Long Term Variations of Uranium Isotopes and Radiocarbon in the Surface Seawater Recorded in Corals

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Abstract. U-series isotopes and radiocarbon are extensively used for dating and as tracers of various processes during the late Quaternary. Advanced, mass spectrometric U-Th and radiocarbon isotope ratio measurement techniques, as opposed to detection of decay products, routinely achieve high temporal precision with smaller sample sizes. Thermal ionization mass spectrometry (TIMS) in U-series dating, and accelerator mass spectrometry (AMS) in ¹⁴C dating, have enabled significant advances in each field. In this paper, we review the techniques of TIMS U-series dating and AMS methods for radiocarbon dating as applied to corals. Coupled measurements of U-isotopes and ¹⁴C in corals provide enhanced insights into past changes in climate. Radiocarbon measurements in Papua New Guinea corals from Huon Peninsula terraces of the last glacial period, dated by U-series, show large discrete ¹⁴C peaks which appear to be correlated with reorganizations of the North Atlantic thermohaline circulation and Heinrich events. Residence time of Uranium in the oceans with respect to riverine inflow is estimated to be about 300–600 thousand years, a time span accessible to U-series disequilibrium dating of corals which concentrate U from seawater in their skeletons. Measurements of the ²³⁴U/²³⁸U ratio in the glacial-age Huon Peninsula corals, when combined with previous data, indicate long term variations in ²³⁴U in seawater by up to about 7%. The variations appear to be linked to major glacial-interglacial climate transitions and to sea-level changes.

Keywords: uranium series dating, radiocarbon, ice age, sea-level, TIMS, AMS, heinrich event, ²³⁴U/²³⁸U in seawater

1. INTRODUCTION

Uranium series nuclides can often be successfully used to date carbonate samples from the marine environment. The dating methods are applicable over an age range from a few tens of years to over half a million year before present (BP). Using techniques of thermal ionization mass spectrometry (TIMS) for U and Th nuclides in corals, a precision better than 0.5% can be routinely achieved in 100,000 year old samples.
Radiocarbon is produced in the upper atmosphere through the interaction of cosmic rays with the atmosphere and is rapidly distributed over the earth and surface oceans. Radiocarbon dating is widely used for samples containing carbon younger than about 50,000 years. In contrast to older radioactive-decay counting techniques, accelerator mass spectrometry (AMS) has been used over the past 20 years to date samples of organic material containing amounts of carbon as small as 0.5 mg with superior precision. Independently, both the radiocarbon and uranium series techniques are currently in widespread use in studies of the late Quaternary.

Among other factors, radiocarbon production rate depends on the flux of cosmic rays as well as on the variations of the Earth’s geomagnetic field. Hence, past levels of atmospheric radiocarbon are known to have been highly variable. Another cosmic ray produced radionuclide, $^{10}$Be, that can also be determined with AMS (Finkel and Nishiizumi, 1997), shows a dependence on paleogeomagnetic intensity variations recorded in volcanic rocks and sediments (e.g., Channell et al., 1997).

Apart from production rate variations, atmospheric radiocarbon levels are dependent on changes in the carbon cycle. As the bulk of the terrestrial carbon is partitioned into the deep oceans, changes in ocean circulation due to climate variability is likely to significantly perturb atmospheric carbon and radiocarbon levels (Broecker, 1998). Through combined Uranium series and radiocarbon dating, where the former method provides an absolute reference time scale, radiocarbon levels in coral samples can reveal past reorganizations in the carbon cycle.

Fossil corals dated using TIMS provide constraints on past sea-levels. Previous studies have concentrated on Interglacial periods, where due to high sea-levels most of the corals are now located above present sea-level and accessible for collection. At tectonically active, uplifting areas such as the Huon Peninsula, Papua New Guinea, coral reefs form during times when sea-level rise overtakes local uplift. At Huon Peninsula, coral reef terraces of the last glacial period, which formed 50 to 80 m below present sea-level, have been uplifted above the current sea-level and can easily be sampled. Such corals provide a unique resource for investigating variations in glacial age sea-levels, changes in atmospheric radiocarbon, and possibly glacial interglacial variations in the U-isotopic composition of the oceans (Bard et al., 1991, 1992; Hamelin et al., 1993; Richter and Turekian, 1993; Henderson, 2002). This period, also known as marine oxygen isotope stage-3 (OIS-3), has been the subject of intense study in deep-sea cores and in ice records as it shows unusual high frequency climate variability (e.g., Alley, 1998).

In this paper, we review the techniques of U-series dating as well as of radiocarbon dating using mass spectrometry. We illustrate the techniques with two examples related to climate change and possible variations of uranium isotopes in the oceans over the past 150,000 years.
2. URANIUM SERIES GEOCHEMISTRY

Uranium series disequilibrium dating methods are based on the following radio-nuclide decay chain

\[
\begin{align*}
{^{238}\text{U}} & \rightarrow {^{234}\text{U}} \rightarrow {^{230}\text{Th}} \rightarrow {^{206}\text{Pb}} \\
(4.49 \times 10^7 \text{ yr}) & \rightarrow (2.48 \times 10^7 \text{ yr}) & \rightarrow (7.5 \times 10^4 \text{ yr}) & \rightarrow \text{stable}
\end{align*}
\]

where the numbers in brackets are half-lives of the decay from one element or isotope to another.

The method relies on the presence of excess \(^{234}\text{U}\) in the system, thus \(^{230}\text{Th}\) is produced by both the decay of \(^{234}\text{U}\) in secular equilibrium with \(^{238}\text{U}\) and by the decay of the excess \(^{234}\text{U}\). The half life of \(^{234}\text{U}\) to \(^{230}\text{Th}\) decay is \(\approx 10^5\) years, and within the age range for dating suitable Pleistocene samples. Uranium content of sea-water is high, whereas the very low Th content is due to its absorption and fixation onto particulate material and sediments. Thus, living corals have negligible thorium abundances; the subsequent \(^{230}\text{Th}/^{238}\text{U}\) ratio is mainly the result of \(^{234}\text{U}\) decay after the coral has died, provided there is no exchange of U and Th through diagenesis (closed system requirement).

