Sea-level change in Australasia and the Radiocarbon time scale calibration during the last 50,000 years

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The work described in this thesis was carried out while I was a full-time student at the Research School of Earth Sciences, at The Australian National University, between October 1995 and May 1999. Except where mentioned in the text, the research described here is my own. No part of this thesis has been submitted to any other university or similar institution.

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Abstract

Uranium series and radiocarbon ages were measured in corals from the uplifted coral terraces of Huon Peninsula (HP), Papua New Guinea, to provide a calibration for the radiocarbon time-scale of the past 30,000 years to 50,000 years. Improved analytical procedures, and quantitative criteria for sample selection, helped screen diagenetically altered samples. The base-line of the calibration curve follows the trend of increasing divergence from calendar ages, as established by previous measurements. In addition, four well defined peaks of excess atmospheric radiocarbon concentration were observed correlated with the timing of reef growth at HP. These peaks appear to be synchronous with Heinrich events and concentrations of ice-rafted debris found in North Atlantic deep sea cores. The time sequence of events are as follows: An initial sea level high is followed by a large increase in atmospheric radiocarbon as the sea-level subsides. Over 3000 years to 4000 years the atmospheric radiocarbon drops to below present ambient levels. This cycle bears a close resemblance to ice-calving episodes of Dansgaard-Oeschger and Bond cycles and the slow-down or complete interruption of the North Atlantic thermohaline circulation. The increases in the atmospheric radiocarbon levels are attributed to the cessation of the North Atlantic circulation.

The measured initial $^{234}$U/$^{238}$U ratio of last glacial period corals from HP, when compared with previously published data for the Holocene and Last Interglacial, appears to be about 1% lower. This suggests shorter ocean $^{234}$U residence times than previously believed. It appears that chemical weathering and terrestrial-ocean transport of $^{234}$U was more efficient during interglacials than in ice-ages.

Sea-level changes, at locations far away from former ice sheets, are relatively immune from isostatic effects; expressed as equivalent sea-level (esl), they relate to variations in ice volume. The tectonically stable North Australian continental shelf, and the tectonically uplifting HP were examined to construct equivalent sea levels for the past 50,000 years. Sedimentological, micropalaeontological and radiocarbon ($^{14}$C) analyses of gravity-core samples, from the North Western Australian shelf, show details of the esl during the Last Glacial Maximum (LGM) and the timing of the termination of LGM, which appears to have been in two steps. During the LGM, maximum esl occurred at about 22,000 yr (BP, calendar timescale), at a depth of -134±4 m, followed by a slightly higher period of esl from 21,000 to 20,000 yr BP.
The end of LGM, at 19,500 yr BP, marks the start of major melting. These results are in excellent agreement with previous studies from the same area and Barbados.

Radiocarbon dated, Holocene corals, from (HP) coral reefs, confirm the occurrence of meter-scale co-seismic uplift events. Using previously published up-lift rates, equivalent sea-levels (esl) derived from U-series dated 30,000 year to 50,000 year old HP corals show similar variations as recorded in deep sea core $^{18}$O based sea-levels.
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Chapter One

Introduction

Variations in world wide (eustatic) sea-levels since the late Pleistocene reflect changes in global ice volumes and observations of the former provide estimates of the changing mass balance between the oceans and ice sheets. Except for the Holocene period, the eustatic sea-level curve is poorly constrained and improved estimates would be important in studies of climate change.

Evidence for past sea-level variations include the positions of former shorelines with respect to present sea-level. Current interglacial ocean volumes are close to their maximum and much of the past record now lies below present sea-levels. However, where tectonic processes have uplifted the crust, as in the Huon Peninsula of Papua New Guinea or where, as in Scandinavia or Canada, glacio-isostatic processes have resulted in major crustal uplift, some of the former shorelines are exposed.

There are two parts to a complete sea-level specification: firstly, the identification of the sea level indicator and measurement of its position relative to present sea-level; and secondly, the measurement of the age of the indicator. Age measurement of suitable remains of organisms that lived within the past 40,000 years can be determined by radiocarbon dating. However, it is well known that the radiocarbon time scale is not coincident with calendar time, nor is it linear. This has implications for diverse areas of study, where rates of processes are important or where time scales are relative to specific methods of dating, as in pollen chronologies, uranium series (U-series) dating or archaeological dating. A significant part of the present study is therefore devoted to the calibration of the $^{14}$C time scale beyond 30,000 years. Additional complications arise due to variable partitioning of $^{14}$C between the atmosphere and the sea and between distinct but dynamic reservoirs in the oceans inter-connected by major circulation systems (the conveyor belt model of
Broecker, (1984)). During deglaciation, fresh meltwater can affect $^{14}$C concentrations in the ocean circulation, and at times of extreme climate change can interrupt the conveyor belt. Therefore, $^{14}$C variability in marine based sea-level indicators, such as corals, could partly be due to a redistribution of $^{14}$C in the oceans. In turn, this effect can be used as indicator of severe climatic change if the corals are dated independently using U-decay series. This is one of the major objectives of this thesis.

Records of variation in sea-level provide constraints on numerical models of sea-level change related to mass exchange between the oceans and land-based ice-sheets. However, sea-level change is not spatially uniform due to the isostatic response of the earth to variable loading. At sites near the former ice sheets this response is amplified and the predictions are strongly dependent on the choice of rheology for the Earth model. At sites far from the former ice sheets, isostatic factors are less important and less sensitive to choices of mantle rheology. Thus observations from these locations are mainly dependent on changes in ocean volume and they provide the best estimates of land based ice volumes during glacial periods.

Particularly important is the sea-level minimum at far-field sites which constrains ice volumes at the time of the last glacial maximum (LGM). In addition, the rise in sea-level across continental shelves during the deglaciation phase determines the rate of ice sheet decay and may establish whether melting occurs at a uniform rate or consists of a series of pulses.

A second major objective of this thesis is to quantify sea-levels at and immediately after the LGM by examining the locations of submerged shorelines from tectonically stable areas, in particular, from the Bonaparte Gulf of North Western Australia. The sediment record within cores from this region contain information on the transgression of the sea from the time of the Last Glacial Maximum up until the mid-Holocene. Cores from different depths, where this transition can be defined, provide constraints on the sea-level curve after applying isostatic corrections to extract the eustatic component of the sea-level change.

The appropriate sediment layers, within cores, which usually contain foraminifera and other crustaceans can be radiocarbon dated. The age range of interest is from $\sim$20,000 to present. Calibration of the $^{14}$C time scale within this age range is again a pre-requisite. The number of calibration points presently available between 15,000 and 30,000 years are barely adequate and some controversy exists as to the accuracy of these data. However, corals or other calcareous organisms from within this time period are rare and it has been possible to add only a few points to the available data base for the comparison of calibration $^{14}$C ages and U-Th dates.
In summary, the aims of the thesis are:

1) The reconstruction of sea-level history from far-field sites to establish constraints on ice models at the time of the LGM and during the interval immediately preceding and following this peak in glaciation.

2) The calibration of radiocarbon ages, particularly those older than 30,000 years.

3) The use of the constraints provided by the new chronological scale and far-field data, to test models of glacio-hydro isostasy.

The outline of the following chapters is as follows: Chapter 2 describes $^{14}$C dating methods for Pleistocene samples. The next chapters deal with methods of mass spectrometric Th-U dating of corals. Chapter 4 presents the results of $^{14}$C and Th-U dating. The second part of the thesis deals with observations and models of sea-level change for constraining ice volumes. The record of sediment cores collected offshore from North-West Australia are discussed in Chapter 7 and 8. Finally, chapter 9 includes a summary of conclusions.
Part I.

Radiocarbon timescale calibration
Chapter Two

Radiocarbon dating of late Pleistocene and Holocene samples

§ 2.1 Introduction

Organic samples and atmospheric CO₂ preserved from the late Pleistocene can be radiocarbon dated. The half-life of ¹⁴C is 5730 years and the method has a potential range of up to 50,000 years. In the 1930’s, some naturally radioactive elements, including ¹⁴C, were suspected to be formed in the atmosphere by cosmic radiation. However, ¹⁴C in natural samples, was not discovered until 1947 when Libby, Anderson and co-workers were able to concentrate it from methane originating from sewage and used for lighting in the city of Baltimore (Anderson and Libby, 1947).

Cosmic ray protons from space interact with atmospheric oxygen and nitrogen to produce neutrons in the lower stratosphere and upper troposphere at altitudes of 15 to 18 km. Neutrons, slowed down by numerous collisions, interact with nitrogen in air to produce ¹⁴C through the following reaction:

\[ ^{14}\text{N} + ^{1}\text{n} \rightarrow ^{14}\text{C} + ^{1}\text{H} \]  

Other reactions with stable isotopes of N, O, and C, which also produce ¹⁴C are insignificant (Délibrias, 1989).
There are three naturally occurring carbon isotopes, made up of 99% $^{12}$C, 1% of $^{13}$C and only 1.2 X $10^{-10}$% of $^{14}$C. After $^{14}$C is produced, it rapidly combines with oxygen to form carbon dioxide and is chemically indistinguishable from the other carbon isotopes (Fig. 2.1). It is rapidly distributed in the atmosphere and the oceans and it enters the biosphere through photosynthesis and the food chain. If $^{14}$C production was uniform in the past, then the relationship between production and decay over time are constant.

Living organisms, such as plants and animals, directly or indirectly assimilate atmospheric $^{14}$C when they are alive. In this way, the $^{14}$C radioactivity within living organisms is in equilibrium with the atmospheric $^{14}$C radioactivity. However, after death, carbon exchange with the atmosphere ceases, and $^{14}$C concentration halves every 5730 ± 40 years (Godwin, 1962). The $^{14}$C decay occurs according to the following reaction:

$$^{14}\text{C} \rightarrow ^{14}\text{N} + \beta^- + v + Q \quad (2.2)$$

$\beta^-$ is a negatively charged beta particle, which is identical to an extranuclear electron, and $v$ is an antineutrino. $Q$ is the end point energy (0.156 MeV). The half-life of $^{14}$C is 5730 years. However, for historical reasons, radiocarbon dates are calculated with the so called “Libby half-life” of 5568 years.
The number of decayed atoms $\Delta N$ of a radionuclide in time $\Delta t$ is proportional only to the amount remaining, $N$ and can be written as:

$$\frac{\Delta N}{\Delta t} \propto N \quad (2.3)$$

The constant of proportionality is called the decay constant, $\lambda$. The differential equation from (2.3) is written as:

$$dN / dt = -\lambda N \quad (2.4)$$

Therefore, the amount of $^{14}$C in a sample at any time $t$ is given by,

$$N = N_0 e^{-\lambda t} \quad (2.5)$$

where, $N_0$ is the initial amount of $^{14}$C at $t = 0$. The relationship between decay constant and half-life, $T_{1/2}$, is as follows:

$$\lambda = \frac{\ln 2}{T_{1/2}} = 0.693 / T_{1/2} \quad (2.6)$$

Therefore, from equation (2.5), the formula for radiocarbon age is:

$$t = \frac{-1}{\lambda} \ln \left( \frac{N_0}{N} \right) = \frac{- T_{1/2}}{0.693} \ln \left( \frac{N_0}{N} \right) \quad (2.7)$$

When the current amount of $^{14}$C ($N$) and the half-life ($\lambda$) are known, the radiocarbon age $t$ can be calculated assuming that production rate of $^{14}$C carbon has remained constant ($N_0$ is known). For a chain of nuclides decaying from $N_1$ to $N_3$ via an intermediate nuclide $N_2$, production rate can be written as:

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \quad (2.8)$$

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad (2.9)$$

and the solution is:

$$N_2 = \left[ \frac{\lambda_1}{(\lambda_2 - \lambda_1)} \right] N_1^0 (e^{\lambda_1 t} - e^{\lambda_2 t}) \quad (2.10)$$

where $N_1^0$ is initial number of atoms of parents nuclei $N_1$ at time 0 (Faure 1986).

This formula can be adopted for production of short lived $^{14}$C ($N_2$) assuming a constant rate of production $R$ ($N_1 \lambda_1$) by cosmic rays. From eqn. (2.10), with $\lambda_1 = 0$

$$^{14}C = \frac{R}{\lambda} (1 - e^{\lambda t}) \quad (2.11)$$
where $R$ is the rate at which $^{14}$C is produced, $\lambda$ is the decay constant of the product $^{14}$C. After a long time equilibrium is reached when:

$$\lim_{t \to \infty} (1 - e^{-\lambda t}) = 1$$

(2.12)

and,

$$\lambda (^{14}\text{C}) = R$$

(2.13)

This is the maximum theoretical concentration $^{14}$C can attain in the atmosphere, assuming there are no sinks of $^{14}$C. The production rate of $^{14}$C is 7.5 kg per year and the maximum concentration of $^{14}$C in the atmosphere above present levels would be 5780% (Eqn. 2.13; Siegenthaler et al. 1980). A plot of equation 2.11 is shown in figure 2.2 for cosmic ray produced $^{14}$C.

Fig. 2.2 A simple model calculation of $\Delta^{14}$C increase in the atmosphere, assuming there were no $^{14}$C sinks. The production rate of cosmic ray produced $^{14}$C is taken as 7.5 kg/year. The level of $\Delta^{14}$C in the atmosphere increases rapidly to the saturation point after which production and decay are balanced. The diagram shows the theoretical extreme $\Delta^{14}$C increase in the atmosphere.

Although, basic principles of radiocarbon dating are quite simple, many unknown factors affect the interpretation of the results. Firstly, radiocarbon dating assumes that the radiocarbon production in the past has been constant. However, as tree ring observations have shown, atmospheric radiocarbon concentration has systematically varied in the past. Radiocarbon is produced through reactions induced by cosmic rays. Hence, any fluctuation in the cosmic ray flux, at the source, or due to geomagnetic field fluctuations will affect the rate of radiocarbon
production in the atmosphere. Secondly, isotopes of carbon are fractionated by physical and chemical processes in nature. In general plants and animals tend to preferentially take up the lighter isotopes of carbon so that a modern sample may appear to be older. A correction for this mass dependent isotope fractionation can be applied with reference to standards (see below). Thirdly, introduction of fossil CO₂, after 1860 during the industrial revolution, has resulted in the lowering of ¹⁴C in the atmosphere. In contrast, atmospheric nuclear weapon explosions have produced enormous amount of excess ¹⁴C. Fourthly, although the distribution of ¹⁴C within the atmosphere, the biosphere and surface ocean waters can be relatively fast (<30 years), exchange with the deep ocean waters is more difficult and time scales for mixing can be of the order of 1000 years.

The limit of ¹⁴C dating using conventional β-counting methods is about 35,000 years. In principle, Accelerator Mass Spectrometry (AMS) dating could double this limit, but realistically, the background age at most laboratories is about 40,000 to 45,000 years due to various sources of contamination. Contamination by modern carbon, can be significant for samples older than 20,000 years. For these samples, strategies for minimising contamination during sample preparation and measurement are essential.

To determine past sea-level variations, suitably documented samples including information on location and height above local sea level are required. Sea-level age indicators, such as molluscs, corals or basal peats can be used as ¹⁴C dating materials. Unlike the conventional β-counting methods, AMS requires significantly smaller sample size and small samples such as foraminifera, plant remains, and ostracoda can be used for dating. One milligram of graphite is sufficient for routine dating, and the precision is usually better than one per cent, for example, for Holocene samples.

§ 2.2 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 consists of calcium carbonate, and is therefore suitable material for ¹⁴C dating.

The measured carbon isotope ratios can then be used to calculate the radiocarbon age. The "fraction modern", F, is defined as:

\[ F = \frac{N_0}{N} = \frac{\left(^{14}C / ^{12}C\right)_{\text{sam}}}{\left(^{14}C / ^{12}C\right)_{\text{std}}} \]  

(2.14)
Where \((^{14}C/^{12}C)_{sam}\) is the sample ratio (fractionation corrected and referenced to wood for which the average \(\delta^{13}C = -25 \%_o\), see section 2.3.3), and \((^{14}C/^{12}C)_{std}\) 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 \(-19\%_o\)). The radiocarbon age of the sample is then calculated from (cf., equation 2.7):

\[
\text{Radiocarbon Age} = -\tau \ln F
\]

(2.15)

where \(\tau\) is the Libby mean life \((5568/\ln 2 = 8033\text{ years})\). The age limit of radiocarbon is

\[
F_{\text{limit}} \leq (F_{\text{measured}}^2 + (2\Delta f)^2)^{1/2}
\]

(2.16)

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

§ 2.3 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 (Table 2.1).

§ 2.3.1 Half-life of \(^{14}C\)

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.
Table 2.1 Possible causes of radiocarbon fluctuations (Damon et al., 1978)

I. Variations in the rate of radiocarbon production in the atmosphere
   (1) Variations in cosmic ray flux throughout the solar system
      (a) Cosmic ray bursts from supernova and other stellar phenomena
      (b) Interstellar modulation of cosmic ray flux
   (2) Modulation of the cosmic ray flux by solar activity
   (3) Modulation of the cosmic ray flux by changes in the geomagnetic field
   (4) Antimatter meteorite collisions with the Earth
   (5) Nuclear weapons testing and nuclear technology
II. Variations in the rate of exchange of radiocarbon between the various geochemical reservoirs and changes in the relative carbon dioxide content of these reservoirs
   (1) Control of CO$_2$ solubility and dissolution as well as residence times by temperature variations
   (2) Effect of sea-level variations on oceanic circulation and capacity
   (3) Assimilation of CO$_2$ by the terrestrial biosphere in proportion to biomass and CO$_2$ concentration, and the dependence of CO$_2$ on temperature, humidity and human activity
   (4) Dependence of CO$_2$ assimilation by the marine biosphere upon ocean temperature and salinity, availability of nutrients, upwelling of CO$_2$ rich deep water and turbidity of the mixed layer of the ocean
III. Variations in the total amount of carbon dioxide in the atmosphere, biosphere and hydrosphere.
   (1) Changes in the rate of introduction of CO$_2$ into the atmosphere by volcanism and other processes that result in the CO$_2$ degassing of the lithosphere
   (2) Various sedimentary reservoirs serving as a sink for CO$_2$ and hence $^{14}$C. The tendency for changes in the rate of sedimentation to cause changes in the total CO$_2$ content of the atmosphere
   (3) Combustion of fossil fuels by human industrial and domestic activity

§ 2.3.2 Global radiocarbon distribution

The $^{14}$C produced in the atmosphere is partly exchanged with oceans and partly enters the biochemical carbon cycle. Although there is rapid mixing between the atmosphere, biosphere and surface waters, mixing rates between the atmosphere and the deep ocean are slow and radioactive decay is significant such that waters in deep Pacific trenches can be as old as 2000 years. Surface waters exchange CO$_2$ rapidly with the atmosphere, however, there is a difference between atmospheric and surface waters, called the marine reservoir effect, due to mixing with older deep water in regions of upwelling dependent on latitude. On average, $^{14}$C in surface waters is depleted by about 5%, which is equivalent to a residence time of 400 years (Bard, 1988). Therefore, an age correction for each of these factors may need to be applied to dated samples.
§ 2.3.3 Isotopic fractionation

When plants use CO₂ from the atmosphere for photosynthesis, they preferentially take up ¹²CO₂ rather than ¹³CO₂ or ¹⁴CO₂. Similarly, incomplete conversion of CO₂ during sample processing can affect carbon isotope composition in a mass dependent fashion. This isotopic fractionation is quantified by the ratio of ¹³C to ¹²C relative to PDB (Peedee belemnites) standard, *Belemnitella americana*, collected from the Cretaceous Peedee Formation. The fractional difference relative to standard, δ¹³C is defined as:

\[
\delta^{13}C = \left[ \frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{PDB}}}{(^{13}C/^{12}C)_{\text{PDB}}} \right] \times 1000 \quad (\%) \quad (2.17)
\]

Uncertainty in δ¹³C and by inference in the ¹⁴C/¹²C ratio contributes to the age error, although this can be minimised by measurement of δ¹³C using mass spectrometry. Some naturally occurring δ¹³C variations are listed in Table 2.2. The age correction is 16 years per % difference from -25%, illustrating the need for fractionation correction to be made to the measured radiocarbon results.

<table>
<thead>
<tr>
<th>Material</th>
<th>Δ³C Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood, peat and many C₃ plants</td>
<td>-25%</td>
</tr>
<tr>
<td>Bone collagen</td>
<td>-19%</td>
</tr>
<tr>
<td>Freshwater plants</td>
<td>-16%</td>
</tr>
<tr>
<td>Arid zone grasses</td>
<td>-13%</td>
</tr>
<tr>
<td>Marine plants</td>
<td>-12%</td>
</tr>
<tr>
<td>Maize</td>
<td>-10%</td>
</tr>
<tr>
<td>Atmospheric CO₂</td>
<td>-8%</td>
</tr>
<tr>
<td>Marine carbonates</td>
<td>0%</td>
</tr>
</tbody>
</table>

* The ranges on these data are typically ±2 or 3% but substantially more variability is possible.

The NBS oxalic acid standard is widely used as reference in carbon isotope work (Olsson, 1970). The δ¹³C of NBS oxalic acid is equivalent to -19 % of PDB. The activity of the oxalic acid is referenced to wood grown between 1840 and 1860 AD to avoid contamination from use of fossil fuels later in the century. It is equal to 95% of the ¹⁴C activity of NBS oxalic acid, in AD 1950, normalised to δ¹³C = -19 per mil with respect to PDB (Stuiver and Polach, 1977) and corrected for isotope fractionation arising from conversion of oxalic acid to CO₂. Craig studied the dependency of oxalic acid’s δ¹³C value under different experimental conditions. When combusted dry, δ¹³C is -19.3%; when combustion is wet, it is -19.6% (Craig, 1954; 1961). Most laboratories around the world use CO₂ from the oxalic acid
standard, in each batch, to determine the correction factor. As the isotopic fractionation factor depends on mass differences, the $^{14}\text{C}/^{12}\text{C}$ fractionation factor is double that of $^{13}\text{C}/^{12}\text{C}$. Hence, measured radiocarbon activity is corrected using the approximate expression:

$$A_N = 0.95 A_{\text{ox}} \left[1 - 2(19 + \delta^{13}\text{C})/1000\right]$$  \hspace{1cm} (2.18)

where $A_N$ is 95% of measured oxalic activity, corrected for fractionation, with $\delta^{13}\text{C} = -19 \%o$, and $A_{\text{ox}}$ is the activity of CO$_2$ gas prepared from the oxalic acid standard.

When samples with isotopic composition that differ from the value for average wood ($\delta^{13}\text{C} = -25\%o$) are measured, the measured activity is corrected using:

$$A_{\text{SN}} = A_s \left[1 - 2(25 + \delta^{13}\text{C})/1000\right]$$  \hspace{1cm} (2.19)

where $\delta^{13}\text{C}$ is the difference between the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample and that of the standard (PDB). $A_s$ is the measured activity of the sample that has not been corrected for isotope fractionation. $A_{\text{SN}}$ is the normalised activity. The radiocarbon age can be derived using equation (2.9) where:

$$F = A_{\text{SN}} / A_N$$  \hspace{1cm} (2.20)

The $^{14}\text{C}$ age, corrected using the relevant isotopic fractionation factors, with the Libby half-life of 5568 years (equivalent to $1/\lambda = 8033$ years, mean life), is referred to as the conventional radiocarbon age (Stuiver and Polach, 1977). Calibration procedures and various geochemical parameters related to radiocarbon dating are summarised in the Table. 2.3 (Stuiver and Polach, 1977).

Usually, marine carbonates have $\delta^{13}\text{C}$ values around -2 to +3 %o in comparison to wood with $\delta^{13}\text{C} = -25\%o$. If isotope fractionation is ignored, the marine samples would be ~400 years younger; and the effect is important for relatively young samples. In comparison, the difference in $^{14}\text{C}$ activity between surface ocean water and the atmosphere is about -4% to -5%, which is equivalent to 320-400 years (450±40 year older in the North Atlantic). Therefore, corrections for $^{13}\text{C}$ fractionation and reservoir $^{14}\text{C}$ deficiency approximately cancel each other out for carbonate shells from non-polar regions (see below).
Table 2.3. Calibration and geochemical parameters for conventional radiocarbon dating

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxalic acid (standard)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net activity</td>
<td></td>
</tr>
<tr>
<td>Normalisation for isotopic fractionation. All $\delta^{13}C$ values with respect to PDB.</td>
<td>$A_{SN} = A_S \left[1 - \frac{2(25 + \delta^{13}C)}{1000}\right]$</td>
</tr>
<tr>
<td></td>
<td>$A_{OX} = 0.95A_{OX} \left[1 - \frac{2(19 + \delta^{13}C)}{1000}\right]$</td>
</tr>
<tr>
<td>Absolute international standard activity (Oxalic acid activity). Correlated for decay since 1950.</td>
<td>$A_{ABS} = A_{ON}e^{\lambda(y-1950)}$</td>
</tr>
<tr>
<td>$x$ = year of growth</td>
<td>$\lambda$ in Table always (1/8267) yr$^{-1}$</td>
</tr>
<tr>
<td>$y$ = year of measurement</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Geochemical samples</th>
<th>Geochemical samples without age correction</th>
<th>Geochemical samples with age correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per mil depletion or enrichment with regard to standard</td>
<td>$\delta^{14}C = \left[\frac{A_S}{A_{OX}} - 1\right] \times 1000$ (%)</td>
<td>$\delta^{14}C = \left[\frac{A_S}{A_{ABS}} - 1\right] \times 1000$ (%)</td>
</tr>
<tr>
<td>Equivalent equation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Per mil depletion or enrichment relative to standard normalised for isotope fractionation</td>
<td>$D^{14}C = \left[\frac{A_{SN}}{A_{OX}} - 1\right] \times 1000$ (%)</td>
<td>$\Delta^{14}C = \left[\frac{A_{SN}}{A_{ABS}} - 1\right] \times 1000$ (%)</td>
</tr>
<tr>
<td>Equivalent equation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Approximate relationship</td>
<td>$\delta^{14}C = \delta^{13}C - 2(5\delta^{13}C - 25)(1/8267) \times 1000$</td>
<td>$\delta^{14}C = \delta^{13}C - 2(5\delta^{13}C - 25)(1/8267) \times 1000$</td>
</tr>
<tr>
<td>Conventional radiocarbon age BP, based on 5568 yr half life</td>
<td>$t = -8033\ln \frac{A_{SN}}{A_{ON}}$</td>
<td></td>
</tr>
<tr>
<td>$\lambda = (1 / 8033)^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Always report</td>
<td>$\delta^{13}C$ and conventional radiocarbon age</td>
<td>$\Delta^{14}C$, $\delta^{14}C$ and $\delta^{13}C$</td>
</tr>
<tr>
<td>Optional</td>
<td>$d^{14}C$ and $D^{14}C$</td>
<td>$p.M = \frac{A_{SN}}{A_{ABS}} \times 100$ (%)</td>
</tr>
</tbody>
</table>
§ 2.3.4 Marine reservoir effect

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 \(^{14}\text{C}\) 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. 2.3). 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 \(^{14}\text{C}\) 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).

![Fig. 2.3. Natural \(^{14}\text{C}\) in surface waters of three oceans reconstructed from various sources (after Bard, 1988).](image)

Ages of various marine reservoirs have been estimated by numerical modelling, and combined with measurements of shell and coral \(^{14}\text{C}\) ages, with known calendar ages (ie. 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 (ie; 0 to -75m) 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. 2.4; 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.

Fig. 2.4. Regional-specific surface ocean reservoir age, $\Delta R$, in world oceans (after Stuiver and Braziunas, 1993). In the Southern Hemisphere, the correction to $\Delta R$ is 362 years. For the northern oceans the correction to $\Delta R$ is 402 years.

§ 2.3.5 Variation of the radiocarbon production rate

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).

§ 2.3.6 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 (Fig. 2.5). 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 will be discussed further in a later chapter.

§ 2.3.7 Anthropogenic effects

Combustion of fossil fuels since the beginning of the industrial revolution resulted in the release of $^{14}$C depleted CO$_2$ into the atmosphere. Suess observed that activity of 20th century wood was ≈2% lower than that of 19th century wood (Fig 2.6). The phenomenon is known as the Suess effect.

Another effect resulted from testing of nuclear weapons in the atmosphere which caused a temporary increase in atmospheric $^{14}$C levels by more than a factor of 2 during 1962-63, compared to the pre 1950 levels (Fig. 2.6). Due to rapid mixing between the northern and southern hemispheres (~4 years) and exchange with the oceans, the atmospheric $^{14}$C levels are now less than 15% above natural levels. The $^{14}$C pulse has also been useful as a tracer to study the rates of exchange between various reservoirs.

Fig. 2.6. Atmospheric $^{14}$C variation deduced from the tree-rings (after Bowman, 1990).
§ 2.4 Methods of radiocarbon dating

There are two methods of \(^{14}\text{C}\) dating. The original method involved counting \(\beta^\text{-}\) rays from the decay of \(^{14}\text{C}\) (eqn. 2.2), called the conventional radiocarbon dating. In the more recently devised method the relative number of \(^{14}\text{C}\) atoms in the sample are counted directly using accelerator mass spectrometry, AMS.

