)}$ error. Values marked in bold are those that have corrected $(^{230}\text{Th}/^{234}\text{U})$ within 3% of that expected and are therefore considered more reliable.

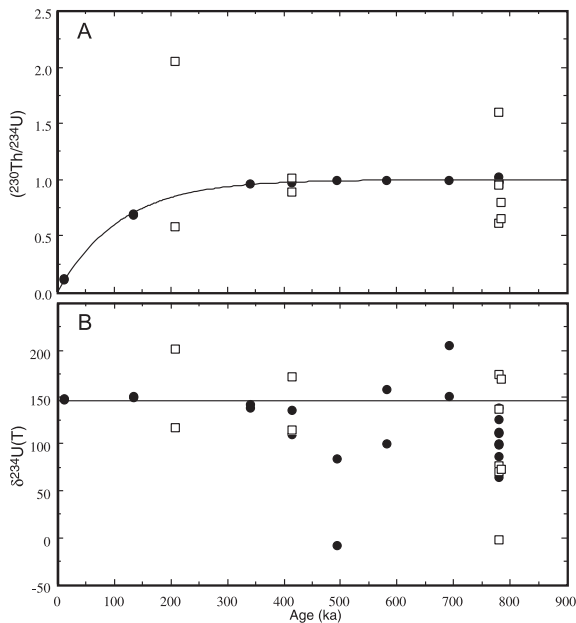


Fig. 3. (A) $(^{230}\text{Th}/^{234}\text{U})$ for Leg 166 samples with independent age control (Table 1, Fig. 2). The curve represents the expected $(^{230}\text{Th}/^{234}\text{U})$ for closed-system samples of that age. Data have been corrected for initial ^{230}Th using the measured $(^{230}\text{Th}/^{232}\text{Th})$ as described in Section 4. Filled circles are data falling within 3% of the expected closed-system value. Note that, in all cases, filled circles represents more than one data point lying directly above one other. Open squares are data falling more than 3% from the expected value which are therefore not considered to have remained as closed systems. (B) $\delta^{234}\text{U}(\text{T})$ for the same samples. $\delta^{234}\text{U}(\text{T})$ is calculated from the measured $\delta^{234}\text{U}$ using the age model of Kroon et al. [21] (Fig. 2). Filled circles are those data with acceptable $(^{230}\text{Th}/^{234}\text{U})$ as above, and open circles are those with unacceptable $(^{230}\text{Th}/^{234}\text{U})$. The horizontal line is the modern seawater $\delta^{234}\text{U}$ for reference. 2σ errors are within symbol size for both panels.

ern seawater value, ranging from 65‰ to 139‰ and averaging 102‰.

5. Discussion

5.1. Simple box model for $\delta^{234}\text{U}$

An understanding of the U isotope budget of the ocean is important if the new $\delta^{234}\text{U}$ results are to be put into context [4,7,29,30]. Both isotopes enter the oceans predominantly via river waters. Measured $\delta^{234}\text{U}$ for 25 rivers around the world

ranges from 70‰ to 1030‰ [30]. A flux-weighted global average is difficult to assess because large rivers with high U loads have been well sampled but tend to have low $\delta^{234}\text{U}$, while smaller rivers have not been so well sampled, but tend to have higher $\delta^{234}\text{U}$. The flux-weighted average is likely to lie somewhere in the range 200–300‰ [31], but further work is required to better constrain this. Removal of U does not fractionate the isotopes from one another and is therefore not a primary controlling influence on seawater $\delta^{234}\text{U}$. Because the oceans have excess ^{234}U , ^{234}U loss by decay more than outweighs ^{234}U input by ^{238}U decay. This loss term accounts for the fact that the oceans have a lower $\delta^{234}\text{U}$ than the riverine input. In fact, the loss by decay is sufficiently fast that, in order to keep the oceans at a value of ~ 145 ‰ [1], an additional source of excess ^{234}U is required to account for roughly half the excess ^{234}U decay. Since the pioneering work of Ku [4] this extra source has been assumed to be diffusion of ^{234}U from marine sediment porewaters where it is enriched due to α -recoil from sediment grains. A modern-day balanced budget for ^{234}U and ^{238}U is presented in Fig. 4. This