The \(^{230}\text{Th}\) age is derived from the following equation (Kaufman and Broecker, 1965; Edwards et al., 1987):

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

where \(T\) is the age in years, \(\lambda\) represents the decay constant for each nuclide, and \((\text{act})\) refers to activity ratio.

\[
\begin{align*}
\lambda_{^{238}\text{U}} &= 1.551 \times 10^{-10} \text{ yr}^{-1} \\
\lambda_{^{234}\text{U}} &= 2.835 \times 10^{-6} \text{ yr}^{-1} \\
\lambda_{^{230}\text{Th}} &= 9.195 \times 10^{-6} \text{ yr}^{-1}
\end{align*}
\]

\(\delta^{234}\text{U}\) is a reformulation of the \(^{234}\text{U}/^{238}\text{U}\) ratio introduced by Edwards et al. (1987):

\[
\delta^{234}\text{U}(0) = \left[ \left( \frac{^{234}\text{U}}{^{238}\text{U}} \right) / \left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{eq}} \right] - 1 \times 10^3
\]

where, \(\left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{eq}} = \frac{\lambda_{^{238}\text{U}}}{\lambda_{^{230}\text{Th}}} = 5.472 \times 10^{-5}\) is the atomic ratio at secular equilibrium. The half-lives of \(^{230}\text{Th}\) and \(^{234}\text{U}\) were recently revised using several electron multipliers for the measurement of the low intensity \(^{234}\text{U}\) and \(^{230}\text{Th}\).
beams (Cheng et al., 2000). The results differed from those determined in previous studies but were within the range of reported uncertainties (De Bievre et al., 1971; Lounsbury and Durham, 1971; Meadows et al., 1980). However, more recently, Bernal et al. (2002) re-determined the $^{234}$U-half-life using high intensity U beams from a secular equilibrium uraninite standard measured in a Faraday cup array. Their results are consistent with the earlier reported half-life value for $^{234}$U and we use the previously determined U and Th half-lives in this paper.

Figure 1(i) shows the relationship between the measured $^{234}$U/$^{238}$U ratio, $\delta^{234}$U(0), and $[^{230}$Th/$^{238}$U] activity ratio. The contours are in units of $\delta^{234}$U(T)
(quasi horizontal curves) and time, $T$ (quasi vertical lines). The expected variation of both $[^{234}\text{U}]/[^{238}\text{U}]_{\text{act}}$ and $[^{230}\text{Th}]/[^{234}\text{U}]_{\text{act}}$ with time are shown in Figs. 1(ii) and (iii). The two figures indicate that both rates approach unity (secular equilibrium) with time. $[^{230}\text{Th}]/[^{234}\text{U}]$ equilibrates after $\approx 350$ kyr whereas $[^{234}\text{U}]/[^{238}\text{U}]$ takes longer $\approx 1200$ kyr. For coral samples, older than 280 kyr, the $[^{230}\text{Th}]/[^{238}\text{U}]$ activity ratio can be larger than 1.

If there were no initial $[^{230}\text{Th}]$ present in the coral, the age, $T$, can be calculated using the measured $[^{234}\text{U}]/[^{238}\text{U}]$ ratio ($\delta[^{234}\text{U}(0)]$), and assuming that the $[^{234}\text{U}]/[^{238}\text{U}]$ ratio at the time of coral growth ($\delta[^{234}\text{U}(T)]$) was the same as the present day seawater value:

$$\delta[^{234}\text{U}(T)] = \delta[^{234}\text{U}(0)] e^{^A_{234}T}.$$  

However, by measuring both $[^{234}\text{U}$ and $[^{230}\text{Th}$ abundances, no assumptions need be made about the $[^{234}\text{U}]/[^{238}\text{U}]$ sea-water ratio at the time of coral growth (Eq. (2)). This parameter can then be used to assess the closed system history of the sample or, if systematic variations can be established, investigate the past seawater concentration of $[^{234}\text{U}$.

3. METHODS OF URANIUM SERIES DATING

Over the past decade, the traditional $\alpha$-counting method has been superseded by direct measurement of the abundances $\text{U}$ and $\text{Th}$ isotopes using thermal ionization mass spectrometry TIMS (Chen et al., 1986). Previously, $\alpha$-counting was used to measure the activities of $\text{U}$-series isotopes in the samples. This is the conventional method for Uranium series dating where $\alpha$-particles from decay are counted. The various isotopes can be recognized from their $\alpha$-particle energy spectrum and isotope ratios as well as concentration of isotopes in the sample can be determined by adding enriched isotope tracers. However, relatively large amounts of sample are required (5–10 g for dating late Pleistocene age samples) and long counting times (days) limit the precision achievable by this method relative to TIMS (e.g., Veeh, 1966; Omura 1988).

Advantages of TIMS compared with conventional $\alpha$-counting methods include a) higher-precision (conservatively a factor of 2 to 3), b) applicability over an extended age range (months to $\approx 500$ ka), c) smaller sample size ($\approx 1$ g compared with $\approx 5$ g), d) rapid analysis (hours instead of days) and, e) clearer appraisal of the degree of open system behaviour by precise measurement of $\delta[^{234}\text{U}(T)]$ and $[^{232}\text{Th}]$.

The first measurement of Uranium and Thorium isotopes by TIMS was performed by Edwards et al. (1987) using the Lunatic 1 single-collector mass spectrometer. In the studies conducted by the present authors (e.g., Stirling et al., 1995, 1998; Yokoyama et al., 2000a, 2001a, 2001c), uranium isotopes were measured using a Finigan MAT 261 mass spectrometer and thorium isotopes were measured using the 61-cm TIMS in charge collection mode (Esat, 1995).
3.1 Chemical separation of Uranium

The measurement of the $^{230}\text{Th}/^{238}\text{U}$ relative abundance is based on TIMS isotope dilution methods. Isotope dilution involves adding a known amount of an enriched isotope tracer to the sample. For U and Th the tracer is an artificially produced long-lived radionuclide of U and Th.

The pretreatment techniques employed by Yokoyama et al. (2000a, 2001a, 2001c) follow the methods previously used by Stirling et al. (1995). Chemical procedures for the extraction, separation and purification of U and Th in the coral samples are based on methods that are similar to those described by Edwards et al. (1986).

Coral samples were crushed to sub-cm sized pieces to expose multiple surfaces that could be inspected in sunlight for traces of “glitter” from calcite. In most cases, presence of 4% or greater amounts of calcite in the coral skeleton can be identified visually prior to x-ray diffraction analysis for quantitative determination of calcite content. Selected coral pieces were physically cleaned using a dental drill under a magnifying lens to remove delicate lattice and septa structures that are susceptible to alteration or to filling with extraneous material relative to solid wall sections. This method can be applied to favid species of corals which have solid wall sections but not to *Porites* corals. The samples cleaned this way yielded $^{234}\text{U}/^{238}\text{U}$ ratios closer to the sea-water value (Stirling et al., 1995), and hence, favids are preferred whenever available. Following physical cleaning, the corals were cleaned in an ultrasonic bath, in turn, in acetone, alcohol and de-ionized water.