§ 2.4.1 Conventional radiocarbon dating

The \(\beta^\text{-}\) ray method has been in use since the radiocarbon method was first introduced. Several variations of the method depend on the nature of the sample after preparation. However, only liquid scintillation and gas counting are now widely used. All analyses carried out at the \(^{14}\text{C}\) dating laboratory at ANU are based on the liquid scintillation counting using benzene (\(\text{C}_6\text{H}_6\)).

§ 2.4.1.1 Liquid scintillation counter technique

Liquid scintillation counting (LSC) involves converting carbon dioxide from the sample into benzene. Liquid benzene, which has 6 atoms of carbon per molecule, minimises the volume of the sample container. The benzene synthesis reaction is as follows (Polach and Stipp, 1967).

\[
2\text{CO}_2 + 8\text{Li} \rightarrow 2\text{C} + 4\text{Li}_2\text{O} \quad (2.21)
\]

\[
2\text{C} + 2\text{Li} \rightarrow \text{Li}_2\text{C}_2 \quad (2.22)
\]

by (2.21) + (2.22), we obtain

\[
2\text{CO}_2 + 10\text{Li} \rightarrow \text{Li}_2\text{C}_2 + 4\text{Li}_2\text{O} \quad (2.23)
\]

The \(\text{CO}_2\) from the sample is released in a metal reaction vessel, which is then heated to high temperature. The reaction between the sample \(\text{CO}_2\) and molten lithium produces lithium carbide (Gupta and Polach, 1985):

\[
4\text{Li} + 2\text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{O} + \text{C} \quad (2.24)
\]

\(\text{Li}_2\text{C}_2\) is then hydrolysed to make acetylene.

\[
\text{Li}_2\text{C}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + 2\text{LiOH} \quad (2.25)
\]

\[
2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2 \quad (2.26)
\]
Finally, $\text{C}_2\text{H}_2$ is trimerised to benzene with the catalyst ($\text{V}_2\text{O}_5$).

$$\text{V}_2\text{O}_5$$

$$3\text{C}_2\text{H}_2 \longrightarrow \text{C}_6\text{H}_6$$  \hspace{1cm} (2.27)

The resulting benzene (1-3 cc and equivalent to 0.9-2.7 g of carbon) is then mixed with scintillator liquid to detect β emissions.

Features of benzene LSC are as follows:
1. Low β background.
2. High yield of carbon from the samples.
3. Low running cost.
4. Counting of β emissions from sample, background, and standards can be automated (Groots et al., 1983).

Disadvantage of this method is larger sample requirement (~10 – 30 g of CaCO$_3$).

Thus, the LSC technique is widely used when sufficiently large samples are available.

§ 2.4.2 Accelerator Mass Spectrometry

In Accelerator Mass Spectrometry, $^{14}$C atoms are counted directly. In a mass spectrometer, the magnetic field deflects a moving, usually singly charged, particle. Charged particles of different mass, but the same velocity, are deflected along different trajectories and collected in multiple Faraday cups along the focal plane. Alternatively the magnetic field can be cycled to deflect different masses into the same Faraday cup. Standard mass spectrometers do not have the sensitivity to separate $^{14}$C from atoms or molecules with similar mass, such as $^{14}$N, $^{12}$CH$_2$ and $^{13}$CH$_2$. The accelerator mass spectrometer follows the same principles, but by coupling the mass spectrometer with an accelerator, it is possible to accelerate the particles to MeV energies as opposed to 5-10 keV in conventional mass spectrometers. A multi-wire gas proportional detector sorts the incoming ions by mass, atomic number and charge state.

Direct counting of $^{14}$C atoms results in significant improvement in efficiency and reduction in sample size. A 1 mg modern carbon sample can produce 10 to 20 μA of current (60-120 x10$^{12}$ atoms of $^{12}$C and 70-140 atoms of $^{14}$C per second) in a caesium ion source. Two minutes of collection is sufficient to achieve a statistical precision of 1%. The equivalent β$^-$ counting time is about 1.4 years (Duplessy and Arnold, 1989).
There are several methods for producing graphite targets from CO₂ (Table 2.4). The methods used in the present work were adopted from those described by Vogel et al. (1984, 1987). This method has advantages compared with others, not only in minimising contamination by 'young' carbon, but also, because it has a high yield of C, from the reduction of CO₂. In addition, isotopic fractionation during the reduction process is minimal. The procedure will be described in greater detail in below.

Table 2.4 Conversion methods graphite target from sample CO₂

<table>
<thead>
<tr>
<th>Methods</th>
<th>Reaction(s) to produce the carbon</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Li conversion</td>
<td>2CO₂ + 10 Li -&gt;4Li₂O + Li₂C₂</td>
<td>1) Memory effects from the Li reactor.</td>
</tr>
<tr>
<td>via C₂H₂ to C</td>
<td>Li₂C₂ + 2H₂O-&gt;C₂H₂+ 2Li₂C₂</td>
<td>2) Beam intensity of C is low because of the carbon polymers.</td>
</tr>
<tr>
<td>b) Reduction of CO₂ with Zn and dissociation CO</td>
<td>CO₂ --------&gt; CO</td>
<td>1) Background level, 2.5% MODERN.</td>
</tr>
<tr>
<td></td>
<td>400°C</td>
<td>2) The typical yield is about 80%.</td>
</tr>
<tr>
<td></td>
<td>CO + H₂---------&gt; C + H₂O</td>
<td></td>
</tr>
<tr>
<td>c) Reduction of CO₂ with Fe catalyst</td>
<td>CO₂ + 2H₂ --------&gt; C+ 2H₂O</td>
<td>1) High C yielded (&gt; 90%) can be succeeded by controlling the H₂ pressure.</td>
</tr>
<tr>
<td></td>
<td>650°C</td>
<td>2) Backgrounds are equivalent to 40 ka to 50 ka.</td>
</tr>
</tbody>
</table>

(Data from: Duplessy and Arnold, 1989; Andree et al., 1984; Kitagawa, 1993)

§ 2.5 Tandem Accelerator Mass Spectrometry

§ 2.5.1 Accelerator mass spectrometry at ANU

The AMS facility of the Department of Nuclear Physics, Research School of Physical Sciences and Engineering is used for the study of ¹⁰Be, ¹⁴C, ²⁶Al, ³⁶Cl, ⁵⁹Ni, and ¹²⁹I isotopes. This is a large accelerator that can reach up to 15MV on the terminal (Fig. 2.7).
Fig. 2.7 14UD AMS at ANU (after Fifield et al., 1992).
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 $^{12}\text{C}$ beam is chopped by a factor of about 89 to 1 so that $^{12}\text{C}$ and $^{13}\text{C}$ have roughly equal intensities. The terminal voltage is set to 6MV and 30 MeV $^{14}\text{C}^{4+}$ is selected for the analysing magnet. The $^{12}\text{C}$ and $^{13}\text{C}$ beams are measured in a Faraday cup placed behind the analysing magnet. The $^{14}\text{C}$ beam is detected in a heavy ion gas proportional counter (Fig. 2.8). For 1mg of graphite sample, the ion source can produce 10-20 μA of carbon ions. Typical precision of $^{14}\text{C}$ measurement is 1%. This is not as good as achieved at other dedicated $^{14}\text{C}$ laboratories (eg. < 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.

The AMS equipment can be divided into three parts: the ion source and first separation section, acceleration section and the detection section (Fig. 2.9).
Fig. 2.8. Figure showing the clear separation of $^{14}$C signal using AMS.
§ 2.5.2 The ion source and first separation

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

\[
E = qeV = \frac{1}{2}mv^2
\]  
(MeV) \hspace{1cm} (2.28)

where \(m\) is the mass, \(V\), 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 \(V\). However, velocities of these ions differ depending on their masses:

\[
v = \sqrt{\frac{2qeV}{m}}
\]  \hspace{1cm} (2.29)

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

$$R = \frac{mv}{qeV_1} \tag{2.31}$$

From equations (2.20) and (2.22), velocity can be eliminated to give:

$$\frac{2qeV_1}{m} = \frac{B^2q^2e^2R^2}{m^2} \tag{2.32}$$

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.

§2.5.3 Ion acceleration and detection section

Negative ions injected into the accelerator are first accelerated to the positive terminal voltage $V_2$ (Fig 2.9) which is at a few megavolts. At the terminal, polyatomic molecules, such as $^{13}$CH$^-$ and $^{12}$CH$_2^-$, 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 $^{14}$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 $^{14}$C:

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

§ 2.6 Sample preparation for AMS $^{14}$C measurement

There are several methods for preparing AMS targets for $^{14}$C 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). In the present study, the latter method was employed using Fe powder to catalise graphite.

§ 2.6.1 Design of the $^{14}$C preparation system

To reduce the possibility of contamination during the CO$_2$-graphite conversion process we have strived to exclude all sources of organic contamination. For this purpose an all metal high-vacuum system was constructed with strict control protocol on its use including the type and age of samples allowed to be processed. The conversion line was made using 1/4” stainless steel tubing with ‘Swage-Lock’ joints and stainless steel bellow valves (Fig. 2.7). All of the component parts were cleaned to remove organic residues and baked under vacuum for extended periods. The line is evacuated using a turbo-molecular pump with a liquid nitrogen trap to prevent oil contamination from the pump. Vacuum of $>10^4$ Torr can be maintained during sample processing.

Vacuum is monitored using two thermocouple gauges and quantitative CO$_2$ and H$_2$ pressures are measured by two pressure transducers, Baratron, which have accuracies of ±0.05% and ±0.5%. The more precise Baratron is used for low pressure measurements to monitor the yield of the gasses produced from the sample within a calibrated volume, and other is used to monitor H$_2$ pressure, at the output, for the reduction process and has a higher pressure capacity. The volume of the Baratron, sample-gas storage vessel, and connecting spaces was calibrated using CO$_2$ produced from precisely weighed amounts of ANU sucrose ($C_{12}H_{22}O_{11} = 342g/mol$). The results are shown in Fig. 2.11. The measured pressure and weight of sucrose vary in proportion, confirming the accuracy and linearity of the Baratron, within errors.
Fig. 2.10. Diagram of reactor apparatus used for the graphitisation CO$_2$ on a Fe powder catalyst. Also shown is the reaction vessel in which the samples are dissolved and the graphitisation apparatus with attached pressure transducer. Numbers correspond to explanations in the text.

Fig. 2.11. Volume-pressure calibration of the CO$_2$ storage volume.
§ 2.6.2 Preparation of all equipment and reagents

A modified graphite production method as described by Vogel et al., (1984) was employed in the present study. This graphitisation method reliably produces high graphite yields (>85-95%). Water is produced as the by-product of the reaction:

\[
\text{(Fe)} \quad 2\text{H}_2 + \text{CO}_2 \rightarrow \text{C} + 2\text{H}_2\text{O} \quad (2.33)
\]

\[625^\circ\text{C}\]

The addition of dry ice cold traps efficiently trapped water vapour away from the sample and even higher graphite yields (~100%) could be achieved.

To obtain approximately 1 to 1.5 mg of graphite, ~1.2 to 1.8 mg of pre-reduced 325 mesh iron powder was used, typically, with C:Fe ratio of 1 to 1.2. A Vycor thimble cup (6mm diameter and ~1cm long) with iron powder was then placed in a larger diameter Vycor tube (9mm diameter and ~15 cm long) and labelled. All Vycor glass-ware were pre-cleaned ultrasonically with distilled water and baked over-night at 900 °C. The reaction tube and connecting pieces were cleaned in 1:1 HNO₃ and rinsed with distilled water, then stored in an oven at ~60 °C until needed. Phosphoric acid (85%) was concentrated on a hot plate with an equal amount of H₂O₂ (30%) to oxidise and remove organic impurities.

§ 2.6.3 Textural inspection under the microscope

Coral samples were inspection under an optical microscope. For each sample, thin sections along the coral longitudinal and latitudinal growth axes were prepared. In general, secondary alteration was present at the interstices but not within wall structures as shown in Fig 2.12.
Fig. 2.12a Photomicrographs of latitudinal section of a favid coral from Huon Peninsula, reef II in cross-polarised light. Well preserved original aragonite structures are found in both cases. Minor, needle-like secondary fillings are found only around the edge of "septa", not in thick "wall" sections. The field of view is 400 μm.
Fig. 2.12b Photomicrographs of latitudinal section of a favid coral from uplifted Holocene reef at Madang, at Huon Peninsula, in cross-polarised light. Well preserved original aragonite structures are found in both cases. Minor, needle-like secondary fillings are also found in this late Holocene coral. The field of view is 400 μm.
Fig. 2.12c Photomicrographs of longitudinal section of a favid coral from reef III of Kanzarua section, Huon Peninsula. Lower picture is a blown up view. Cross-polarised light. Well preserved original aragonite structures are found in this section, with minimal secondary filling. The field of view is 400 μm and 800 μm, respectively.
Fig. 2.12d  (a) Photomicrographs of *Porites* coral from reef IIa from Kanzarua, Huon Peninsula in crossed polarised light. Well preserved original aragonite structures can be seen. (b) Photomicrographs of diagenetically altered coral from LIG reef in Huon Peninsula. This coral has ~10% of calcite. Secondary calcite appears to be replacing primary aragonite. Field of view for both pictures is 400 μm.
§ 2.6.4 XRD calcite measurements

Calcite content of each sample was determined from X-ray powder diffraction spectrum. The measurements utilised CuKα radiation (40 kV, 30 mA) and a scintillation counter. The scan rate was 2°20 per minute. Approximately 300 mg of powdered coral was used for each test. The detection limit for calcite in this procedure for was about 2 %. (Klug and Alexander 1974).

![XRD traces of corals](image)

Fig. 2.13. Example of XRD traces of corals used in the present study.

§ 2.6.5 Pre-cleaning of samples

Both corals and bivalves were inspected under a magnifier and, where possible, physically cleaned using a dental drill to remove interstitial structures other
than walls. The samples were cleaned with distilled water in an ultrasonic bath. They were then dried in an oven (\(-40-60^\circ C\)) and weighed. Minimum required amount of CaCO\(_3\) to yield 1 mg of carbon is approximately 8.5 mg. However, we used larger sample sizes (2-3 mg), for step-wise selective dissolution, to check for \(^{14}C\) contamination.

\(\S\ 2.6.6\) CO\(_2\) production and purification

Contamination by material containing younger carbon shifts "true" radiocarbon ages to younger values. This might occur not only during the laboratory process, but also in the natural environment through diagenesis and recrystallisation. Selective dissolution by step-wise leaching could help to identify contaminated samples.

For bivalves and forams, the first \(\sim 40\%\) of evolved CO\(_2\), corresponding to 40 % of its total weight was discarded, and the remainder was used for graphitisation. With corals, the first 50% of CO\(_2\) was discarded and the last 50% was collected in three or four steps.

The reaction vessel was designed to facilitate selective dissolution. It consisted of three separate compartments, the main chamber for sample dissolution, and two accessory branches for phosphoric acid. The vessel was connected by a Cajon Ultra torr fitting (1) to the main vacuum line (2; Fig. 2.10). After 1.5 hours of pumping and out-gassing of the acid, a vacuum of \(10^{-4}\) Torr could be achieved. The vessel was then tilted to drip acid (3) onto the sample (4) to start the reaction. The CO\(_2\) produced was dried by passing through two spiral traps (5) immersed in a dry ice-ethanol mixture (-78.8 °C), and cryogenically collected (6) at liquid nitrogen temperature. The CO\(_2\) pressure (7) was measured at intervals to determine the amount of sample dissolved. The dried CO\(_2\) was then transferred \textit{via} one of several outlets (8) to the graphitisation apparatus that consisted of a 6 mm diameter Vycor thimble containing iron powder placed inside a \(\sim 15\) cm long, 9 mm diameter Vycor tube. The iron powder had previously been reduced \textit{in-situ} with \(\sim 400\) Torr H\(_2\) at 400 °C for several hours. The set-up includes a cold finger to trap water vapour, and a pressure transducer to monitor the progress of the conversion reaction. The apparatus has a double valve system for isolating and removing it from the vacuum system (see Fig. 2.10). ANU sucrose, whose \(^{14}C\) activity corresponds to \(1.5061 \pm 0.11\) pM (per cent modern) was used as a standard (Rozanski et al., 1992). The sucrose was weighed and placed in a Vycor tube (6 mm diameter and \(\sim 20\) cm long), with CuO and Ag wire. The tube was evacuated and sealed with a torch and placed in an
oven at 900 °C for 8 to 10 hours to combust and convert the sucrose to CO₂. The rest of the procedure is the same as that used for samples.

§ 2.6.7 Graphitisation

Approximately 2.2 times more molar fraction of H₂ than CO₂ was used for the graphitisation reaction. After evacuation (<10⁻⁴ Torr), the valves to the apparatus were closed and the end of the tube inserted into a high temperature oven at 625 °C. Water vapour produced by the reaction was removed by a cold finger in a dry-ice ethanol bath attached to the graphitisation apparatus. The variation in pressure was monitored with the pressure transducers (Fig. 2.14). The pressure readings indicate that most of the conversion had occurred during the first 0.5 to 1 hour and almost completed within 3 hours. However, to ensure complete reaction, the process was continued for at least 6 hours (Fig. 2.15).

Graphite yields were calculated by both weighing the residue and from the measured pressure difference, and range from 82% to 100%. Typically they were greater than 95%. We have not observed any significant carbon isotope fractionation related to the graphitisation procedure (e.g., McNichol et al., 1992; Kitagawa et al., 1993; Brown and Southon, 1997).
§ 2.6.8 Background of the system

Background $^{14}$C levels have been monitored constantly using the international old calcite standard, IAEA-C1 (Rozanski et al., 1992). The range of background values are from 0.04 pM to 0.30 pM, and typically 0.25 pM which corresponds to 48,000 years (Fig. 2.16). Thus, it should be possible to reliably measure samples as old as 40,000 years using the present system and procedures.

Fig.2.16. Example of measured value of IAEA-C1 (international carbonate standard that has no $^{14}$C) used to monitor total procedural blank. Wheel number are in time sequence. In this figure, most recent run is #94.
§ 2.7 Summary

Radiocarbon dating is widely used for samples up to 45,000 years old. Carbon-14 is produced in the upper atmosphere through the interaction of cosmic rays with atmospheric $^{14}$N. Shortly after its production, $^{14}$C is oxidised and distributed globally as CO$_2$. Through respiration, photosynthesis and the food chain, the concentration of $^{14}$C in organisms equilibrates with atmospheric values. After death, there is no more exchange and $^{14}$C is depleted by decay. Knowing the initial $^{14}$C concentration in the atmosphere and the half life, the timing of the death can be determined.

Although radiocarbon dating is quite a useful tool in various Quaternary studies, deriving 'true' ages may not be straightforward. Among the many factors affecting age determinations, isotope fractionation, assumption of closed system behaviour, past fluctuations in the radiocarbon production rates, and past re-distributions in the atmosphere-ocean-biosphere carbon reservoirs need to be considered.

Diagenetic processes can alter the original $^{14}$C concentration in a sample. Alteration in corals or marine carbonates, through secondary carbonate deposition and/or recrystallization is one of the main causes of carbon contamination. In particular, older age samples, greater than 20,000 years old, are much more susceptible to contamination by younger age carbon than from dilution by 'old' carbon. Hence, it is important to screen samples for indications of open system behaviour. In the present work, we consider that the most reliable test of open system behaviour involves screening of each sample through stepwise dissolution followed by $^{14}$C age measurement on each aliquot. Only those samples that show a consistent age, from interior material, are deemed to exhibit true $^{14}$C ages. However, even for these, it is not possible to be 100% decisive.

Sample from a marine environment require additional corrections. The reservoir correction reflects the difference in $^{14}$C levels between the atmosphere and the surface ocean. On average, the difference is approximately 5% or $\sim$400 years.

Past variations in atmospheric radiocarbon concentrations are well known. The variation is monotonic and corresponds to a gradual increase in the strength of the geodynamic filed during the past 50,000 years to 10,000 years. Over the past 10,000 years there have been higher frequency components superimposed on the gradual variation that are best explained by solar magnetic fluctuations. For most of
the time through the last 50,000 years, radiocarbon concentrations in the atmosphere were higher than present, biasing the sample ages toward younger values. These issue are further discuss in detail in a later chapter.
Chapter Three

Uranium series dating of corals

§ 3.1 Introduction

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

\[
238 \text{U} \rightarrow 234 \text{U} \rightarrow 230 \text{Th} \rightarrow 206 \text{Pb}_{\text{stable}} \tag{3.1}
\]

(4.49x10⁹ yr) (2.48x10⁵ yr) (7.5x10⁴ yr)

where the numbers in brackets are half-lives of the decay from one element or isotope to another. The full decay scheme is shown in Fig. 3.1.

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 into sediments. Thus, living corals have negligible thorium abundance; the subsequent $^{230}\text{Th}/^{238}\text{U}$ ratio is the result of $^{238}\text{U}$ decay after the coral has died, provided there is no exchange of U and Th through diagenesis (closed system requirement).
The $^{230}$Th age is derived from the following equation (Kaufman and Broecker, 1965; Edwards et al., 1987):

$$ (3.2) $$
where $T$ is the age in years, $\lambda$ the decay constant for each nuclide act refers to activity ratio:

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

(3.3)

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

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

(3.4)

where, $\left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{eq}} = \frac{\lambda_{238}}{\lambda_{230}} = 5.472 \times 10^{-5}$ is the atomic ratio at secular equilibrium.

Figure 3.2 (i) shows the relationship between the measured $^{234}$U/$^{238}$U ratio, $\delta^{234}$ U (0), and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$. The contours are in units of $\delta^{234}$U(T) (quasi horizontal curves) and $T$ (vertical lines). The decays of excess $^{238}$U with time is shown in Fig. 3.2 (ii). Fig3.2 (iii) shows the simultaneous growth of $^{230}$Th. $^{230}$Th equilibrates after $\approx 350$ kyr whereas $^{234}$U takes longer $\approx 1200$ kyr. For coral samples, older than 280 kyr, the $^{230}$Th/$^{238}$U activity ratio can be larger than 1. If there were no initial $^{230}$Th present in the coral, the age, T, can be calculated using the measured $^{234}$U/$^{238}$U ratio ($\delta^{234}$ U (0)), and assuming that the $^{234}$U/$^{238}$U ratio at the time of coral growth ($\delta^{234}$ U (T)) was the same as the present day sea-water value:

\[
\delta^{234} \text{U}(T) = \delta^{234} \text{U}(0) e^{-\lambda_{234} T}
\]  

(3.5)

However, by measuring both $^{234}$U and $^{230}$Th abundances, no assumptions need be made about the $^{234}$U/$^{238}$U sea-water ratio at the time of coral growth (Eq. 3.2). 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 sea-water concentration of $^{234}$U.
Fig. 3.2 (i) Measured $^{234}$U/$^{238}$U plotted as a function of $^{230}$Th/$^{238}$U activity ratio. Contours depict variations in $\delta^{234}$U(T) (horizontal), and age T (vertical lines). Unaltered corals lie along the $\delta^{234}$U(T) = 150% contour. Open system behaviour results in departures from this line in a loose array to older ages and higher values of $\delta^{234}$U(T). Curves (ii) and (iii) show the decay of the excess $^{234}$U and simultaneous growth of $^{230}$Th, respectively and approach secular equilibrium.
§ 3.2 Uranium series dating

Over the last decade, the traditional α-counting method has been superseded by direct measurement of the abundances U and Th isotopes using thermal ionisation mass spectrometry TIMS (Chen et al., 1986).

§ 3.2.1 α-counting

This is the conventional method for Uranium series dating where α- particles from decay are counted. The various isotopes can be recognised from their α- 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 (5-10g 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 1995).

§ 3.2.2 Thermal Ionisation Mass Spectrometry

Advantages of TIMS compared with conventional α-counting methods include a) higher-precision (conservatively a factor of 2 to 3), b) applicable over an extended age range (months to ~ 500 ka), c) smaller sample size (=1g compared with =5g), d) rapid analysis (hours instead of days) and, e) clearer evaluation of the degree of open system behaviour by precise measurement of δ²³⁴U (T) and δ²³²Th.

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 present study, 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).

§ 3.3 Chemical separation of Uranium

The $^{230}$Th/$^{238}$U relative abundance and the $^{234}$U/$^{238}$U isotope ratio are measured using TIMS and methods of isotope dilution. Isotope dilution involves adding a known amount of enriched isotope tracer to the sample. For U and Th the tracer is an artificial long-lived radionuclide of U and Th.
The presently used pre-treatment technique follows the method of 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).

§3.3.1 Pre-cleaning of samples

Coral samples are inspected in sunlight for traces of "glitter" from calcite and then broken to cm-sized pieces to expose many surfaces. We have established that samples with greater than 4% calcite can be visually identified in this way. Selected pieces are then physically cleaned using a hand held diamond abrasive wheel under a magnifying lens to remove delicate lattice structures and septa that are presumably easier to alter or fill with extraneous material than solid wall sections. This is possible for Favid species corals which have solid wall sections but not for Porites corals. It has previously been established that samples cleaned in this way yield $^{234}\text{U}/^{238}\text{U}$ ratios closer to the sea-water value (Stirling et al., 1995). Therefore, Favids are preferred whenever available. The physically cleaned coral pieces are then rinsed in acetone, alcohol and de-ionised water in an ultrasonic bath.

§3.3.2 Sample dissolution and addition of spike

For samples up to 50,000 years old, we have used approximately 2 to 3 g of cleaned coral, which contain 25 to 35 pg of $^{230}\text{Th}$ and 5 to 8 pg of Uranium. The cleaned samples were dried in a laminar air-flow chamber and weighed. The samples were then covered with distilled water and slowly dissolved by adding concentrated HNO$_3$. Weighed, mixed-spikes ($^{230}\text{Th} - ^{233}\text{U} - ^{236}\text{U}$) were then added after first drying the sample to remove trace amounts of HF which help keep Th in solution in the spike bottle. To eliminate any remaining organic matter in the solution, concentrated H$_2$O$_2$ is added. The solution is then slowly dried, usually overnight, to drive off CO$_2$ and to ensure complete sample-spike equilibration. The residue is then dissolved in 1N-HNO$_3$.

§3.3.3 Co-precipitation of hydrolysable metals and separation of U and Th

In corals, both U and Th exist only in relatively small amounts (parts per million and parts per billion, respectively). A small amount of FeCl$_3$ is added to the sample as carrier of U and Th. The sample solution now includes Fe, Ca, Sr, and Mg as major elements and U and Th as trace elements. The U and Th are then co-precipitated with Fe by adding NH$_4$OH. The solution changes colour from clear to
yellow and a brown deposit containing ferric hydroxide forms that includes oxides and hydroxides of U and Th. The mixture is then centrifuged and the supernate containing Ca is discarded. The remaining ferric hydroxide precipitate is washed several times in de-ionised water and dissolved in 7N HNO₃.

Chemical separation of U and Th is by anion exchange resin using standard methods. Pre-cleaned 2 ml columns are used for this step and Fe is eluted with 7N HNO₃. Then, Th is eluted by adding 2 ml (x 3 times) of 8N HCl followed by U with 2 ml (x twice) of 0.5N HCl. Both Th and U fractions are dried, then re-dissolved in 7N HNO₃ and loaded separately onto small anion exchange columns (0.15 ml). Any remaining Fe is cleaned by 7N HNO₃ and U and Th are recovered using 0.5 HCl and dried on a hotplate. They are stored as small dry drops ready for mass spectrometry.

§ 3.4 Thermal Ionisation Mass Spectrometry

The advantages of TIMS compared with conventional α-counting methods have already been mentioned. More importantly, the measurement of δ²³⁴U (T) and ²³²Th provide the only quantitative reliable indicator for assessing the degree of closed system behaviour in coral samples and will be further discussed below.

§3.4.1 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, OsO₅ 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 vaporised sample will actually be ionised and these are focussed 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 $10^8$, $10^{10}$, $10^{11}$, or $10^{12}$ 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 ($I=c \frac{dv}{dt}$) (Fig. 3.3). 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 x10⁻¹⁷ peak to peak).
Fig. 3.3 An example of simultaneous output from three electrometers operating in charge mode. (a), (b) and (c) correspond to $^{229}\text{Th}$, $^{220}\text{Th}$ and $^{232}\text{Th}$, ion beams respectively. A steady Th ion current produces a monotonic increase in output voltage as charge accumulates on 20 pF capacitors. Each set consists of 60 data points with 1.28 seconds of integration time.

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.

§3.4.2 Charge Collection Thermal Ionisation Mass Spectrometry (CCTIMS)

CCTIMS is useful when only small (<10\(^{14}\) A) ion currents can be generated because of small available sample size or low ionisation efficiency such as for Th and Os. In the 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.3.5). Background values of each run are measured for at least 20 blocks of 60 ratios and have remained constant within statistical error for over the past five years. The background values are determined before the sample reaches optimal running temperature so that to maximise 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 ionisation current of approximately 3 x 10\(^{15}\) C that can easily be detected and then subtracted from the background level (Fig. 3.4).

