

Variability in the uranium isotopic composition of the oceans over glacial–interglacial timescales

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Abstract

Uranium-series mass spectrometric analyses of corals from the uplifted last glacial terraces at Huon Peninsula, Papua New Guinea, that grew from 50,000 years ago to 30,000 years ago show systematically low values of $^{234}\text{U}/^{238}\text{U}$, at the time of coral growth, compared with modern corals. When combined with coral data from other studies a systematic trend emerges indicating shifts in the $^{234}\text{U}/^{238}\text{U}$ ratio at times of major glacial–interglacial transitions that involve large variations in sea-levels. From last glacial to Holocene, the rate of change in $\delta^{234}\text{U}$ is approximately 1‰ per thousand years. The variations in the U budget of the oceans appear to be due to accumulation of excess ^{234}U in near shore areas in anoxic and suboxic sediments, in salt marshes and mangroves, in estuaries, and in continental margins during periods of warm climate and high sea-levels. These near-shore areas are exposed during periods of low sea level resulting in rapid oxidation of U into highly soluble phases. The subsequent release of ^{234}U -enriched uranium into the oceans occurs over a sustained period, in step with rising sea-levels.

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1. Introduction

Oceanic residence times of dissolved chemical elements, defined as the total number of atoms of an element relative to amounts added to or precipitated from the oceans per year, can extend to over hundreds of thousands of years but may be sensitive to extreme changes in climate during much shorter timescales, such as those between glacial and interglacial transitions that involve major shifts in global sea levels. Residence time of Uranium in the oceans, with respect to riverine inflow, is estimated to be about 300–600 thousand years (Henderson and Anderson, 2003), a time span accessible to U-series disequilibrium dating of corals which concentrate U from seawater in their skeletons. The principal supply of dissolved U to the

oceans is derived from chemical weathering of continents and is transported by rivers. Dissolution of limestones and weathering of uraniumiferous black shales supply the bulk of U with only a small contribution from silicate weathering of shield terrains (Klinkhammer and Palmer, 1991; Palmer and Edmond, 1993; Chabaux et al., 2001; Dunk et al., 2002).

Radioactive decay, and α -recoil of ^{238}U , and subsequent preferential leaching from damaged sites results in excess of ^{234}U relative to equilibrium levels and $^{234}\text{U}/^{238}\text{U}$ activity ratios greater than unity are found in river waters. Current oceanic $^{234}\text{U}/^{238}\text{U}$ activity ratio (relative to the secular equilibrium value of $(^{234}\text{U}/^{238}\text{U})_{\text{atom}} = 5.472 \times 10^{-5}$; the decay constants used are listed in footnotes to Table 1) ranges from 1.143 ± 0.004 (Chen et al., 1986) to 1.153 ± 0.001 (Delanghe et al., 2002; Robinson et al., 2004a), whereas a value of 1.149 ± 0.002 (Stirling et al., 1998; Delanghe et al., 2002; Robinson et al., 2004a) is found in modern corals.

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Table 1
U isotopic composition and ^{230}Th ages of glacial age corals

Sample ^a	^{232}Th (ppb) ^b	^{234}U (ppm)	$\delta^{234}\text{U}(0)$ (‰) ^c	$\delta^{234}\text{U}(T)$ (‰) ^c	$(^{230}\text{Th}/^{234}\text{U})$ (activity) ^d	Age (kyr) ^e	Height (masl) ^f
<i>Kanzarua section</i>							
Kanz 4	0.022	2.73	118.3 ± 1.4	137 ± 1.7	0.4247 ± 0.0100	51.5 ± 1.6	86
Kanz 9	0.067	2.73	119.4 ± 1.2	139 ± 1.4	0.4379 ± 0.0013	53.4 ± 0.3	78
Kanz 11 ^P	0.086	2.41	119.9 ± 1.0	139 ± 1.1	0.4245 ± 0.0011	51.3 ± 0.3	78
Kanz 13 ^P	0.048	3.26	118 ± 12	132 ± 12.9	0.3339 ± 0.0008	38.3 ± 0.5	48
Kanz 15 ^P	0.038	2.68	127.0 ± 2.2	143 ± 2.4	0.3633 ± 0.0041	42.0 ± 0.6	39
Kanz U8 ^P	0.380	2.70	129.9 ± 3.7	144 ± 4.1	0.3276 ± 0.0042	37.0 ± 0.6	27
Kanz U9	0.483	2.70	125.3 ± 0.9	141 ± 1.1	0.3652 ± 0.0007	42.3 ± 0.2	28
Kanz U10 ^P	0.539	2.50	121.2 ± 1.2	137 ± 1.4	0.3734 ± 0.0006	43.7 ± 0.3	49
Kanz U11	0.017	1.99	127.4 ± 3.0	142 ± 3.3	0.3340 ± 0.0009	37.9 ± 0.3	27
Kanz U12	0.015	2.19	122.1 ± 3.0	136 ± 3.4	0.3289 ± 0.0049	37.5 ± 0.7	26
Kanz U13	0.005	3.26	128.6 ± 8.2	142 ± 9.1	0.3187 ± 0.0008	35.8 ± 0.4	26
Kanz U15	0.038	3.36	120.5 ± 1.2	132 ± 1.3	0.2977 ± 0.0005	33.4 ± 0.2	23
Kanz U16 ^P	0.056	3.36	130.5 ± 3.2	142 ± 3.5	0.2770 ± 0.0031	30.4 ± 0.4	29
Kanz A	0.510	3.07	123.7 ± 1.3	138 ± 1.5	0.3293 ± 0.0008	37.5 ± 0.2	25
<i>Bobongara section</i>							
Bobo U10	0.114	2.78	127.6 ± 1.2	142 ± 1.3	0.3283 ± 0.0008	37.2 ± 0.2	49
Bobo U11	0.227	2.39	128.8 ± 1.7	143 ± 1.9	0.3338 ± 0.0015	37.9 ± 0.3	49
Bobo U17	0.013	1.98	128.9 ± 2.5	141 ± 2.8	0.2892 ± 0.0008	32.0 ± 0.2	20
Bobo U18	0.083	2.06	126.7 ± 1.7	143 ± 1.9	0.3663 ± 0.0007	42.4 ± 0.2	37
Bobo U20	0.098	2.02	126.9 ± 1.2	141 ± 1.3	0.3313 ± 0.0004	37.6 ± 0.2	40
Bobo U21	0.064	2.47	128.4 ± 2.3	140 ± 2.6	0.2709 ± 0.0005	29.7 ± 0.2	30
Bobo U24	0.010	2.51	131.2 ± 1.3	144 ± 1.4	0.2914 ± 0.0006	32.2 ± 0.2	30
Bobo U28	0.011	2.44	127.5 ± 1.7	140 ± 1.8	0.2909 ± 0.0032	32.3 ± 0.5	22
Bobo U30	0.007	2.25	131.0 ± 1.2	143 ± 1.3	0.2861 ± 0.0005	31.5 ± 0.2	27
<i>Others</i>							
SEN(N)8 ^P	0.176	2.21	121.6 ± 1.4	140 ± 1.7	0.4320 ± 0.0081	52.4 ± 1.3	nA
GBR-A	1.142	2.61	133.0 ± 1.2	140 ± 1.3	0.1642 ± 0.0006	17.0 ± 0.1	-175

^a Except where indicated, all samples are from the *Faviidae* family; the superscript ^P denotes *Porites* corals. Analyses of *Faviidae* corals are for the wall fractions only.