Approximately 2 to 3 g of cleaned coral are required for samples younger than 50,000 years old which contain 25 to 35 pg of $^{230}\text{Th}$ and 5 to 8 µg of Uranium. The samples were dried in a laminar air-flow chamber and weighed. They were covered with de-ionized water and slowly dissolved by adding concentrated HNO$_3$. Weighed, mixed-spikes ($^{229}\text{Th}-^{233}\text{U}-^{236}\text{U}$) were added as well as concentrated H$_2$O$_2$ to eliminate any organic residues in the solution. To ensure complete sample-spike equilibration and to drive off CO$_2$, the solution was slowly dried over night.

Since corals contain relatively small amounts of uranium and thorium, parts per million and parts per billion, respectively, a small amount of FeCl$_3$ was added to the sample as a carrier for uranium and thorium as well as for some other trace elements. By adding NH$_4$OH, U and Th were co-precipitated with Fe. The color of the solution changed from clear to yellow to a brown deposit containing ferric hydroxide forms that includes oxides and hydroxides of U and Th. The mixture was centrifuged and the supernate which mainly contains Ca was discarded. De-ionized water was used to wash the ferric hydroxide precipitates several times which were then dissolved in 7N HNO$_3$.

Uranium and thorium were separated by column chromatography with anion exchange resin using standard methods. All columns used for this step (2 ml) are pre-cleaned and Fe is eluted with 7N HNO$_3$. Thorium is then eluted by adding 2 ml ($\times$3) of 8N HCl, and 2 ml ($\times$2) of 0.5N HCl is added to elute uranium. The Th
and U solutions were dried and re-dissolved in 7N HNO₃. They were loaded separately onto small anion exchange columns (0.15 ml) for further cleaning of any remaining Fe. The recovered U and Th were dried and stored as small drops ready for mass spectrometry.

3.2 Charge collection mass spectrometer

The mass spectrometer for CCTIMS (Charge Collection Thermal Ionisation Mass Spectrometry; Esat, 1995) consists of a 180° sector, 61 cm radius, double focusing magnet with a non-uniform radial field (Esat, 1984). The machine has five faraday cups and can be used for measurement of isotopes up to mass 260 such as, U, Th, OsO₃ and ReO₄. The non-uniform radial field enhances the dispersion along the focal plane and at mass 260 the separation per mass unit is 4.5 mm. The thermal ionization source is Dietz type (Dietz, 1959; Wasserburg et al., 1969), which consists of (1) filament and source casing, (2) split first focus, (3) split second focus, (4) collimator, (5) Z-plate, and (6) adjustable slit. Samples are loaded onto a filament and placed at (1). The filament is then slowly heated up to the evaporation temperature of the sample. Only a small fraction of the vaporized sample will actually be ionized and these are focused and accelerated within the ion source. The beam then passes through elements (2) and (3) which steer and accelerate the beam. The collimator and the adjustable slits constrain the beam divergence and the Z-plates allow steering of the beam in the non-dispersive plane.

Five 4.5 mm wide Faraday cups with 1.2 mm slits are installed at the focal plane. The cups consists of an inner and an outer cup insulated by sapphire spacers to maintain the highest possible resistivity to ground. Each Faraday cup has a suppressor voltage plate at its entrance, behind the main slit, to prevent ions and electrons from escaping the cup. The Faraday cups are connected to Keithley low-noise 642 electrometers. Each electrometer has a selectable resistive feedback element 10⁸, 10¹⁰, 10¹¹, or 10¹² Ω where the measured voltage (V) is proportional to the current (V = IR) or a 20 pF capacitor (c) where the rate (dt) of charging of the capacitor is proportional to the current I, (I = c dv/dt). Because capacitors are inherently less noisy than high-value resistors, lower background noise levels can be achieved in CCTIMS. To maintain the electrical resistivity of the system, all critical connections are made through sapphire insulators and the electrometers are kept in a temperature controlled enclosure (±0.01°C) in a dry nitrogen atmosphere. This provides for very low background noise levels (<2–3 × 10⁻¹⁷ peak to peak).

Zone-refined rhenium dimple filaments for Th measurements with CCTIMS were first out-gassed at about 1500°C for 30 minutes and then loaded with graphite for a second stage of out-gassing at more than ~2000°C for 2 hours. The first out-gassing is intended to remove oxygen from the filament to prevent oxidation and volatilization of the following graphite load. Filaments were stored in high vacuum until the sample was loaded. Filaments left in air for extended periods tend to oxidize and yield poor ion currents. No ²³⁰Th, ²³²Th or U isotopic
Signals have been detected above background levels from blank filaments. Calibration of the relative gain of the five electrometers is done simultaneously. Each electrometer is connected to a common, variable-rate, ramp generator through 100 pF reference capacitors. The electrometers are supplied the same current and can be calibrated over a range of currents. Errors are adjusted for the contribution of background currents.

CCTIMS is useful when only small (<10^{-14} A) ion currents can be generated because of small available sample size or low ionization efficiency such as for Th and Os. In charge mode, a constant input current results in a monotonic increase in Voltage (V) across the feed-back capacitor.

The output is integrated over 1.28 sec intervals, and the range of typical
measurement current is approximately $10^{-15}$ A to $10^{-12}$ A with a background level of approximately $10^{-17}$ A. Sixty 1.28 sec. measurements are grouped in each block and depending on sample size, 20 to up to 60 blocks of data can be collected (Fig. 2).

Background values of each run are measured for at least 20 blocks of 60 ratios and have remained constant within statistical error for over many years. The background values are determined before the sample reaches optimal running temperature to maximize the time available for collecting sample data. The actual background levels during the sample runs may actually be lower. The material of the field-effect transistors in the electrometer contain small amounts of radioactive impurities which decay by the emission of $\alpha$-particles approximately once every 5 minutes. The $\alpha$-decay events appear as sharp jumps in background signal with ionization current of approximately $3 \times 10^{-15}$ C that can easily be detected and then subtracted from the background level (Fig. 3).

### 3.3 Measurement of Thorium isotopes

Th isotope ratios were measured with the 61-cm TIMS in charge collection mode (Esat, 1995). Previous methods employed peak hopping using a single electron multiplier (Edwards et al., 1986) or a Daley detector (Bard et al., 1990) which enabled measurement of very low intensity ion beams ($< ca. 10^{-15}$ A). However, the precision obtainable was limited due to beam intensity variations and poor duty cycle in data-acquisition.

Internal statistical precision for a 45 minutes data acquisition period is typically 0.6‰ using CCTIMS as shown in Fig. 4, better than what has been achieved in other laboratories by about a factor of three (Esat, 1995).