§3.4.2.1. Measurement of Uranium isotopes

Uranium measurements have not been previously attempted on the 61 cm mass spectrometer with CCTIMS. To obtain sufficient \(^{234}\)U beam, approximately 3 to 5 x 10\(^{11}\) A of \(^{238}\)U beam current is required (\(^{235}\)U/\(^{238}\)U = 1/137.88 and \(^{235}\)U/\(^{234}\)U = 100). An attempt was made to enhance the thermal ionisation efficiency of U for this purpose. The sample loading technique for Th utilises a "graphite sandwich" method, on a rhenium filament, where the sample is loaded in between two layers of graphite and provides sufficient beam current. Although the same method was tried for U, the \(^{238}\)U signal was too small (<1 x 10\(^{11}\) A) for 1\(\mu\)g load of U. Since UO\(_2\) evaporates at significantly higher temperatures than U the high temperature reducing environment provided by the graphite load presumably helps increase the ionisation efficiency. Following this assumption, the amount of graphite on the filaments was increased, which resulted in higher but unstable beam currents.
Fig. 3.4 Background level of an electrometer operating in charge mode. An occasional (ca. Less than 1 in 5 minutes) $\alpha$-decay event, in the active input node, results in a transient current pulse (less than $3 \times 10^{-15}$ Coulombs). After subtracting the $\alpha$-particle decay event, the mean background current is obtained from the slope of a straight-line fit. The mean background for this data was $2.4 \times 10^{-17}$ A. Although the background current can be highly variable over short time scales (<20 sec.), it reproducibly constant over longer periods (several minutes).

Several previous studies employed single ion-exchange resin beads to load U and Pu (e.g., Fassett, and Kelly, 1984). In the present study, U samples were loaded onto single ion exchange resin beads and covered with a thin layer of graphite. Significant improvement in beam intensity was achieved, although the beam often could not be stabilised, possibly due to the non-uniform distribution of U within the resin. To eliminate the fluctuations, the resin was crushed to smaller size before loading with U and graphite. This technique provided very high and relatively stable beam intensities (> ~3 to $6 \times 10^{11}$ A of $^{238}$U) and required lower filament temperatures.

No background signal could be detected by scanning the U region with a filament loaded with beads and graphite only and it appeared that the ion exchange resin method would be adequate for U isotope measurements.
Fig. 3.5 Thorium isotope data for an entire run consisting of 37 sets of 60 data points each. Thorium was extracted from a 32.2 ka coral in this example. At the beginning of the experiment the beam intensity was low ($^{230}$Th $=0.6 \times 10^{14}$ A), the error for one set ranged from 5-8%. The statistical accuracy improved and dropped to 1 % or less with increasing beam intensity ($^{230}$Th $>3 \times 10^{14}$ A).

Several measurements of a U standard (HU-1, a Precambrian uraninite that has been shown to be in secular equilibrium, Ludwig et al., 1993) showed variations in the fractionation corrected (normalised to the $^{233}\text{U}/^{238}\text{U}$ double spike value) $^{232}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{235}\text{U}$ ratios, outside of the statistical uncertainties. During measurements the large $^{238}\text{U}$ beam was confined in a Faraday cup to avoid scattered beam entering the other Faraday cups. The two ratios appeared to vary in step, suggesting variations in the common $^{235}\text{U}$ isotope or a variable background contribution proportional to separation from the $^{238}\text{U}$ beam. To investigate the possible scattering of the $^{238}\text{U}$ beam, the suppressor plate voltage at the Faraday cups was increased from −180V up to −400V. This resulted in a significant reduction in the offset and variability in the $^{233}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios between runs.

Although variations in the isotope ratios were reduced (∼6% external reproducibility, with 2σ internal precision of ±0.6%), they could not be completely eliminated. Therefore, the 61 cm instrument was not used for the measurement of U isotopes in the present study.

§3.4.2.2. 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., 1990c) which enabled measurement of very low intensity ion beams (< ca. $10^{13}$ A). However, the precision obtainable was limited due to beam intensity variations and poor duty cycle in data-acquisition.

In the present work, internal statistical precision for a 45 minutes data acquisition period is typically 0.6 % as shown in Fig. 3.6, better than what has been achieved in other laboratories by about a factor of three (Esat, 1995).

![Fig. 3.6 External reproducibility of thorium measurements using a mixture of $^{230}$Th spike and uraninite standard. Solid symbols are from the present study; the open circle corresponds to the best that has been reported from other laboratories. The mean value for each measurement is calculated from the weighted average of 20 to 70 sets of 60 ratios. The error bars are $2\sigma_m$ statistical uncertainties.](image)

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 focussing and centring 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 x $10^{15}$ 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. 3.5).

§3.4.3 Measurement of Uranium isotopes using Finnigan MAT 261

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 ETP multipliers, optimised 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 $10^{11}$ Ω 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 μg 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 ionisation 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 normalised 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 % (2σM).

§3.4.4 Calibration of the Mixed spikes

In the present study, two types of mixed spikes have been used. One is a mixed solution of $^{229}$Th and $^{233}$U (U-1) and the other spike is a mixture of $^{229}$U, $^{233}$U, and $^{236}$U (U-3). The double spike was prepared for U measurements on the 61-cm Mass spectrometer with CCTIMS method. $^{232}$U/$^{235}$U is approximately 1 and samples spiked so that $^{235}$U/$^{236}$U would be approximately 10. Spike solutions were stored in teflon 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, $^{234}$U/$^{235}$U = 2.3378, $^{233}$U/$^{235}$U = 1259.38, and $^{229}$Th/$^{230}$Th = 20,000. While U-3 has the same-isotopic
composition but additionally $^{233}\text{U}/^{235}\text{U} = 0.523$. 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 solutions yielded $^{233}\text{U}/^{229}\text{Th} = 53.18 \pm 0.05 (2\sigma_m)$ (Stirling et al., 1995) and for the HU-1 plus U-3 solution $^{233}\text{U}/^{229}\text{Th} = 37.312 \pm 0.05 (2\sigma_m)$.

§3.4.5 Calibration of $^{234}\text{U}/^{238}\text{U}$

Analytical bias in the machine can be monitored and corrected using HU-1 and assuming that it is in secular equilibrium. Since the installation of the new electron multiplier, the value obtained for $\delta^{234}\text{U}$ has been $0.599 \pm 0.270 \%$ (Fig. 3.7). Previously a small bias in the SEM produced a systematically lower value of $-2.1 \pm 0.5\%$. This offset was used to correct the measured values (Stirling et al., 1995). In the present case there is no need for any correction factors for $\delta^{234}\text{U}$ data with error of $\pm 1$ to 2 \%.

§3.4.6 Filaments

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 oxidisation and volatilisation 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 oxidise and yield poor ion currents. No $^{230}\text{Th}$, $^{232}\text{Th}$ or U isotopic signals have been detected above background levels from blank filaments.
§3.5 Criteria for assessment of open system behaviour

Extensive efforts have previously been made to establish quantitative criteria for recognising U and Th open-system behaviour in corals (e.g., Stein et al., 1993; Bar-Matthews et al., 1993). Currently, none of the established procedures can identify altered samples with certainty. We have used a combination of criteria to select out likely samples suspected of open system behaviour.
§3.5.1 Microscopic analysis

Alteration of normal aragonitic coral textures, in fossil coral skeletons, were studied using a petrographic microscope. Both longitudinal and latitudinal thin-sections, relative to coral growth axis, were checked for secondary void filling and alteration, including coarsening due to re-calcification (Bar-Mathews et al., 1993). In most cases, for favid corals, traces of alteration were confined to the delicate lattice-work or septa in between solid wall sections. These structures are routinely removed during sample cleaning (section 3.3.1). Other samples, with extensive alteration features were not used for dating.

§3.5.2 XRD analysis

In corals exposed to freshwater, secondary calcite can replace the original aragonite as calcite in such environments is more stable than aragonite (Deer et al., 1967). Presence of calcite is indicative of U and Th exchange and can be detected by x-ray diffraction analysis. Samples with 4% or greater calcite content can be visually identified in sunlight. The sensitivity of XRD analysis is limited to ≈2% calcite. (section 2.63, 2.64). In most cases, where calcite is detected above background levels, cleaned wall fractions were found to have less or negligible amounts of calcite.

§3.5.3. Trace elements and stable isotopes

There have been numerous attempts to establish a correlation between trace elements, stable isotopes and spurious U-Th ages (eg., Chen et al., 1991; Stein et al., 1993; Bar-Matthews et al., 1993). Trace elements and isotopes studied include Na, Mg, Sr, δ13C and δ18O. However, the results have been inconclusive. Stein et al., (1993) concluded: "Trace element and stable isotope data are insensitive to low-level leakage". In two papers, on corals from the Bahamas, Chen et al., (1991) and Bar-Matthews et al., (1993), have reported generally lower concentrations of Na, Mg, and Sr compared with modern corals. They attributed this to secondary calcite growth. However, the relationship between this and U/Th age of the corals, if any, have not been established.

§3.5.4 δ234U(T)

Corals that remain as closed systems with respect to U and Th exchange should have 234U/238U ratios similar to those found in modern corals where δ234U(T)=149±1 % (Gallup et al., 1994, Stirling et al., 1995), or in present sea-water where δ234U(T)=144±7 % (Chen et al., 1986) with the expectation that the sea-water
value remained unchanged over time. T. Stein et al., (1993) used a value of $\delta^{234}U(T)$ from 140 to 150%, for acceptable Last Interglacial samples from Hon Peninsula, within an uncertainty of $\pm 9\%$. In contrast, stricter limits of $\pm 4\%$ could be applied for the majority of Last Interglacial corals from Western Australia (Stirling et al., 1995). Gallup et al., (1994) have demonstrated a direct correlation between U-Th ages and high $\delta^{234}U(T)$ values. In all cases, high $\delta^{234}U(T)$ values, outside of 149$\pm 4\%$, were approximately correlated with older apparent ages. Similar trends can be seen in Last Interglacial Huon corals (Stein et al., 1993), and in Western Australian corals (Stirling et al., 1998). We consider the $\delta^{234}U(T)$ criterion to be the only quantitative indicator for U and Th open system behaviour.

§3.5.5 Total U concentration

Uranium concentration in modern corals is approximately 3 ppm and is only weakly dependent on species. Fossil corals, acceptable for dating in general have 2.5 to 3.5 ppm of uranium.

§3.5.6 $^{232}Th$ 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 Th addition and results in older measured ages. The measured concentration of $^{235}Th$ 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.

§3.6 Summary

The $^{238}U$, $^{234}U$, $^{230}Th$ decay system can be used for dating Pleistocene and Holocene corals, and in particular samples which can be used as indicators for variations in past sea-levels. Suitably selected coral samples can ensure closed system integrity for U and Th isotopes. In corals, the absence of initial $^{230}Th$, simplifies dating and isochrons are not required.

Development of TIMS methods has led to reduction in sample size, faster analyses times and higher precision. In the present study, U 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. In particular, the $^{234}U/^{238}U$ ratio provides the only quantitative means of ensuring closed system U and Th behaviour and the most reliable ages.

In the present work coupled U-Th and $^{14}C$ ages are used to define a $^{14}C$ calibration curve for the period 30 ka to 50 ka. 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. To ensure sample integrity, we have employed additional strict test procedures specifically for carbon, and these are described in the following chapter.
Chapter Four

Radiocarbon and Uranium series dating of corals from Huon Peninsula, Papua New Guinea: Connections between Last Glacial sea-levels, Heinrich events, ocean circulation, and atmospheric $^{14}$C

§4.1. Introduction

Variance between the $^{14}$C and actual age of a historic object was first noted for an Egyptian artefact accurately dated by the ancient Egyptian Old Kingdom calendar (Ralph, 1959). This demonstrated the existence of discrepancies between radiocarbon and calendar ages. Calibration of the $^{14}$C time scale over the last ~11 ka has been secured using tree-ring chronology (Becker and Kromer, 1993), however, data beyond this period is not extensive (Bard 1998).

The original aim of this project was to extend the $^{14}$C time scale calibration to beyond ~30 ka using well dated corals from the uplifted coral terraces of Huon Peninsula, Papua New Guinea. Tree-ring calibration extends over the last ~11 ka (Beckker and Kromer, 1993); coral drill-cores enabled U-Th-$^{14}$C cross-calibration to beyond ~20 ka (eg., Bard et al., 1990a,b; 1999; Edwards et al., 1993); however, beyond 30 ka the data are particularly sparse. Calibration over the period from ~30 to ~50 ka has been attempted using annually laminated lake sediments (eg., Goslar et al., 1995; Hughen et al., 1998; Kitagawa and van der Plicht, 1998), speleothems (eg., Vogel and Kronfeld 1997), deep sea cores (Volker et al., 1998), and travertine and tufa samples (Bischoff et al., 1994; Lin et al., 1998). All of the data are in general agreement that the divergence of the $^{14}$C time-scale from calendar-dates continues...
over the measurable range of the $^{14}$C clock. However, the existing data beyond 30 ka suffer variously from a lack of precise absolute chronology, sufficient time resolution, and reliability of measured $^{14}$C as representative of atmospheric $^{14}$C (Bard, 1998). In spite of the ambiguities, the data also show possible, large peaks and excursions (greater than 1000‰) over and above the general trend away from the 1:1 time equivalence line.

Radiocarbon ($^{14}$C-dating) and calendar ages ($^{238}$Th/$^{234}$U-dating) of corals can be determined directly (Bard et al., 1998), an advantage that is particularly relevant for time periods beyond ~25 ka. Coral samples from drill-cores offshore from Barbados (Bard et al. 1990a,b, 1993, 1998) and from Huon Peninsula (Edwards et al., 1993) have been dated with high precision accelerator mass spectrometry (AMS, $^{14}$C, Nelson et al., 1977) and thermal ionization mass spectrometry (TIMS, Th/U, Edwards et al., 1987). Where there is an overlap in calendar ages determined from tree-rings and Th/U dating, the two methods are in good agreement (Bard et al., 1998, Kromer and Spurk, 1998).

We have extended the previous coral based radiocarbon calibration from 30 ka to beyond 50 ka using mass spectrometric $^{14}$C and Th/U dating techniques on corals collected from Reefs II and III at Huon Peninsula, Papua New Guinea. Some Th/U ages were already available for a subset of the same corals (Chappell et al., 1996). In the first instance, the present results are in accord with previous observations that there is a large secular difference between $^{14}$C and Th/U ages, and that the difference increases with age.

The present data, which I describe below, also show huge (>15,000 years) discrete deviations toward younger $^{14}$C ages superimposed on the long-term trend from ~30 ka to ~54 ka. They correspond to highly elevated $^{14}$C levels in equatorial surface waters, and by implication in the atmosphere. Peaks of excess $^{14}$C have been reported previously at ~23 ka and ~32 ka (equivalent to age shifts of ~4000 and ~5500-7000 years respectively; Kitagawa and van der Plicht, 1998) and at ~33 ka and ~39 ka (age shifts of ~5000 and ~8000 years respectively; Voelker et al., 1998). However, exact timing, magnitude or the cause of these shifts could not be established unambiguously and varies from one study to another.

Huon Peninsula Reefs II and III, and associated sub-reefs, represent discrete episodes of reef building, mostly at times when sea-levels rose faster than local uplift. A remarkable finding of the present study is the coincidence in timing of excesses in $^{14}$C, in all cases, with either Heinrich Events (HE) or high levels of ice-rafted debris (IRD) deposits as established in deep sea cores (Bond et al. 1992; Bond
and Lotti, 1995). The generally accepted cause of HE involves periodic disintegration of large ice sheets, including the Laurentide ice sheet, and other northern hemisphere minor ice sheets such as the Greenland and Iceland ice sheets. In what follows, I discuss the evidence for these assertions in the context of the present data and previous work.

§4.2. Previous calibrations of the radiocarbon time scale

Radioactive $^{14}$C is produced in the upper atmosphere when cosmic ray produced secondary neutrons interact with nitrogen. Therefore, the production rate of $^{14}$C is strongly dependent upon solar magnetic activity and the strength of the terrestrial geomagnetic dipole. It can also be influenced by re-distributions in the Earth's carbon reservoirs, such as the biosphere, atmosphere and especially the oceans.

Three distinct components have been recognised in the past atmospheric or surface ocean $^{14}$C variations: (i) High-frequency (century scale) deviations during the Holocene can be related to solar brightness and sunspot activity, (ii) Long term decrease in $^{14}$C and other cosmogenic nuclides which appear to be related to the strengthening of the geomagnetic field, and (iii) millenial scale changes in the rates of exchange within the global carbon cycle (Bard 1998).

§4.2.1. High frequency variations in atmospheric $^{14}$C

Rapid, century-scale variations in $^{14}$C have been observed in tree-rings during the Holocene period (Stuiver 1993). They have been related to solar magnetic variations linked to sunspot activity. For example, in the 17th century, during the so called Maunder Minimum Period, sunspots were almost absent (de Mairan 1733; Maunder 1894). During the last four centuries, low sunspot periods coincide with high concentrations of $^{14}$C in the atmosphere (Stuiver and Quay, 1980). The record of other cosmogenic isotopes such as $^{10}$Be and $^{36}$Cl, from polar regions, confirms the dominant underlying mechanism as driven by solar modulation (Raisbeck et al. 1981; Beer et al. 1988; Finkel and Nishiizumi 1996).
§4.2.2. Long term variations in atmospheric $^{14}$C

Existence of a relatively smooth secular variation in $^{14}$C ages, relative to calendar ages, from 30 ka to 5 ka, is evident in the coral record established mainly from the work of Bard et al. (1990a, 1998) and Edwards et al., (1993). Similar trends have also been reported from Speleothems (eg., Vogel and Kronfeld 1997; Richards et al. 1997), lacustrine inorganic material (Schramm et al., 1997), and a $^{14}$C and U/Th dated archaeological site (Bishoff et al., 1994). The $^{14}$C age shift from calendar time scale is almost linear, and ranges from a shift of $\approx500$ years to as large as $\approx5000$ years from 7 ka to 30 ka respectively. The effect is attributed to a long term variation in the geomagnetic dipole (Bard 1998; Fig. 4.1) and is supported by the observation that variations in $^{10}$Be and $^{36}$Cl fluxes are present at mid- to low-latitudes but absent from polar regions (Raisbeck et al. 1992; Yiou et al. 1988; Finkel and Nishizumi 1998) due to the shielding provided by the geomagnetic field at lower latitudes. Bard et al. (1999) have provided equations to describe the long-term trend beyond 11 ka:

$$Y_{\text{cal}} = 1.168 \times Y_{^14\text{C}}$$ \hspace{1cm} (4.1)

or a second order polynomial equation:

$$Y_{\text{cal}} = [(-3.0126 x 10^{-6}) \times (Y_{^14\text{C}})^2] + (1.2896 \times Y_{^14\text{C}}) - 1005$$ \hspace{1cm} (4.2)

where $Y_{\text{cal}}$ is calendar age and $Y_{^14\text{C}}$ is $^{14}$C age (yr BP).
Fig. 4.1 An example of palaeomagnetic intensity reconstruction from deep sea-sediments (after Schneider and Mello 1996). Geomagnetic intensity was weaker around 40 ka, shown as lower values of the Virtual Axial Dipole Moment.

Large age shifts, at \(\approx 33\) ka (5000 years) and \(\approx 39\) ka (8000 years), superimposed on the smooth secular trend, as reported by Voelker et al. 1998 (Fig.4.2) from \(^{14}\)C dated deep sea core foraminifera were calibrated using the \(^{18}\)O record from GISP2 Greenland ice core as calendar time scale indicator (Meese et al., 1994). However, beyond \(\approx 25\) ka the calibration is reported to be unreliable due to insufficient data.
Fig. 4.2 Age differences between deep-sea core radiocarbon ages and calendar ages derived from GISP2 ice core (Voelker et al. 1998). Radiocarbon ages and oxygen isotope ratios were measured using North Atlantic deep sea core planktonic foraminifera. Calendar ages were derived from a match of oxygen isotopes in deep sea cores and GISP2 record. The graph also includes previous calibration points from tree rings, lake sediments and corals. The three continuous lines represent age shifts and error envelope derived from various paleomagnetic data (Laj et al. 1996; Bard, 1998). Dotted lines show corresponding Δ14C values. The peak value is approximately 1200 ‰.
Fig. 4.3 Variations in atmospheric Δ¹⁴C derived from annually laminated sediments of Lake Suigetsu, Japan (Kitagawa and van der Plicht 1998). There is a good match between the data and tree-ring based Δ¹⁴C during the Holocene period. Two peaks are evident at 23 ka and 32 ka. Beyond 30 ka, accumulate varve counting errors can amount to 2000 years as shown by the dotted line. The magnitude of the 32 ka peak, including counting errors, can range from 600‰ to 900 ‰.

Data from Lake Suigetsu in Japan (Kitagawa and van der Plicht, 1998) show a similar magnitude shift at ≈32 ka (5500 years) and a smaller peak at 23 ka (4000 years) as shown in Fig.4.3. In this work the calendar time scale was constructed from grey-scale images that mirror annual laminated bands. The data set extends up to 45,000 ka, however, samples older than ≈38 ka were dated by assuming a constant sedimentation rate. If there were no interruptions in sedimentation, counting of varves alone can accumulate errors of up to 2,000 years for 40,000 year old samples (Kitagawa and van der Plicht, 1998). In an earlier report, on the same data set, Kitagawa et al., (1995) derived a very different trend, even though the time scale was adjusted using well known volcanic ash layers. In methods, where the calendar age of samples cannot be directly measured, as in varve counting, discrepancies can arise; these should be considered as minimum ages. All of these data are compiled in figure 4.4.
§4.2.3. Global carbon reservoir exchanges: The Younger Dryas Cold Episode

The third possible cause of atmospheric $^{14}C$ excursions relates to changes in exchange rates of carbon among various reservoirs. The largest carbon reservoir is the deep ocean (>90%); carbon content of the oceans is a factor of ≈60 larger than the atmospheric carbon budget. Currently, about 80% of $^{14}C$ required to maintain a steady state abundance of $^{14}C$ in the atmosphere and in deep ocean is mediated through the North Atlantic thermohaline circulation (Broecker, 1998). It is widely believed that a perturbation in the Atlantic circulation was the cause of the Younger Dryas (YD) cold episode around 11.5 – 13 ka. A slowdown in the $^{14}C$ exchange between the atmosphere and the deep ocean resulted in elevated levels of atmospheric $^{14}C$ (=50 % increase $\Delta^{14}C$; Fig. 4.5) and constant radiocarbon ages for over a millennium during the YD episode (Bard et al., 1990a,b; 1999; Bard, 1998; Edwards et al. 1993; Hughen et al. 1998, Kromer and Spurk 1998; Hajdas et al. 1998). Box-model, and elaborate general circulation model simulations of a
perturbation in the conveyor belt circulation, with suitable boundary conditions, have been able to reproduce the observed elevated $^{14}$C levels (Hughen et al. 1998; Stocker and Wright 1996; Oeschger et al. 1980; Mikolajewicz, 1998; Schiller et al., 1998; Goslar et al. 1999). However, problems remain (Bard, 1998). In particular, if the North Atlantic circulation supplies $\approx80\%$ of deep sea $^{14}$C atoms, and the circulation were interrupted over a 1000 year period, very large offsets in radiocarbon ages may be expected (Broecker, 1998). In contrast, over the YD period the offset is equivalent to about 120 years.

Fig. 4.5 Atmospheric $\Delta^{14}$C variations during the Younger Dryas event (Bard 1998). There is a sharp rise at the onset of the YD at 13 ka followed by a smooth and prolonged drop to 11.5 ka.

The YD event is often classified together with “Heinrich Events”, (HE) as the HE-0 event. Heinrich events, as discussed in detail below, arise from episodic partial disintegration of Northern Hemisphere ice sheets, in particular the Laurentide ice sheet, during the last glacial; they are characterised in northern Atlantic sediments by detrital limestone fragments, clay minerals, and deficiency of foraminiferal shells (Broecker, 1994). The accompanying fresh water injection is likely to have slowed or
completely shut down the North Atlantic deep water (NADW) formation. Although the YD event appears to have some of the same features, in scale it is minor when compared to HE during the last glacial. Younger Dryas occurred during a period of major deglaciation and rapid sea-level rise (4-5 m per century, over 400 years) labelled “melt-water-pulse-1A” (Fairbanks, 1989; Bard et al., 1990a,b, 1996; Edwards et al., 1993), a circumstance distinct from other HE episodes. In contrast, discharge of icebergs into oceans is expected to raise sea-levels by 3-4 m over 250 years (Mac Ayeal 1993; Elliot et al., 1998).

Atmospheric radiocarbon production is estimated to be 7.5 kg per year. If all carbon sinks were to be temporarily disabled the increase in atmospheric $^{14}$C would follow the pattern shown in Equation 2.11 (Chapter 2). In 1000 years the increase is close to 500%, and the theoretical maximum is 5870% (Siegenthaler et al., 1980). The YD increase of 50% indicates either NADW formation was only slightly slowed or as advocated by Broecker (1998) enhanced deep water production in the Southern Ocean prevented the rise in atmospheric $^{14}$C. Currently, deep water production in the Southern Ocean is approximately equal to that produced in North Atlantic. The shut-down of the Atlantic circulation is likely to have increased the advection of warm surface waters to low southern latitudes and caused mixing and transport of heat to deeper ocean. The lowered density, then allows dense southern surface ocean waters to penetrate the deep ocean (Broecker, 1998). Presumably, these waters were better aerated than transpires at present.

§4.3. Thermohaline circulation and Heinrich Events

Global thermohaline circulation (THC) originates in the North Atlantic (Fig.4.7). Warm surface waters moving north from the tropics increase in salinity by evaporation and cool down in the North Atlantic. The dense surface waters sink to the bottom and flows south toward the tip of Africa where they mix in with the current circulating around the Antarctic continent. Here, formation of ice increases the salinity and density of surface waters which flow into deep ocean off the shelves around Antarctica. Two deep ocean branches supply the Indian and Pacific Oceans and surface water flows north into the Atlantic Ocean (Broecker, 1997).
Fig. 4.6 A schematic pattern of ocean thermohaline circulation. Darker lines represent deep water flows, and lighter lines show surface water flows. Deep water is mainly produced in the North Atlantic, but also significantly around Antarctica (cross symbols). Deep water proceeds from the North Atlantic, past the tip of Africa and joins in with the Antarctic deep water. It resurfaces in the Indian and Pacific oceans (filled circles).

Fig. 4.7 A similar diagram as in Fig. 4.6 but in cross section. In the southern ocean, the circum-Antarctic deep water current connects to Atlantic, Pacific and Indian oceans. Deep water around Antarctica is produced as ice forms at the margins and produces brine-rich water that sinks down the continental shelves.
Climate records from Greenland ice cores were the first to show abrupt climate oscillations during the last glacial. Numerous studies of Atlantic and Pacific deep sea cores point to similar climatic variability associated with periodic weakening, and possibly complete shut-down of the North Atlantic circulation, with global climatic effects that extend beyond the North Atlantic. The transitions appear to have been triggered by fresh meltwater from iceberg discharges that transport and deposit layers of debris first noted by Hartmut Heinrich (1988). A schematic of a typical cycle is shown in Fig 4.8 (Alley, 1998), composed of so-called Dansgaard-Oeschger and Bond cycles. The cycle starts with several warm to cold climate Dansgaard-Oeschger transitions, each lasting ≈1500 years, and progressively range to cooler temperatures. The magnitude of the climatic signal is up to about half that occurs between major glacial-interglacial transitions. Abrupt warming at the end of the coldest oscillation completes a 5 to 7 thousand year Bond cycle. Heinrich debris layers occur at the start of the coldest period and, presumably, correspond to massive iceberg discharges. The Dansgaard-Oeschger oscillations are related to perturbations of the North NADW formation. Recent evidence (Elliot et al., 1998) that more frequent but smaller scale distinct detrital layers occur before and at the start of HE may provide a clue to the origin of Dansgaard-Oeschger transitions. These smaller-scale iceberg discharges appear to originate from Iceland and other coastal ice sheets in the Nordic area and could be re-charged on a similar time scale as Dansgaard-Oeschger events. The small scale sea level rises that may coincide with a particularly unstable period in the growth of the Laurentide ice sheet could tip the balance and cause a large scale collapse, possibly every 5-10 ka as in Bond cycles.
Fig. 4.8 Schematic diagram of Bond and Dansgaard-Oeschger (DO) climate cycles (Alley, 1998). The 1,500 year DO cycles, related to weakening of deepwater formation in the North Atlantic (NADW), are also associated with ice-rafted debris in deep sea cores. Only the minor or coastal ice-sheets may be responsible for this process. The shut-down of NADW causes a cold snap by preventing warm equatorial waters from travelling into the North Atlantic and results in re-growth of ice-sheets. Re-start of the NADW circulation causes a warm stadial and the cycle repeats. Several such cycles lead to progressive cooling and growth of the major Laurentide ice sheet, over Hudson Bay; the cycle is eventually terminated by a large surge and an armada of icebergs in the North Atlantic. These low frequency 5-7 ka oscillations define a Bond cycle. Bond cycles may be modulated externally by ice-age transitions, or may be related to internal ice sheet dynamics. The coldest part is marked by a Heinrich ice-rafted debris layer mainly originating from the Hudson Bay area.