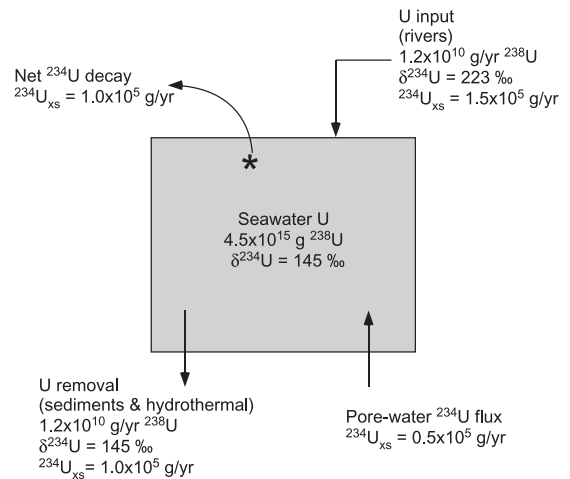


Fig. 4. A simple balanced budget for ^{234}U in the oceans. Note that the decay of excess ^{234}U in the oceans is balanced by the difference in input and output of ^{234}U accompanying ^{238}U , and by the input of ^{234}U from sediment porewaters. These two sources play a roughly equivalent role in supporting the oceanic $\delta^{234}\text{U}$.

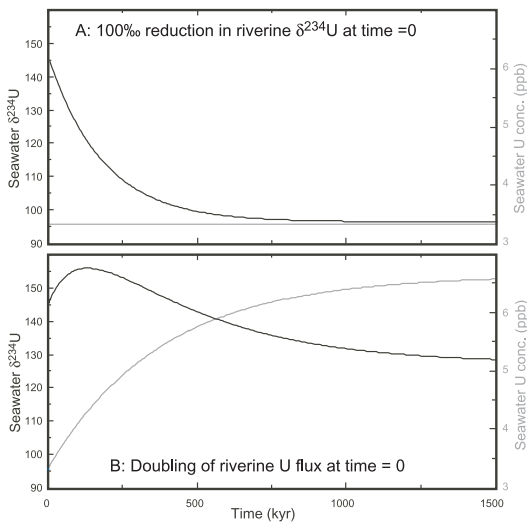


Fig. 5. Effect of changing riverine input on seawater $\delta^{234}\text{U}$ and U concentration, assessed by perturbing the simple model shown in Fig. 4. (A) Effect of reducing riverine $\delta^{234}\text{U}$ by 100% at time zero. Note that seawater U concentration remains unchanged while $\delta^{234}\text{U}$ decreases to a new steady state value on a time scale dependent on the residence time of ^{234}U ($=180$ kyr). (B) Effect of doubling the riverine U flux at time zero. Note that the U concentration increases to achieve a new steady state at twice the original concentration, following the assumption of removal proportional to concentration. Note also that $\delta^{234}\text{U}$ initially increases due to increased riverine input of ^{234}U , but then decreases due to the larger amount of excess ^{234}U decay occurring in the oceans.

budget indicates a residence time for ^{238}U of 380 kyr. The residence time for ^{234}U is shorter (180 kyr) due to its turnover, not only by fluxes into and out of the oceans, but also by decay.

Perturbation of seawater $\delta^{234}\text{U}$ is possible by changing the riverine U flux or average riverine $\delta^{234}\text{U}$. Other fluxes are less important because the sediment diffusion source of ^{234}U is unlikely to alter significantly on a time scale of 10^5 – 10^6 years and because the removal of U does not fractionate the isotopes. The effect of changing either the riverine U flux or U isotope ratio can be assessed with a simple box model (Fig. 4). If $\delta^{234}\text{U}$ of the riverine input is altered, ocean $\delta^{234}\text{U}$ changes to achieve a new steady state. Because the balance of riverine U input to sediment U removal is responsible for half of the excess ^{234}U decay in the

ocean, the seawater response to a change in riverine $\delta^{234}\text{U}$ is half that change, i.e. for every 1‰ that the rivers increase, the ocean increases by 0.5‰ (although this sensitivity would change if the contribution of excess ^{234}U was significantly different in the past from the modern value of 50%). The new steady state is achieved with an e-folding time equivalent to the residence time of ^{234}U (i.e. 63% of the change is achieved in 180 ka).