Thorium sample fractions were dissolved with 1N HNO$_3$ and loaded onto a
zone-refined Re “dimple” filaments (Esat et al., 1979) between two layers of graphite. No evidence for interferences have been found in the vicinity of the Th isotopes. Peak scanning of Th isotopes in the Faraday cups shows flat topped peaks with widths less than one third of the Faraday cup slits. For focusing and centering, the electrometers were switched to resistor mode, with $10^{12} \Omega$ resistors, when the beam intensity increased to approximately $6 \times 10^{-15}$ A. Although the $^{230}$Th current is typically 2 to $4 \times 10^{-15}$ A, at the beginning of a run with 15 to 30 pg of $^{230}$Th loaded onto the filament, it grows to more than $5 \times 10^{-14}$ A. As the run proceeds, $^{230}$Th intensity builds up to $6 \times 10^{-14}$ A over 1 hour. No appreciable within-run shift in the $^{229}$Th/$^{230}$Th ratio has been observed during any of the runs (Fig. 2).

3.4 Measurement of Uranium isotopes

The attempt to measure U isotopes using the 61-cm instrument was prompted by the deterioration of the analogue mode electron multiplier in the Finnigan MAT 261. Alternative multipliers, optimized for pulse counting, were found to be unsuitable when operated in the analogue mode and produced intensity dependent shifts in the U isotope ratios. Eventually a replacement for the original multiplier could be obtained from the manufacturer that produced reliable data. Features of the MAT 261 include a multi-collector Faraday cup system which makes it possible to measure up to seven isotopes simultaneously. Electrometers with $10^{11} \Omega$ feedback resistors are used to detect large currents. The single electron multiplier (SEM) with an overall gain of ca. 100 allows the measurement of very low level currents (from $10^{-16}$ to $10^{-13}$ Ampere) and can be operated simultaneously with the Faraday cups.

Approximately 1 g of total Uranium was loaded onto a Re double filament. Uranium isotopes, $^{238}$U, $^{235}$U, and $^{233}$U, were measured in the Faraday cups and $^{234}$U ($^{238}$U/$^{234}$U = ca. 13800) was measured with the SEM at the same time. Fifteen blocks of data, corresponding to 150 sets of ratios, were acquired over a 40 minute interval at evaporation filament temperatures ranging from 1050 to 1150°C and ionization filament temperatures of 2000°C.

Measured U isotope ratios, $^{234}$U/$^{235}$U and $^{233}$U/$^{235}$U, were corrected for isotopic mass fractionation, using the measured $^{235}$U/$^{238}$U ratio normalized to the natural value (137.88), with appropriate corrections for the contributions of various isotopes in the spikes. The uncertainty of each run was typically 1–2‰ ($2\sigma_m$).

3.5 Calibration of the mixed spikes

In the studies by Yokoyama et al. (2000a, 2001a, 2001c), two mixed spikes were used. One was a mixed solution of $^{229}$Th and $^{233}$U (U-1) and the other of $^{229}$Th, $^{233}$U and $^{236}$U (U-3). In U3 the $^{233}$U/$^{236}$U ratio was approximately 1 and samples spiked so that $^{235}$U/$^{236}$U would be approximately 10. Spike solutions were stored in PTFE bottles with a trace amount of HF to prevent Th from precipitating out of solution. The isotopic composition of U-1 is; $^{238}$U/$^{235}$U =
2.8937, $^{234}\text{U}/^{238}\text{U} = 2.3378$, $^{233}\text{U}/^{235}\text{U} = 1259.38$, and $^{229}\text{Th}/^{230}\text{Th} = 20,000$. While U-3 has the same isotopic composition but additionally $^{233}\text{U}/^{236}\text{U} = 0.523$. Corals which are 20,000–50,000 years old were spiked so that $^{233}\text{U}/^{235}\text{U}$ ca. 0.3–0.4 and $^{229}\text{Th}/^{230}\text{Th}$ ca. 3–5.

Uraninite standard HU-1, which is in secular equilibrium, was used to calibrate the relative abundance of the U and Th mixed spikes. Calibration using this standard has several advantages, including the elimination of uncertainty arising from gravimetric measurements of the sample and the standard, and also reduces systematic biases due to errors in the decay constants. Mass spectrometric analyses of particular mixtures of HU-1 plus U-1 yielded $^{233}\text{U}/^{229}\text{Th} = 53.18 \pm 0.05 (2\sigma_m)$ (Stirling et al., 1995) and for HU-1 plus U-3 yielded $^{233}\text{U}/^{229}\text{Th} = 37.312 \pm 0.05 (2\sigma_m)$.

### 3.6 Calibration of $^{234}\text{U}/^{238}\text{U}$

The secular equilibrium uranium standard HU-1 is used to monitor and correct for any instrumental bias in the mass spectrometer. For example, the instrument at the Australian National University, originally yielded a $\delta^{234}\text{U}$ value

![Fig. 5. Repeat measurements of $^{234}\text{U}/^{238}\text{U}$ using the HU-1 standard (upper figure) and the NBS SRM 960 uranium standard (lower figure). Open symbols are results from Chen et al. (1986).]
of \(-2.1 \pm 0.5\%\) which was attributed to a bias in the electron multiplier (Stirling et al., 1995). However, a newly installed electron multiplier yielded a mean value of \(\delta^{234}\text{U} = 0.599 \pm 0.270\%\) for six repeat measurements. Typical \(2\sigma_m\) errors in measured \(\delta^{234}\text{U}\) are within \(\pm 1\%\) to \(\pm 2\%\) and no correction was applied to the measurements reported in this paper (Yokoyama et al., 2000a, 2001a, 2001c).

4. CRITERIA FOR ASSESSMENT OF OPEN SYSTEM BEHAVIOUR

Numerous studies have established qualitative and quantitative criteria for recognizing uranium and thorium open-system behavior in corals (e.g., Stein et al., 1993; Bar-Matthews et al., 1993). However, exact mechanisms for open system behaviour appear to be complicated and none of the established procedures are able to identify diagenetically altered samples with certainty. Most studies

Fig. 6. Photomicrographs of Porites coral from reef (a) IIa (ca. 30 ka BP) from Kanzarua, and from Last interglacial reef (b) Huon Peninsula in crossed polarized light. Well preserved aragonite structures can be seen in (a) whereas diagenetically altered portion of the coral is evident from this picture (b). Approximately 10% of secondary calcite was detected in the coral (b).
used a combination of criteria to select out likely samples suspected of open system behavior and we outline those in below.

4.1 Microscopic analysis

Original textures of coral aragonitic skeletons are examined under the petrographic microscope (Fig. 6). To increase the reliability of the results, both longitudinal and latitudinal thin-sections are made and checked for secondary void filling and alteration, including coarsening due to re-calcification (Bar-Mathews et al., 1993). Often evidence for alteration is found around delicate lattice-work or septa in between solid wall sections in Favid corals. During mechanical sample cleaning, these structures are routinely removed. Those samples that contain extensive alteration features are rejected.