Growth of the Laurentide ice sheet could eventually cause sufficient geothermal heating and melting at the base of the ice sheet to trigger an ice surge. In this picture HE occur because of local conditions. Alternatively, the global nature of climate shifts that extend beyond the North Atlantic argue for an external, possibly Milankovitch type forcing as the initiator of rapid glacial climate changes. Discharge of icebergs into North Atlantic is bound to be accompanied by sea-level rise. A sea-level rise of 4-10 m is bound to mobilise that portion of the Antarctic ice sheet grounded under sea and cause a surge in the inland Antarctic ice sheet. In this way, local effects in North Atlantic could propagate globally.
A local-cause model for surges in the Laurentide ice sheet has been described previously (eg. McAyeal 1993; Alley 1998). It can be illustrated as simple bamboo oscillator ("Shi-shi odoshi") often found in Japanese gardens (Fig. 4.10). Initially, water fills the bamboo "bucket" over a relatively long interval (binge phase of the ice sheet); as the bamboo becomes top heavy, it suddenly tips over on its axis and fast flowing water drains into the pond below (purge phase of the ice sheet) and the process restarts (McAyeal 1993).

Fig. 4.9 The bamboo see-saw in a Japanese garden which captures the basic principles of the oscillation of the Laurentide ice sheet; from an idea originally proposed by MacAyeal (1993).
§4.4. Cosmogenic isotopes $^{10}$Be and $^{36}$Cl

Records of cosmogenic isotopes such as $^{10}$Be and $^{36}$Cl can provide additional constraints on solar and geomagnetic variations when considered together with $^{14}$C data. Due to the shape of the geomagnetic field, maximum shielding against cosmic rays is provided at mid- to low-latitudes such that cosmogenic isotope production at the poles is relatively insensitive to variations in the geomagnetic field. Whereas radiocarbon is oxidised and rapidly mixed in with atmospheric CO$_2$, and it is widely distributed in the atmosphere and the oceans, $^{10}$Be becomes attached to atmospheric aerosol particles and is rapidly removed in precipitation. Behaviour of $^{36}$Cl may be more complex as it forms several gaseous species. In Greenland ice cores the $^{10}$Be record shows a strong correlation with Dansgaard-Oeschger events but these appear to be related to precipitation rate changes. In contrast, a peak both in $^{10}$Be and $^{36}$Cl has been observed in ice cores at GRIP and a similar peak in $^{10}$Be at Vostok that represents an approximate doubling of cosmic ray flux (Raisbeck et al. 1981; Beer et al. 1988; Finkel and Nishiizumi 1996; Yiou et al., 1997; Aldahan and Possnert, 1998). The timing of the peak is uncertain and ranges from 37 ka at GRIP to 43 ka at Vostok. The duration of increased flux is approximately 2000 to 3000 years. A similar peak has also been observed in deep sea sediment cores in the Mediterranean, Gulf of California and more recently in a core from the Caribbean, a low-latitude location that is sensitive to changes in the geomagnetic field and insulated from polar climate extremes that may modulate deposition rates. It is dated at 37,000 $^{14}$C years or $\approx$42,000 calendar years (Aldahan and Possnert, 1998).

The 35 ka to 45 ka time interval includes the Laschamp geomagnetic excursion (Levi et al. 1990; Baumgartner et al. 1998). At $\approx$48 ka the field was greater than present, followed by a sharp decline to about 30% of the present field for over 15 ky. Bard (1998) considers the enhanced $^{10}$Be-$^{36}$Cl levels to be the combined result of low solar activity superimposed on slow variations of geomagnetic field (Fig.4.10). However, the duration of the excess flux over several million years poses a problem in maintaining low solar activity for such a long time. Other hypothetical explanations have included extreme long-term solar activity (Raisbeck et al. 1987; McHargue et al. 1995), and increased cosmic ray flux due to a supernova explosion (Sonett et al. 1987).
Fig. 4.10 Long-term variations in $\Delta^{14}C$ (Bard 1998); data from measurements in corals. The line shows expected variations in atmospheric $\Delta^{14}C$ by doubling of cosmonuclide production around 42-40 ka as observed in numerous $^{10}Be$ records.
§4.5. Radiocarbon and Th-U dating of corals from Huon Peninsula

Veracity of the results from radiocarbon and Th-U dating of corals ultimately depend on the quality of the samples. This is a vexed issue that cannot be resolved with complete certainty, but relies on a battery of tests each of which provide, at best, circumstantial evidence for or against. It has been previously established that the “quality” of favid-type coral samples can be significantly improved by removing the septa and only analysing the wall fractions (Stirling et. al, 1995, 1998). We have followed this procedure in the present work. Where possible we have placed added weight on quantitative tests rather than qualitative assessment. The best quantitative test for Th-U dates is the deviation of the $^{234}\text{U}/^{238}\text{U}$ ratio from the modern sea-water value (Gallup, et al., 1994, Stirling et al., 1995, 1998). Similarly, we have devised a quantitative test of radiocarbon dates that relies on progressive dissolution of coral samples. We have determined empirically that first 50% of a leached coral sample is more likely to have been contaminated by extraneous, younger age carbon, than the last 50% (Burr et al., 1993; Fig. 4.11). We have adopted a procedure whereby the first 50% leach of a sample was discarded. The remainder was leached in at least three steps and each aliquot was $^{14}\text{C}$-AMS dated (Chapter 2). This procedure was applied to each dated sample. The data for all of the samples can be found in the appendix. In every case, within twice the statistical uncertainty, the last three aliquots have identical radiocarbon ages. Ancillary tests were also performed that include: Microscopic inspection of thin-sections for traces of secondary alteration and x-ray diffraction analysis to detect calcite; stable isotope carbon and oxygen analysis; and checks to ensure $^{238}\text{U}$ and $^{232}\text{Th}$ were within acceptable concentration limits. Samples included in the discussion below pass all of these tests within limits of assigned errors. A major concern with radiocarbon dates for samples older than 30,000 years is the possibility of contamination with younger age or modern carbon. There is no absolute a priori test to determine the issue. In particular, for the 52 ka samples reported below, the radiocarbon ages range from 35 to 45 ka and may need to be viewed with some caution. However, we consider that the selective dissolution test is the best quantitative indicator that can be devised at present. These issues are discussed in detail in the appendix.
Fig. 4.11a Step-wise dissolution of a Last Interglacial (LIG) coral (124.7 ± 0.9 ka and $\delta^{18} \text{O} = 152 ± 2\%$; Stirling, 1996), present work; and a stage 4 coral (72.8 ± 2.2 ka; Chappell et al. 1996) from Burr et al. (1993). Shaded columns are for bulk samples that result in significantly younger ages than expected. In both cases, the first 30% appears to have substantial amounts of contamination. The results appear to be valid for different types of coral (LIG coral is a Favid whereas the stage 4 coral is a Porites.)
Fig. 4.11b Selective dissolution of a giant clam from upper sections of reef III shows analytical background levels of $^{14}C$ after ~50% dissolution. GBR-A coral was obtained by a submersible from a depth of 175 m at the Great Barrier Reef (Veeh and Veevers 1970).
Fig. 4.11c All the samples used in the present study were subjected to step-wise dissolution as shown in these examples. The shaded columns show the results of bulk analysis for a different piece of the same coral. Results for all the other samples are compiled in the Appendix.
### Table 4.1 U/Th isotope ratios and $^{230}$Th ages of the corals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{232}$Th (ppb)</th>
<th>$^{238}$U (ppm)</th>
<th>$\delta^{234}$U(0) (%)</th>
<th>$\delta^{234}$U(T) (%)</th>
<th>$(^{230}$Th/$^{238}$U)_{act}</th>
<th>Age (kyr)</th>
<th>Height (masl)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kanzaruia section</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Kanz 4</td>
<td>0.022</td>
<td>2.73</td>
<td>118.3±1.4</td>
<td>137±1.7</td>
<td>0.4247±0.0100</td>
<td>51.5±1.6</td>
<td>86</td>
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<tr>
<td>Kanz 9</td>
<td>0.067</td>
<td>2.73</td>
<td>119.4±1.2</td>
<td>139±1.4</td>
<td>0.4379±0.0013</td>
<td>53.4±0.3</td>
<td>78</td>
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<tr>
<td>Kanz 11$^p$</td>
<td>0.086</td>
<td>2.41</td>
<td>119.9±1.0</td>
<td>139±1.1</td>
<td>0.4245±0.0011</td>
<td>51.3±0.3</td>
<td>78</td>
</tr>
<tr>
<td>Kanz 13$^p$</td>
<td>0.048</td>
<td>3.26</td>
<td>118.4±11.6</td>
<td>132±12.9</td>
<td>0.3339±0.0008</td>
<td>38.3±0.5</td>
<td>48</td>
</tr>
<tr>
<td>Kanz 15$^p$</td>
<td>0.038</td>
<td>2.68</td>
<td>127.0±2.2</td>
<td>143±2.4</td>
<td>0.3633±0.0041</td>
<td>42.0±0.6</td>
<td>39</td>
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<tr>
<td>Kanz U8$^p$</td>
<td>0.380</td>
<td>2.70</td>
<td>129.9±3.7</td>
<td>144±4.1</td>
<td>0.3276±0.0042</td>
<td>37.0±0.6</td>
<td>27</td>
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<tr>
<td>Kanz U9</td>
<td>0.483</td>
<td>2.70</td>
<td>125.3±0.9</td>
<td>141±1.1</td>
<td>0.3652±0.0007</td>
<td>42.3±0.2</td>
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<tr>
<td>Kanz U10$^p$</td>
<td>0.539</td>
<td>2.50</td>
<td>121.2±1.2</td>
<td>137±1.4</td>
<td>0.3734±0.0006</td>
<td>43.7±0.3</td>
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<tr>
<td>Kanz U11</td>
<td>0.017</td>
<td>1.99</td>
<td>127.4±13.0</td>
<td>142±9.1</td>
<td>0.3187±0.0008</td>
<td>35.8±0.4</td>
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<tr>
<td>Kanz U12</td>
<td>0.015</td>
<td>2.19</td>
<td>122.1±3.0</td>
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<td>Kanz U13</td>
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<td>35.8±0.4</td>
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<td>Kanz A</td>
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<td>0.3293±0.0008</td>
<td>37.5±0.2</td>
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<td><strong>Bobongara section</strong></td>
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<tr>
<td>Bobo U10</td>
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<td>127.6±1.2</td>
<td>142±1.3</td>
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<tr>
<td>Bobo U11</td>
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<td>128.8±1.7</td>
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<td>0.3338±0.0015</td>
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<tr>
<td>Bobo U17</td>
<td>0.013</td>
<td>1.98</td>
<td>128.9±2.5</td>
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<tr>
<td>Bobo U18</td>
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<td>2.06</td>
<td>126.7±1.7</td>
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<td>0.3663±0.0007</td>
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<td>Bobo U20</td>
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<td>2.02</td>
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<td>0.2914±0.0006</td>
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<td>Bobo U28</td>
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<td>143±1.3</td>
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<tr>
<td><strong>Others</strong></td>
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<td>SEN(N)$^8$P</td>
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<td>133.0±1.2</td>
<td>140±1.3</td>
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<td>17.0±0.1</td>
<td>-175</td>
</tr>
</tbody>
</table>

† Except where indicated, all samples are from the Faviidae family; the superscript p denotes Porites corals. Analyses on Faviidae corals are for the wall fractions only.

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

‡ $\delta^{234}$U = \[\frac{([^{234}U]/[^{238}U])_{eq}}{([^{234}U]/[^{238}U])_{eq} - 1}] \times 10^3$. $([^{234}U]/[^{238}U])_{eq}$ is the atomic ratio at secular equilibrium and is equal to $\frac{\lambda_{239}}{\lambda_{234}} = 5.472 \times 10^{-6}$ where $\lambda_{238}$ and $\lambda_{234}$ are the decay constants for $^{238}$U and $^{234}$U, respectively. $\delta^{234}$U(0) is the measured value, the initial value is given by $\delta^{234}$U(T) = $\delta^{234}$U(0)$e^{\lambda_{234}T}$, where $T$ is the age in years.

$^8$ $(^{230}$Th/$^{238}$U)_{act} = (^{230}$Th/$^{238}$U)/($\lambda_{238} / \lambda_{234}$).

$^9$ $^{230}$Th-ages are calculated iteratively using $1 - \frac{\Delta^{230}$Th}{\Delta^{238}$U}_{act} = e^{-\lambda_{230}T} \left( \frac{\delta^{234}$U(0)}{\lambda_{230} - \lambda_{234}} \right) (1 - e^{(\lambda_{230} - \lambda_{234})T})$ where $T$ is the age in years and $\lambda_{230}$ is the decay constant for $^{230}$Th. $\lambda_{238} = 1.551 \times 10^{-10}$ y$^{-1}$; $\lambda_{234} = 2.835 \times 10^{-6}$ y$^{-1}$; $\lambda_{239} = 9.195 \times 10^{-6}$ y$^{-1}$. Ages considered "reliable" have $\delta^{234}$U(T) values overlapping the range 149 ± 10%.

The $\Delta^{230}$ uncertainty in the age is determined by propagating the $\Delta^{230}$ analytical contribution from the parameters $\delta^{234}$U(0) and $(^{230}$Th/$^{238}$U)_{act}, as well as the systematic contributions from the decay constants $\lambda_{230}$ and $\lambda_{234}$ through the age equation. The uncertainty in the age is largely due to the decay constant errors which contribute ~950 years to $\Delta^{230}$ at 125 ka.
The new data comprise of twenty five new TIMS Th-U dates and over two hundred AMS radiocarbon dates (Table 4.1; 4.2). The radiocarbon ages and Th-U calendar ages are plotted in Figure 4.12 together with data from other studies. The oldest radiocarbon age from the three available ages was selected; average of the three ages is within twice the experimental error in each case. Results from one coral, from the Great Barrier Reef, originally dated by Veeh and Veevers, (1970) with conventional radiocarbon and Th-U (13.600 to 13.860 ± 0.220 ka and 17.000±1.000 ka respectively), are in good agreement with present results (14.390±0.150 ka and 16.981±0.112 ka). This sample is well within the field of other data of similar age (Fig. 4.12). All of the other corals are from the uplifted Huon Peninsula coral terraces of Papua New Guinea collected during the 1992 international expedition (Ota et al. 1993; Figs. 4.12, 13, 14). Four samples were previously Th-U dated using TIMS and five others by α-spectrometry (Chappell et al., 1996), they are included with the new results in Fig. 4.12. The previous data have larger analytical uncertainties (Omura et al., 1995; Chappell et al., 1996), however, they are in good agreement with the new TIMS data.

Table 4.2 U/Th results and 14C data

<table>
<thead>
<tr>
<th>Sample *</th>
<th>U/Th age (k cal yr BP)</th>
<th>U/Th age 14C age (k 14C yr BP)</th>
<th>pM*</th>
<th>Δ14C (‰) †</th>
<th>δ13C (‰) †</th>
<th>Reef ‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kanzarua</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Kanz 4</td>
<td>51.5±1.6</td>
<td>33.7±0.5</td>
<td>1.50±0.13</td>
<td>6576</td>
<td>-0.762</td>
<td>IIIa</td>
</tr>
<tr>
<td>Kanz 4a</td>
<td>51.2±0.8</td>
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<td>8644</td>
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</tr>
<tr>
<td>Kanz 9</td>
<td>53.4±0.3</td>
<td>44.2±1.0</td>
<td>0.41±0.05</td>
<td>1310</td>
<td>-0.833</td>
<td>IIIa</td>
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<tr>
<td>Kanz 9T</td>
<td>54.6±0.7</td>
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<td>1659</td>
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<tr>
<td>Kanz 11f</td>
<td>51.3±0.3</td>
<td>36.5±0.5</td>
<td>1.07±0.06</td>
<td>4317</td>
<td>-0.576</td>
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<tr>
<td>Kanz 13f</td>
<td>38.3±0.5</td>
<td>39.1±0.5</td>
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<td>Kanz 15f</td>
<td>42.0±0.6</td>
<td>38.9±1.2</td>
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<td>IIIc</td>
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<tr>
<td>Kanz U8f</td>
<td>37.0±0.6</td>
<td>33.9±0.6</td>
<td>1.47±0.11</td>
<td>289</td>
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<td>Kanz U9</td>
<td>42.3±0.2</td>
<td>35.3±0.9</td>
<td>1.24±0.14</td>
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<td>Kanz U9T</td>
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<td>Kanz U10f</td>
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<td>Kanz U11</td>
<td>37.9±0.3</td>
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<td>Kanz U12</td>
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<td>Kanz U13</td>
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<td>Kanz U14f</td>
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<td>Kanz U15</td>
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Table 4.2 continued

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<tr>
<th>Sample *</th>
<th>U/Th age (k cal yr BP)</th>
<th>¹⁴C age (k ¹⁴C yr BP)</th>
<th>pM°</th>
<th>Δ¹⁴C (%) †</th>
<th>δ¹³C (%) ‡</th>
<th>Reef³</th>
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<tr>
<td>Bobo U30</td>
<td>31.5±0.2</td>
<td>26.5±0.6</td>
<td>3.70±0.24</td>
<td>673</td>
<td>0.165</td>
<td>IIc</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEN(N)8p</td>
<td>52.4±1.3</td>
<td>43.0±1.7</td>
<td>0.48±0.09</td>
<td>1719</td>
<td>-0.992</td>
<td>IIIc</td>
</tr>
<tr>
<td>GBR-A</td>
<td>17.0±0.1</td>
<td>14.4±0.3</td>
<td>16.67±0.64</td>
<td>300</td>
<td>-1.963</td>
<td></td>
</tr>
<tr>
<td>GBR-Aa</td>
<td>17.0±1.0</td>
<td></td>
<td></td>
<td>300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# Except where indicated, all samples are from the Faviidae family; the superscript p denotes Porites corals. Analyses on Faviidae corals are for the wall fractions only. The superscript a and T are indicate previously reported values by means of α-counting method and TIMS method, respectively (Chappell et al., 1996).

† Using Libby’s half-life (5568 years).

@ Percent Modern (Stuiver and Polach, 1977) defined as (Aₚₓ / Aₚₓₛ) x 100, where Aₚₓ and Aₚₓₛ are activities of sample and standard material, respectively. Although Aₚₓ is normalised for isotopic fractionation conventionally, it was not applied in the present study. Because small isotopic fractionation is not affected such as old samples dealt with present study. Also isotopic fractionation usually cancelled out by reservoir correction for shallow marine carbonates. Aₚₓₛ is activity of 19th wood.

‡ The Δ¹⁴C value is the per mil difference between the initial ¹⁴C / ¹²C of a sample (normalised for isotopic fractionation) and the ¹⁴C / ¹²C of a standard; the standard has a value similar to the initial ¹⁴C / ¹²C ration of 19th century wood. The Δ¹⁴C is defined and discussed in Stuiver and Polach (1977) and equals (Fe^⁻¹7 - 1)x1000 per mil, where F is the fraction modern (Donahue et al., 1990), λ is the decay constant that corresponds to the 5730 year half-life, and T is the age in calendar years B.P. In the present study, Δ¹⁴C is calculated by the measured ¹⁴C / ¹²C ratio and then the calculation of the initial ¹⁴C / ¹²C ratio with the use of the ²³⁰Th age. Quoted error include errors in the measured ¹⁴C / ¹²C ratio and ²³⁰Th age.

§ Results are expressed as relative value against V-PDB in per mil.

Fig. 4.12 The present data set and previously published data.
Fig. 4.13 Location of Kanzarua and Bobongara reef sections.

Fig. 4.14 A view of Kanzarua section. Well developed uplifted coral terraces are evident.
Chapter 4

Bobongara (Bobo) 100

---

Kanzarua (Kanz) 500

---

Fig. 4.15 Profiles of coral terraces at Kanzarua and Bobongara sections.
The measured Th-U ages of corals, from the uplifted Huon Peninsula Reefs II and III (Chappell, 1970; Chappell et al., 1996), range between 29 ka to 55 ka. Several trends are apparent in the data; firstly, there is an apparent increase in the divergence of the radiocarbon ages from calendar dates, from 30 ka to 50 ka, that follows the same trend as the bulk of the previous data; secondly, there are significant (from 7 ka up to 17 ka or 1000‰ to 7000‰ in Δ¹⁴C) excursions at periods that correspond to particular reef-building episodes at Huon; and thirdly, some radiocarbon ages in between the “peaks” that are older than calendar ages.

That the Th-U ages cluster at particular times is no surprise as we are specifically dating corals from discrete reef sections; we do not have a continuous record of coral growth over this time period. However, the magnitude of the radiocarbon age excursions from calendar ages is unprecedented. The present data are shown on an expanded scale in Fig 4.16. It is clear that data with radiocarbon ages older than calendar ages is distributed in-between the peaks. Two previous coral data points are within the range of present ages; one is a 30,200 year coral from Barbados and the other 42,000 year old coral from Huon (Bard et al., 1993; 1998, Fig 4.4). Both of these overlap with the baseline defined by the present measurements (Fig. 4.12). At tectonically uplifting sites coral terraces grow when sea-level rise overtakes uplift. Corals can also grow during a fall in relative sea-level; these are termed regressive reefs. The uplift rate along the Huon coast is variable but typically of the order of 3 m per ky. The sea-level history derived from the present, and previous similar data (Chappell et al. 1996), is discussed in Chapter 6. The coincidence between sea-level rise and large excursions in ¹⁴C is at first sight puzzling. However, we believe that these events can be directly linked to rapid global climate changes, in particular, in the North Atlantic, and are also connected with Heinrich events and reorganisations of the North Atlantic thermohaline circulation.
Fig. 4.16 Radiocarbon and Th-U ages plotted in an expanded scale diagram. Errors are 2σ mean.

There are large variations in the reported calendar ages of various Heinrich events (Andrews, 1998). This arises, in part, from mishandling of radiocarbon to calendar age conversions. Some radiocarbon ages are not even corrected, but reported as absolute ages. Secondly, as the present data shows, the variability in radiocarbon ages may be due to rapid variations in atmospheric ^14C. We consider that data obtained by Bond et al., (1993) on the abundance of *Neogloboquadrina pachyderma* (s) from the North Atlantic core V23-81 to represent one of the best examples of the timing and signature of Heinrich events. The radiocarbon scale of this data set was converted to calendar ages using the prescription given by Bard et al (1998; Equations 4.1 and 4.2). The result is shown in Fig. 4.17 from a paper by Lund and Mix (1998). Inspection of Figures 4.16 and 4.17 shows that the radiocarbon peaks in the calibration curve match almost exactly with the timing of maxima in the foraminiferal abundance and Heinrich Events. The 32 ka (calendar age) ^14C peak matches with H3. The 37.5 ka ^14C peak matches with the sharp cold stadial at 37.5 ka that is not marked as a Heinrich event but appears to belong to the same class. The 42.3 ka ^14C peak matches with H4 at ~42 ka and the 52 ka ^14C peak matches with H5 at 52 ka. This correspondence is remarkable and is highly unlikely to be coincidental. The important point is that the Huon Peninsula terraces which represent episodes of sea-level rise, appear to have been built as a direct consequence of large scale discharges of icebergs into the North Atlantic and the associated sea-level rise. The present data assert that, concurrent with each episode, there was a huge rise in atmospheric radiocarbon.
Fig. 4.17 North Atlantic deep-sea core V23-81 showing systematic fluctuations in the abundance of *N. pachyderma* (s.) correlated with the timing of Heinrich events and cold stadials (from Lund and Mix 1998). The time scale was derived from radiocarbon data using the calibration recommended by Bard et al., 1993. Between H3 an H4, a brief duration sharp peak corresponds to an excess 14C peak found in the present data at 37.5 ka. This peak is not labelled as an Heinrich event but appears to belong to the same class. Heinrich events H3, H4 and H5 correspond to peaks of 14C in the present data. Such a correlation is unlikely to be coincidental.

The 14C excess, Δ14C, calculated from the present level is shown in Fig 4.18. As outlined in section 4.2 the theoretical maximum 14C excess in the atmosphere, if all the sinks are cut off, is 5870% and 2000‰ level can be reached within a few hundred years (Fig2.2). It appears that the present data provide the first direct evidence for the slow-down or shut-down of the North Atlantic thermohaline circulation as expounded by Broecker (1997,1998). Furthermore, it solves a puzzle, again put forward by Broecker (1998): quote “Currently, ≈80% of the 14C atoms required to replace those undergoing decay in the deep sea enter via the Atlantic’s conveyor circulation. Hence, if this route were to be shut down during the course of the 1200-calendar-year duration of the Younger Dryas, an enormous offset in the 14C timescale might be expected.” Of course the YD event is comparatively a minor event in relation to the massive Heinrich events.
As shown in Figure 4.18, $\Delta^{14}C$ varies from 1000$\%_o$ to 2000$\%_o$ except for the 52 ka event. However, it is possible that corals of this age may be more susceptible to contamination by younger age $^{14}C$. All possible precautions and cross checks were followed in the analysis of these samples; nevertheless, possibility of contamination cannot be ruled out and pending confirmation the $=7000\%_o$ excess $\Delta^{14}C$ for the 52 ka corals should be considered tentative.

The radicarbon ages, older than calendar ages, appear in between the large $^{14}C$ excursions. Presumably, they correspond to the resumption of the thermohaline circulation and transport of radiocarbon to deep sea, initially at a rate greater than present. There is theoretical support for such age reversals in the calculations by Stocker and Wright (1998), when surface reservoir ages increase rapidly at the time of the commencement of the circulation. Alternatively, at other oceans enhanced ventilation may tip the balance toward old ages. Interruption of the thermohaline circulation may be expected to re-direct the northward movement of warm equatorial waters in the Atlantic to the Southern Ocean. Coupled with 5-10 m sea-level rise from North Atlantic icebergs, the Antarctic ice sheet may also be destabilised. The possibility that fresh water injection into Antarctic waters may interrupt the Antarctic deep-water formation has not been assessed in detail. However, Clark et al., (1996) consider a contribution to the melt-water-pulse-1A from the Antarctic ice sheet most likely.

Fig. 4.18 A plot of $\Delta^{14}C$ against Th-U ages. Note the negative values in between the first three peaks.
The 37 ka peak in the present data and the nominal 37 ka peaks in $^{10}$Be and $^{36}$Cl polar and deep sea records, at first sight, appear to be generic. However, there is considerable uncertainty in the calendar age of the $^{10}$Be/$^{36}$Cl peak. Various studies place this peak anywhere from 37 ka to 42 ka (calendar years). It corresponds to a relatively long period when the geomagnetic field was low. Similarly the $^{10}$Be peak is broad (=3000 years). Whether the 37 ka peak in the present data is the same as the $^{10}$Be and $^{36}$Cl peaks remains an open question.

The $\Delta^{14}$C peaks have been observed by Kitegawa and van der Plicht (1998) at 30-32 ka ($\Delta^{14}$C up to 850‰); by Voelker et al., (1998) at 33 ka ($\Delta^{14}$C =700‰) and 39 ka ($\Delta^{14}$C =1200‰) and by Bard (1998) at 41 ka ($\Delta^{14}$C =700‰). Given the uncertainties in exact timing of these events, they could be related to the radiocarbon-excesses found in the present work. The magnitude of present $\Delta^{14}$C range from 1000‰ to 2000‰ to 7000‰, with a question mark on the last figure. These values are within a factor of two to three of the previously determined highs.

Finally we consider the timing of sea-level rises in relation to Heinrich events. Icebergs released into the ocean need not melt rapidly, however, their effect on sea-level, once released, is immediate. Presumably sufficient fresh water is released into the North Atlantic to perturb the thermohaline circulation. In a few hundred years, beyond this time, atmospheric $^{14}$C levels could reach 200% to 300% above ambient. Following the HE and the associated cold period, the deep sea records show abrupt warming indicating the return of warm equatorial water into North Atlantic and presumably the re-start of the thermohaline circulation. If this scenario is correct, we expect the Huon coral reefs to respond to the rise in sea-level, over the rate of uplift, and try and keep up with the rising sea-level. Thus new growth, at Huon, would occur during the cold phase of the HE and record the rise in the atmospheric and surface-ocean rise in $^{14}$C. There is some confirmation for this in the present data. In Figure 4.19 we show the variation in sea level recorded at Huon Peninsula after correcting for uplift (Chapter 6) and the corresponding variation in $^{14}$C. There may be up to a +20 m uncertainty in sea-level due to the possible range in depth that corals can grow in. We have the most data for the ~37.5 ka peak (Fig. 4.19b) which shows an early sea-level rise immediately followed by a rise in $^{14}$C levels. The $^{14}$C peak subsides after a few hundred years and eventually decreases beyond the initial ambient levels over 4,000 years. At the same time sea-level stabilises. The drop in sea-level from an initial peak, over 500 years, presumably reflects the regrowth of the large ice-sheets, and in particular the Laurentide ice sheet. Small variations in sea-level may relate to the range in growth habitat of corals rather than actual sea-level rises. Nevertheless, the basic scenario depicted in this graph appears to be robust. The picture represents the strongest and the best evidence, up to this time, for the
climate changes first discovered in polar ice cores and deep sea sediments, for 
Dansgaard-Oeschger and Bond cycles and ice calving and associated oscillations in 
the North Atlantic thermohaline circulation. The data for the 32 ka and 42 ka peaks 
(Figs. 4.19a and c) show a similar structure within uncertainties; in each case there is 
an early rise in $^{14}$C, but the trend in the sea-level curve is mixed. The data for the 52 
ka peak are too few and scattered to draw any meaningful conclusions.