^b Error in ^{232}Th is dominated by the uncertainty in the ^{232}Th blank correction (5 ± 2 pg).

^c $\delta^{234}\text{U} = \{[(^{234}\text{U}/^{238}\text{U})/(^{234}\text{U}/^{238}\text{U})_{\text{eq}}] - 1\} \times 10^3$. $(^{234}\text{U}/^{238}\text{U})_{\text{eq}}$ is the atomic ratio at secular equilibrium and is equal to $\lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$, where λ_{238} and λ_{234} are the decay constants for ^{238}U and ^{234}U , respectively. $\delta^{234}\text{U}(0)$ is the measured value, the initial value is given by $\delta^{234}\text{U}(T) = \delta^{234}\text{U}(0)e^{-\lambda_{234}T}$, where T is the age in years.

^d $(^{230}\text{Th}/^{238}\text{U})_{\text{act}} = (^{230}\text{Th}/^{238}\text{U})/(\lambda_{238}/\lambda_{230})$.

^e ^{230}Th -ages are calculated iteratively using

$$1 - \left[\frac{^{230}\text{Th}}{^{238}\text{U}} \right]_{\text{act}} = e^{-\lambda_{230}T} - \left(\frac{\delta^{234}\text{U}(0)}{1000} \right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) (1 - e^{(\lambda_{234} - \lambda_{230})T}),$$

where T is the age in years and λ_{230} is the decay constant for ^{230}Th . $\lambda_{238} = 1.551 \times 10^{-10} \text{ yr}^{-1}$; $\lambda_{234} = 2.835 \times 10^{-6} \text{ yr}^{-1}$; $\lambda_{230} = 9.195 \times 10^{-6} \text{ yr}^{-1}$. Ages considered “reliable” have $\delta^{234}\text{U}(T)$ values overlapping the range $149 \pm 10\%$. The $2\sigma_{\text{M}}$ uncertainty in the age is determined by propagating the $2\sigma_{\text{M}}$ analytical contribution from the parameters $\delta^{234}\text{U}(0)$ and $(^{230}\text{Th}/^{238}\text{U})_{\text{act}}$, as well as the systematic contributions from the decay constants λ_{230} and λ_{234} through the age equation. The uncertainty in the age is largely due to the decay constant errors which contribute ~ 950 years to $2\sigma_{\text{M}}$ at 125 ka.

^f Meters above present day sea-level.

Uranium is unique among other dissolved chemical elements in the oceans in several respects. It carries an in-built clock in ^{234}U , enabling high precision dating of corals that grew during the late Quaternary over the past 500,000 years. The $^{234}\text{U}/^{238}\text{U}$ ratio in seawater, at the time of coral growth, can be derived from coral age and $^{234}\text{U}/^{238}\text{U}$ measurements (Edwards et al., 1986; Bard et al., 1992; Stirling et al., 1998) and can provide a precise chronology for possible variability in the abundance of ^{234}U in the oceans over major climate cycles. As a means of gauging the veracity of samples a limited range of values spanning the oceanic $^{234}\text{U}/^{238}\text{U}$ ratio, equivalent to an error range in age, is used as a quantitative indicator of coral diagenesis. Coral sam-

ples with measured $^{234}\text{U}/^{238}\text{U}$ ratios that fall outside of this band are excluded (Stirling et al., 1998; Gallup et al., 1994).

2. Variability in $^{234}\text{U}/^{238}\text{U}$ observed in previous studies

During periods of intense weathering and inflated riverine transport, ^{234}U in the oceans may vary independently of total U (essentially ^{238}U) inventory. Uranium is highly soluble under oxidizing conditions, in reducing environments it can be particle reactive and insoluble. Therefore, global climatic changes influencing the extent of oxic, anoxic zones in ocean sediments can influence U concentrations. However, the expected long residence time of U in

the oceans, over several glacial–interglacial cycles, reduces its usefulness over shorter time periods. Searches for variations in U concentration in oceans have focused primarily on corals but one study, involving U/Ca ratio measurements in foraminifera tests in deep sea sediments, found a 25% decrease in seawater U concentration during the last glacial compared to Holocene levels (Russell et al., 1996). However, in contrast to corals, foraminifera do not include significant U within their structure and have adsorbed metallic coatings, including U, that may be difficult to remove quantitatively and could confuse the results.

Variations in the measured $^{234}\text{U}/^{238}\text{U}$ ratio of corals that grew during interglacial and interstadial periods, over the past 300,000 years, have mainly been attributed to diagenetic effects (Gallup et al., 1994). Previously, Hamelin et al. (1991); Richter and Turekian (1993) and Henderson (2002) considered variations in the input of ^{234}U into the oceans over glacial–interglacial and longer timescales and subsequently additional insights into the problem were provided by Scholz et al. (2004), Villemant and Feuillet (2003). However, the available data at the time did not allow definitive conclusions outside of broad limits. Larger than present values of the $^{234}\text{U}/^{238}\text{U}$ activity ratio (1.149), expressed as $\delta^{234}\text{U} = 149\text{‰}$, often linearly correlate with anomalously old ages and can be modeled by assuming continuous addition of both ^{234}U (or equivalently ^{230}Th), and ^{230}Th at approximately equal constant rates (Gallup et al., 1994; Thompson et al., 2003). Samples collected from fossil-coral outcrops from different continents, exposed to diverse climatic conditions, appear to have been altered similarly that otherwise might be expected to show random open system behaviour between age and $\delta^{234}\text{U}$. The same general pattern has been found in Last Interglacial age corals from Huon Peninsula (Stein et al., 1993), Barbados (Gallup et al., 1994; Thompson et al., 2003), and Western Australia (Stirling et al., 1998). Data from other interglacial periods, Marine Isotope Stages (MIS) 7 and 9, show analogous variability (Gallup et al., 1994; Stirling et al., 2001) as do coral samples from major interstadials, MIS 5a and 5c (Thompson et al., 2003; Potter et al., 2004).