4.2 XRD analysis

Once corals exposed to freshwater environment, original aragonitic skeleton can be replaced by secondary calcite since calcite is more stable than aragonite in such environments (Deer et al., 1967). Presence of calcite may be indicative of U and Th exchange after their deposition. Presence of calcite can be detected using X-ray diffraction analysis (XRD). However the sensitivity of XRD is usually limited to ≈2% calcite.

4.3 Trace elements and stable isotopes

A number of studies have attempted to establish a correlation between trace elements, stable isotopes and spurious U-Th ages (e.g., Chen et al., 1991; Stein et al., 1993; Bar-Matthews et al., 1993). In one such work, Na, Mg, Sr, δ¹³C and δ¹⁸O were studied by Stein et al. (1993) in corals from Huon Peninsula. They concluded that neither trace element nor stable isotope analyses were sensitive to low levels of alteration. In two papers, on corals from the Bahamas, Chen et al. (1991) and Bar-Mattews et al. (1993), have reported generally lower concentrations of Na, Mg, and Sr compared with modern corals. They attributed this to secondary calcite alteration. However, the relationship between this and U/Th age of the corals, if any, has not been established.

4.4 δ²³⁴U(T)

Assuming that the sea-water ²³⁴U/²³⁸U ratio has remained constant over time, δ²³⁴U(T) in fossil corals should be similar to that in modern corals and in sea-water where δ²³⁴U(T) = 149 ± 1‰ (Gallup et al., 1994; Stirling et al., 1995) and 144 ± 7‰ (Chen et al., 1986) respectively. The acceptance criteria for δ²³⁴U(T), adopted for Huon Peninsula coral samples, ranged from 140‰ to 158‰, an uncertainty range of ±9‰ (Stein et al., 1993). In contrast, a narrower limit of ±4‰ was employed by Stirling et al. (1995) for Last Interglacial corals from Western Australia. We consider the δ²³⁴U(T) criterion to be the only quantitative indicator for U and Th open system behaviour. Gallup et al. (1994)
have shown a direct correlation between high $\delta^{234}$U($T$) values and Uranium series ages. Increase in $\delta^{234}$U($T$) beyond 149‰ is approximately correlated with older apparent ages in all cases. Similar trends can be seen in Last Interglacial Huon corals (Stein et al., 1993), and in Western Australian corals (Stirling et al., 1998). A demonstrable explanation for such a correlation remains elusive, however, Thompson et al. (2003) have recently proposed a plausible mechanism.

4.5 Total U concentration

Modern corals contain approximately 3 ppm U and have an approximate range from 2.5 ppm to 3.5 ppm. Within these limits, uranium concentration in corals can also be used for checking the quality of corals for uranium series dating.

4.6 $^{232}$Th concentration

Pristine corals from oceanic islands normally contain less than 0.5 ppb of $^{232}$Th (Edwards et al., 1987; Chen et al., 1991). In continental rocks $^{232}$Th is a common isotope (>1 ppm concentration). Excess $^{232}$Th in corals is indicative of external U and $^{230}$Th addition and results in older measured ages. The measured concentration of $^{232}$Th and the expected $^{238}$U/$^{232}$Th ratio can therefore be used to correct for the contribution of detrital materials. In the present study none of the dated corals had significant $^{232}$Th abundances.

5. RADIOCARBON DATING OF CORALS

Reef forming coral habitats occur over a range of water depths, down to about 50 m, and the upper growth limit is generally at the mean water spring level (Hopley, 1986). The coral skeleton mainly consists of calcium carbonate, and is therefore suitable material for $^{14}$C dating. The measured carbon isotope ratios can then be used to calculate the radiocarbon age. The “fraction modern”, $F$, is defined as:

$$F = \frac{N}{N_0} = \frac{\left( ^{14}C/^{12}C \right)_{sam}}{\left( ^{14}C/^{12}C \right)_{std}}.$$  (6)

Where $\left( ^{14}C/^{12}C \right)_{sam}$ is the sample ratio (fractionation corrected and referenced to wood for which the average $\delta^{13}$C = $-25$‰), and $\left( ^{14}C/^{12}C \right)_{std}$ is the standard ratio (National Bureau of Standards, NBS oxalic acid standard, referenced to age-corrected activity of wood grown between 1840 and 1860, which has 95% of oxalic acid activity; and is corrected for isotope fractionation and referenced to PDB standard value of $-19$‰). The radiocarbon age of the sample is then calculated from.

$$\text{Radiocarbon age} = -\tau \ln F$$  (7)
where $\tau$ is the Libby mean life ($5568/\ln2 = 8033$ years). The age limit of radiocarbon is

$$F_{\text{limit}} \leq \left\{ (F_{\text{measured}})^2 + (2\Delta f)^2 \right\}^{1/2} \quad (8)$$

where $\Delta f$ is the uncertainty in the system background. Isotope ratio calculations and contamination corrections are presented and summarized in Donahue et al. (1990a, b).

### 5.1 Possible cause of fluctuations in radiocarbon ages

Several assumptions are implicit in deriving radiocarbon ages: (1) accuracy of the half-life, (2) uniform global distribution of radiocarbon, (3) closed system assumption and (4) constant rate of radiocarbon production. However, these assumptions are only approximately valid and need to be verified.

The half-life of $^{14}C$ was determined to be 5568 years by Libby in 1947. However, later experiments showed 5730 years to be more accurate (e.g., Nakamura, 1988). But, to avoid confusion in comparing ages obtained at different times, the older value (5568 years) continues to be used by convention (Godwin, 1962) unless otherwise stated.

Atmospheric radiocarbon equilibrates rapidly. However, ocean mixing is slower. For example, surface water radiocarbon is approximately 400 years older than atmospheric. Bard (1988) examined the problem using $^{14}C$ measurements in molluscs and corals compared with total dissolved carbon content of surface sea water from different latitudes in the Atlantic, Pacific and Indian oceans (Fig. 2.2). He concluded that the “apparent age” of carbonate shells from surface ocean water ranges between 400 to 1,200 years depending mainly on latitude (Bard, 1988). In upwelling areas such as the Southern Ocean, where $^{14}C$ depleted deep ocean water mixes with surface waters, samples have older apparent ages (Stuiver and Braziunas, 1985; Bard, 1988); while in brackish waters in estuaries where open ocean and riverine flux mix, the correction is smaller (Stuiver and Braziunas, 1993).