Fig. 4.19a Sea-levels (a) and $\Delta^{14}$C (b) derived from present data for the 32 ka 
peak. A distinct $^{14}$C peak occurs in the early part of the cycles. About a 1000 
years prior to this, there is a sea-level rise followed by a fall in sea-level, 
presumably reflecting the re-building of the ice sheets. All this is as expected. 
However, sea-level appears to rise by another 15 m towards the end of the 
cycle, but this is based on a single data point. Clearly more data are required to 
confirm this pattern before placing too much weight on it.
Fig. 4.19b Sea-levels (a) and $^{14}$C (b) derived from present data for the 37.5 ka peak. There are sufficient data points for this peak to define a definite trend. The cycles starts with a sea-level high, presumably corresponding to ice sheet calving. At the same time $^{14}$C levels start rising and peak about 500 years later and slowly decline thereafter for the next $\approx 4000$ years to below current levels; that reflect the resumption of the North Atlantic circulation or ventilation of oceans at other localities. Over the same interval the sea-level falls by about 15 m followed by a gradual rise which may reflect the range in growth habits of corals rather than an actual sea-level rise. The 15 m drop in sea-level, over 500 years, presumably reflects the re-growth of the Laurentide ice-sheets. The data provide very strong support for the causes of Dansgaard-Oeshger and Bond cycles derived from polar and deep-sea cores that involve the slowdown and secession of the North Atlantic thermohaline circulation coupled to massive iceberg discharges and up 15 meter sea-level rises.
Fig. 4.19c Sea-levels (a) and $\Delta^{14}C$ (b) derived from present data for the 42 ka peak. Refer to Figs 4.26 and 4.27.
Fig. 4.19d Sea-levels (a) and $\Delta^{14}C$ (b) derived from present data for the 52 ka peak. The number of data points for this peak are insufficient to define a trend.
§4.7. $^{234}\text{U}/^{238}\text{U}$ in sea-water during the past 150000 years

Apart from the correlated variations between $^{14}\text{C}$ and $\text{U}/\text{Th}$ ages, the other interesting finding during the present work relates to variation in the $^{234}\text{U}/^{238}\text{U}$ ratio in corals and hence in the oceans. It is known that the residence time of Uranium in the sea water is relatively long, $\approx 3.3 \times 10^5$ years (Ku et al., 1977; Richter and Turekian, 1993). Tetravalent uranous ions ($\text{U}^{4+}$) readily form uranyl ions ($\text{UO}_2^{2+}$) under oxidising conditions, and remain stably dissolved in sea water, because they form water soluble compounds (Ivanovich and Harmon, 1992). On the other hand, Thorium is quickly removed from sea-water as it remains in the tetravalent state (Ivanovich and Harmon, 1992) by absorption onto particle surface, through co-precipitation with other elements (Fe, Mn) and 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 the result of this, Uranium stays in the sea-water for long periods at a uniform value as $\approx 3.2$ ng/g (Chen et al., 1986). In turn, the initial $^{234}\text{U}/^{238}\text{U}$ isotope ratio in corals ($\delta^{234}\text{U}(T)$) has been used as a indicator of degree of closed system behaviour for Uranium and Thorium isotopes (e.g., Gallup et al., 1994; Stirling et al., 1995; 1998) on the exception that the residence time of $^{238}\text{U}$ is equally long.

The $^{234}\text{U}/^{238}\text{U}$ ratio in Huon Peninsula corals used in the present study are shown in figure 4.20 together with the usual screening criteria of $149\pm10$ % which most previous studies employed (Stirling et al., 1998). The data from the present study clearly plot at lower value of $\delta^{234}\text{U}(T)$ than others, with a weighted average of 139.8 % (Fig. 4.20). This is approximately 10 % lower than that reported from other studies (Edwards et al., 1986, 1987; Stirling et al., 1995; 1998).
Most of the TIMS Th-U work in corals has been targeted at dating Last Interglacial (LIG) corals (eg., Chen et al., 1991; Stein et al., 1993; Stirling et al., 1995). Stirling (1996) dated LIG corals from Western Australian reefs and noticed that the $\delta^{234}$U(T) values were slightly (= 3 - 4 %o) higher than the present sea-water value. Due to the high precision achieved in TIMS measurements (approximately a factor of 5 better precision in CCTIMS), the difference could be verified outside of analytical uncertainties. However, Gallup et al. (1994) and Stirling et al. (1995, 1998) also observed an approximate linear variation between Th-U ages and $\delta^{234}$U(T) in corals from the same stratigraphic time horizon (Fig. 4.21). This was attributed to diagenetic alteration. The higher value of $\delta^{234}$U(T) for most of the WA corals was shown to be unaffected by this process. Previously reported results from LIG reefs also exhibited higher values of $\delta^{234}$U(T), but with larger errors that overlapped with the sea water value. The proposed higher value for the LIG period was 152 % (Stirling et al., 1995). In all of the high precision TIMS dating reported so far, there are few indications for diagenetic effects that tend to cause lower values of $\delta^{234}$U(T); this is also true for LIG corals from the Huon Peninsula (Stein et al., 1993; Fig. 4.21)
The weighted average value for last glacial Huon corals is $\delta^{234}\text{U}(T) = 139.8 \%\text{o}$ which is approximately 10 \% lower than that of present day sea water. Similarly, lower value were also reported from Barbados (for 14 – 30 ka samples; Bard et al., 1990a) and from Florida and Bermuda (for 77-116 ka samples; Ludwig et al., 1996). All of the available data is compiled in Fig. 4.22 including data from WA for Holocene corals (Eisenhauer et al., 1993). The cluster with the highest $\delta^{234}\text{U}(T)$ values are the LIG corals from WA (Stirling et al., 1998) and the lowest cluster correspond to the glacial period corals from PNG. It is interesting to note that corals from Florida and the Bahamas, for the 80 ka interstadial, plot at intermediate values, whereas similar age corals from Barbados have higher $\delta^{234}\text{U}(T)$. Holocene corals from WA cluster around the modern value (149\%). Huon corals that grew during the transition from the penultimate glacial to LIG (Esat et al., 1999) show a range of values, from low to high, as may be expected; as do the corals that grew during termination I (Bard et al., 1990a).
Fig. 4.21 Shifts in $\delta^{234}$U(T) to higher values appears to be correlated with shifts to older Th-U ages, from Stein et al. (1993) for Huon Peninsula Last Interglacial corals. Data reflect typical pattern of diagenetic alteration as also observed at Barbados (Galup et al. 1994) and Western Australia (Stirling et al. 1995, 1998).
These results are contrary to previous expectations for a constant $\delta^{234}\text{U}(T)$ in sea water for the last several hundred thousand years. Instead, $\delta^{234}\text{U}(T)$ appear to shift with changes in sea-level. During Holocene, sea-level observation at far-field sites indicate that melting of major ice sheets had ceased by $\sim 6.2$ ka and that the Antarctic ice sheet had contributed $\sim 3$ m of sea-level (Nakada and Lambeck, 1988). Therefore, ocean volume during the past $\sim 6000$ years was approximately constant. Sea-levels during the LIG were up to several meters higher than present (Stirling et al., 1995). In contrast, during the last glacial, average sea-level has been approximately 50 meter lower level in average (e.g., Chappell et al., 1996; Linsley 1996) and $\sim 80$ ka coral reefs at Florida and Bahamas were at most only 10 m lower than present (Ludwig et al., 1996; Stieling et al., 1998). It appears that $^{234}\text{U} / ^{238}\text{U}$ in the sea-water has varied in step with climate changes, possibly reflecting changing denudation rates, and hence variation of $^{234}\text{U}$ and U flux into the oceans. It may be expected that during glacial periods increases in dust levels may also reflect enhanced weathering and higher levels of $^{234}\text{U}$ input into oceans. However, the present data show lower concentrations of $^{234}\text{U}$ in oceans during glacial periods and higher levels during interglacials. This is presumably due to decreased chemical weathering rates during glacial periods, notwithstanding enhanced activity due to glacial erosion, and perhaps reflect higher riverine and continental precipitation fluxes into ocean during interglacials.

Richter and Turekian (1993) used simple models to predict the geochemical response of oceans to periodic forcing and to estimate residence times in oceans. They concluded that Sr and U had remained at constant levels during the past several hundred thousand years and that samples indicating variability more likely reflected local conditions or diagenetic (Richter and Turekian, 1993). The present data indicate that changing fluxes of $^{234}\text{U}$, mediated by climate cycles, indicate residence times shorter than a few thousand years.
If $^{234}$U input into oceans is influenced by continental weathering patterns, due to climate change, then similar variations may be expected in osmium isotopes. Osmium isotope composition of sea water has been measured in several laboratories (Pegram et al., 1992; Sharma et al., 1997; Oxburgh, 1998; Levasseur et al., 1998). Oxburgh (1998) has measured Os in marine sediments over the last two glacial cycles. She finds $^{187}$Os/$^{188}$Os in sea-water has varied from an almost constant value of 8.5 to 8.6 to lower values, up to 8.1, during the last glacial maximum and the penultimate glacial maximum. She attributes the lower values to reduced chemical weathering of the continents during periods of extreme glaciation; and that the response of ocean composition to changes in input flux to be less than 12,000 years. These results are in agreement with present observations of $^{234}$U behaviour in the oceans.
Fig. 4.22 Present $\delta^{234}$U(T)/Age measurements plotted together with previously published data. The present day sea-water value is 149 $\%_o$. Holocene samples lie close to 149 $\%_o$ but Last Interglacial (LIG) corals are slightly higher by about 3 – 4 $\%_o$ in step with 3 – 4 m higher sea-levels during the LIG. In contrast, during the last glacial period, the present data, and other data, show consistently lower values by about 10 $\%_o$, correlated with lower sea-levels. It appears that chemical weathering and continental fluxes of 234U were lower during the last glacial than during the Holocene or LIG.
Part II.

Sea-level observations and predictions for the MIS 3-1: Evidence from Huon Peninsula and North Western Australia
Chapter Five

Principles of Sea-level change and Glacio-hydro isostasy

§ 5.1 Introduction

Sea-level change, the sea-water level change relative to land, is a result of various phenomena such as climate change, tectonic processes and geoidal change (Fig. 5.1). Late Quaternary sea-level variation is mainly attributed to the global waxing and waning of former ice sheets over a time scale of 10^3-10^5 years.

Major changes in late Pleistocene ice volumes occurred in northern hemisphere, in large ice sheets, over North America and Northern Europe. During the last termination, partial melting of these ice sheets started at about 20 000 -18 000 ^14C yr BP; much of the ice had vanished by about 9000 ^14C yr BP, resulting in a globally averaged sea-level rise of about 120 m. This change did not occur uniformly over the oceans because of the spatial variation in the earth’s response to the changing ice-water surface load distribution. These are the glacio-hydro isostatic effects that will be discussed in this chapter.

§ 5.2 Definition of sea-level equations

Throughout this work we take sea-level at a given time and locality \((t, \phi)\) is the mean sea-level relative to the land. Past sea-level relative to the present level, relative sea-level, is defined by the equation

\[
\zeta_{\text{rel}} (t, \phi) = \zeta_{\text{fossil}} (t, \phi)
\]

where \(\zeta_{\text{fossil}} (t, \phi)\) is present day mean sea-level and \(\zeta_{\text{fossil}} (t, \phi)\) is the elevation of the fossil shoreline. Farrell and Clark (1976) first introduced the sea-level equation of
Chapter 5

**Ocean Steric (thermohaline) Volume Changes**

- **Shallow (0-500m)**: \(10^{-1}\) to \(10^{2}\) years*
  - \(10^9\) to \(10^3\) mm#
- **Deep (500-4000m)**: \(10^1\) to \(10^4\) years*
  - \(10^9\) to \(10^3\) mm#

**Liquid water on Land**

- **Groundwater Aquifers**: \(10^2\) to \(10^5\) years*
  - \(10^2\) to \(10^4\) mm#
- **Lakes and Reservoirs**: \(10^2\) to \(10^5\) years*
  - \(10^9\) to \(10^2\) mm#

**Sea level change**

**Glacial Accretion and Wastage**

- **Mountain Glaciers**: \(10^1\) to \(10^2\) years*
  - \(10^2\) to \(10^3\) mm#
- **Greenland Ice Sheet**: \(10^2\) to \(10^5\) years*
  - \(10^1\) to \(10^4\) mm#
- **East Antarctic Ice Sheet**: \(10^3\) to \(10^5\) years*
  - \(10^4\) to \(10^5\) mm#
- **West Antarctic Ice Sheet**: \(10^2\) to \(10^4\) years*
  - \(10^3\) to \(10^4\) mm#

**Crustal Deformation**

- **Lithosphere formation and Subduction**: \(10^5\) to \(10^8\) years*
  - \(10^3\) to \(10^5\) mm#
- **Glacial Isostatic**: \(10^2\) to \(10^4\) years*
  - **rebound**: \(10^2\) to \(10^4\) mm#
  - **continental**
    - **collision**: \(10^5\) to \(10^8\) years*
    - \(10^4\) to \(10^5\) mm#
- **Sea floor and epirogeny**
  - \(10^5\) to \(10^8\) years*
  - \(10^4\) to \(10^5\) mm#
- **Sedimentation**: \(10^4\) to \(10^8\) years*
  - \(10^3\) to \(10^5\) mm#

* Time scale (years)
# Order of change (mm)

Fig. 5.1 Processes of sea-level change.
global mass redistribution due to growth and decay of former ice sheets. If we assume that the melt water from ice sheets is uniformly distributed over the oceans at time $t$, then to a first approximation sea-level change will be

$$\Delta \zeta_{\text{eq}} (t) = \frac{A_{\text{ice}}}{A_{\text{ocean}}} \rho_{\text{ice}} - \frac{A_{\text{water}}}{A_{\text{ocean}}} \rho_{\text{water}}$$

(5.2)

where $\rho_{\text{ice}}$ and $\rho_{\text{water}}$ are the densities of ice and water respectively. Global, land based ice volume difference, between the time $t$ and the present, is described as $\Delta V_{\text{ice}}$. The surface area of the ocean is $A_{\text{ocean}}$. $\Delta \zeta_{\text{eq}}$ is then termed the change in equivalent sea-level (esl) and is one of the important inputs in glacial rebound modelling. ESL provides only a zero-order approximation of sea-level and the actual change is different from this because of tectonic and glacio-hydro-isostatic effects. When ice sheets melt, the corresponding surface load is reduced and the lithosphere beneath the former ice sheet tends to rebound as mantle material returns to the region beneath the formerly depressed lithosphere. At the same time, meltwater loads the oceanic lithosphere and induces further mantle flow, interalia from oceanic lithosphere to beneath the continental lithosphere. Because of (i) redistribution of surface load, (ii) deformation of the earth’s surface, and (iii) redistribution of mantle material beneath the surface, the gravitational attraction of the earth also changes and the final relative sea-level change will be a consequence of (i) changing ocean volumes (the esl contribution, eqn. 5.2), (ii) crustal displacement due to the changing load, and (iii) change in the shape of gravitational potential surfaces due to internal and external mass redistribution. Combined effects of (ii) and (iii) are the glacio-hydro-isostatic contributions. In addition to this, crustal displacement may result from a range of tectonic processes that contribute to changing sea-levels. Because of earth’s viscous characteristics, crustal displacement persists long after the melting of the ice sheets. For example, the last termination, relative sea-level change continues to the present, even though most of the ice sheet decay ceased by about 6000 about 6000 $^{14}$C yr BP.

In view of these various contributions, the sea-level change at time $t$ at a site $\phi$, can be written schematically as (eg., Farrell and Clark, 1976; Nakada and Lambeck, 1987):

$$\Delta \zeta_{\text{rel}} (t, \phi) = \Delta \zeta_{\text{eq}} (t) + \Delta \zeta_{\text{iso}} (t, \phi) + \Delta \zeta_{\text{tecl}} (t, \phi)$$

(5.3)

where $\Delta \zeta_{\text{rel}}$ is the change in relative sea level, $\Delta \zeta_{\text{eq}}$ is the previously defined equivalent sea-level contribution, $\Delta \zeta_{\text{iso}}$ is the total isostatic effect associated with the glacial rebound process and $\Delta \zeta_{\text{tecl}}$ is any additional tectonic contributions. $\Delta \zeta_{\text{iso}} (t, \phi)$ includes the glacio-isostatic component and hydro-isostatic component which are described as $\Delta \zeta_{\text{ice}} (t, \phi)$ and $\Delta \zeta_{\text{water}} (t, \phi)$, respectively. The two terms include the effects of changes in the gravity field caused by both loads. Then,
\[ \Delta \zeta_{\text{iso}} (t, \phi) = \Delta \zeta_{\text{rig}} (t, \phi) + \Delta \zeta_{\text{ice}} (t, \phi) + \Delta \zeta_{\text{water}} (t, \phi) \]  

(5.4)

In the equation (5.4), the isostatic term has been split into two parts in order to highlight the role of the gravitational attraction on sea-level change. The first part, \( \Delta \zeta_{\text{rig}} (t, \phi) \) describes sea-level change on a rigid earth when the only contribution to change arises from equivalent component and gravitational terms. The second part, \( \Delta \zeta_{\text{ice}} (t, \phi) + \Delta \zeta_{\text{water}} (t, \phi) \), consists of two elements that contribute to the isostatic adjustment and include modifications to gravity terms arising from deformation. The rigid terms are usually included in the isostatic formulation but for the present we have kept them separate.

The total sea-level change is expressed as:

\[ \Delta \zeta_{\text{tot}} (t, \phi) = \Delta \zeta_{\text{rel}} (t) + \Delta \zeta_{\text{rig}} (t, \phi) + \Delta \zeta_{\text{iso}} (t, \phi) + \Delta \zeta_{\text{water}} (t, \phi) + \Delta \zeta_{\text{tect}} (t, \phi) \]  

(5.5)

The first is the equivalent sea-level contribution term defined in the previous section. The second term \( \Delta \zeta_{\text{rig}} (t, \phi) \), describes additional contributions to sea-level change from eustasy on the rigid earth by allowing for variations in the gravitational attraction between ice and water, as the ice sheets melt, and between the water and land, as the ocean volume increases. \( \Delta \zeta_{\text{rig}} \) is therefore a function of both ice sheet geometry through time and of the geometry of the ocean basin from which water is extracted. This term is significant near ice sheets. Other terms are functions of temporal and spatial variables. They are discussed in later sections. \( \Delta \zeta_{\text{tect}} (t, \phi) \) is dominant at tectonically active areas such as Papua New Guinea.

All of the above components are included in the model for predicting sea-level changes based on theories outlined by Nakada and Lambeck (1987), and Johnston (1993) with subsequent modification by P. Johnston.

§ 5.3 Sea-level modelling

Input parameters required for sea-level calculations in solving equation 5.5 include the ice distribution with time, the rheological structure of the earth and a description of the ocean geometry. Each of these requirements are discussed briefly below.
§ 5.3.1 Earth Models

The behaviour of the internal structures of the earth is highly dependent on the time scale of the loading function. For very long time scales, it behaves as a viscous fluid (e.g. mantle convection) whereas for very short time scales, the earth responds to external forces primarily as an elastic body (e.g. as in seismic wave propagation through the mantle and lithosphere).

Earth models used are radially symmetric; that is their physical properties vary only with depth. They consist of a number of spherical shells; several layers of linear Maxwell viscoelastic mantle underlying an elastic lithosphere, and a liquid core. Rheological properties of each layer of the earth model are described by depth-dependent bulk modulus (K), shear modulus (μ), and density, all of which are obtained from the seismic velocity model PREM (Dziewonski and Anderson, 1981), and shear viscosity (η) defined by discrete values for each layer.

The models used for here are limited to two viscoelastic mantle layers, with viscosities of η_{\text{um}} and η_{\text{lm}} respectively. The upper mantle is taken to extend from the base of the lithosphere to the major seismic discontinuity at 670 km depth, and the lower mantle to extend from the 670 km discontinuity to the core-mantle boundary at a depth of 2891 km. The lithosphere is characterised by an effective elastic thickness H_L (Table 5.1).

<table>
<thead>
<tr>
<th>Model</th>
<th>H_L</th>
<th>η_{\text{um}}</th>
<th>η_{\text{lm}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA0</td>
<td>65</td>
<td>4 × 10^{20}</td>
<td>10^{22}</td>
</tr>
<tr>
<td>EA1</td>
<td>50</td>
<td>3 × 10^{20}</td>
<td>10^{22}</td>
</tr>
<tr>
<td>EA2</td>
<td>100</td>
<td>3 × 10^{20}</td>
<td>10^{22}</td>
</tr>
<tr>
<td>EA3</td>
<td>80</td>
<td>3 × 10^{20}</td>
<td>5 × 10^{22}</td>
</tr>
<tr>
<td>EA4</td>
<td>80</td>
<td>3 × 10^{20}</td>
<td>5 × 10^{21}</td>
</tr>
</tbody>
</table>

It should be noted that these parameters are effective only over time scales of 10^3 to 10^5 years. The viscoelastic formulation is noteworthy for both its mathematical convenience and for the good agreement it provides with the observed behaviour of the earth on these time scales. However, the actual rheology of the mantle will be more complex.
§ 5.3.2 Ice Models

As far as has been possible ice models used in this study are based on detailed reconstructions from the available geomorphological evidence. For the Northern hemisphere the major ice sheets located in Fennoscandia, the Barents-Kara sea (LSJ-98; Lambeck et al., 1998), North America and Greenland (a derivative of ICE 1; Peltier and Andrew, 1976), and Great Britain (GB-3; Lambeck, 1995b) are used. The Antarctic ice model used here is a scaled version of the ANT3 model of Nakada and Lambeck (1988) and assumes a maximum volume of ice at LGM equivalent to 25 m of sea-level. The loading and unloading cycles before LGM are based on a model by Lambeck (1999; unpublished) derived from oxygen isotope data. Figure 5.2 depicts the melting history of ice sheets employed in the present study.

The melting history of the Pleistocene ice sheets since the LGM was constrained by equivalent sea-level estimates inferred from the isostatically and tectonically corrected observations from at Barbados (Fairbanks, 1989; Bard et al., 1990a), Papua New Guinea (Chappell and Polach, 1991), Tahiti (Bard et al., 1996) and other data (Fleming et al., 1998). Only the Barbados cores reach back to LGM and

---

Fig. 5.2 Equivalent sea-level used in the present study (Lambeck, in prep). Details are provided in the text.
the eustatic sea-level history reconstructed from this observation is in good agreement with the ice models used in the present study. Fleming et al (1998) concluded that the eustatic sea-level at the LGM was \( ca. 125 \pm 5 \) m which also agrees well with the Ice models used in the present study.

§ 5.3.3 Ocean geometry

The changing shape of the coastlines during glacial melting affects the sea-level predicted at the coastline through the water load term \( \Delta \zeta_{\text{water}} \) as well as through the equivalent sea-level contribution term \( \Delta \zeta_{\text{eul}} \). The geometry of the ocean surface is time dependent and the sea surface area expands as ice sheets melt (Lambeck and Nakada, 1990; Johnston, 1993). The effect of time dependent coastline geometry, on the sea-level change at broad continental shelves, such as north western Australia, is particularly large and cannot be neglected. In the model an iterative procedure is used to allow for time dependent variations in coastlines and solutions usually converge, to cm precision, after three iterations.
§ 5.4 Geographical variation of sea-level change

Sea-level change resulting from isostasy are global, and geographically different depending on the position relative to the former ice sheets (Fig. 5.3). It is
convenient to discuss this spatial variability by grouping the sea-level response into three categories: near-, intermediate-, and far-field sites. The first corresponds to localities within or very close to the former ice margins where the response is dominated by crustal rebound. The second corresponds to localities beyond ice margins where the response is still strongly affected by glacial rebound but the contribution of equivalent sea-level is dominant. The third zone corresponds to areas well away from ice margins where the response is essentially the equivalent sea-level term modified by the effects of hydro-isostatic rebound (Fig. 5.4).

Fig. 5.4 Variation in the ice load component with distance from the ice sheet. Although the ice load component is large near the ice sheet, a constant small ice load component persists out to far-field site.

To illustrate these variations, a simple axi-symmetric ice model is used which has an ice sheet at the north pole (20 degree radius) and a far-field continent (60 degree radius) at the other pole (Fig. 5.5). The amount of ice at the pole is 80.4 m in equivalent sea-level, corresponds roughly to the size of the Laurentide ice sheet. The rheological model used for this axi-symmetric ice-ocean model is shown in Table 5.1.
§ 5.4.1 Model predictions for Near-field changes

Sea-level change in the near-field is primarily the sum of two contributions: the change in equivalent sea-level and crustal rebound, with the second term usually being dominant (Fig. 5.3a; 5.4). For small ice sheets, or near the margin of a large ice sheet, the two contributions may be comparable in magnitude, but opposite sign, and the sea-level signal will be a more complex (Fig. 5.3b; 5.4). The detail of the actual sea-level response for a given locality, in the near-field will, therefore, depend on the magnitude of the ice load. Due to the large mass of ice sheets, surfaces of constant gravitational potential are deformed and, because the ocean approximates such a surface, sea-level is also modified (Fig. 5.6). This effect is prominent for an rigid earth model. However, for a more realistic viscoelastic model, the magnitude of relative sea-level change is smaller than for the rigid earth case because gravitational mantle deformation is partly cancelled by gravitational effects from the ice sheets themselves (Fig. 5.5b).
Fig. 5.6  (a) Schematic diagram of the shape of the sea surface both before and after the deglaciation in the interior- and near-field regions on a rigid earth. (b) the same diagram for a visco-elastic earth (after Zwartz 1995). Prior to melting of ice, the sea surface is pulled up adjacent to the ice load due to the strong gravitational attraction between the ice sheet and the ocean.

The near-field relative sea-level, characterised by a large ice load component, is shown in Fig. 5.7. In this case the crustal rebound dominates and the land is uplifted so that sea-level is seen to fall relative to the land. For a locality near but outside the ice sheet or within the ice margin, crustal rebound is smaller in magnitude so that ice load and equivalent sea-level components are comparable but of opposite sign (Fig. 5.8).
Fig. 5.7 Relative sea-level change near the centre of the ice sheet (colatitude = 10 degree). EA0 is used as earth model for this calculation. The relative sea-level change in this region is characterised as continuously falling since the LGM (~21 ka) to the present. Ice load component is the most dominant component for sea-level change.

Sea-level is also sensitive to the rheological structure of earth as shown in Fig.5.9. In this particular example, the largest difference in sea-level occurs around 20,000 years BP. There is ~50 m variance in sea-level when the lower mantle viscosity is changed from $5 \times 10^{21}$ Pa s to $5 \times 10^{22}$ Pa s. Changing upper mantle viscosity by a similar amount leads to a sea-level difference of ~20. However, lithospheric thickness is less sensitive to sea-levels in the central region. The relative contribution of these parameters can be estimated by studying ice sheets of different dimensions.
Fig. 5.8 Near-field, distance from centre of the ice sheet is 18 degree. Although the Ice load component decreased dramatically, it is still the dominant factor for sea-level in this area.
Fig. 5.9 Dependence of sea-level change on the rheological structure of the earth at the center of an ice sheet (a), and at the edge of the former ice sheet (b). Relative sea-level response to changes in rheological parameters appears to be reasonable. The maximum rsl difference is about 50 m for extreme values of parameters at the LGM.

§ 5.4.2 Intermediate-field sea-level change

Further away, beyond areas of former glaciation, crustal response to unloading of ice is one of subsidence, mainly in reaction to the flow of the underlying mantle material towards the formerly loaded areas. Thus, here sea-level is mainly
dependent on the result of the equivalent sea-level and glacio-isostatic terms, the latter a rising relative sea-level (subsiding crust). Relative sea-level curves from intermediate-field regions are, therefore, characterised by continuously rising sea-levels from LGM to the present (Fig. 5.10).

\[ inter-mEDIATE \, fIeld \]

Fig. 5.10 Relative sea-level at an intermediate-field site (a). Ice load component is much smaller than that for the near-field, but still larger than water load (b).