In contrast to positive age correlated excursions in $\delta^{234}\text{U}$, relative to 149‰, similar systematic negative variations had not been documented until recently (Thompson et al., 2003; Potter et al., 2004). There is an indication of low $\delta^{234}\text{U}$ values in 30–50 ky corals from Huon Peninsula (Yokoyama et al., 2001a; Cutler et al., 2003) and in Last Interglacial age corals from Hateruma Atoll (Henderson et al., 1993). Very low $\delta^{234}\text{U}$ values have been measured in 370–600 ka submarine corals from the New Hebrides Arc (Edwards et al., 1991). Recent age measurements in corals sampled from MIS 5a and 5c terraces at Barbados, show the usual correlated distribution between older ages and $\delta^{234}\text{U}$, except the correlation extends to values of $\delta^{234}\text{U}$ significantly below 149‰ (Thompson et al., 2003; Potter et al., 2004). The correlated and seamless variation in $\delta^{234}\text{U}$ above and below 149‰ implies either that the cou-

pled ^{234}U (or ^{234}Th) ^{230}Th diagenetic addition model is not applicable or that the addition started from a low baseline, below $\delta^{234}\text{U} = 149\text{‰}$. It is highly unlikely that corals, in proximity to each other in a reef, exchanged U and Th, both in and out of their skeletons, in such a way to maintain the trend line between age and $\delta^{234}\text{U}$ above and below 149‰. Furthermore, a substantial sized coral reef or other carbonate mass in close proximity is needed to supply the large amounts of ^{230}Th and ^{234}U (^{234}Th) even if the exchange process is spread over a long time period (Thompson et al., 2003).

In contrast to MIS 5a and 5c corals, well characterized, pristine samples from the Holocene, the Last Interglacial, MIS 7 or MIS 9, in each case spanning an age range of at least 10 ky, appear to have $^{234}\text{U}/^{238}\text{U}$ ratios exclusively at or above 149‰ (Stein et al., 1993; Gallup et al., 1994; Stirling et al., 1998, 2001; Thompson et al., 2003). There is sufficient high quality data, in one instance, for a comparison of oceanic ^{234}U levels between the Last Interglacial and the Holocene. Last Interglacial coral reefs in Western Australia exhibit a tight clustering of measured ages between 128 and 122 ka at elevations of +3 to +5 m relative to present sea-level. When strict selection criteria are applied, to select samples within a range of $\pm 4\text{‰}$ in $\delta^{234}\text{U}$, they form a band that is displaced systematically higher than the modern 149‰ value by about 4‰ (Stirling et al., 1995, 1998). Analysis of previous, less precise data from other localities, distributed worldwide, yield a similar result (Stirling et al., 1995).

Recently, Robinson et al. (2004b) have published $^{234}\text{U}/^{238}\text{U}$ activity ratios of some New Zealand rivers which range up to a maximum of 4.6 but with an average of 2.24 for the low rainfall east coast rivers. They assumed that a percentage of global rivers, proportional to the continental area uncovered during the glacial ($\approx 15\%$), had increased activity ratios due to subglacial weathering resulting in an average global riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio of about 1.45. They find that over a 10,000 year deglaciation the change in $\delta^{234}\text{U}$ in could be as high as 10‰. A summary of previous work, to evaluate changes in the ocean $^{234}\text{U}/^{238}\text{U}$ activity ratio due to variations in riverine ^{234}U , was provided by Edwards et al. (2003). They concluded that a minimum detectable change of 10‰ in the ocean uranium isotopic composition would require an activity ratio change of 0.2 in riverine values over a period of 100,000 years or longer.

3. Results

In this paper, we discuss the significance of systematically low $^{234}\text{U}/^{238}\text{U}$ ratios in 30,000–50,000 year old corals sampled from Huon Peninsula, Papua New Guinea, terraces II and III (Chappell et al., 1996; Yokoyama et al., 2001a). We combine these results with additional literature data, including data from other localities. The results when viewed together reveal a consistent picture of low $\delta^{234}\text{U}$ during the last glacial period, lower than the modern coral

value of 149‰. The data show a systematic and correlated variation in $\delta^{234}\text{U}$ from low to higher values in step with major climate change and low-to-high sea-level transition from the last glacial to Holocene. Similar changes occur from the Last Interglacial to last glacial transition with $\delta^{234}\text{U}$ changing from high to low values.

The measurements were undertaken as part of a sea-level variation and radiocarbon timescale calibration study described in detail previously (Yokoyama et al., 2000, 2001a,b). The coral samples selected for analysis were subjected to a full battery of tests that help verify their quality for U-series dating. The results of these tests have been documented in previous publications (Stirling et al., 1995; Yokoyama et al., 2001a,b). They included, selection of best available interior pieces; mechanical cleaning of samples to select wall fractions whenever possible; X-ray diffraction analysis; trace element and stable isotope analysis including ^{232}Th , $^{18}\text{O}/^{16}\text{O}$, and $^{13}\text{C}/^{12}\text{C}$; SEM and optical petrographic analysis of thin-sections.

The $\delta^{234}\text{U}$ data from the present work are shown in Fig. 1 and Table 1. Details of U-series mass spectrometric methods and analysis procedures employed in our laboratories, at the Australian National University, have been published previously (Stirling et al., 1995; Yokoyama et al., 2001a,b; Yokoyama and Esat, 2004). Fig. 1 includes a compilation of previously published coral $\delta^{234}\text{U}$ data as well as a sea-level curve representing ice volume changes over the past 135,000 years. The total range in $\delta^{234}\text{U}$ is from 132‰ to over 160‰ whereas the modern coral value is 149‰. The present results from 30 to 60 ka plus data from at least six other studies (Dia et al., 1992; Bard et al., 1990a,b, 1996; Chappell et al., 1996; Esat et al., 1999; Thompson et al., 2003; Cutler et al., 2003; Potter et al., 2004; Yokoyama and Esat, 2004), over a similar age range, merge in at the young end of the trend with the data extending from Holocene to last glacial, over the past 30 ka (Fig. 1). The accuracy, or the relative calibration of the data from various laboratories cannot explain the variations in $\delta^{234}\text{U}$ shown in Fig. 1. Most laboratories routinely measure certified NIST U-standards and modern corals which, for high precision measurements, yield consistent results to within $\pm 2\%$.

There is some uncertainty in the estimated height of sea levels during the 80 and 100 ka interstadials (Potter and Lambeck, 2004). Although sea-levels during both interstadials are believed to have been similar, estimates range from less than 10 m below present, to 35 m below present. Corals of this period from Barbados, Florida and the Bahamas (Gallup et al., 1994; Ludwig et al., 1996; Toscano and Lundberg, 1999; Muhs et al., 2002; Thompson et al., 2003; Potter et al., 2004) have a range in $\delta^{234}\text{U}$ from values as low as 138‰ to as high as 160‰. The low values fit in with the MIS 3 data set. The data from Barbados (Thompson et al., 2003; Potter et al., 2004) vary approximately linearly with age from low to high $\delta^{234}\text{U}$. The exact mechanism for such a variation is controversial and probably involves diagenesis leading to open system behaviour

for both U and Th isotopes (Gallup et al., 1994; Thompson et al., 2003). Similar variability is observed in the data for the period just prior to Last Interglacial from 140 to 130 ka (Esat et al., 1999). However, all of the data for the Last Interglacial period (130–116 ka), as well as for MIS-7 (Gallup et al., 1994) and MIS-9 (Stirling et al., 2001) interglacials, that indicate a correlated $\delta^{234}\text{U}$ -age variation do so starting from a base of $\delta^{234}\text{U} = 149\%$. Detailed discussion of such behaviour is outside the scope of the present paper.