Ages of various marine reservoirs have been estimated by numerical modelling, and combined with measurements of shell and coral $^{14}C$ ages, with known calendar ages (i.e., known collection age and U/Th age) have been used to establish the local reservoir effect, $\Delta R$ (Stuiver et al., 1986; Stuiver and Braziunas, 1993). The simulations indicate that marine reservoir age of samples from surface ocean waters within the mixing layer (i.e., 0 to –75 m) in the northern hemisphere is 402 years, and 362 years in the southern hemisphere (Stuiver and Braziunas, 1993). These results were compared with observed $^{14}C$ ages using data from all over the world’s oceans, except the Indian Ocean, to establish $\Delta R$ values (Fig. 2.3; Stuiver et al., 1986; Stuiver and Braziunas, 1993). Thus, the correction for reservoir effect for radiocarbon dated near surface carbonate marine samples, is $\sim$402 years in the northern hemisphere and $\sim$362 years in the southern hemisphere.
The initial concentration of atmospheric radiocarbon is a required parameter in calculating the age of $^{14}$C dated samples. It is now well established that the $^{14}$C in the atmosphere was systematically different in the past. Detailed information about these variations has been obtained from $^{14}$C analyses of wood from tree rings that extend back in time up to about 8000 years and show rapid century-scale variations. They appear to be correlated with solar magnetic activity. Superimposed over the rapid variations there is a long term (from 30,000 to 3,000 years BP) decrease in atmospheric $^{14}$C levels that is best explained by a two-fold increase in the geomagnetic field over the same time interval (Bard, 1998).

5.2 Variations in reservoir carbon content

After $^{14}$C is produced in the atmosphere, it is oxidised and converted to $^{14}$CO$_2$, and distributed over the Earth’s surface. The marine environment is one of the biggest reservoirs of $^{14}$C because it can both fix carbon as carbonate by the organisms living in the ocean and release the $^{14}$CO$_2$ by respiration of these organisms. The main concentration of $^{14}$C (>95%) is in the oceans in the form of bicarbonates and carbonates.

In the terrestrial environment, large forests and peat lands or lakes are also important reservoirs of carbon and exchange CO$_2$ with the atmosphere through respiration and photosynthesis over time scales of ~30 years, which is small compared to the half life of $^{14}$C. In contrast, exchange between deep ocean reservoirs and the atmosphere is slow, 700 years for deep Atlantic water, 1600 years in the Indian Ocean and up to 2000 years in the Pacific trenches.

Both marine and terrestrial reservoirs are also affected by large scale glacial-interglacial climate changes that would also affect the distribution of $^{14}$C. This can be used as tracer of oceanic deep water circulation since deep water is the major reservoir of atmospheric $^{14}$C through the North Atlantic region (Broecker et al., 1998). Given that the paleomagnetic intensity is known at some time in the past, proxy recorded variations of atmospheric $^{14}$C can be attributed as intensification/cessation of the Thermohaline circulation.

5.3 Radiocarbon dating using Accelerator Mass Spectrometry

In this section, we review basics of $^{14}$C measurement using Accelerator Mass Spectrometry (AMS). In convention, we take the AMS currently being used at the Department of Nuclear Physics, Research School of Physical Sciences and Engineering, as an example (Fig. 7). The AMS is used for the study of $^{10}$Be, $^{14}$C, $^{26}$Al, $^{36}$Cl, $^{59}$Ni, and $^{129}$I isotopes. This is a large accelerator that can reach up to 16 MV on the terminal (Fig. 7). It has an ion source with a multi-cone target wheel with capacity for 24 samples. The inflection magnet is cycled to inject each of the carbon isotopes into the accelerator. The $^{12}$C beam is chopped by a factor of about 89 to 1 so that $^{12}$C and $^{13}$C have roughly equal intensities. The terminal voltage is set to 6 MV and 30 MeV C$^{4+}$ is selected for the analysing magnet. The $^{12}$C and $^{13}$C beams are measured in a Faraday cup placed behind the analysing magnet. The $^{14}$C beam is detected in a heavy ion gas proportional counter (Fig. 8). For 1
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mg of graphite sample, the ion source can produce 10–20 µA of carbon ions. Typical precision of 14C measurement is 1%. This is not as good as achieved at other dedicated 14C laboratories (e.g., <0.5% at Groningen (Wijma et al., 1996)). However, for 30–40 kyr old coral samples the uncertainty is dominated by external factors such as in situ sample contamination and any contamination introduced during the sample preparation.

There are several methods for preparing AMS targets for 14C measurements. Two methods are commonly used among various laboratories. One is the two-steps reduction method using Zn and Fe as catalysts and the other is the single-step reduction method using Fe or Co powder as a catalyst (Vogel et al., 1984).

The AMS equipment can be divided into three parts: the ion source and first separation section, acceleration section and the detection section.

At the ion source, a low energy caesium beam sputters carbon from the target, negatively charged C is extracted by a lens system and focused into a magnetic mass analyser. The ions are deflected by 90° and injected into a tandem accelerator. The singly charged C ions are accelerated to energy $E$ given by

\[ E = \frac{m v^2}{2} \]

where $m$ is the mass of a carbon ion and $v$ is its velocity.

Fig. 7. Relationship between observed (a) $^{232}\text{Th}$ and $^{234}\text{U}(T)$ and (b) actual age. No systematic variations were found.
where \( m \) is the mass, \( V_1 \) the extraction voltage (100 keV), \( v \) the velocity and \( q (=1) \) the charge of the carbon ions.

All C\(^-\) ions have the same charge and are accelerated by the same potential difference \( V_1 \). However, velocities of these ions differ depending on their masses:

\[
v = \sqrt{\frac{2qeV_1}{m}}.
\]

When the ions are injected into the magnetic mass analyzer, their circular
trajectories are based on the condition:

\[ qe v B = \frac{mv^2}{R} \]  

(11)

where \( R \) is the radius of the ion’s path and \( B \) is the strength of the magnetic field. Therefore, the circular path is described by:

\[ R = \frac{mv}{qeV_2}. \]  

(12)

From above described equations, velocity can be eliminated to give:

\[ \frac{2qeV_1}{m} = \frac{B^2 q^2 e^2 R^2}{m^2}. \]  

(13)

This describes the radius of circular paths as a function of \( V \) and \( B \). Thus, if the magnetic field strength is fixed, the particles which have same \( m/q \) would follow the same path. Therefore, ions of same charge (–1) will be separated by the injection magnet as a function of their mass.

Negative ions injected into the accelerator are first accelerated to the positive terminal voltage \( V_2 \) which is at a few megavolts. At the terminal, polyatomic molecules, such as \( ^{13}\text{CH}^- \) and \( ^{12}\text{CH}^- \), are dissociated and produce positively charged atoms as their outer electrons are stripped in passing through a thin foil or gas stripper. The positively charged atoms are further accelerated, away from the terminal, by an amount \( qV_2 \). Total energy at this point is \((1 + q)V_2\).