§ 5.4.3 Far-field sea-level change

The far-field sites are distant from ice sheets, and even during the last glacial maximum sea-level changes are sensitive mainly to the equivalent sea-level and hydro-isostatic terms as illustrated schematically in Fig. 5.11. During the melting phase, \( \Delta \zeta_{\text{esl}} \gg \Delta \zeta_{\text{ice}} \) and it is the eustatic change that dominates the sea-level
characteristics. But during the postglacial period (PGP) $\Delta z_{\text{est}} = \Delta z_{\text{water}} > \Delta z_{\text{est}}$ and hydro-isostatic component that dominates, resulting in the characteristic mid-Holocene highstands (HHS) of continental margins. In the far-field, there is almost no spatial variation in the ice-load component of sea-level change (Fig. 5.12), and sea-level prediction is insensitive to the choice of earth-model parameters. Observations from these localities are relevant to estimates of changes in ocean volume.

The HHS result from a combination of two factors; the water loading of the adjacent ocean floor, and the on-going adjustment of the shape of the ocean basin due to ice unloading. Both effects are included in the model. But the second effect is overestimated in the axi-symmetric model used here because the “peripheral bulge” of the intermediate-field a occurs entirely in an oceanic environment whereas for realistic models it lies largely within the continents and its “collapse” does not modify ocean basin shape.
Fig. 5.11 Relative sea-level change at a far-field site (a). A high stand can be observed at ~7000 years BP when the ice sheet melting stopped. Water load component is large in this region, whereas the ice load contribution is minimal (b).

The HHS result from a combination of two factors; the water loading of the adjacent ocean floor, and the on-going adjustment of the shape of the ocean basin due to ice unloading. Both effects are included in the model. But the second effect is overestimated in the axi-symmetric model used here because the "peripheral bulge"
of the intermediate-field $a$ occurs entirely in an oceanic environment whereas for realistic models it lies largely within the continents and its "collapse" does not modify ocean basin shape.

Fig. 5.12 Ice load component of relative sea-level change as a function of distance from centre of the ice sheet for intermediate- to far-field sites.
Fig. 5.13 Schematic diagram of relative sea-level change in the far-field; along the continental margin (a), and small island in the middle of ocean (b), after Lambeck and Nakada (1990). At the time $t_a$, sea-level started to rise rapidly up to time $t_2$ and shoreline moved from A to B at the continental margin. When melting ceased, sea-level change at each site continued as a consequence of the earth's deformation. Sea-floor subsides due to newly added water, and sea-level appears to fall relative to the shoreline (point C) at time $t_3$. As a result the sea-level curve at the site develops a characteristic high stand. A very small ocean island will shift with ocean floor and record no differential sea-level change during $t_2$ to $t_3$. For the case of relatively small melt-water addition, continuous sea-level change is observed at an island near the continent (c).
During deglaciation, water loading is restricted to the oceanic side, mantle material flows from beneath the ocean to beneath the continent resulting in crustal tilting. Relatively high sea-level evidence is found in-land, and evidence of submergence sea-ward (Fig. 5.13). Following the melting of most of the ice sheets by ≈7000 years BP, water loading was the dominant component of sea-level in the far-field sites (Fig.5.11). Along continental margins, in the far-field, the contribution of the water load to sea-level change is larger than the glacio-isostatic contribution. The effect of the water load decrease smoothly with time during deglaciation and throughout the subsequent interglacial period (Fig.5.11). The relative sea-level falls from the maximum level to the present level with time. The water load component is also dependent on the position of the site relative to the shoreline and of the shape of the coastline in the area of the site (Fig.5.14).

![Diagram](image)

Fig. 5.14 Water load component of the far-field continental margin for five different epochs.

Hence, it is essential to use detailed models of coastal geometry for predictions of far-field sea-levels. Large differences, in relative sea-level, occur between off shore sites and coastal areas due to tilting of the continental margins. High-stand differences for each site are plotted in Fig. 5.15 to illustrate this effect. The amplitude of the far-field high stand depends on the distance from the coastline but also on earth model parameters. Observations of this tilting constrain earth model
parameters and provide a test of the assumption that there has been no increase in ocean volume after 7 ka. (Nakada and Lambeck, 1988; Yokoyama et al., 1996).

Fig. 5.15 Predicted amplitude of the far-field sea-level highstand versus distance from the coastline. Three different curves represent the results obtained using different earth models. At far-field sites, rsl is less dependent on details of earth models.

§ 5.5 Sea-level observations

There are many sea-level indicators, including geomorphological, biological and geochemical ones. A basic principle in documenting sea-level change evidence is to ensure that the sample is in situ and indicative of sea-level height, within a known uncertainty, and that it provides a reliable age of formation. A series of tropical or subtropical sea-level indicators are summarised in figure 5.16 (Kelletat, 1988). Notches, basal peat, coral reefs and micropalaeontological methods are preferred as reliable in-situ indicators of palaeo-sea-level markers. It should be noted that the possibility of compaction renders basal peat data prone to uncertainty. Contamination of ages by modern or old carbon can also be a concern with peat data. Biological carbonate samples such as corals and molluscs, including microfossils comprise an important source of information and were used in the present study. Their use as sea-level indicators has been widespread and their growth relationship to sea-level are reasonably well understood. Also the material lends itself to both $^{14}$C and U-series dating and methods have been developed to test for whether the original samples have been adequately preserved. These include
mineralogical observations with a binocular microscope, XRD (X-Ray Deflection), FT-IR (Fourier Transfer function - Infra Red analysis), and $^{234}\text{U}$ (see chapter 3).

§ 5.5.1 Biological indicators of sea-level

Researchers have used a broad array of fauna and flora as sea-level indicators, particularly corals, forams, ostracods, diatoms and mangroves. In tropical regions, coral reefs are very good indicators of sea-level. Although corals live at various depths, palaeo-water depth may be reconstructed from investigation of assemblages in the reef structure. In tectonically active areas, palaeo reefs have been uplifted above present sea-level. If we assume a fixed history of uplift, it becomes possible to use uplifted coral data to reconstruct palaeo sea-level. This type of study has been conducted in many parts of the world, and most notably Papua New Guinea (eg., Chappell, 1974; Bloom et al., 1974; Chappell, et al., 1996; Esat et al., 1999), Barbados (eg., Bloom and Yonekura, 1985) and the Ryukyu Islands (eg., Ota and Omura, 1992).

Coral drill-cores have been obtained off the coast of Barbados (Fairbanks, 1989) and provide very reliable sea-level data for the last deglaciation. Currently, Atlantic ocean, *Acropora Palmata*, in the Atlantic ocean, live at depths shallower than 5 m so that sea-level can be determined within an uncertainty of 5 m. Similar studies have been conducted in Papua New Guinea (Chappell and Polach, 1991) and Tahiti (Bard et al., 1996).

Microfossil evidence from diatoms, foraminifera and ostracoda are also useful indicators of palaeo sea-level. Many taxa are distributed in various salinity ranges and are relatively indifferent to other environmental factors such as temperature. Therefore if sediments are used for microfossil assemblage analysis, the horizons for these taxa can be identified with respect to marine transitions. For Holocene sediments, diatoms whose frustules are silica-based are often preserved in sediments in good conditions. Additionally, diatom assemblages have the advantage of relatively narrower ranges of occurrence in terms of salinity, particularly, at the boundary between fresh and brackish water (Sato et al., 1996). Thus many constraints on Holocene sea levels have been obtained to ~20 cm resolution using data from diatoms (eg., Yokoyama et al., 1996). However, diatom assemblages in sediments deposited before the Holocene are relatively poorly preserved except in uplifted areas. These sediments generally experience inundation by sea water during deglaciation and the frustules are susceptible to dissolution due to under saturation of silica in sea water. In particular, tropical sediments strongly indicate silicate dissolution. However, foraminifera and ostracoda assemblage analysis are relatively
well preserved and can instead be used. Many studies have also been conducted to
reconstruct palaeo environments using both ostracoda and foraminifera data (eg.,
Scott et al., 1995; Murray, 1991). Resolution in sea-level height reconstruction is not
as good as for diatom analyses; though because, both foraminifera and ostracoda
have calcium carbonate shells it is occasionally possible to find direct evidence of
reworking. In particular, some ostracoda species live in brackish water and have
fragile shells; thus, if re-deposited due to secondary sediment transportation, they
are very unlikely to retain both shells (DeDeckker, 1988). The micropaleontological
methods described above complement each other and in unison may be used to
provide precise sea-level history.

Fig. 5.16 Sea-level indicators at site in tropical or subtropical environment
(after Kelletat 1988).

§ 5.5.2 Oxygen isotopes as a proxy for equivalent sea-level

Oxygen isotope analysis in foraminifera, as a sea-level change indicator, relies
on their retaining a record of oxygen isotopes in sea-water in their CaCO₃ skeletons.
The value is defined relative to the Standard Mean Ocean Water (SMOW):

\[ \delta^{18}O = \left[ \frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{standard}}}{(^{18}O/^{16}O)_{\text{standard}}} \right] \times 1000 \]  (5.6)
Variations in δ¹⁸O reflect changes in ice volumes in the polar regions, salinity, or sea-water temperatures or a combination of these factors. Chappell and Shackleton (1986) obtained a sea-level curve by using both coral terrace data and deep-sea oxygen isotope data from sediment cores. A distinction between global ice volume, and the sea-water temperature contribution can be made by comparing δ¹⁸O in planktonic and benthic forams, as the latter are less affected by temperature variations (Shackleton, 1987). Scaling of the δ¹⁸O sea-level curve using uplifted coral reef data results in reasonable agreement between the two methods (Chappell et al., 1996), although the details are not exactly matched, especially during the last glacial.

§ 5.6 Summary

Variations in sea-level occur not only with time but also by location. Observed values of sea-level heights vary depending on the distance from former ice sheets. Far-field sea-level observations are best-suited to constraining the ocean volumes through time. Loading by polar ice sheets is minimal, and equivalent sea-level component can be determined from relative sea-level observation in the far-field.

Past sea-level changes can be successfully derived from various indicators during the Holocene or the Last Interglacial. However it is difficult to obtain sea-level information for the last interstadial as most coral reefs, of this period, are below the present sea-level.

Indirect sea-level observations are used to establish the equivalent sea-level change. Deep-sea δ¹⁸O records reflect ice volume history, but also ambient sea water temperature and salinity. Far-field sites in tectonically active areas have been used to provide a time scale for equivalent sea-levels obtained from the deep-sea sediment δ¹⁸O measurements. Tectonically uplifted areas preserve palaeo sea-level information above the present sea-level, particularly at the Huon Peninsula, Papua New Guinea. This area lies in close proximity to the North coast of Australia where tectonic stability and a large continental shelf shelters and allows preservation of palaeo sea-level indicators. Studies of sea-level change in these areas has the potential to reliably establish past sea-levels and provide constraints to glacio-hydro-isostatic models.
Chapter Six

Late Pleistocene sea-level observations from the Huon Peninsula, Papua New Guinea

§ 6.1 Introduction

In this chapter, we introduce chronological data of sea-level change and tectonic activity at Huon Peninsula (HP), Papua New Guinea (PNG). As a by-product of the time-scale calibration study reported in Chapter 4, the coral data collected from the HP reefs may also contain information on sea-level fluctuations during the oxygen isotope stages 3 and 4 if the growth positions of the corals can be related to sea-level at the time of growth, and if the elevations of the dated corals have been measured. It also relies on the assumption that the rate of tectonic uplift in the region is known over the same time period.

The HP is located on the north eastern coast of PNG at the boundary between the converging Australian and Pacific plates (Fig.6.1). The tectonism of this area is further complicated by the presence of the North Bismarck, South Bismarck, Solomon Sea and Woodlark Plates. HP itself lies on the north eastern side of the Ramu-Markham fault where the Australian plate thrusts against the South Bismarck plate and it has been possible, using geodetic techniques, to observe crustal movement in this region over relatively short time periods (Tregoning et al., 1998; Stevens et al., 1998). The extremely high rate of tectonic uplift along the HP has preserved palaeo coral reefs at heights well above present sea-level. Last interglacial lagoons, for example, can be found at elevations above 200 m (Chappell, 1974). These uplifted coral reefs can provide useful sea-level information if the rate of uplift can be accurately determined. Bloom and Yonekura (1985;1990) have
examined the reef elevations of Last interglacial (LIG) age and concluded that the uplift rate over these time scales can be linearly interpolated assuming that sea-levels were at their present level during the LIG. Chappell et al (1996) and Ota and Chappell (1996) found evidence for meter scale co-seismic uplift in the Holocene period, although direct observation of a 1992 earthquake revealed that the associated uplift was only 10 cm (Pandolfi et al., 1994). Therefore, Chappell et al. (1996) concluded that the tectonism in HP region can be characterised by two distinct classes of event, distinguished by the frequency and scale of uplift; m-scale uplift at a frequency of once per 1200 years for one class, and cm-scale uplift at a much greater frequency for the second.

For more than 20 years, HP has provided some of the most reliable sea-level data available for the late Pleistocene (Chappell, 1974; Bloom et al., 1974; Chappell and Shackleton, 1986). Uplifted terraces have been dated using conventional counting methods by both $^{14}$C and U/Th, and recent mass spectrometric measurements have yielded more precise results (Chappell et al., 1996). However, to date not many coral terrace dates have been measured using TIMS (Thermal Ionisation Mass Spectrometry). In the present study, more than 20 corals collected from Reefs II and III have been dated using this technique. A detailed description of the corals and the associated results can be found in the appendix and Chapter 4.
§ 6.2 Sample locations

Most of the corals used in this study were collected from Bobongara (Bobo) and Kanzarua (Kanz) sections that have some of the highest uplift rates on HP (Fig.6.2). All of the samples were collected from reefs II and III. In these two sections, the rapid uplift has allowed several sub-reefs to be identified. The reef III complex consists of three sub-reefs IIIa upper (ca. 60 ka), IIIa middle (ca. 52 ka), and IIIb (ca. 44 ka) (Chappell et al., 1996). The reef II complex has two sub-reefs on the Bobo transects, IIa (ca.38 ka) and IIb, though no discrete sub-reefs were found in the Kanz section (Pandolfi and Chappell, 1994). Most of the corals were obtained from reef cliffs. The reef III complex (ca. 44-60 ka) is located between ~130 m and ~100 m above present sea-level (Chappell et al., 1996), while the LIG reef is located at 320 m at Kanz and 403 m at Bobo (Fig.6.3). The LIG reef elevations were used for
calculation of the first order uplift rate. As mentioned above, a linear uplift rate can be assumed for time scales upward of several thousand years for HP (Bloom and Yonekura, 1985) and this is supported by similar values of uplift rate obtained using both the LIG reef and Holocene reef data (Ota et al., 1993; Chappell et al., 1998). Other localities where the LIG reef could be identified but with different uplift rates, lead to similar inferences of sea-levels at the time of formation of the intermediate reefs so that the assumption of linear uplift rate at each site appears to be reasonable even though the rates themselves vary substantially from site to site. In the present study, uplift rates of 2.8m/kyr for Kanz transection and 3.3m/kyr for Bobo transection (Chappell, et al., 1996) are adopted.

Fig. 6.3 Reef profiles of Kanzarua and Bobongara sections at Huon Peninsula. Numbers show U-series dates reported by Chappell et al., (1996) with sample names (K=Kanz, B=Bobo).

§ 6.2 Evidence of co-seismic uplift

Detailed examination of the reef structures has shown that the HP has experienced a number of major seismic uplift events over the past 100 000 years and it has been possible to estimate the timing and amount of uplift from the regressive
reef structures formed after the earthquakes. Several meter-scale events have been identified in this way (Ota et al., 1993; Ota and Chappell, 1996).

There have been four earthquakes of magnitude >7 in the past 60 years in this region (Ripper and Letz, 1991). However the only documented co-seismic event is one that occurred in 1992 and which produced 7 to 13 cm uplift (Pandolfi et al., 1994). Historical documents of the record of earthquakes goes back only about 100 years in PNG and the fossil reefs provide a possible record of the earlier events.

Fig. 6.4 Same as Fig. 6.2 but for Madang.

A question that arises is whether the meter scale events or the centimetre scale events are dominant in PNG. Ota and Chappell (1996) concluded that meter scale uplifting events were dominant because of the distinct morphological features formed in the reefs. If the observed regressive terraces had been formed by repeated small uplifting events (cm scale uplift event) with small intervals (<~200 years), then the morphologic record, such as the sharply defined cliffs, notches and platforms, should show greater signs of significant erosion (Ota and Chappell, 1996).
During a geodetic field survey carried out by Research School of Earth Sciences, Australian National University, corals were sampled in July 1998 from uplifted reefs at Kalibobo point near Madang on the North Western coast of Huon Peninsula (Fig. 6.4). Several studies have been made of corals from Madang reefs (eg. Tudhope et al., 1995; Pandolfi and Minchin 1995), but $^{14}$C dates have not been reported. In this area a ca. 2.5 m uplifted reef platform has been preserved which extends for more than 2 km along the coast (Fig. 6.5); three coral samples were collected from this reef for $^{14}$C dating (Fig 6.6). Optical microscope investigation of textures, and XRD analysis revealed distinct aragonite structures for all samples with $\approx$100 % aragonite content. The $^{14}$C results obtained from these samples are shown in Figure 6.6. Mada-1 was sampled from the upper part of the present notch just above current mean sea-level which is presently located at the middle of the notch so that this sample would be expected to yield the most recent age of formation. Mada-2 and Mada-3 were sampled at 1.9 and 2.4 m above present sea-level, respectively. Radiocarbon dates, corrected for $\delta^{13}$C and reservoir age, record two separate events. Mada-2 and Mada-3 indicate an age of $\sim$550 ($^{14}$C yr) BP whereas Mada-1 gives a date of formation of $\sim$300 ($^{14}$C yr) BP. The age difference between Mada-1 and the other two samples shows a discrete jump at the time of reef development due to vertical movement.

![Fig. 6.5](image)

Fig. 6.5 The uplifted coralline terrace at Madang.

We conclude that approximately 550 $^{14}$C years ago, a substantial co-seismic event occurred with a magnitude of $\sim$3m. This supports the findings of Ota and Chappell (1996) that meter scale uplift can be produced by distinct large magnitude tectonic events.
§ 6.3 Results from corals at Kanzarua and Bobongara sections

Twenty three new U/Th ages, including 8 duplicate samples originally reported by Chappell et al (1996), have been obtained (Table 6.1; also see Chapter 4). Although results from the present study have better precision than the earlier results, the agreement with the previously reported values is satisfactory. For instance, the ages for Kanz U9 previously measured with both conventional α-spectrometry (Omura et al., 1995) and TIMS (Esat, 1995) methods are in good agreement, with the value obtained in this study (Table 6.1).

As described in Chapter 4, four discrete age groups are found which correspond to periods of main reef (or sub-reef) growth. Sub-reef b is higher than sub-reef a, while c is the highest of the three. Reefs IIIa, IIc, IIb, and IIa were found to have formed at approximately 52 ka, 42 ka, 37 ka, and 32 ka respectively (see Fig.6.3). Figure 6.7 shows the tectonically-corrected elevations of the corals as a function of age, assuming there were no sudden tectonic uplift events. These elevations represent a lower limit to sea-level during the interval 30 – 50 ka: sea-levels must have been higher than these heights. Individual corals can grow at various
depths below sea-level and the relationship between the individual coral’s growth position and the coeval upper limit to coral growth needs to be established from the facies examination of the reef within which the coral is located.

Two of the Kanz points lie well above the other data, by approximately 12 m (Fig.6.7) and sea-level must have been higher than the height of these corals. However, further data are required to confirm these elevations. One coral at ~42 ka from Bobongara is situated well below others. This is the only species of *Platygira* coral used in this study. It can grow at close to sea-level when *Platygira* makes microatoll. However in other circumstances, these species can be found up to about 20 m below sea-level. We take this data point to be a limit of sea-level for this period.
Table 6.1 Height and U-series dates of corals from Reef II and III

<table>
<thead>
<tr>
<th>Sample</th>
<th>Height (m)</th>
<th>Reef Number</th>
<th>Age (ka)</th>
<th>Sea-level (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kanz-9</td>
<td>78</td>
<td>IIIa</td>
<td>53.4±0.3</td>
<td>-72</td>
</tr>
<tr>
<td>Kanz-11</td>
<td>78</td>
<td>IIIa</td>
<td>51.3±0.3</td>
<td>-65</td>
</tr>
<tr>
<td>Kanz-U10</td>
<td>49</td>
<td>IIIc</td>
<td>43.7±0.3</td>
<td>-73</td>
</tr>
<tr>
<td>Kanz-4</td>
<td>86</td>
<td>IIIa</td>
<td>51.5±1.6</td>
<td>-60</td>
</tr>
<tr>
<td>Kanz-13</td>
<td>60</td>
<td>IIIb</td>
<td>38.3±0.5</td>
<td>-47</td>
</tr>
<tr>
<td>Kanz-15</td>
<td>39</td>
<td>IIIc</td>
<td>42.0±0.6</td>
<td>-79</td>
</tr>
<tr>
<td>Kanz-A</td>
<td>25</td>
<td>II</td>
<td>37.5±0.2</td>
<td>-80</td>
</tr>
<tr>
<td>Kanz-U15</td>
<td>23</td>
<td>II</td>
<td>33.4±0.2</td>
<td>-71</td>
</tr>
<tr>
<td>Kanz-U16</td>
<td>29</td>
<td>II</td>
<td>30.4±0.4</td>
<td>-56</td>
</tr>
<tr>
<td>Kanz-U9</td>
<td>28</td>
<td>IIa</td>
<td>42.3±0.2</td>
<td>-91</td>
</tr>
<tr>
<td>Kanz-U11</td>
<td>27</td>
<td>IIa</td>
<td>37.9±0.3</td>
<td>-79</td>
</tr>
<tr>
<td>Kanz-U12</td>
<td>26</td>
<td>IIa</td>
<td>37.5±0.7</td>
<td>-79</td>
</tr>
<tr>
<td>Kanz-U13</td>
<td>26</td>
<td>IIa</td>
<td>35.8±0.4</td>
<td>-74</td>
</tr>
<tr>
<td>Kanz-U8</td>
<td>27</td>
<td>IIa</td>
<td>37.0±0.6</td>
<td>-77</td>
</tr>
<tr>
<td>Bobo-U10</td>
<td>49</td>
<td>IIa</td>
<td>37.2±0.2</td>
<td>-79</td>
</tr>
<tr>
<td>Bobo-U11</td>
<td>49</td>
<td>IIa</td>
<td>37.9±0.3</td>
<td>-76</td>
</tr>
<tr>
<td>Bobo-U20</td>
<td>40</td>
<td>IIb</td>
<td>37.6±0.2</td>
<td>-84</td>
</tr>
<tr>
<td>Bobo-U18</td>
<td>37</td>
<td>IIb</td>
<td>42.4±0.2</td>
<td>-103</td>
</tr>
<tr>
<td>Bobo-U17</td>
<td>20</td>
<td>IIc</td>
<td>32.0±0.2</td>
<td>-86</td>
</tr>
<tr>
<td>Bobo-U28</td>
<td>22</td>
<td>IIc</td>
<td>32.3±0.5</td>
<td>-84</td>
</tr>
<tr>
<td>Bobo-U24</td>
<td>30</td>
<td>IIc</td>
<td>32.2±0.2</td>
<td>-76</td>
</tr>
<tr>
<td>Bobo-U30</td>
<td>27</td>
<td>IIc</td>
<td>31.5±0.2</td>
<td>-77</td>
</tr>
<tr>
<td>Bobo-U21</td>
<td>30</td>
<td>IIc</td>
<td>29.7±0.2</td>
<td>-68</td>
</tr>
</tbody>
</table>

Chappell et al (1996)*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Height (m)</th>
<th>Reef Number</th>
<th>Age (ka)</th>
<th>Sea-level (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRT-F1</td>
<td>183</td>
<td>IV</td>
<td>72.8±2.2</td>
<td>-72</td>
</tr>
<tr>
<td>Kanz-1(TIMS)</td>
<td>105</td>
<td>IIIa</td>
<td>61.4±0.6</td>
<td>-70</td>
</tr>
<tr>
<td>Kanz-3</td>
<td>96</td>
<td>IIIa</td>
<td>51.8±0.8</td>
<td>-53</td>
</tr>
<tr>
<td>Kanz-4</td>
<td>86</td>
<td>IIIa</td>
<td>51.2±0.8</td>
<td>-60</td>
</tr>
<tr>
<td>Kanz-33</td>
<td>77</td>
<td>IIIa</td>
<td>45.8±0.7</td>
<td>-53</td>
</tr>
<tr>
<td>Kanz-9(TIMS)</td>
<td>78</td>
<td>IIIa</td>
<td>54.6±0.7</td>
<td>-59</td>
</tr>
<tr>
<td>Kanz-34</td>
<td>56</td>
<td>IIIb</td>
<td>44.5±0.7</td>
<td>-71</td>
</tr>
<tr>
<td>Kanz-U10</td>
<td>49</td>
<td>IIc</td>
<td>43.9±0.7</td>
<td>-73</td>
</tr>
<tr>
<td>Kanz-U9</td>
<td>28</td>
<td>IIa</td>
<td>41.8±0.6</td>
<td>-92</td>
</tr>
<tr>
<td>Kanz-U9 (TIMS)</td>
<td>28</td>
<td>IIa</td>
<td>42.2±0.3</td>
<td>-92</td>
</tr>
<tr>
<td>Kanz-U14(TIMS)</td>
<td>26</td>
<td>IIa</td>
<td>34.8±0.0</td>
<td>-72</td>
</tr>
<tr>
<td>Bobo-U10(TIMS)</td>
<td>49</td>
<td>IIa</td>
<td>37.8±0.3</td>
<td>-79</td>
</tr>
<tr>
<td>Bobo-U24</td>
<td>30</td>
<td>IIc</td>
<td>33.0±0.5</td>
<td>-82</td>
</tr>
<tr>
<td>Bobo-U21</td>
<td>30</td>
<td>IIc</td>
<td>33.4±0.6</td>
<td>-84</td>
</tr>
</tbody>
</table>

*Ages were obtained using ⁰⁻spectrometric conventional U/Th method except
“TIMS” labelled samples.
The evidence suggests that throughout MIS 3, from about 30 000 – 45 000 yr BP sea-level at the Huon Peninsula was about 70 m below present and that major excursions from this level did not occur during this interval. In contrast, from about 45 000 – 55 000 yr BP, which corresponds to the latter part of MIS 4, sea-level may have been somewhat higher, at about 55 m below present.

The sea-level curve inferred from the oxygen isotope record, corresponding to equivalent sea-level, is compared with present observations in Figure 6.7. The curve is established from two deep-sea oxygen isotopic data sets (Lambeck et al., 1999 in prep.), from the eastern equatorial Pacific (Shackleton, 1987), and from the Sulu Sea (Linsely, 1996), and is scaled by the previously reported Huon terrace data of Chappell et al. (1996). Agreement between the two, with the exception of the previously noted points, is quite satisfactory. A possible envelope of the sea-level curve is indicated by the dashed line which correspond to uncertainties in the $\delta^{18}O$ results revealed when the different data sets are compared. While agreement between the two is satisfactory, the importance of isostatic corrections remains to be examined. The observations refer to relative sea-levels at the Huon, whereas the $\delta^{18}O$ results refer to the changes in ice volume which in turn relate to sea-level according to eqn. 5.6.
§ 6.4 Comparison with glacio-hydro-isostatic modelling

Glacial isostatic modelling was undertaken for both the Bobo and Kanz sections. The rheological model employed here is a nominal 3-layer model found to be representative for many locations. It consists of a 65 km elastic lithosphere, $4 \times 10^{20} \text{ Pa s}$ upper mantle viscosity and $1 \times 10^{22} \text{ Pa s}$ lower mantle viscosity. Site locations used for modelling are given in Table 6.2. The ice model is based on glacial cycles from about 220,000 yr BP to the present with the ice partitioned between the various ice sheets as shown in Fig. 5.2.

Table 6.2 Sites used for sea-level prediction

<table>
<thead>
<tr>
<th>Reef section</th>
<th>Site</th>
<th>Longitude (E degree)</th>
<th>Latitude (S degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kanzarua</td>
<td>K1</td>
<td>147.650</td>
<td>6.225</td>
</tr>
<tr>
<td></td>
<td>K2</td>
<td>147.675</td>
<td>6.200</td>
</tr>
<tr>
<td></td>
<td>K3</td>
<td>147.700</td>
<td>6.175</td>
</tr>
<tr>
<td></td>
<td>K4</td>
<td>147.725</td>
<td>6.150</td>
</tr>
<tr>
<td></td>
<td>K5</td>
<td>147.750</td>
<td>6.125</td>
</tr>
<tr>
<td>Bobongara</td>
<td>B1</td>
<td>147.780</td>
<td>6.350</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>147.813</td>
<td>6.325</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>147.840</td>
<td>6.300</td>
</tr>
<tr>
<td></td>
<td>B4</td>
<td>147.863</td>
<td>6.275</td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>147.888</td>
<td>6.250</td>
</tr>
<tr>
<td>Madang</td>
<td>M1</td>
<td>145.880</td>
<td>5.630</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>146.000</td>
<td>5.500</td>
</tr>
<tr>
<td></td>
<td>M3</td>
<td>146.130</td>
<td>5.380</td>
</tr>
<tr>
<td></td>
<td>M4</td>
<td>146.250</td>
<td>5.250</td>
</tr>
<tr>
<td></td>
<td>M5</td>
<td>146.380</td>
<td>5.130</td>
</tr>
</tbody>
</table>

Figure 6.8 illustrates the late Holocene predicted sea-levels for a section through Madang. It shows the characteristic trend in the high stand amplitude predicted for 6000 $^{14}$C years ago with high levels at the coast decreasing with distance offshore. This is the result of water loading of the adjacent ocean floor. Note that the amplitudes are over-estimated because the model here assumes that ice volumes have not changed over the past 6000 $^{14}$C years. If the uplift of the Madang terrace occurred at about 500 $^{14}$C yr BP then the isostatic correction to uplift is about 0.3 m, and the tectonic uplift would be about 2.2 m. Figure 6.9 illustrates the predicted sea-levels for the Kanz and Bobo sites where locations are sufficiently near to each other for there to be negligible differential change in the isostatic contribution. For both sites, the predicted sea-levels are above the nominal equivalent values by about 10 m.
Relative sea-level calculated for all three sites and equivalent sea-level for the period between 25 ka and 60 ka is shown in Figure 6.9. Two sites, Kanzarua and Bobongara, are only separated by ca. 2.5km so that the glacio-isostatic effect for these areas is identical (Fig. 6.9). The values for equivalent sea-level is consistently deeper than relative sea-level value maximum by ca. 10 m through period.
Fig. 6.9 Predicted sea-level variations at Kanzarua and Bobongara. The predicted values are always higher than esl.