The $\delta^{234}\text{U}$ data in Fig. 1 over the last glacial period, from the last glacial maximum up to the Last Interglacial, indicates low oceanic $^{234}\text{U}/^{238}\text{U}$ ratio compared with the same ratio during interglacial periods. There is scatter in the glacial $\delta^{234}\text{U}$ values ranging from about 136‰ to about 145‰. However, there is a sufficient number of measurements over the transition period from last glacial to Holocene indicating a smooth glacial-interglacial transition rather than an abrupt shift in $\delta^{234}\text{U}$. This observation plus the systematically low values of MIS-3 data from Huon Peninsula and Barbados from four different laboratories argues for a cause other than some unspecified open system behaviour.

Corals recovered from a Huon peninsula drill core dated by Edwards et al. (1993) range in age from 13 to 7 ka. They all have $\delta^{234}\text{U}$ values close to modern seawater and show no variability with sea-level change in contradiction to the results described above. However, Huon Peninsula corals recently analyzed at the same laboratory (Cutler et al., 2003) do show low $\delta^{234}\text{U}$ during the last glacial and trend to higher $\delta^{234}\text{U}$ values in step with sea-level change from the last glacial to Holocene (Fig. 1). In what follows, we will assume the coral data to represent a change in the oceans balance of ^{234}U between glacial and interglacial periods by about 7–9‰ and investigate possible causes for it.

4. Uranium isotopes in the oceans

Variability in $\delta^{234}\text{U}$ in the oceans can occur independently from variations in total U concentration. The flux weighted mean dissolved riverine $\delta^{234}\text{U}$ input to the oceans is thought to range from 170‰ to 270‰ (Russell et al., 1996; Dunk et al., 2002), although, large variations in particular rivers, over 1000‰ are common (Palmer and Edmond, 1993; Chabaux et al., 2001). Changes in $\delta^{234}\text{U}$ imply changes in either ^{234}U or ^{238}U , where the latter can be equated with the total amount of U in the oceans. The current atomic $^{234}\text{U}/^{238}\text{U}$ ratio in modern corals is 6.287×10^{-5} so that changes in ^{234}U are easier to contemplate than wholesale changes in ocean U budget. The fluctuations observed in the $^{234}\text{U}/^{238}\text{U}$ isotope ratio, when compared with reasonable expectations of variability in the concentrations of ^{234}U and ^{238}U , in the oceans, lead to the same conclusion that any variability is likely in ^{234}U and not in ^{238}U .

In oxygenated seawater dissolved U forms carbonate complexes in the +VI oxidation state (Langmuir, 1978).