The effect of changing the riverine U flux on seawater $\delta^{234}\text{U}$ is more complex. It changes both the input flux of excess ^{234}U , and also the total amount of U in the oceans. As an example, consider a doubling of the riverine flux from modern values (Fig. 5). Initially, the increased flux of excess ^{234}U to the oceans causes the seawater value to increase at a rate dependent on the residence time of ^{234}U . But at the same time, the U concentration of seawater increases at a rate dependent on the residence time of ^{238}U . As this occurs, there is now more excess ^{234}U in the oceans so the loss of ^{234}U by decay increases. If rivers were the only source of excess ^{234}U these effects would exactly cancel one another. But because rivers only supply half the excess ^{234}U (but all the ^{238}U) the net effect of increasing riverine U fluxes is, somewhat counter-intuitively, to decrease seawater $\delta^{234}\text{U}$. The overall effect is a small one with, for example, a doubling of modern riverine flux causing only a 19‰ decrease in $\delta^{234}\text{U}$ (Fig. 5).

U concentrations in corals are broadly constant during the Pleistocene [32] suggesting that riverine fluxes have not varied by anything approaching the doubling discussed above. Any observed changes in past seawater $\delta^{234}\text{U}$ are therefore more likely to reflect changes in the average $\delta^{234}\text{U}$ of rivers. The controls on riverine $\delta^{234}\text{U}$ are still poorly constrained, but probably relate to the ratio of physical to chemical weathering [10]. In areas where physical weathering dominates, fresh mineral surfaces are exposed which can readily lose ^{234}U from α -damaged sites and the associated increase in surface area also increases active recoil of ^{234}U . In areas where chemical weathering dominates, on the other hand, both ^{234}U and ^{238}U are dissolved and pass into the fluid phase at close to secular equilibrium.

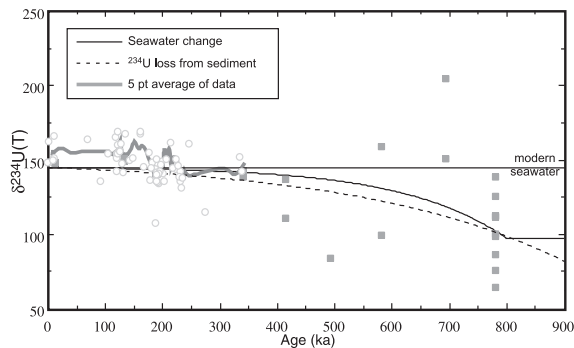


Fig. 6. Summary of Bahamas sediment $\delta^{234}\text{U}(\text{T})$ data and its possible explanations. $\delta^{234}\text{U}(\text{T})$ data are shown in gray with those age-corrected by U/Th as open circles and those age-corrected by stratigraphic ages as filled squares. The solid gray line is a five-point smoothing of all < 360 ka data. The horizontal line is the modern seawater value ($= 145\text{‰}$). The solid black curve is the expected seawater history for a 100‰ increase in average riverine $\delta^{234}\text{U}$ occurring at 800 ka. The dashed black curve is the expected sediment value if 0.54% of ^{234}U atoms are ejected from the sediment as they are formed from ^{238}U decay.

Changes in seawater $\delta^{234}\text{U}$ in the past are therefore expected to broadly reflect changes in the ratio of physical weathering to chemical weathering on the continents.

5.2. Constant $\delta^{234}\text{U}$ for the last 360 ka

Bahamas sediment data indicate that seawater $\delta^{234}\text{U}$ has remained within 15‰ of its present value for at least the last 360 ka. A total of 67 measurements for this period, from the literature and from this study, range from 108‰ to 169‰. This range clearly incorporates a degree of diagenetic change as samples of very similar age have different $\delta^{234}\text{U}$ which cannot represent genuine change in seawater $\delta^{234}\text{U}$. Using a five-point smoothing of the data in order to remove some of this diagenetic scatter suggests a maximum range of seawater $\delta^{234}\text{U}$ of 135–160 during the last 360 ka, at least for interglacial periods (Fig. 6). Changes outside this window during glacial periods seem unlikely based on the response time of ocean $\delta^{234}\text{U}$, but cannot be ruled out by the Bahamas data.