§ 6.6 Equivalent sea-level from 25 ka to 60 ka

As can be seen from figure 6.7, the first order correlation between nominal esl and coral based sea-level is quite good. In the present study area, the isostatic component is ca. 10 m. If this is taken into account, and a possible coral formation depth of 10-20 m below sea-level is assumed then an esl curve with uncertainties of ~10 m can be drawn. For the period from 25 ka to 60 ka, sea-level fluctuated between ~80 and ~50 m with a period of ca. 4000 (Fig.6.9). This may correspond to the change in oceanographic and climatological conditions recorded in the Greenland ice core. This was discussed in greater detail in Chapter 4.
Chapter Seven

Late Pleistocene Sea-level observations from Australia: A review

§ 7.1. Introduction

The Australian margin is tectonically stable on time scales of $10^4$-$10^5$ years as evidenced by the occurrence of the last interglacial shorelines at a few meters above present sea-level in Western Australia (Stirling et al., 1995), South Australia (Schwebel, 1984; Belperio et al., 1995) and northern New South Wales (Marshall and Thom, 1976). The Australian coastal environment is therefore suitable for determining the position of sea-level during late glacial time without the need to allow for vertical tectonic movement. Several attempts have been made to constrain sea-level change using coral data from the late Pleistocene. However, the coral record provides only a limit to the sea-level curve; depending on the depth at which a particular coral may have grown and this can be uncertain by up to 10-20 m. At the Great Barrier Reef, for example, there is considerable evidence that coral reef growth may not have been able to keep up with rapidly rising sea-levels (Davis et al., 1995; Zwartz 1995; Marshall et al. 1998). Individual corals may have lived at a considerable depth below sea-level so that their age-depth relationship may not provide a reliable indicator of sea-level change. For example, Veeh and Veevers (1970) reported a coral from 175 m depth with an age of 13,600 yr $^{14}$C BP. There are distinct advantages to using sediment cores to reconstruct palaeo environmental histories. Sediments can record environmental change precisely and contain microfossils that provide a variety of information, such as salinity, temperature, depositional conditions and whether they have been subsequently reworked.
Sediment cores from the sea floor are used in the present study to obtain precise palaeo sea-level data. In this chapter, some previous studies are reviewed and then some observational data from the new sediment cores is reported.

§7.2. Previous studies of sea-level during the LGM and late glacial period

Sea-level data for the LGM is rare because of inundation after the last deglaciation during the late Pleistocene and early Holocene. Around the coast of Australia, a number of isolated data points have been reported but no systematic study has yet been made. Much of this information has come from sediment cores (Table 7.1.) but most is not very precise.

<table>
<thead>
<tr>
<th>Region</th>
<th>Reference</th>
<th>Depth (m)</th>
<th>Age (yr $^{14}$C BP)</th>
<th>MIS*</th>
<th>$^{14}$C dated material or method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf of St Vincent</td>
<td>Cann et al. (1993)</td>
<td>27-30 m</td>
<td>32,000-40,000</td>
<td>3</td>
<td>LSC</td>
</tr>
<tr>
<td>Off shore of Sydney</td>
<td>Ferland et al. (1995)</td>
<td>&lt; 130 m</td>
<td>11,870, 17,320, and 40,990</td>
<td>2</td>
<td>AMS and LSC</td>
</tr>
<tr>
<td>Gulf of McCulloch</td>
<td>McCulloch et al. (1989)</td>
<td>&gt; 53 m</td>
<td>~35,000</td>
<td>3</td>
<td>LSC</td>
</tr>
<tr>
<td>Central GBR</td>
<td>Veeh and Veevers (1970)</td>
<td>150-175 m</td>
<td>13,600 and 13,900</td>
<td>2</td>
<td>Coral</td>
</tr>
<tr>
<td>Timor Sea</td>
<td>van Andel and Veevers (1967)</td>
<td>130-135 m</td>
<td>17,400-19,100</td>
<td>2</td>
<td>total carbon LSC</td>
</tr>
<tr>
<td>Arafura Sea</td>
<td>Jongsma (1970)</td>
<td>130-175 m</td>
<td>18,700</td>
<td>2</td>
<td>Beach rock LSC</td>
</tr>
</tbody>
</table>

*MIS = Marine Oxygen Isotope Stage

At the Spencer Gulf (Fig. 7.1), Cann et al (1993) extensively examined foraminifera from vibrocores and discussed the sea-level change of the last glacial period. They used the shallow-water species *Elphidium crispum* as the sea-level indicator. However, their radiocarbon dates were obtained by conventional methods and the samples were only minimally etched (<10% of total weight loss). Samples of such old age may need more severe etching to remove all traces of younger carbon contamination. The same concern applies to all of the reported data in Table 7.1. In particular, the Timor Sea and Arafura Sea observations have all dated total carbon.
in sediment layers, and are much more susceptible to secondary carbon contamination.

Fig. 7.1 Map of Australia and the locations referred to in the text.

Samples from the outer continental shelf, offshore of Sydney, have been dated both by radiocarbon methods (AMS and conventional) and amino acid racemization analysis (AAR) (Ferland, et al., 1995). This study confirmed the deposition sequence by AAR which clearly resolves the boundaries of depositional events. They established the upper limit of maximum sea-level fall as less than 150 m at the LGM but a more precise constraint could not be established.
Fig. 7.2 Maps of the palaeo-shore lines in the Joseph Bonaparte Gulf at 18 ka, 12 ka, 10 ka and 8 ka in 14C time scale.

Continental shelf areas with shallow sea-floor depressions, better lend themselves to a systematic study of sea-level change. During the LGM large parts of the Australian continental shelf were exposed (Fig 7.2), and any exposed shallow depressions may have served as environments for the collection and preservation of lagoonal or terrestrial material. The subsequent inundation of these features may then be recorded as transitions from terrestrial or fresh-water conditions to marine
conditions in either floral or faunal remains within the sediments. If depressions with
different sill heights occur, it becomes possible to map the sea-level change through
time (Fig 7.3).

Fig. 7.3 Schematic diagram of sea-level change across the continental shelf. If
sea-level has fluctuated over the past, sediment cores taken from various
depths across continental shelf would preserve facies boundaries between
marine and non-marine environments. $^{14}$C dating can be applied to these facies
boundaries to obtain the timing ($T_a$, $T_b$, $T_c$, and $T_d$; sea-level at a, b, c and d) of
these events.
The results in Figure 7.2. are based on approximate bathymetric data only (ETOPO-5) and ignore the effects of glacial-hydro isostasy. But it does point to one locality that merits examination. Other examples include (i) the Gulf of Carpentaria, a giant basin in late glacial time well separated from the sea by sills in the Arafura Sea (at -53 m depth) and in the Torres Strait (at -12m depth); (ii) areas within the Great Barrier Reef; (iii) Bass strait and (iv) the Bonaparte Depression and the North Western Shelf. It is this last area that is of particular interest here as an opportunity arose to obtain new cores from a number of sites in this region.

§ 7.3. Sea-level change around the Timor Sea

§ 7.3.1. Regional background

The Timor Sea is located off the northern coast of Australia (Fig 7.4), where there is a well developed continental shelf, the Sahul Shelf, one of the broadest shelf areas in the world. The climate of this area is influenced by both monsoon and trade winds, mostly affected by the Asian-Australian monsoon circulation and the Intertropical Convergence Zone (ITCZ). During the southern winter and spring, the ITCZ is not stable but ranges from around 23°N near the Himalayas and the Gulf of Bengal, to 32°N at the south coast of Honshu, Japan and to near the equator, east of Papua New Guinea. By contrast, during the southern summer, the ITCZ moves along an almost parallel track at 10-12°S and the SW trade winds are deflected along the west coast of Australia, such that the NW monsoon brings large amounts of moisture from the northern warm seas to the Australian continent (Van Andel, et al., 1967; van der Kaars, 1991). Cyclic aeolian dust in gravity core sediments from the Gulf of Carpentaria indicates that the ITCZ, during the last glacial, did not extend as far south as it does today (De Deckker, et al., 1991).
The mean annual precipitation in the Timor Sea area is 500-1000 mm (van der Kaars, 1991), while the evaporation rate is twice as much from ~953 mm/yr to 1816 mm/yr (Van Andel and Veevers, 1967). According to palynological studies of the last ice age, this area was much drier than today. This is evident from the advanced condition of grassland vegetation, contraction of the coastal tropical lowland and
eucalypt woodland forests, and maximum expansion of grasslands between 19,000 to 17,000 yr BP when the annual precipitation was ~100 - 500 mm (van der Kaars, 1991). The current drainage discharge rates rivers adjacent to the Timor Sea is approximately $6.1 \times 10^{10}$ m$^3$/yr. Off shore limits of quartz distribution in sediment samples and the planktonic foraminiferal distribution patterns indicate that the Bonaparte Depression at that time had an area of ca. $10^{11}$ m$^2$. The annual precipitation/evaporation compared was about 87% of today's value (Wyrtki, 1961) such that the Bonaparte Depression would have rapidly become a freshwater lagoon (Van Andel, et al., 1967). However, sedimentological and micropalaeontological analyses show no evidence for a freshwater lake even during the lowest sea-level period. It is therefore likely that the last ice age was much more arid in this area, a condition supported by Wyrtki (1961). This argument is consistent with 50 – 65 % lower rainfall in the Timor Sea during the LGM when compared to present day values (van der Kaars, 1991). Alternatively, it could mean that sea-levels were higher than has previously assumed. An improved model of the coastline than used in figure 7.2 is required.

In summary, observations from off shore northern Australia can be significant for sea-level studies for the following reasons:
1) This area, being located in the far-field of the late Pleistocene ice sheets, and being tectonically stable will potentially produce a reliable estimate of sea level fall during the LGM and late glacial phase.
2) It will provide tests of numerical models of past sea-level reconstructions.
3) If sea-level change can be independently determined, it may contribute to the calibration of the Oxygen isotopic records in terms of climate parameters.

§ 7.3.2. Descriptions of Gravity cores and Vibro cores

53 Gravity cores, 31 Vibro cores and 7 Grab samples have been collected by AGSO (Australian Geological Survey Organisation) and ANU from the Timor Sea (see Figs. 7.4 and 7.5). The surface sediment can mainly be divided into two different types; carbonate rich sandy calcareous sediment and inner shelf silty clay (see also van Andel and Veevers, 1967). The former is distributed seaward, whereas the fine muddy sediment is dominant along the coastline. Gravity and Vibro cores from the Berri Bank (122/VC/1, 2) (see Fig. 7.4 for locations) are composed of gravel to sand-size sediments with superimposed gravel size material as turbidity deposits (Fig 7.6). Their colour is olive grey. Samples taken from the Bonaparte Depression are dominated by a very dark brown to black color, suggesting organic rich mangrove facies (Fig 7.7).
§ 7.3.3. Microfossil analysis

Sediment samples have been analysed for presence of diatoms, foraminifera and ostracods. Although at present this area does have a high production rate, few diatom fossils were found, probably the result of diatom dissolution (eg., Hurd, 1973; Johnson, 1974; McManus, et al., 1995). For diatoms to reproduce, silica is essential, however this is known to be extremely scarce in the upper water column, and is also recycled through frustule dissolution (Leventer and Harwood, 1993). Figure 7.8 describes this through pictures of smear slides from samples of Antarctic Holocene and Bonaparte depression sediments. The Antarctic sediments, which are sometimes referred as low silicate sediments due to silicate dissolution, have well-preserved diatom frustules, whereas the Bonaparte sediments do not.
Fig. 7.6 a Columnar sections of sediment cores from the Berri Bank and the Lambert Shelf. VC indicates Vibrocore, and GC indicates Gravity core.
Foraminifera and ostracods were found in most of the facies. Analyses to date have been mainly of samples from the Bonaparte Depression. One common method of reconstructing palaeoenvironments is by the use of foraminifera wall structures, particularly useful when dealing with shallow-water species (Murray, 1973). There are three different types; Miliolids (porcellaneous), Rotaliids (or Hyaline, Spirillina, Lagenina, Robertinina), and Textulariids (or Agglutinated).
Their distribution as a function of deposition environment can be described by triangular plots as illustrated in Fig 7.9.

Fig. 7.7 Columnar sections of sediment cores from the Bonaparte Depression.
Fig. 7.8 Images of smear slides under the microscope. Samples from (a) Timor sea (176/GC9/130, 10 x 40; *Thalassiosira* spp.) and (b) Antarctic Holocene borehole sediments (10 x 20; *Thalassiosira* spp., *Nitzschia* spp., and so forth).
Chapter 7

Foraminifera wall structure analysis of Bonaparte Depression samples showed that there was a normal marine to brackish deposition environment (Fig. 7.10). Marine ostracods, such as *Cytherella*, *Cytheropteron* and *Praemunita*, are found in many horizons, however it is difficult to find any freshwater species. Shallow marine to brackish species, such as *Calistocythere*, *Cyprideis* and *Neocytheretta*, were found in cores 176/GC/2, GC/3, GC/6, GC/8, GC/9, and also in the upper portion of GC/3 and GC/5 (Fig. 7.7). Samples including shallow-water ostracods are in good accord with the results of foraminiferal analyses indicating a preponderance of shallow-water foraminifera such as *Ammonia*, *Elphidium* and so on. The description and radiocarbon ages of the grab samples are shown in Table 7.2.
Fig. 7.9 Schematic diagram of the triangular plot using foraminiferal wall structures to indicate the associated local environments (Murray, 1973).
§ 7.4. Summary

The results of lithological micropalaeontological analyses, indicate that each core displays a transitions from the LGM to Holocene condition. Shallow saline water species of foraminifera and ostracod indicate that sea-level was lower than present in the past, but there is no evidence for a freshwater lake at any time in the Bonaparte bay area. This is consistent with previous studies (e.g. van Andel and Veevers, 1967) and in line with past climatological conditions, in particular the evaporation rate exceeding precipitation. The Bonaparte depression therefore seems to have remained in contact with the open sea via the Marita shelf or other valleys even during the last glacial maximum.

Grab samples have been ^14C dated by conventional methods (Table 7.2). Samples ANU-10 427, 10428 and 10 429 were a mixture of shell species and calcareous rubble. Inspection under a microscope showed micrite filled textures.
indicating that at least two generations of growth had occurred within the rubble. It appears that this rubble was reworked from a shallower site to their current position. Nevertheless, sample ANU-10 430 consisted only of the shallow-water species, *Antigona puerpera*. Two of these bivalves had both valves intact, indicative of *in situ* deposition. This species today lives in littoral sand to -9m water depth around the Australian coast (Lamprell and Whitehead, 1992). There is still some ambiguity in this sample's reliability; as to whether it was, or was not reworked. The apparent age is ca. 18 000 $^{14}$C yr BP, indicating little sedimentation had taken place since the last glacial maximum. However, the age and depth is consistent with observations from older Bonaparte depression core sample $^{14}$C dates (van Andel and Veevers, 1967), data from off shore New South Wales (Ferland et al., 1995) and model predictions (Nakada and Lambeck, 1989; Zwart, 1995).

<table>
<thead>
<tr>
<th>Table 7.2 Location and $^{14}$C results for Grab samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>site 12 b</td>
</tr>
<tr>
<td>site 12 c</td>
</tr>
</tbody>
</table>

Age: 10,440± 110 yr $^{14}$C BP  
Lab.No.: ANU-10428
Calcareous sand with gravel sample was obtained. They consisted with mainly coralline rubble, include some bivalves and stone coral such as *Lima lima*, *Diaseris* sp. and so forth. Textural investigation under the optical microscope for cemented coralline algae, benthic forams and *Halimeda*. detected two different depositional generations of coralline rubble. Bulk samples, approximately 40g, were used for $^{14}$C dating using LSC method.

Age: 14,900±150 $^{14}$C BP  
Lab.No.: ANU-10429

12c2 Age: 18,630±150 $^{14}$C BP  
Lab.No.: ANU-10430

Gravel and calcareous sand mixture was recovered, which was mainly composed of coralline rubble. Some bivalves, such as scallops, *Lima lima*, and *Antigona puerpera* were included. A thin section of coralline rubble was made to examine the petrological structure. Then benthic forams and crusted coralline algae as secondary concreted inclusion were found under the optical microscope. Mixtures of coralline cement and shells were used for radiocarbon dating, laboratory number ANU-10429, whereas the single bivalve species, *Antigona puerpera*, was used for ANU-10430.

The cores from the Bonaparte depression indicate that the maximum sea-level during the last glacial maximum fell as low as *ca.* 120 to 127m below present day.
sea-level. Detailed micropalaeontological analysis and $^{14}$C AMS dating of the cores from Bonaparte Gulf was undertaken to construct a precise palaeo sea-level change record for this region. The details of this analysis will be discussed in the next Chapter.
Chapter Eight

Late Pleistocene sea-levels and ice volumes: Evidence from North Western Australia

§ 8.1. Introduction

The geographic distribution and volume of ice during the Last Glacial Maximum and the subsequent Late Glacial stage remain uncertain quantities despite recent progress in understanding the evolution of the large Late Pleistocene ice sheets. Some constraint on the total volumes of ice locked up in these ice sheets is provided by observations of past sea levels but such data have remained uncertain because of the limitations in the observational record and because of the necessity to correct such data for both isostatic and tectonic displacements of the crust.

Estimates of sea level during the Last Glacial Maximum have remained uncertain and controversial. Nakada and Lambeck (1988) reviewed the limited available data and concluded that, globally, sea levels were some 130 m lower than their present. Table 8.1 summarizes some observational estimates of sea levels at sites far from the former ice sheets at the time of the Last Glacial Maximum. However, new data from Barbados, indicated about 120 m below present levels (Fairbanks 1989, Bard 1990a), whilst others have argued that sea-level may have been only about 105 m lower (Peltier 1994). The volume of ice locked up in the second-largest northern hemisphere ice sheet, that of Northern Europe, is estimated to have contained only enough ice to raise sea level globally by some 15-20 m (e.g. Denton and Hughes, 1981). These various estimates of the Last Glacial Maximum sea level have major glaciological implications and improved estimates are clearly desirable.
Table 8.1 Some published eustatic sea-level values of LGM.

<table>
<thead>
<tr>
<th>Reference</th>
<th>esl</th>
<th>locality or method*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nakada &amp; Lambeck (1988)</td>
<td>130 m</td>
<td>Isostatically corrected data from intermediate- and far-field</td>
</tr>
<tr>
<td>Tushingham &amp; Peltier (1992)</td>
<td>115 m</td>
<td>Isostatically corrected data mainly from near- and intermediate-field</td>
</tr>
<tr>
<td>Peltier (1994)</td>
<td>105 m</td>
<td>Data from Barbados corrected for isostasy but not for tectonics.</td>
</tr>
<tr>
<td>Fleming et al (1998)</td>
<td>125 m</td>
<td>Isostatically and tectonically corrected data from intermediate- and far-field</td>
</tr>
<tr>
<td>Denton &amp; Hughes (1981)</td>
<td>127-163 m</td>
<td>GL</td>
</tr>
<tr>
<td>Chappell &amp; Shackleton (1986)</td>
<td>130 m</td>
<td>$\delta^{18}O$</td>
</tr>
<tr>
<td>van Andel &amp; Veevers (1967)</td>
<td>120-130 m</td>
<td>Timor Sea, sed</td>
</tr>
<tr>
<td>Jongsma (1970)</td>
<td>150-175 m</td>
<td>Arafura Sea, sub.Coral</td>
</tr>
<tr>
<td>Veeh &amp; Chappell (1970)</td>
<td>120 m</td>
<td>PNG, up.Coral</td>
</tr>
<tr>
<td>Carter &amp; Johnson (1986)</td>
<td>114-133 m</td>
<td>GBR, sed</td>
</tr>
<tr>
<td>Fairbanks (1989), Bard et al (1990a)</td>
<td>117 m</td>
<td>Barbados, dr.Coral</td>
</tr>
<tr>
<td>Ferland et al (1995)</td>
<td>&lt; 130 m</td>
<td>off Sydney, sed</td>
</tr>
<tr>
<td>Colonna et al (1996)</td>
<td>145 m</td>
<td>Mayotte, sub.Coral</td>
</tr>
</tbody>
</table>

* GL = Glaciological method; $\delta^{18}O = Foraminiferal \delta^{18}O$ record obtained from deep-sea sediment core. GBR = the Great Barrier Reef; PNG = Huon Peninsula, Papua New Guinea sed = sediment core taken from sea floor; up.Coral = uplifted coral reefs; dr.Coral = drilled coral obtained from offshore; sub.Coral = coral obtained by submergible from sea floor.

A second approach to estimating the total ice volumes during the Last Glacial Maximum is to constrain the ice sheets by a combination of geomorphological observations to define the boundaries of ice through time and numerical modelling of ice accumulation and ablation. There are few direct estimates of past ice sheet thickness, those that do exist being limited to areas where mountain tops protruded above the ice cap so as to leave differential erosion characteristics above and below ice limits. These observations are restricted to the smaller ice caps, such as those formerly over the British Isles (Stone et al., 1998a) or over parts of Antarctica (Stone et al.1998b). In consequence, the geomorphological and glaciological ice models rest on a number of assumptions that aim to constrain the ice thickness. These include assumptions concerning the basal conditions at the ice-rock interface and of the flow...
properties of ice, and the different climatological conditions that control the accumulation and ablation of the ice (Boulton et al. 1985; Nicholls, 1997). There are sufficient uncertainties in all of these procedures to render the resulting ice height and ice volume estimates quite uncertain.

The ice models can be partly constrained by observations of crustal rebound and relative sea-level change within and near the periphery of the former ice sheets (e.g., Lambeck et al., 1998). For example, if the Last Glacial Maximum ice thickness over Scandinavia exceeds a certain limit, then the crustal subsidence is so great that much of Finland and southern Sweden remain below sea level until well after the ice has disappeared, thus leaving the Baltic Sea open to widespread marine influence from both the Atlantic and Arctic Oceans. However, this is not observed and the absence of such connections for periods of time helps constrain the ice heights (Lambeck 1999). Similarly, the crustal rebound centred over western Scotland argues against a Last Glacial Maximum ice sheet over the British Isles that was driven by the Scandinavian ice sheet (Lambeck 1991, 1993a,b).

One of the conclusions generally reached from these rebound considerations is that the ice heights and volumes at the time of the Last Glacial Maximum are often less than those assumed in glaciological models. Thus, for the small British ice sheet, Lambeck (1993a,b) concluded that the ice thickness at the Last Glacial Maximum is unlikely to have exceeded about 1500 m, in contrast to more than 2000 m proposed by Denton and Hughes (1981) in their northern Europe ice model. This lower estimate is consistent with ice models in which the ice is only loosely coupled to the underlying bedrock (e.g. the minimum model of Boulton et al. 1985). Similarly Lambeck et al. (1990, 1998) concluded that the ice volumes in the Scandinavian ice sheet are likely to have been substantially smaller than those in the Denton and Hughes (1981) model, a conclusion also reached by Tushingham and Peltier (1992). Similar conclusions have been drawn for the Barents Sea ice sheet (Lambeck 1995a, 1996) and for the Laurentide ice sheet (Quinlan and Beaumont, 1981; Wu and Peltier 1983; Nakada and Lambeck 1991).

The Australian margin is well suited for studies of sea-level change during the Last Glacial Maximum (see Chapter 7). The margins are tectonically stable, as witnessed by the occurrence of Last Interglacial Shorelines (OIS; Marine Oxygen Isotope Stage- 5e; often contracted to MIS by other studies) near present-day sea level (Veeh 1966; Veeh et al., 1979; Veeh and France, 1988; Marshall and Thom, 1976; Stirling, et al., 1995). Also, the continent lies far from the former ice sheets so that the isostatic corrections, due mainly to the hydro-isostatic effects, are small and not strongly dependent on the details of the ice-load geometry. Finally, there are
wide and shallow shelf areas with depressions where conditions may have been favourable for the preservation of evidence for former, and now submerged shoreline positions. The Timor Sea and Northwest Shelf as well as the Arafura Sea (Fig. 8.1) provide environments suitable for sea level studies, and this area has provided one of the few reliable estimates of sea level at the time of the Last Glacial Maximum (van Andel and Veevers 1967; van Andel et al. 1967).

In this Chapter I report on new data that provide evidence for sea levels during the OIS 2 as well as for the period leading into the Last Glacial Maximum. The data are based on core and dredge samples from localities in the Timor Sea that may have existed as lagoonal or very shallow coastal environments when sea levels were much lower. Shallow marine molluscs and brackish lagoonal sediments have been identified and radiocarbon dated to determine the relative sea levels about the time of the Last Glacial Maximum.

These observations have then been combined with the results of glacio-hydro-isostatic modelling to estimate equivalent sea-level change and the volumes of land-based ice over and above the present-day volumes.
Fig. 8.1 Map showing the location of the Timor Sea with bathymetric contours. Filled circles represent sampling sites for the present study except LSDH-57 and V-229 previously reported by van Andel and Veevers (1967).
§8.2. New observational evidence for Last Glacial Maximum sea levels

§8.2.1. Regional setting

The Timor Sea, located off the northwestern coast of Australia, includes a broad and well-developed shallow continental shelf, the Sahul Shelf, and local bathymetric depressions, of which the Bonaparte Gulf is the largest. During times of sea-level lowstands much of the shelf would lie exposed and its outer edge provide protection against wave action for sediments deposited in some of the depressions. At these times the Bonaparte Depression was connected to the open ocean via narrow channels and, depending on the sea level, may have oscillated between marine and freshwater conditions. A total of 23 gravity cores, 10 vibrocores and 3 dredge sedimentary samples were collected in water depths from 34 to 147 m as part of a wider sedimentological investigation. Among the gravity cores, 9 were taken from the Bonaparte Depression. The location of these and other shallow water cores are illustrated in Fig. 8.1 and Table 8.2, along with the locations of two cores discussed by van Andel et al. (1967).
Fig. 8.2 Columnar sections of gravity cores obtained from the Timor Sea for the present study. Cores were collected from -88 to -128 m water depth so that they contain preserved sea-level information of the LGM. Note that most of $^{14}$C ages are stratigraphically in order thus reworking of sediments is unlikely.
§8.2.2. Analytical Methods

Lithological descriptions of all retrieved cores have been made and 11 gravity cores were selected for detailed micropalaeontological analysis of foraminifera, ostracoda and diatoms. Remains of calcareous organisms were radiocarbon-dated using, depending on sample size, either scintillation counting (LSC) or accelerator mass spectrometry (AMS) methods. The conventional dates were obtained using the standard procedures of the Australian National University (ANU) radiocarbon laboratory (Gupta and Polach 1985). For AMS dates, samples were prepared in a newly-built graphitisation line as discussed in Chapter 2.