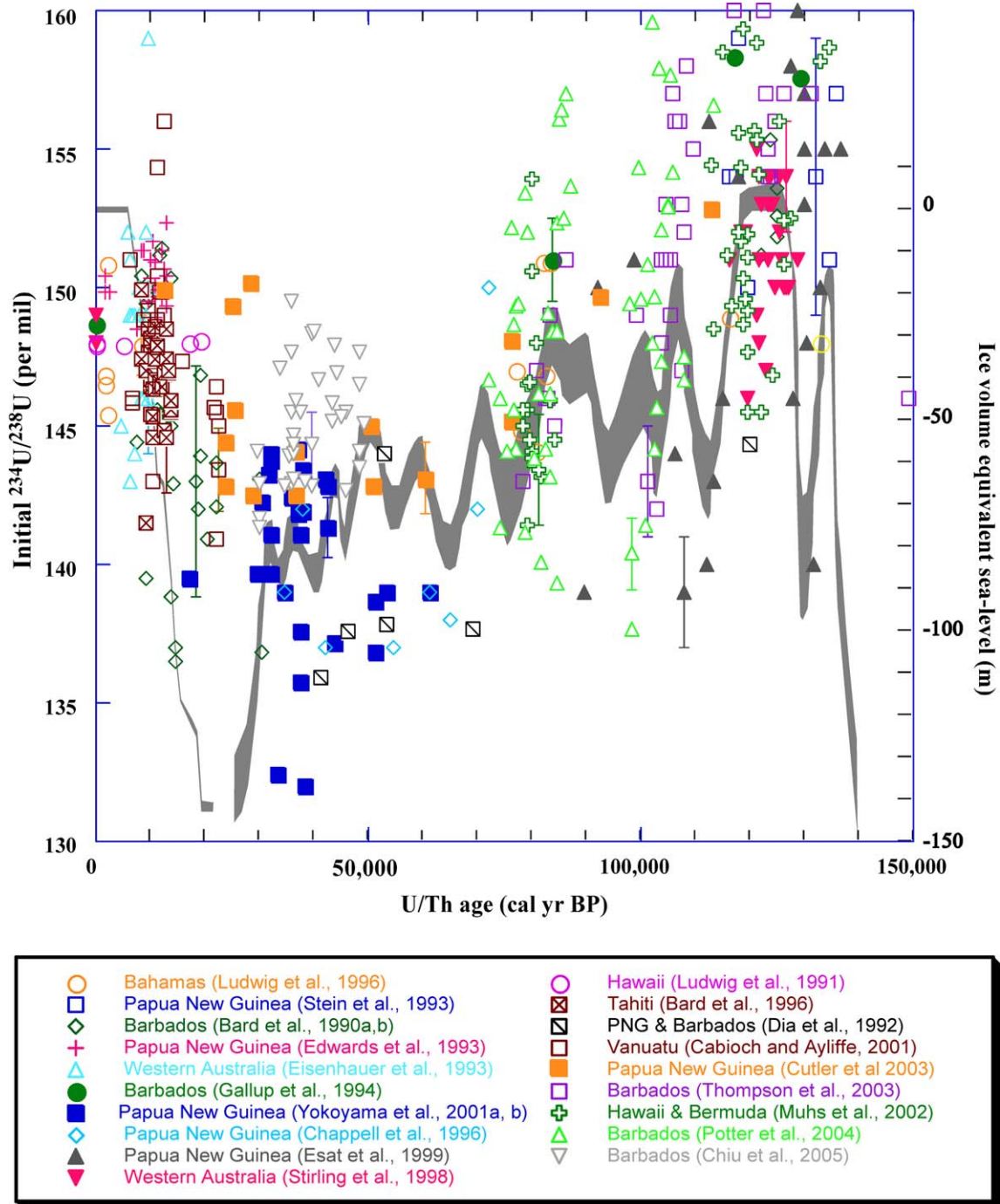


Fig. 1. A compilation of $\delta^{234}\text{U}$ values in U-series dated corals from the Last Interglacial, the last glacial, and the Holocene. For each data set representative uncertainties are as shown. The sea-level curve is from Lambeck et al. (2002) and is intended only as a guide for the eye in contrasting the trend in $\delta^{234}\text{U}$ with changes in sea-level. The shaded band represents the uncertainty in sea-level estimations. The Last Interglacial sea-level was 3–5 m above the current sea-level and we have placed it at $\delta^{234}\text{U} \approx 153\text{‰}$, as explained in the text. The general resemblance of the $\delta^{234}\text{U}$ variations to the sea-level curve for this period is remarkable. In living coral $\delta^{234}\text{U} = 149 \pm 2\text{‰}$. There is a systematic rise in $\delta^{234}\text{U}$ from a low of 132‰ , during the last glacial, up to about 153‰ at the start of the Holocene, corresponding to an extra ≈ 20 Mmol of ^{234}U . There is considerable variability during the 30–60 ka period over a range of 10‰ in $\delta^{234}\text{U}$. The prominent sea-level high-stands around 80–110 ka display a large range of low to high values of $\delta^{234}\text{U}$. The Last Interglacial is represented by a mass of points that appear randomly distributed, and may reflect increased variability in measurements due to older ages and diagenesis in comparison to samples from the Holocene (see above-mentioned references for further information).

However, in anoxic basins including salt marshes and mangrove swamps, continental margins and slope, overlain by oxygen-depleted waters, U can be reduced to a particle reactive +IV state and forms authigenic minerals by diffu-

sion into the sediments (Klinkhammer and Palmer, 1991; Barnes and Cochran, 1993; Dunk et al., 2002). At present, the sources and sinks of U in oceans appear to be in balance within a range of 34–60 Mmol/yr (Dunk et al., 2002).

It is estimated that about 80% of dissolved river flux accumulates in organic rich continental margin sediments that cover about 8% of sea floor area (Morford and Emerson, 1999). In contrast, anoxic deep ocean sediments comprise about 0.3% of the ocean floor but may play a role in the U budget of glacial oceans due to enhanced productivity and accumulation of U facilitated by up to a factor of 10 increase in the areal extent of sediments overlain by oxygen-depleted seawater (Emerson and Husted, 1991; Rosenthal et al., 1995). Rivers transport U both in dissolved and in suspended particulate phases that include colloids, consisting of organic compounds, clays, and Fe–Mn–oxyhydroxide particles. The particulate material appears to be involved in the removal of U, as it changes from U6⁺ to U4⁺ state, it is adsorbed from river water as it coagulates and settles out, but may also release U from sediment porewaters of sufficient alkalinity during estuarine mixing depending on degree of turbulence and flow rates in particular rivers (McKee et al., 1987; Barnes and Cochran, 1993; Swarzenski et al., 1995). In most studies of riverine supply of U, and other trace elements to oceans, river-water samples are passed through 0.45 μm filters before analysis for dissolved metals (Porcelli et al., 1997; Andersson Per et al., 1998). Larger sized particulates presumably would settle out of the flow and never reach the ocean. However, a significant fraction (>80%) of the total U load of rivers may be transported by >0.45 μm particles. Based on several different lines of argument, there is general consensus that the average particulate to dissolved flux of U in rivers is at least 5:1 (Martin and Whitfield, 1983; Klinkhammer and Palmer, 1991; Palmer and Edmond, 1993; Swarzenski et al., 1995; Porcelli et al., 1997; Morford and Emerson, 1999), although, much larger values may occur in some rivers (Martin and Meybeck, 1979; Porcelli et al., 1997; Andersson Per et al., 1998). In general, tropical rivers carry much higher particulate loads compared with temperate and arctic rivers. However, in all cases estuaries and shelves may sequester large quantities of detrital and scavenged U enriched in ²³⁴U. For example, in the Mississippi delta, it is estimated that 90% of suspended sediment load is deposited in an area around the delta smaller than 1% of the area of Gulf of Mexico (Martin and Meybeck, 1979).

We propose to account for the apparent change in the ²³⁴U/²³⁸U ratio of the oceans during deglaciations by the following mechanism: Large quantities of U enriched in ²³⁴U are transported by particulates in rivers and accumulate in coastal margins under relatively reducing conditions during interglacials. Exposed and oxidized to a soluble form throughout the glacial, enriched U is released back to oceans as sea levels rise during deglaciation. In the following section we quantify these considerations and show that, within the bounds of available riverine flux and U isotope data, the proposed mechanism is viable.

5. A simple box model of uranium balance in the oceans

Fluctuations in the U balance of the oceans in response to variations in riverine transport, or changes in the area of anoxic sediments, can be investigated through a simple box model that considers idealised inputs and outputs of U in oceans, including radioactive decay and growth (Russell et al., 1996). Initial concentration of U is represented by $U_{8,0}$ (19×10^{12} mol) and $U_{8,\text{in}}$ ($47 \pm 12 \times 10^6$ mol/yr) is the dissolved riverine input rate of U. The removal rate $k = U_{8,\text{in}}/U_{8,0}$ per year is assumed to be constant for steady state conditions and changes in ²³⁸U due to decay are negligible over Quaternary timescales. Then:

$$\frac{dU_8}{dt} = U_{8,\text{in}} - kU_8$$

and the solution, assuming $U_8(t) = U_{8,0}$ at $t = 0$, is

$$U_8(t) = U_{8,0}e^{(-kt)} + \frac{U_{8,\text{in}}}{k} [1 - e^{(-kt)}]. \quad (1)$$

The companion equation for ²³⁴U can be constructed similarly by defining R as the ²³⁴U/²³⁸U ratio where R_{sw} (6.287×10^{-5} mol/mol; activity ratio 1.149) is the current value and R_{in} (6.651×10^{-5} mol/mol; activity ratio 1.22) is the mean riverine ²³⁴U input ratio and λ are the decay constants (Table 1, footnote). The equation is

$$\frac{dU_4}{dt} = R_{\text{in}}U_{8,\text{in}} + \lambda_8U_8(t) - (k + \lambda_4)U_4.$$