The constancy of seawater $\delta^{234}\text{U}$ for the last

360 ka confirms the rejection of coral U/Th ages which have $\delta^{234}\text{U}(\text{T})$ different from modern seawater [6,9]. Although a $\delta^{234}\text{U}(\text{T})$ close to seawater is not a guarantee of the validity of a U/Th age, it is clear that a $\delta^{234}\text{U}(\text{T})$ which deviates significantly from the modern seawater value reflects open system behavior for U isotopes and the age cannot be assumed to be reliable.

The constancy of seawater $\delta^{234}\text{U}$ over this period also suggests that the weathering regime on the continents has remained approximately the same, at least from one glacial/interglacial cycle to the next. For seawater $\delta^{234}\text{U}$ to remain within 15‰ of the modern value requires that the riverine input has not changed its $\delta^{234}\text{U}$ by more than 65‰ for more than 100 kyr. Because modern rivers have a range in $\delta^{234}\text{U}$ of nearly 1000‰ a shift of the average value by 65‰ is not difficult to imagine and the constancy of seawater $\delta^{234}\text{U}$ therefore indicates that the ratio of physical to chemical weathering has remained rather constant for the last 360 ka.

5.3. The earlier record of $\delta^{234}\text{U}$

Prior to 360 ka the data from Site 1006 exhibit scatter with samples from each interglacial period disagreeing with one another. Within each interglacial, measured $\delta^{234}\text{U}$ varies by up to 21‰, even after rejection of samples with open-system ($^{230}\text{Th}/^{234}\text{U}$), leading to very large variations in $\delta^{234}\text{U}(\text{T})$ (Fig. 6). Because seawater $\delta^{234}\text{U}$ cannot have varied this rapidly, the scatter must reflect diagenesis of these samples. The extent of such diagenesis contrasts with the younger samples and may reflect the lower U concentration and ($^{230}\text{Th}/^{232}\text{Th}$) of the older samples from Site 1006. Any movement of U isotopes, either by α -recoil processes within the sediment, or by addition of pore-water U with anomalous $\delta^{234}\text{U}$, is expected to be more significant for low U samples. The diagenetic scatter of these samples prevents an accurate reconstruction of seawater $\delta^{234}\text{U}$ for the period between the B/M and 360 ka. There is, however, no obvious trend with age towards higher or lower $\delta^{234}\text{U}$.

The samples from close to the B/M from Sites 1003 and 1004 have high U concentrations and

($^{230}\text{Th}/^{232}\text{Th}$) and their $\delta^{234}\text{U}$ is therefore expected to be more robust to diagenesis than the Site 1006 samples. Although their $\delta^{234}\text{U}(\text{T})$ values vary considerably, much of this variation is due to the fact that these samples are three half-lives of ^{234}U old. The measured scatter is much smaller and is only $\sim 8\%$. It is striking that all eight samples which pass the ($^{230}\text{Th}/^{234}\text{U}$) criteria have lower $\delta^{234}\text{U}(\text{T})$ than modern seawater, averaging 102‰. Two explanations can be put forward for this lower value. The first is that it is caused by lower seawater $\delta^{234}\text{U}$ at that time. And the second is that it is caused by gradual diagenetic loss of ^{234}U from the sediment by α -recoil over the lifetime of the samples.