The accelerated ions are then focused into the analysing magnet that selects a particular mass/charge (\( m/q \)) combination. The \( ^{14}\text{C} \) ions are then separated from ions with similar energy, mass and charge states into a multi-wire proportional gas counter.

In summary, the AMS system has a number of advantages in detecting small amounts of \( ^{14}\text{C} \):

1) Elimination of \( ^{14}\text{N} \) by the use of a negative ion source.
2) Elimination of molecular ions which have the same mass.
3) Separation of \( ^{14}\text{C} \) atoms by using a heavy ion detector.
4) Precise determination of the relative abundances of \( ^{14}\text{C} \), \( ^{13}\text{C} \) and \( ^{12}\text{C} \) in a sample.

6. CLIMATE CHANGE RECORDED AS LONG-TERM VARIATIONS OF SEAWATER RADIOCARBON IN CORAL SKELETONS

Twenty five U-series dates were obtained using TIMS from corals at Huon Peninsula collected from terraces corresponding to OIS-3 time period (Yokoyama et al., 2000a, 2001a). They are plotted with \(^{14}\text{C} \) dating results in Fig. 10. Uranium
Fig. 9. Figure showing the clear separation of $^{14}$C signal using AMS.
Fig. 10. Radiocarbon results plotted against U-Th based calendar age (upper panel). The lower panel is the abundance of cold water species in the deep sea sediments for the same time intervals (Bond and Lotti, 1995; Lund and Mix, 1998). The large positive peaks of $^{14}$C corresponding well with the low sea surface temperature at the North Atlantic. Each of these cold snaps are accompanied with IRD in the cores and defined as Heinrich events (Bond and Lotti, 1993).

series ages are within the age range between 29,700 years to 54,600 years and correspond to terraces labeled as II and III (Chappell, 1974; Chappell et al., 1996). The ages in Fig. 10 are grouped in discrete clusters. However, within each time interval there is a large spread in $^{14}$C ages which stand out as sharp peaks. Typically, they correspond to excursions of 1000–2000‰ in $\Delta^{14}$C (Yokoyama et al., 2000a). In comparison, one of the largest previously established peaks in atmospheric radiocarbon corresponds to the Younger Dryas period, which is associated with a 300‰ $^{14}$C peak. A speleothem from a Bahamian cave dated by uranium series and radiocarbon (Beck et al., 2001) shows a peak in atmospheric
radiocarbon, at about 44 ka, with a magnitude over 1000‰. The present data also show negative $\Delta^{14}C$ in between the $^{14}C$ peaks, which correspond to older $^{14}C$ ages than the uranium series ages (Fig. 10). This negative shift in $\Delta^{14}C$ cannot be explained by contamination with secondary, dead carbon (Yokoyama et al., 2000a). The veracity of the data ultimately depends on the quality of samples. All the data shown in Fig. 10 was screened through the previously described tests. However, for radiocarbon dating, each sample was also subjected to selective dissolution, ranging from three to five steps, and each aliquot was radiocarbon dated and results accepted only when at least two of the final aliquots gave consistent ages within errors (Yokoyama et al., 2000a).

Timing of the radiocarbon peaks appear to correlate with the published timing of millennial scale climate variability during the last ice age (Fig. 10). Heinrich events are periods of extreme cold that occurred periodically during the last ice age (Bond et al., 1992; Bond and Lotti, 1995). Deep sea records from numerous localities and Greenland ice records show a periodicity ranging from 4 ky to 7 ky. Heinrich events are attributed to the partial disintegration of northern hemisphere ice sheets. The large amounts of freshwater influx into the North Atlantic is thought to be the cause of the intense cold snaps due to the interruption of the Thermohaline circulation and the associated transport of heat from the equatorial regions to the North Atlantic (Bond et al., 1992; Bond and Lotti, 1995). The interruption of the Thermohaline circulation is also expected to affect the production rate of North Atlantic Deep Water. In this scenario, the enhanced atmospheric radiocarbon peaks would be attributed to the interruption of the Thermohaline circulation which is thought to carry with it up to 80% of the radiocarbon production (Broecker et al., 1998).

The exact timing of the Heinrich events is difficult to determine from deep-sea cores or from ice-records. Different studies have assigned differing dates for the various events with extreme variations up to 4–5 ky. Dates based on radiocarbon suffer from the absence of appropriate calibration when converting to calendar ages. The sharp excursions in radiocarbon in the present data would result in unreliable $^{14}C$ dates at the time of Heinrich events. Therefore, dating of Heinrich events with other methods, such as U-series would be more appropriate.

Chapman et al. (2000) have assessed the dates assigned to Heinrich events from various studies and have compiled a set of reliable dates. There is a remarkable correlation between these and the timing of the $^{14}C$ anomalies in the present data (Yokoyama and Esat, in prep.). The progression of a Heinrich event starts with the partial disintegration of the Laurentide ice sheet and presumably leads to a correlated rise in sea-level. As sea-level changes propagate rapidly on a global scale they will also affect the Antarctic ice sheet grounded below sea-level. There is evidence for this from ice-rafted debris events in South Atlantic deep-sea cores (Kanfoush et al., 2000). There is a possibility that the surge of the continental Antarctic ice sheet could also lead to the interruption of the circumpolar Antarctic deep water formation. Given that Antarctic deep water formation is thought to sink as much water as the Atlantic deep water formation the effect on enhanced $^{14}C$ retention in the atmosphere could be significant (Yokoyama and
Icebergs released into the ocean need not melt rapidly. Yet, their effect on sea-level, once released is immediate. In principle, it is possible that the interruption of deep water formation could affect atmospheric $^{14}$C levels by more than 200–300% within a few hundred years. Following a Heinrich event cold period, the deep sea records show an abrupt warming indicating the return of warm equatorial waters to the North Atlantic and the re-start of the Thermohaline circulation. The return of warm conditions will presumably lead to an increase in moisture transport and the rebuilding of the Laurentide ice sheet (Lambeck et al., 2002).
Thus, in this scenario, the OIS-3 Huon coral reefs were constructed due to rapid, periodic rises in sea-level when there was a spurt in coral growth to catch up to the rising sea-level. Coral growth, relative to the Heinrich event cycle would occur during the initial cold phase. Some time later, the interruption of the thermohaline circulation would result in the rise of the atmospheric and surface ocean $^{14}$C levels. As the Heinrich event terminates after 1–2 kyr the atmospheric $^{14}$C levels would drop as the thermohaline circulation re-established with the return of warm waters to the North Atlantic.