With the initial conditions: $U_4(t) = U_{4,0} = R_{\text{sw}}U_{8,0}$ at $t = 0$, and including the previous expression for $U_8(t)$, the solution can be written as

$$U_4(t) = a + be^{(-kt)} + c[e^{-(k+\lambda_4)t}], \quad (2)$$

where

$$a = \frac{kR_{\text{in}}U_{8,\text{in}} + \lambda_8U_{8,\text{in}}}{k(k + \lambda_4)}, \quad b = \frac{\lambda_8(kU_{8,0} - U_{8,\text{in}})}{\lambda_4k}, \quad \text{and}$$

$$c = R_{\text{sw}}U_{8,0} - \frac{U_{8,\text{in}}(\lambda_4R_{\text{in}} - \lambda_8)}{\lambda_4(k + \lambda_4)} - \frac{\lambda_8U_{8,0}}{\lambda_4}.$$

The definition of k as $U_{8,\text{in}}/U_{8,0}$ ($=2.47 \times 10^{-6}$) ensures a constant concentration of ²³⁸U(t) in the ocean. In Eq. (2) we have assumed the same removal term k as in Eq. (1) as $k \approx U_{4,\text{in}}/U_{4,0}$. The latter accounts for the removal of ²³⁴U from the ocean with a ²³⁴U/²³⁸U ratio that is different than for the general ocean. It is likely to be smaller than the removal term for bulk U. The values for the various parameters used in the above equations are shown graphically in Fig. 2. In Fig. 3(a) we show that the variation in the ²³⁴U/²³⁸U activity ratio can be kept constant to 1.149 ± 0.001 over 100,000 years with a removal term $k = 2.26 \times 10^{-6}$.

The rate of observed change in $\delta^{234}\text{U}$, from glacial maximum to Holocene, is at least 1‰ per 1000 years (Fig. 1). If we attribute the change to increases in the riverine output during this time it requires a change in the riverine flux of a factor of 6 (Fig. 3b), assuming the activity ratio does

not change significantly. In comparison, reasonable estimates of variability in glacial–interglacial weathering rates, and U inflow from rivers, are expected to be within $\pm 50\%$ (Russell et al., 1996). Riverine U and ^{234}U supply to the oceans appears to have been constant during the Holocene and the Last Interglacial, over periods up to 10,000 years. This is a stringent condition that would require an increase in riverine outflow of ^{234}U , during glacial–interglacial transitions, which then quickly reverts to a steady state. It is evident that increased riverine inflow cannot reproduce the observed increases in $\delta^{234}\text{U}$ during glacial to interglacial transitions. However, the possibility remains that a reduction in the area of the deep ocean anoxic sink could also influence $\delta^{234}\text{U}$ (Emerson and Husted, 1991; Rosenthal et al., 1995). It is worthwhile to note here that the only opportunity to influence the removal of ^{234}U supply to the oceans has to be close to shorelines before the input is homogenized with the general ocean. Following homogenization, removal of U has no effect on the $^{234}\text{U}/^{238}\text{U}$ ratio.

We have used the present model to simulate the oceans' response to the delivery of additional riverine ^{234}U . As proposed by Robinson et al. (2004b), enhanced subglacial weathering followed by greater Holocene rainfall could increase the average global riverine $^{234}\text{U}/^{238}\text{U}$ activity ratio to 1.45. Fig. 3c shows the predictions over 10,000 years. The change in $\delta^{234}\text{U}$ is about half of that observed in corals. The required change can be generated by assuming $\approx 40\%$ reduction in the removal rate k , which has to revert back to normal values at the end of the deglaciation. We point out that the changes in $\delta^{234}\text{U}$, from the last glacial to Holocene, appear to commence early in the last glacial (Fig. 1). This is contrary to expectations that river volumes are likely to inflate after the start of the Holocene. In fact, it is generally believed that glacial river discharge volumes were not very different relative to interglacial levels to within about 50% (Rosenthal et al., 1995; Russell et al., 1996; Robert, 2004). Therefore, the products of enhanced subglacial weathering and similar river discharge volumes should

have maintained ocean $\delta^{234}\text{U}$ values at high levels during the glacial, which is contrary to observations.

In contrast to the mechanism put forward by Robinson et al. (2004b) we propose to derive the excess ^{234}U from