Lower seawater $\delta^{234}\text{U}$ at the time of the B/M reversal might be explained by decreased physical weathering of the continents prior to the onset of the major 100 kyr glacial cycle. Although the Northern Hemisphere was glaciated prior to 900 ka, it is only since then that it has experienced large amplitude 100 kyr cycles between glacials and interglacials. During glacial periods, large continental areas are ice-covered probably increasing the physical grinding of rocks. During interglacial periods, these freshly ground rocks are exposed so that the newly exposed ^{234}U can be washed to the oceans. A resulting change in seawater $\delta^{234}\text{U}$ can be investigated using the simple box model discussed above. A change in seawater $\delta^{234}\text{U}$ from 102‰ at 780 ka to 145‰ at the present could be caused, for instance, by a step change in average riverine $\delta^{234}\text{U}$ from 123‰ to 223‰ at 800 ka. The response of the ocean with time to this change occurs at a rate dependent on the residence time of ^{234}U in the oceans (Fig. 6). This means that the oceans have nearly fully responded to the change by 360 ka and remain within 10‰ of their modern value since that time, in agreement with observations.

The alternative explanation for lower $\delta^{234}\text{U}(\text{T})$ at the B/M reversal is that sediment grains lose some of their ^{234}U by α -recoil throughout their history. Over long periods, this cumulative loss would become significant for the $\delta^{234}\text{U}$ of the bulk grains, and the effect would be exaggerated as samples approach secular equilibrium. To generate 780 kyr old sediment with $\delta^{234}\text{U}(\text{T}) = 102\%$

from an initial value of 145‰ requires that 0.54% of the ^{234}U created by ^{238}U decay in the grains is ejected to the pore-waters. The evolution of $\delta^{234}\text{U}(\text{T})$ of the grains would be dependent on the half-life of ^{234}U (Fig. 6). At 360 ka, the predicted $\delta^{234}\text{U}(\text{T})$ would be 135‰ which is within the observational constraints. One problem with this scenario, though, is the lack of evidence for ejected ^{234}U . In each volume of sediment, about 6000 times more U is in the sediment grains than in the pore-waters. Alpha-recoil of $\sim 0.5\%$ of the ^{234}U would therefore contribute about 30 times more ^{234}U to the pore-waters than decay within the water. Eventually, this would lead to $\delta^{234}\text{U}$ within the pore-waters of $\sim 30\,000$. In contrast, observed values at ~ 75 m in Leg 166 pore-waters are only ~ 360 [33]. Even if pore-waters are flushed every 100 kyr by fluid flow so that α -recoil ^{234}U never fully accumulates, the expected pore-water $\delta^{234}\text{U}$ is still ~ 8000 .

At this stage, the $\delta^{234}\text{U}$ data are not adequate to distinguish between seawater $\delta^{234}\text{U}$ change and α -recoil loss of ^{234}U . But the difficulties of reconciling the latter model with pore-water observations lend support to the idea that seawater $\delta^{234}\text{U}$ was, indeed, somewhat lower than today at the time of the B/M reversal. Certainly, there is no evidence to suggest that seawater was significantly higher than at present during the last 800 kyr. This suggests that the ratio of physical to chemical weathering on the continents has not been higher than at present for any prolonged period during the last 800 kyr.

6. Conclusions

MC-ICP-MS analysis of Bahamas slope sediments has allowed an assessment of seawater $\delta^{234}\text{U}$ for the last 800 kyr. This indicates that seawater $\delta^{234}\text{U}$ has not varied by more than 15‰ from the modern value for the last 360 kyr. This confirms the rejection of coral U/Th ages with $\delta^{234}\text{U}(\text{T})$ that deviate from modern seawater values. It also indicates that average riverine $\delta^{234}\text{U}$ has not changed by more than 65‰ for any extended period during the last 360 kyr. Prior to 360 ka, $\delta^{234}\text{U}$ data are more scattered but no evidence

for higher values of $\delta^{234}\text{U}$ is seen and, at the B/M reversal, all $\delta^{234}\text{U}$ data are lower than the modern value, averaging 102‰. Although the low value at the B/M reversal might be explained by progressive ^{234}U loss due to α -recoil, it is possible that seawater $\delta^{234}\text{U}$ was lower at that time. This might be explained by lower rates of physical weathering on the continents prior to the advent of the 100 kyr glacial cycle. Certainly, the lack of evidence for seawater $\delta^{234}\text{U}$ above modern values suggests that the rate of physical weathering has not been higher than at present for any extended period during the last 800 ka.

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