This sequence of events is shown in Fig. 11 for the prominent radiocarbon peak at ~38 ka for which we have the most data (Yokoyama and Esat, in prep.). A plot of sea-level and $\Delta^{14}$C versus calendar age shows a progression just as described above. At the start the sea-level is high. This is followed by a rapid increase in $^{14}$C levels. The $^{14}$C peak subsides after a few hundred level returns to previous levels. Small variations in sea-level, seen in the diagram, may represent a range in growth habitat of corals rather than actual sea-level rises. Nevertheless, the basic scenario depicted in this graph appears to be robust. For other $^{14}$C peaks we do not have as much data (Fig. 12). However 32 ka and 44 ka peaks show a similar structure within uncertainties. The 52 ka peak is at the limits of radiocarbon

![Fig. 12. Sea-level changes recorded in the Huon corals correlated well with reported Heinrich events (after Yokoyama et al., 2001a). Arrows in the panel A show the timing of the Heinrich events by (Chapman et al., 2000). Panel B is the record of ice rafted detritus from Antarctic ice sheets. These figures show the strong connection between the Antarctic ice sheet and the global climate change.](image-url)
measurements and is possibly affected by small additions of younger carbon and therefore may not be as reliable.

7. $^{234}$U/$^{238}$U IN SEA-WATER DURING THE PAST 150000 YEARS

The residence time of uranium in the sea water is relatively long, up to 300,000–500,000 years (Ku et al., 1997; Richter and Turekian, 1993). Tetravalent uranous (U$^{4+}$) ions readily form uranyl ions (UO$_2$$^{2+}$) under the oxidizing conditions, and remain stably dissolved in sea-water, because they form water soluble compounds (Ivanovich and Harmon, 1992). On the other hand, thorium is removed from sea-water quickly, due to its tetravalent oxidation state (Ivanovich and Harmon, 1992), by absorption onto particle surfaces and co-precipitating preferentially with some elements such as Fe and Mn, and also through biological processes (Ivanovich and Harmon, 1992). Thorium, therefore, has a very short
residence time in sea-water approximately 350 years (Goldberg and Koide, 1962). As a result of this, Uranium in the sea-water is stable and uniform for long periods at ~3.2 ng/g (Chen et al., 1986). In turn, initial uranium content of corals (δ²³⁴U(T)) can be used as an indicator of possible movement of uranium and thorium isotopes in fossil corals determine if they remained as closed system (e.g., Stirling et al., 1995, 1998).

The present sea-water value is δ²³⁴U = 152.6 ± 1 (Delanghe et al., 2002) which is somewhat larger than δ²³⁴U = 149 ± 1‰ found in modern corals (Edwards et al., 1986, 1987; Stirling et al., 1995, 1998; Delanghe et al., 2002). Present results for Huon Peninsula OIS-3 corals yield a weighted average of 139‰ (Yokoyama et al., 2001c). This is approximately 10‰ lower than the expected value, assuming that the relative abundance of ²³⁴U in the oceans has remained unchanged over the past 50,000 years.

Most of the TIMS U-series coral dating has targeted either interglacial or interstadial periods (e.g., Chen et al., 1991; Stein et al., 1993; Muhs et al., 1994; Stirling et al., 1995; Ludwig et al., 1996; Toscano and Lundberg, 1999; Potter et al., 2002; Thompson et al., 2003 etc.). Stirling et al. (1995) dated Last Interglacial corals from reefs in Western Australia which show a noticeable difference in δ²³⁴U(T) values that are slightly higher (153 ± 2‰) than those for modern corals. In contrast, lower δ²³⁴U(T) values have been reported for interstadial periods, mainly the 80 ka and the 100 ka interstadials. These are from Barbados, Florida and Bermuda (Bard et al., 1990; Muhs et al., 1994; Ludwig et al., 1996; Ludwig et al., 1996; Toscano and Lundberg, 1999; Potter et al., 2001; Thompson et al., 2003, etc.). Figure 13 shows these results including those for Holocene corals from WA (Eisenhauer et al., 1993), and Bermuda and Galapagos (Delanghe et al., 2002).

The data appear to challenge the idea that δ²³⁴U in sea water has been invariant over the last several hundred thousand years, instead ²³⁴U appears to be sensitive to climate and changing sea-levels. Sea-level observations at the far-field sites during the Holocene show that the melting of major ice sheets had ceased by ~6200 cal yr BP (Nakada and Lambeck, 1989). Therefore, ocean volume during the past ~6000 years has been approximately constant. In contrast, sea-levels during the Last Interglacial were several meters higher than present (Stirling et al., 1995). During the last glacial period, sea-levels were approximately 50 meters lower on average (e.g., Chappell et al., 1995; Linsley, 1997) except for the major interstadial periods around 80 and 100 ka (Ludwig et al., 1996). Therefore, the data in Fig. 13 are consistent with variations in ²³⁴U/²³⁸U correlated with changes in climate and sea-level.

8. CONCLUSION

The ²³⁸U-²³⁴U-²³⁰Th decay system can be used for dating Pleistocene and Holocene corals. Suitably selected coral samples can ensure closed system integrity for U and Th isotopes. In corals, the absence of initial ²³⁰Th, simplifies the dating process. Development of TIMS and AMS methods has led to reduction in sample size, faster analysis and higher precision. In the present work U
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isotopes were measured using Faraday cups in combination with an analogue-mode electron multiplier. Thorium isotopes were measured using charge collection in multiple Faraday cups. The latter method provides higher precision relative to other standard methods of measurement. A multiplicity of criteria were employed to ensure the quality of the dated coral samples.

Coupled U-Th and $^{14}$C ages were used to define a $^{14}$C calibration curve for the period 30 ka to 50 ka (Yokoyama et al., 2000a, 2001a). Many of the criteria used for selecting suitable samples for U-Th dating also apply to the selection of $^{14}$C samples. However, the likelihood of carbon contamination is much more severe than for U or Th. However, the use of rigorous screening criteria and the closely correlated behaviour of the $^{14}$C signal with past climate changes points to large and rapid reorganization of ocean circulation due to global climate change rather than to spurious results due to diagentic alteration in the coral samples. The uranium isotopic composition of sea water is thought to have remained invariant over the past 300–600 k years. In previous studies, most of the work was targeted to the study of Interglacial or interstadial period corals that are currently located at or above present sea-level and are readily accessible for sampling. In tectonically active areas, such as the Huon Peninsula, Papua New Guinea, glacial period coral reef terraces, that formed when sea-levels were lower than the present, are currently elevated tens of meters above sea level. Corals collected from these terraces have systematically low $^{234}$U/$^{238}$U ratios than present day seawater that possibly hint at glacial-interglacial scale changes in U isotopes in the oceans. Processes responsible for this variability are not readily apparent and need additional study of U isotopes in sea water, in rivers and in sediment samples.

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