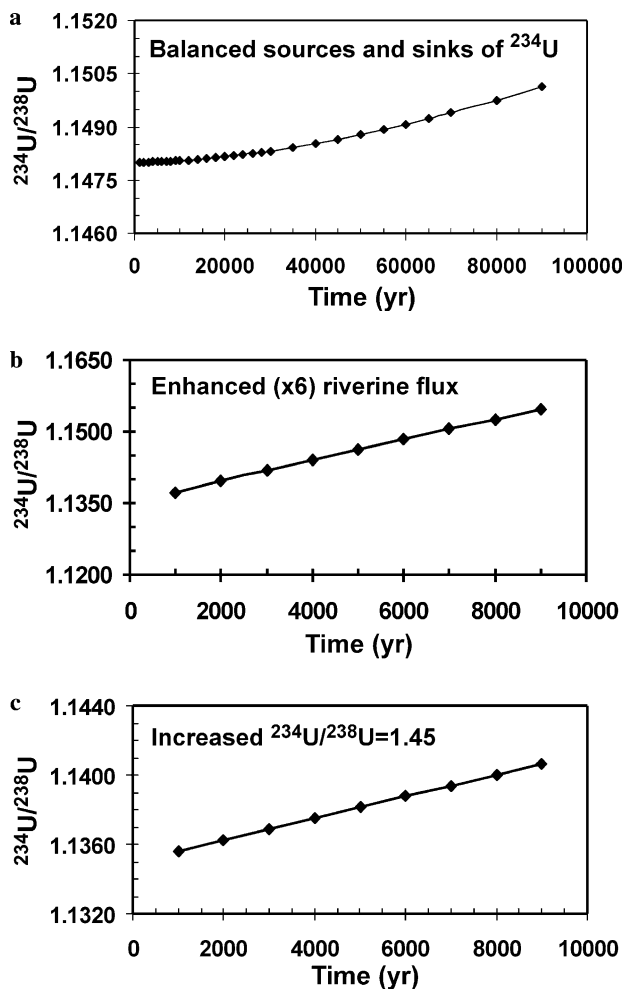


Fig. 3. A simple box model simulation of ^{234}U budget of the oceans as described by Eq. (2). There are large ($\pm 30\%$) uncertainties in the estimates of the fluxes of U and ^{234}U to and from the oceans. However, within these uncertainties the inputs and outputs of U appear to be currently in balance (Dunk et al., 2002). Panel (a) shows the equilibrium in $^{234}\text{U}/^{238}\text{U}$ activity ratio (1.149 ± 0.001) over a 100,000 year glacial–interglacial time period. The parameters used were: $R_{\text{sw}} = 6.264 \times 10^{-5}$ mol/mol (sw, seawater $^{234}\text{U}/^{238}\text{U}$; activity ratio = 1.149); $R_{\text{in}} = 6.651 \times 10^{-5}$ mol/mol (in: riverine input $^{234}\text{U}/^{238}\text{U}$, activity ratio = 1.22); $U_{8,0} = 19 \times 10^{12}$ mol (8,0: initial concentration of ^{238}U in the ocean); $U_{8,\text{in}} = 47 \times 10^6$ mol/yr (8,in: dissolved riverine input of ^{238}U); $k = 2.26 \times 10^{-6}$ mol/mol (k , removal rate of ^{234}U ; at equilibrium defined as $U_{8,\text{in}}/U_{8,0} \approx U_{4,\text{in}}/U_{4,0}$). Within the uncertainties, other combinations of the input and output rates of U and ^{234}U can produce invariant $^{234}\text{U}/^{238}\text{U}$. The decay constants used are listed in footnotes to Table 1. The increase in $^{234}\text{U}/^{238}\text{U}$ from 1.135 to 1.150, from last glacial to Holocene, can be reproduced as shown in panel (b) through increasing river discharge by a factor of six for 10,000 years. However, reasonable estimates of increased river discharge during deglaciation are within $\pm 50\%$ (Russell et al., 1996). All other parameters are as in (a). Panel (c) shows the effects of a sudden change in $^{234}\text{U}/^{238}\text{U}$ to 1.45 as postulated by Robinson et al. (2004b). The change in $\delta^{234}\text{U}$ is about half that observed in corals, but can be reproduced by assuming a 40% reduction in the removal rate k over the equilibrium value in panel (a).

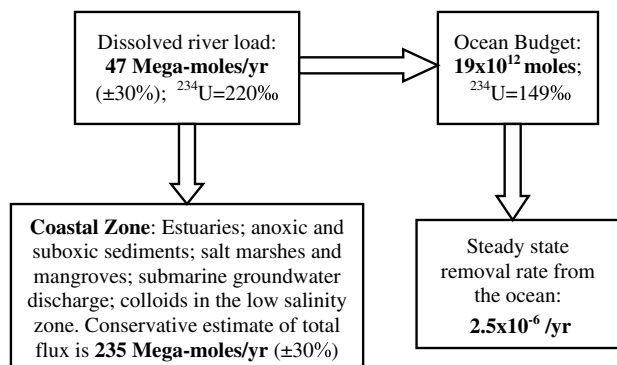


Fig. 2. The partitioning of U between rivers, the ocean and major coastal reservoirs. The flux of U into various coastal sediments has large uncertainties and the average particulate to dissolved flux of U is conservatively estimated to be 5:1. A large fraction of the particulates, including colloids, are sequestered in coastal sediments. The removal of U from the oceans is assumed to be proportional to the input flux to maintain a steady state over 100 ky timescales.

continental margin sediments enriched in ^{234}U , mostly, during the Last Interglacial. Normally, when considering the U budget of the oceans, the relevant factor is the flux of dissolved riverine U. However, in rivers with significant particulate load, 80% of the total U is estimated to reside in the fraction $>0.45\ \mu\text{m}$, most of which is sequestered in near shore sediments, continental margins, and slopes (Klinkhammer and Palmer, 1991; Church, 1996; Church et al., 1996; Morford and Emerson, 1999; Andersson Per et al., 2001). Some of this material may be remobilized and transported to oceans. For example the deep waters of Chesapeake Bay go through cycles of anoxia in summer due to increased productivity and scavenging of U by biodebris (Shaw et al., 1994). Low oxygen in bottom waters in summer results in burial of reduced (+IV) U into sediments. In winter higher oxygen concentrations in bottom waters oxidize U to the soluble (+VI) form which is then recycled back into the river outflow. These considerations indicate a mechanism whereby large fluxes of U, and in particular ^{234}U can be injected into the oceans. The anoxic estuarine, continental margin and slope sediments are exposed during glacial times when sea levels fall. The area exposed for 100 m of sea-level fall corresponds to an additional 3% ($15 \times 10^6\ \text{km}^2$) of Earth's surface area ($510 \times 10^6\ \text{km}^2$). Over a period of approximately 10,000 years, during an interglacial, the amount of ^{234}U that accumulates in estuaries and continental margins can be estimated using the box model and the parameters shown in Fig. 2.

Consider the burial of ^{238}U in estuarine and continental slope sediments. The evolution of ^{234}U can be determined by assuming constant input of ^{238}U :

$$\frac{dU_8}{dt} = U_{8,\text{in}} = \text{const.}, \text{ so that } U_8(t) = U_{8,\text{in}}t,$$

and the solution for $U_4(t)$ is

$$U_4(t) = \frac{\lambda_8 U_{8,\text{in}}}{\lambda_4} t + \frac{U_{8,\text{in}}}{\lambda_4} \left(R_{\text{in}} - \frac{\lambda_8}{\lambda_4} \right) (1 - e^{-\lambda_4 t}) \quad (3)$$

with initial conditions $U_4(t) = U_{4,0} = R_{\text{sw}}U_{8,0} = 0$ at $t = 0$, assuming that there was no initial ^{234}U present.

The accumulation of excess ^{234}U derived from Eq. (3) is about 170 mega ($\times 10^6$) mol, corresponding to $\approx 14\%$ of ocean's inventory. During the same period, ^{238}U build-up amounts to 0.5×10^{12} mol or less than 3% of present ocean budget of 1.9×10^{13} mol; so that the effect on ^{234}U is significantly larger than changes in the total U concentration as argued previously. We propose that most of the ^{234}U locked in sediments during interglacials is exposed, and oxidized, during times of low sea-level, and readily soluble when the sea-level rises again. The rate of sea-level rise during the transition to Holocene is about 15 mm/yr from approximately 18–10 ka, ignoring the Younger Dryas episode and melt-water pulses. A steady input of ^{234}U and to a lesser, relative extent ^{238}U is injected into oceans in step with the sea-level rise. The net decay loss in ^{234}U from Last Interglacial to Holocene reduces the excess ^{234}U from 170 Mmol to about 150 Mmol which equates to about 12%

of the amount in the ocean. The available excess is well within the requirements of the present data of about 20 Mmol (Fig. 1). As the supply of ^{234}U is limited, and sea-levels stabilize during interglacials, this mechanism overcomes the difficulty of assuming abrupt changes in riverine outflow of U, or changes in removal rate of ^{234}U . The ^{234}U concentration in the oceans reverts back to a steady state, possibly with some time delay. In this context, the higher $^{234}\text{U}/^{238}\text{U}$ of 1.153 during the Last Interglacial presumably reflects the higher than present (by up to 5 m) sea levels at that time (Stirling et al., 1998).

Inspection of the coral data (Fig. 1) indicate a noticeable change in $^{234}\text{U}/^{238}\text{U}$ early in the deglaciation starting at ≈ 15 ka. A relevant consideration is the mixing time of ^{234}U -enriched-U diffusing in from coastal margins into the bulk ocean. Corals grow close to shorelines and are likely to be influenced directly by the outflow of ^{234}U enriched fluids. Thus, it is possible that ^{234}U in corals may not be representative of average ocean $^{234}\text{U}/^{238}\text{U}$ values but may reflect local concentration of ^{234}U at a particular time. However, over longer timescales, during the last glacial from 70 to 30 ka, and during interglacials, the $^{234}\text{U}/^{238}\text{U}$ ratios in corals are likely to be representative of the bulk ocean.

The notion of variable $^{234}\text{U}/^{238}\text{U}$ in the oceans during periods of sea level change has consequences for judging the veracity of U-series dates derived from corals. Previously, the $^{234}\text{U}/^{238}\text{U}$ ratio at the time of coral growth provided the only quantitative indicator for closed system behaviour. Tight limits around the modern coral value of $\delta^{234}\text{U} = 149\text{‰}$ ranging from $\pm 2\text{‰}$ to $\pm 4\text{‰}$, or larger, were used to screen samples (Edwards et al., 1986; Gallup et al., 1994; Stirling et al., 1998). Screening interglacial samples during periods of stable sea level in this way may indeed suffice. However, serious biases in the range of “acceptable ages” may arise in the screening of glacial- and interstadial-aged samples where marine $^{234}\text{U}/^{238}\text{U}$ may deviate significantly from the present day value.

6. Sinks of uranium isotopes from the oceans

The scenario discussed in the previous section provides a plausible mechanism to increase $\delta^{234}\text{U}$ in the oceans in step with sea-level rise. However, a mechanism is required to also reduce $\delta^{234}\text{U}$. If all the inputs of ^{234}U were interrupted, it would require about 5000 years to lower the ocean $^{234}\text{U}/^{238}\text{U}$ from 1.149 to 1.135. The drop from a steady state, at the end of the Last Interglacial (or equivalently from Marine Oxygen Isotope Stage 5a) provides an estimate of the rates involved. Fig. 1 has a compressed timescale over this period, however, in expanded scale the change can be better discerned. The variation is from 1.153 at 118 ka (1.150 at 80 ka) to 1.140 at 110 ka (1.138 at 70 ka) a change of $\approx 1.1\%$ over 8000 years in ^{234}U atom concentration. It is worth noting that lowering the bulk U concentration does not change the $^{234}\text{U}/^{238}\text{U}$ isotope ratio. What is needed is either selective lowering of ^{234}U or selective increase in

^{238}U while at the same time keeping the long-term sources and sinks in balance. The first option could be achieved by removing ^{234}U from rivers and from near shore areas before it completely mixes in the oceans, the second option requires significant input of material depleted in ^{234}U . Reducing weathering rates or the riverine discharge is not a realistic choice as we have argued previously.

The drop in the atmospheric CO_2 levels during glacial times may have been due increased productivity at high latitude surface waters, resulting in enhanced transport of organic matter to deep ocean sediments and an increase in the areal extent of reducing sediments by up to a factor of ten, from 0.3% to 3% (Emerson and Husted, 1991; Rosenthal et al., 1995; Morford and Emerson, 1999). As a consequence, removal rates of U would have been enhanced and U concentrations in the glacial oceans may have been lower than the present 3.3 ppb. Alternatively, alkalinity driven carbonate precipitation (Opdyke and Walker, 1992; Walker and Opdyke, 1995) could explain the reduced glacial atmospheric CO_2 levels without causing deepwater oxygen depletion as there is no evidence for extensive glacial ocean anoxia and associated laminated sediments. However, an increase in the extent of anoxic sediments from 0.3% to 3% may not be easily identifiable. It is likely that both processes were involved in lowering atmospheric CO_2 levels during glacial periods. These considerations may also be relevant to the lowering of $\delta^{234}\text{U}$ through periods of low sea-level during glacials. Low sea levels expose shallow-water carbonate deposits that are weathered and also eroded by rivers cutting new channels to the sea. Deep sea carbonate dissolution may also make a contribution. However, consideration of alkalinity changes (Shaw et al., 1994; Walker and Opdyke, 1995) show enhanced dissolution during episodes of sea-level rise and interglacials. We adopt extreme values of carbonate dissolution (Russell et al., 1996; Stoll et al., 1999) of 5×10^{15} mol of carbonate or 6.5×10^9 mol of U in 1000 years. We also assume that the U in these sediments is highly depleted in ^{234}U with an activity ratio of 0.8. The change in the activity ratio of the ocean after 8000 years is very small, approximately 0.001. Clearly, carbonate weathering from exposed, near-shore shelves is unlikely to affect the U balance in the oceans.

Dissolved Fe from mineral dust is a significant regulator of phytoplankton productivity in the oceans which in turn affects the atmospheric CO_2 levels through the flux of carbon in the surface ocean (Martin, 1990). Iron in the oceans is mainly supplied at continental margins in re-suspended sediment. However, Fe-rich aeolian dust levels are significantly enhanced during glacials (Pourmand et al., 2004), in particular, at coastal zones. Uranium readily forms complexes with Fe (Duff et al., 2002). In contrast to the requirement of dissolved Fe for phytoplankton productivity, Fe-rich particulates and Fe-oxides minerals are likely to incorporate U. At coastal zones removal of U will tend to reduce ^{234}U supply to the ocean. There are no estimates for the magnitude of this flux, but it is likely to be significant.

7. Conclusions

We have made a case that glacial–interglacial transitions appear to have influenced the oceans' U budget. The variations appear to involve ^{234}U and not the bulk concentration of U (^{234}U), although changes in U concentration are not ruled out. Some of the measured variability in coral $\delta^{234}\text{U}$, in particular the low MIS 3 values below the current $\delta^{234}\text{U} = 149\text{‰}$, and the systematic increase of $\delta^{234}\text{U}$ from the last glacial to Holocene can be best accounted for by continental weathering cycles and cycles of ocean productivity that influence the accumulation of ^{234}U -enriched U in continental margin sediments. Problems in interpretation may arise when variations in $\delta^{234}\text{U}$ in corals are of diagenetic origin, rather than due to climate change. However, with carefully designed experiments, open system behaviour in corals can be detected. The previous practice of screening corals based on differences between $\delta^{234}\text{U}$ at the time of coral growth and the $\delta^{234}\text{U}$ in modern corals can no longer be justified without qualification. During interglacials and interstadials, U and excess ^{234}U concentrations increase in estuarine, continental margin and slope sediments, as well as in salt marshes and mangroves (Dunk et al., 2002) overlain by oxygen-depleted waters. During low sea-level stands, U in the exposed sediments is oxidized and subsequently returned to the ocean as sea-levels rise. Corals grow close to shorelines and can directly sample fluids diffusing out of margins with variable ^{234}U prior to complete mixing with the bulk ocean. Uniform oceanic ^{234}U concentrations result over longer time periods of relatively stable sea-level during glacials and interglacials.

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