Fig. 8.3a Example of photographic image of a gravity core from Timor Sea. Cores are collected and stored in the refrigerator and opened at the laboratory for sedimentological study. Micropalaeontological work was undertaken, originally, every ~10 cm interval for each core. Material from some facies boundaries, inferred from sedimentological descriptions, were ¹³C dated. If either ¹⁴C dates or micropalaeontological data showed potential transition of facies, further analysis by micropalaeontological inspection and ¹⁴C dating and used to refine the data.
§8.2.3. Results

§8.2.3.1. Sample descriptions

The surface sediments are of two kinds: carbonate-rich sandy calcareous sediments and silty clay (van Andel and Veevers 1967). Lithological logs of the selected cores are provided in Fig. 8.2. Samples from the Bonaparte Depression are dominated by very dark brown to black colours (7.5YR 2/4 to 2.5YR 2/0 based on the Munsell Soil Color Chart, 1954; Fig. 8.3). With the exception of GC9, which is dominated by silts, all cores consist primarily of clay to silt-sized grains. The two cores from the outer edge of the shelf (GC10 and GC11) consist of coarser, mainly silt-sized sediments, grey to olive in colour. The three dredge samples from Gb 1 comprise mostly calcareous sand to gravel sized grains.
Table 8.2. Location of the samples discussed in the present study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Longitude E</th>
<th>Latitude S</th>
<th>Water depth (m)</th>
<th>Sampling method</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC1</td>
<td>127° 55.00'</td>
<td>12° 06.00'</td>
<td>127</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC2</td>
<td>127° 55.03'</td>
<td>12° 06.02'</td>
<td>128</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC3</td>
<td>127° 56.02'</td>
<td>12° 07.00'</td>
<td>127</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC4</td>
<td>128° 00.00'</td>
<td>12° 09.99'</td>
<td>121</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC5</td>
<td>128° 01.50'</td>
<td>12° 11.00'</td>
<td>118</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC6</td>
<td>128° 09.99'</td>
<td>12° 18.00'</td>
<td>110</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC7</td>
<td>128° 15.99'</td>
<td>12° 22.96'</td>
<td>107</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC8</td>
<td>128° 37.04'</td>
<td>12° 38.36'</td>
<td>95</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC9</td>
<td>128° 52.00'</td>
<td>12° 50.01'</td>
<td>88</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC10</td>
<td>126° 19.53'</td>
<td>11° 12.46'</td>
<td>103</td>
<td>gravity core</td>
</tr>
<tr>
<td>GC11</td>
<td>126° 17.49'</td>
<td>11° 13.85'</td>
<td>101</td>
<td>gravity core</td>
</tr>
<tr>
<td>Gb1</td>
<td>124° 28.89'</td>
<td>12° 54.96'</td>
<td>129</td>
<td>dredge</td>
</tr>
<tr>
<td>V-229*</td>
<td>123° 50.40'</td>
<td>11° 57.50'</td>
<td>132</td>
<td>dredge</td>
</tr>
<tr>
<td>LSDH-57*</td>
<td>127° 57.00'</td>
<td>11° 44.00'</td>
<td>132</td>
<td>piston core</td>
</tr>
</tbody>
</table>

* van Andel and Veevers (1967)

§ 8.2.3.2. Micropalaeontological indicators of environmental conditions

Although the area has a high production rate for diatoms (e.g., Burford et al., 1995), few fossil diatoms were found in the gravity cores, probably as a result of diatom dissolution (e.g., Hurd 1973; Johnson 1974; McManies et al. 1995; see also Chapter 7). Other siliceous skeletons were also rare in the core from the Bonaparte Depression examined by van Andel et al. (1967). Benthic foraminifera, ostracoda and pteropods are common in most of the cores.

The environmental interpretations inferred from the faunal assemblages are shown in Fig. 8.4. Well preserved planktonic foraminifera and pteropods, found in the upper parts of the four cores (see Fig. 8.4), are indicative of an open-marine sediment facies and their occurrence is coincident with marine ostracods such as *Argilloecia sp.* and *Bradleya sp.* No freshwater ostracods were observed in any of the cores but euryhaline ostracod taxa *Cyprideis* and *Leptocythere*, indicative of brackish water with some freshwater influence (De Deckker 1988; Yassini and Jones 1995), have been identified. The state of preservation of the valves of these ostracoda provide further information on their transport history. The occurrence of *Elphidium sp.* and *Ammonia beccarii* are further indicators of brackish-water conditions (e.g., Cann and De Deckker, 1981; Murray 1991; Albani 1979; Yassini & Jones 1995; Hayward and Hollis, 1994). Bivalve molluscs and gastropods have also been used to establish palaeoenvironmental conditions.
Fig. 8.4 a Sedimentological description with facies inferred from micropalaeontological methods and $^{14}$C dates for GC2 to GC6.

Fig. 8.4 b Same as Fig 8.4a but for GC7 to GC9.
Based on a combination of faunal assemblages, four facies categories have been identified:

Open marine: presence of the fragile pteropods and planktonic foraminifera; these are indicative of normal sea-water salinity and water depths greater than about 20 m.

Shallow marine: presence of numerous well preserved benthic foraminifera and ostracoda taxa; terrigenous components are rare; these are indicative of normal sea-water salinity and water depths less than ~ 10 m.

Marginal marine: low diversity of benthic ostracod and foraminifera taxa accompanied by scaphopods, all of which show signs of abrasion; molluscs are abundant and often fragmented; occurrence of terrigenous material is frequently high: These are indicative of water depths much less than 10 m being within the tidal zone influence with salinity fluctuating from normal sea-water values.

Brackish: paucity of typical marine foraminifera and ostracoda taxa; presence of *Ammonia beccarii*, *Leptocythere sp.*, *Neocytheretta sp.*, *Cyprideis australiensis* etc.; signs of 'bleaching' on the calcareous shells by corrosive waters; terrigenous clays forming a major fraction of the sample: All these are indicative of salinity values well below normal sea-water and strongly influenced by continental waters.
§8.2.3.3. Radiocarbon dating results.
Table 8.3 summarizes the radiocarbon dates for selected horizons in 9 of the gravity cores and one grab sample as well as 3 dates from earlier work in the region done by van Andel and Veevers (1967). Reservoir (400 years) and δ¹³C corrections have been applied. Calendar ages were obtained using the Calib 3.0.3 conversion (Stuiver & Reimer 1993) for ages up to 17,000 ¹⁴C yr BP and using a polynomial relationship between the two time scales for older material (Bard et al. 1998).
Table. 8.3 $^{14}$C results

<table>
<thead>
<tr>
<th>Core</th>
<th>Water depth core</th>
<th>Water depth in core</th>
<th>Method</th>
<th>$^{14}$C age $^1$</th>
<th>Calendar age $^*$</th>
<th>Sample ID #</th>
<th>Dated material</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC2</td>
<td>128</td>
<td>23</td>
<td>AMS</td>
<td>9,770±100</td>
<td>10,980±40</td>
<td>ANUA-7518</td>
<td>B, F</td>
</tr>
<tr>
<td></td>
<td>434</td>
<td></td>
<td>AMS</td>
<td>39,240±600</td>
<td>44,960±630</td>
<td>ANUA-7514</td>
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</table>

† All dates are calculated using the half-life of 5568 years expressed in yr before 1950 (BP). The errors are one standard deviation of counting.

* Ages obtained using calib 3.0.3 (Stuiver and Reimer, 1993) and a second order polynomial approximation (Bard et al., 1998), for the $^{14}$C ages younger and older than 17,000 $^{14}$C yr BP, respectively. Statistical errors are given at the one sigma level.

# Numbers with prefixes “ANU” and “ANUA” were dated at Quaternary Dating Laboratory and Nuclear Physics Department in ANU, respectively. “LJ” were dated at La Jolla radiocarbon laboratory (van Andel, et al., 1967)


§ 8.2.3.4. Micropalaentological results

Core GC1 was not analyzed in detail, being very similar to cores GC2 and GC3. The palaeontological composition of core GC3 was examined in detail at 14 horizons. The upper-most part of the core is characterised by sediments deposited in an open-marine environment with a change to shallower water conditions occurring at about 60 cm and a further change to a marginal marine environment at about 95 cm. A radiocarbon date for this boundary gave 11,810 ± 130 $^{14}$C BP. Environmental conditions remained similar back to 25,500 ± 380 $^{14}$C BP at which point a return to shallow marine conditions occurred. Nowhere in this interval is there evidence that brackish-water conditions occurred or that the site was subaerially exposed. The shallow-marine conditions persisted down to the base of the core which is dated at 30,430 ± 380 $^{14}$C BP. Core GC2, being essentially located at the same water depth, provides a similar environmental reconstruction down core with decreasing water depth from open marine to marginal marine conditions followed by a return to shallow marine conditions. In both cores, the silty sediments correspond mainly to the open-marine environment within the depression during the Holocene interval whereas the clay sediments correspond mainly to the late glacial and the glacial maximum period.
Core GC4 is from a somewhat shallower depth and exhibits a similar sequence with respect to the inferred environmental conditions except that the transition in the upper part of the core goes from open marine directly to marginal marine without any evidence of well-developed intervening shallow marine conditions. This transition occurred at about 16,000 $^{14}$C yr BP. Core GC5 recorded brackish-water environments, this condition having persisted from about 16,000 $^{14}$C yr BP to about 25,750 $^{14}$C yr BP. The lowest part of this core, below 365 cm depth, is characterised by the presence of marine ostracods and planktonic foraminifera. Above 340 cm, small *Ammonia beccarii* occur along with other shallow water to brackish indicators such as *Elphidium sp.* and *Cyprideis australiasis*. Some of the horizons in this part of the section also contain Scaphopoda and other molluscs.

Figure 8.5 illustrates the depth-age relationship of the radiocarbon samples from GC5. Within the interval between about 40 cm and 340 cm, corresponding to the Late Glacial stage, the sedimentation rate has been relatively constant and high. The two dates near 227 cm depth correspond to one sample based on foraminifera species only (16,240 ± 240 $^{14}$C yr BP) and the other sample is based on small bivalve molluscs from the same horizon (16,540 ± 170 $^{14}$C yr BP). The age agreement within the experimental error indicates that both represent true depositional ages. However, a hiatus occurs at this latter depth lasting from about 18,040 $^{14}$C yr BP to 25,750 $^{14}$C yr BP and corresponds approximately to the time of the maximum glaciation recorded at high latitudes. This hiatus is interpreted as being due to erosion of an aerially exposed surface rather than being due to a starvation of sediment supply since the nearby cores in somewhat deeper waters do not exhibit starvation.
Core GC7, from a water depth of 107m, contained a mixture of well-preserved shallow water bivalves, including *Paphia undulata*, *Marcia japonica*, *Ctenocardia fornicata*, with a characteristic littoral sand habitat (Lamprell and Whitehead 1992). The three conventional radiocarbon ages are also sequentially in order, thus indicating that the sediments have not been disturbed. The AMS ages of the lowest horizon of cores GC10 and GC11 are similar.

The dredged surface sample Gbl contains the bivalve mollusc *Antigona puerpera* (Lamprell and Whitehead, 1992; sample ANU-10 430) whose characteristic habitat is littoral sand. This specimen includes both valves and is well preserved, suggesting that it has been subject to minimal reworking and hence to minimal transport from shallower depths. With an age of 18,630 14C yr BP, this sample implies that the Last Glacial Maximum sea level at this location was above -129 m. The second sample dated from Gbl consists of a mixture of different bivalves which typically live at various water depths such as *Lima lima*, *Antigona puerpera* and so forth. Their age of 14,900 ± 450 14C yr BP is significantly less than that of the single-hinged sample suggesting that some reworking of the sample may have occurred with younger material having been transported from shallower sites.

§8.2.3.5. Discussion

Core GC5 provides the most direct evidence for the position of sea level during the time of maximum glaciation with brackish shallow-water conditions identified in the interval from 18,040 ± 150 14C yr BP to about 16,000 14C yr BP, overlying a hiatus postulated to extend from the older date 18,040 ± 150 to 25,750 ±
overlying a hiatus postulated to extend from the older date 18,040 ± 150 to 25,750 ± 300 ⁰¹C yr BP. This hiatus is attributed to a time of sub-aerial exposure of the sediments indicating that local sea levels for this period was below the -121 m mark. The brackish-water conditions indicate shallow-water depths such that at about 17,500 ⁰¹C yr BP sea-levels were only a few meters above -121 m. The dredged surface sample Gb 1 indicates sea-level to have been above -129 m at 18,630 ⁰¹C yr BP. This is similar to the result obtained by van Andel et al. (1967) from a piston core at a nearby locality at a water depth of -132 m. Silty clays in that core gave radiocarbon ages of 17,400 ± 1000 and 18,900 ± 1000 ⁰¹C yr BP indicating that sea levels were above this depth in the time interval encompassed by these two dates. The littoral-living bivalve *Chlamys senatorius* dredged from the outer edge of the Sahul shelf by van Andel et al. (1967) from a depth of -132 m (V-229, Fig. 1) also indicates that sea level was above -132 m at 16,910 ± 500 ⁰¹C yr BP.

Sea-levels during the Lateglacial are also recorded in the cores from both the outer edge of the shelf and the Bonaparte depression. For example, microfossil analysis of GC-10 and GC-11, at -103 m and -101 m respectively, indicate a marginal marine environment such as a beach or coastal lagoon at between 14,750 ± 170 and 14,570±180 ⁰¹C yr BP. A similar inference is drawn from the upper part of GC7 where, at -105 m, littoral-dwelling bivalves, such as *Ctenocardia fornicata*, *Paphia undulata* and *Marcia japonica*, have been identified with a radiocarbon age of 14,600 ⁰¹C yr BP. Sea levels during the pre-Last Glacial Maximum period are recorded in several cores (GC2, GC3, GC5, GC8 and GC9).

Figure 8.6 illustrates the height-age relationship for the data from the Bonaparte depression. Together, they point to sea levels locally at below -121 m and above -129 m during the Last Glacial Maximum, followed by a rise to above -105 m by about 14,750 ⁰¹C yr BP. Sea-levels first fell below 121 m at about 25,750 ⁰¹C yr BP but the sea-level change before this period, while indicating falling conditions, is not well defined for the period immediately pre-dating the Last Glacial Maximum. The data from the outer shelf (Gb1, GC10, 11 and V-229) provides a comparable result for the Last Glacial Maximum and Lateglacial period (see Fig. 8.6), with a low stand above -129 m during the Last Glacial maximum at about -124 m, followed by a rise of about 25-30 m during the following 3,000 years from -124 m to -100 m.
§ 8.3. Numerical models for sea-level change for the Sahul Shelf and Bonaparte depression.

Sea-level change at sites on the Sahul Shelf and within the Bonaparte depression are determined in the first approximation by the equivalent sea-level change resulting from the expansion and contraction of the continental-based ice sheets. Superimposed on this are the glacio-hydro-isostatic contributions discussed
in Chapter 5. Model calculations by Lambeck & Nakada (1990) indicate that, for the Northwest Shelf of Australia, these contributions can amount to 10% of the equivalent change, with a sign that depends on distance from the present shoreline, and that departures from the equivalent sea level at the time of the Last Glacial Maximum can vary by as much as 20 m across the shelf (see Fig. 2 of Lambeck & Nakada 1990).

Analyses from tectonically stable areas in different locations around the world, have indicated that an adequate representation of isostatic contribution, $\Delta \xi_I$, to sea-level change can be obtained using relatively simple models of the Earth's rheology. Then, from observations, $\Delta \xi_{\text{obs}}$, of relative sea level at time, $t$, the isostatically corrected equivalent sea level $\Delta \xi_{\text{esl}}$ may be written:

$$\Delta \xi_{\text{esl}} (t) = \Delta \xi_{\text{obs}} (\phi, t) - \Delta \xi_I (\phi, t)$$

where the two terms on the right hand side are functions of position $\phi$ and time whereas $\Delta \xi_{\text{esl}}$ is a function of time only.

The theory and model parameterisation used here to compute $\Delta \xi_I (\phi, t)$ have been described in papers by Nakada and Lambeck (1987), Johnston (1993) and Lambeck & Johnston (1998), and applications to shelf environments in regions far from the former ice sheets have been discussed in Lambeck and Nakada (1990), Lambeck (1996, 1997) and Fleming et al. (1998). For the present computations, the earth-models employed assume a three-layered mantle as discussed previously (see Chapter 5). Table 8.4 summarizes a range of earth model parameters that have been found to be consistent with sea level models and data for other regions (Lambeck et al. 1996, 1998).

Because the region of interest lies far from the former ice sheets, details of the melting history of these ice loads is assumed not to be significant, the important requirement being that the total change in ice volume is compatible with the change in sea level at the corresponding time. For the present purpose the ice models ($I_0$) for the two hemispheres discussed in Chapter 5 and the concomitant equivalent sea-level curve are used.
Fig. 8.7 Relative sea-level curve obtained by glacial-hydro-isostatic modelling for three localities in the Timor Sea. (a) is for the last 25 ka and (b) is for the LGM. GC10 is located at the edge of the continental shelf whereas GC9 is the site nearest the present day coastline; GC5 is located in the middle of the Joseph Bonaparte depression.

Figure 8.7 illustrates the predicted sea levels based on models E₀ and I₀ for three localities, GC9, closest to the present continental margin (Fig. 8.1), GC5 within the Bonaparte depression, and GC10 on the edge of the shelf. The model predictions include the consequence of the shoreline having migrated from the edge of the shelf to
the present coastline between the time of the Late Glacial period and about 6000 years ago. It also includes the small change in sea level caused by the Earth’s changing centrifugal force and associated rotational deformation due to shift in the position of the rotation axis as the mass of the earth-ice-ocean system changes through time (Milne and Mitrovica, 1996). The ice models start accreting at the time of the Last Interglacial (OIS 5e) stage. The differences between predictions for the three localities are significant. At the site nearest to the present coast, GC9, sea-level change has been always higher than for the other two localities. The maximum difference between GC9 and the shelf edge site, GC10, is ca. 10 m at the LGM. The sea-level record at all three sites is substantially above esl for the same time periods. Figure 8.8 illustrates the changes in sea level across the shelf relative to present sea level at three selected epochs, the Last Glacial Maximum at 21,000 yr BP, at 13,000 yr BP and at 7,000 yr BP (see Fig. 8.1 for the location of the profile). These curves represent the potential heights of sea-level with respect to the present sea-level if they could have formed (and been preserved) at the epoch in question. The magnitude of change across the shelf is ca. 5 m. For example, 21,000 yr BP sea levels at GC5 would be expected to be shallower with respect to present-day sea-level than the sea-level of the same epoch at GC10, the maximum difference for this choice of model parameters being about 6 m.

![Figure 8.8 The inferred height of sea-level across the shelf during three different time intervals.](image-url)
Uncertainties in the model predictions come from three sources: the choice of earth-model parameters, the ice-sheet parameters, and the assumed equivalent sea-level function. The range of plausible earth-model parameters is summarised in Table 8.4 and Fig. 8.9a illustrates the dependence of the predictions for site GC5 on these parameters.

Table 8.4 Model parameters used for isostatic calculation

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Sea-level values obtained using earth model \( E_6 \) show the lowest value whereas the results for most of the others are the same to within ±3 m. Another source of uncertainty in the modelling is the volume of the LGM Antarctic ice sheet. In the model of Nakada & Lambeck (1988) significant change in Antarctic ice volume was inferred indirectly from a comparison of the northern-hemisphere ice volumes with the observed sea levels in far-field localities. Yet analyses of observed sea-level change from a few localities in Antarctica suggest that the change may have been substantially less than that originally proposed (Zwartz et al. 1998, and see Table 8.5).
Fig. 8.9 Dependence of relative sea-level on the choice of rheological earth-model parameters.
Table 8.5 Published estimates of Antarctic ice volume change since the LGM.

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<td>0.5 - 2.4</td>
<td>Colhoun et al. (1992)</td>
</tr>
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<td>8.0 - 12</td>
<td>Zwartz (1995)</td>
</tr>
<tr>
<td>12 - 16</td>
<td>Huybrechts (1990)</td>
</tr>
<tr>
<td>25 - 30</td>
<td>Hughes et al. (1981)</td>
</tr>
<tr>
<td>37</td>
<td>Nakada &amp; Lambeck (1988)</td>
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</tbody>
</table>

To examine whether the choice of distribution of ice between the two hemispheres is important in the present context, predictions have also been made for the model E₀ but with an ice model in which there is no change in the southern hemisphere ice sheets while the northern hemisphere ice volumes have been increased so as to maintain the same equivalent sea-level change as before. Fig. 8.10 illustrates the results of this comparison. The shallowest sea-level curve in the figure represents predicted relative sea-level for the standard model of ice distribution in Antarctica. The curve next to it is the predicted relative sea-level curve using the scaled northern hemisphere ice sheet. The maximum difference between using the "total" ice-model and the "scaled" model is about 5 m at LGM. Errors in observation of the LGM samples are generally of the order of 5 m, so that sea-level change in the present study may reasonably be taken to be independent of ice sheet distribution.
Fig. 8.10 Evaluation of dependence of sea-level on the choice of geographical distribution of ice. See text for details.
§ 8.4. Inference of the equivalent sea-level change

Isostatically corrected sea-level observations from the present study area can provide constraints on the equivalent sea-level at the Last Glacial Maximum. The $\Delta \zeta_I$ contribution to LGM sea-level for sites, GC5, GC9 and GC10 are summarised in figure 8.11. The total isostatic component is given for the LGM and is found to lie within a range of approximately 6 m for all earth model parameters (Fig. 8.11). In the period between the LGM and 7000 yr BP, the isostatic contribution to sea-level at each site was nearly constant across the shelf and the values obtained for $\Delta \zeta_I$ for this period are the same to within ca. 20 % except for earth model E$_3$, which has the highest lower mantle viscosity.
Fig. 8.11 Isostatic component for three sites. Earth model $E_6$ which has higher viscosity for lower mantle, is always distinct from the others. Largest value is observed in GC9, the closest site to the present day shoreline. The difference is due to the contribution from greater water loading component.
Figure 8.12 depicts isostatically corrected observations obtained from this study and previously published observations from the same area (van Andel and Veevers, 1967) and Barbados (Fairbanks 1989; Bard et al., 1990a). The continuous line represents the equivalent sea-level assumed for the ice models used in this study. The results of the present study and earlier far-field data are in good agreement for the period between 22,000 yr BP and around 18,000 yr BP. The error in sample ages is one sigma except for some U/Th dated Barbados corals (2 sigma; Bard et al., 1990). The estimated uncertainty in $\Delta \varepsilon_{\text{esl}}$ is $(\sigma_{\text{obs}}^2 + \sigma_{\text{pred}}^2)^{1/2}$ where $\sigma_{\text{obs}}$ is the standard deviation of the observed values and $\sigma_{\text{pred}}$ is a measure of the spread of the predicted values for the range of earth rheologies discussed above. The observational uncertainties can not usually be defined by standard probability distributions and estimates of the lower and upper limits of the observed values are used as a measure of $\sigma_{\text{obs}}^2$. The lowest value of equivalent sea-level values at the LGM was ca. $-134 \pm 4$ m and remained at this level until about 19,000 yr BP, at which point there was a rapid rise in sea-level with a magnitude of ca. 10 m (Fig. 8.12).

During the period discussed in the present section, the values obtained for esl from the observations are always lower than the nominal curve (Fig.8.13), though the timing of melting seems to be well represented. The importance of ocean geometry in the calculation of the esl curve suggests that agreement between the nominal and observed esl curves could be substantially improved by either incorporating additional ice into the ice model used or, less obviously, by more accurate representation of Antarctic ice sheet retreat which would effect ocean geometry and thus the water-load component of the isostatic contribution used to obtain our observed esl values.
Fig. 8.12 Equivalent sea-level values obtained from isostatically corrected observational data. Filled symbols are results from the present study. The continuous line represents the nominal equivalent sea-level curve of glacio-isostatic calculation for the present study. The dotted line is the proposed curve.
Fig. 8.13 Evaluation of esl values. (a) Predicted esl values plotted against observations. Error bars represent the range of values due to different earth models used. (b) Differences between observed and predicted esl. The results include a comparison between standard and scaled ice sheets models. Error bars reflect the range due to the variations in earth model parameters. In both cases, predicted values are higher than observed values. Note that the results for the "scaled" ice model are closer to the nominal esl curve.
Table 8.6 Some published ice models

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<td>North America</td>
<td>59.4</td>
<td>54.9</td>
<td>59.0</td>
<td>59.0</td>
<td>76.3 - 89.4</td>
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<td>Greenland</td>
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<td>6.6</td>
<td>2.7</td>
<td>2.7</td>
<td>0.8 - 9.4</td>
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<td>15.1</td>
<td>7.6</td>
<td>15.0</td>
<td>15.0</td>
<td>19.4 - 20.1</td>
</tr>
<tr>
<td>Barents and Kara sea</td>
<td>15.4</td>
<td>12.1</td>
<td>11.8</td>
<td>6</td>
<td>2.1 - 15.5</td>
</tr>
<tr>
<td>Siberia or others</td>
<td>0.0</td>
<td>2.8</td>
<td>0.0</td>
<td>0.0</td>
<td>3.2 - 4.5</td>
</tr>
<tr>
<td>Total (N.H*)</td>
<td>92.2</td>
<td>84.0</td>
<td>88.5</td>
<td>82.7</td>
<td>103.1 - 137.6</td>
</tr>
<tr>
<td>Antarctica</td>
<td>37.1</td>
<td>27.7</td>
<td>27.0</td>
<td>37.3</td>
<td>24.3</td>
</tr>
<tr>
<td>Total</td>
<td>129.3</td>
<td>111.8</td>
<td>115.5</td>
<td>120.0</td>
<td>127.4 - 161.9</td>
</tr>
</tbody>
</table>

*All numbers correspond to equivalent sea level values (m)
*N. H = Northern Hemisphere

The significant point that can be drawn from the present study is that data from the North West shelf provide an accurate indication of (i) the maximum volume of the Late Pleistocene ice sheets (even allowing for uncertainty due to the effects of ocean geometry these data require ice volumes considerably in excess of suggested values in previous studies (eg. Tushingham and Peltier, 1992; Peltier 1994; also see Table 8.6) and (ii) the timing of deglaciation following the LGM. Agreement between observed and nominal esl curves could be improved by including the effect of secondary ice sheets (such as the Tibetan, Siberian, Bering Strait, Swiss Alps, and Patagonian ice sheets not included in this study) which could have accumulative effect of up to 8 m. This should not be relied upon too heavily however since the model of the Laurentide ice sheet used in this study may need to be reduced in size to accord with sea-level data from the North American sites. As mentioned above, more accurate modelling of ice sheets at or near continental margins may also result in changes to ocean geometry and thus the nominal esl curve. Detailed examination of either of these issues is beyond the scope of the current study.
Conclusions

More than two hundred and fifty AMS radiocarbon dates and 25 high precision TIMS U-series ages have been determined for 30,000 year to 50,000 year old corals from the uplifted terraces of Huon Peninsula, Papua New Guinea. Extensive previous efforts to define a radiocarbon calibration curve for the period beyond ~12,000 years, through directly measured calendar ages, only yielded a few scattered points. A new CO₂ extraction and graphisation line was constructed and used for processing "old" carbonate samples only. Radiocarbon dates of samples older than 20,000 years may be affected by secondary younger carbon contamination. For this reason, each coral sample was subjected to partial dissolution, and the results were considered acceptable only when the radiocarbon age of at least three aliquots were self consistent within errors. This is the only quantitative test of diagenetic alteration in corals for radiocarbon dating purposes. In addition, conventional screening methods were applied, including textural investigation of thin sections under a petrographic microscope, XRD and stable isotope analyses. For these reasons, results obtained in the present study are considered to be as reliable as can be ascertained with presently available methods. However, in some
circumstances, it is still possible that contaminated samples could pass through the above tests; for example the high radiocarbon excesses found in \(\approx50\) ka (calendar age) corals need further confirmation. In addition to tests for \(^{14}\text{C}\) contamination, the samples were tested for open system behaviour for U and Th isotopes, such as total U and \(^{232}\text{Th}\) concentrations, and \(^{234}\text{U}(T)\) values. Most samples were within acceptable limits of these tests.

The results of the radiocarbon time-scale calibration experiments can be summarised as follows: Firstly, the trend for increasing divergence between radiocarbon ages and calendar ages appears to continue beyond 30 ka and up to 50 ka; the limit of present measurements. At the younger end, data from the present study overlap with previous data. Secondly, four discrete age peaks of enhanced radiocarbon concentration were observed. The clustering in age is expected as the samples come from distinct, individual reef sections. However, the prominent peaks of \(\Delta^{14}\text{C}\), including some negative values, in between the peaks, were unexpected. It is possible that the peaks are due to, secondary, younger age, or modern carbon contamination. While this is acknowledged, and some of the older \(\approx50\) ka samples may have been affected, it is unlikely to be the dominant cause given the battery of tests the samples were required to pass. The negative values of \(\Delta^{14}\text{C}\), that systematically cluster in between the peaks, could not be produced by such contamination.
The four radiocarbon peaks appear correlated with the timing of North Atlantic Heinrich events and ice-rafted debris deposits in deep sea cores. The accepted explanation for these Dansgaard-Oeschger and Bond cycles involve reorganisations in the global circulation system. The North Atlantic deep water formation, during glacial periods, appears to be sensitive to fresh melt-water input into the North Atlantic by periodic instabilities in the ice sheets that launched armadas of icebergs into Hudson Bay and resulted in sea-level rises. Slowdown or closure of the circulation is expected to significantly rise atmospheric radiocarbon levels. The present data show an initial high sea-level followed by steep rise in atmospheric radiocarbon levels as the sea-level falls. The high radiocarbon concentration lasts for less than \( \approx 1000 \) years and drops below original ambient levels over sever thousand years. The negative values of \( \Delta^{14}C \) indicate the vigorous re-start of the NADW circulation or enhanced ventilation at other oceans. Deep water formation around the Antarctic continent is believed to be equal to that in the North Atlantic. Cessation of the North Atlantic circulation is likely to re-direct warm equatorial waters to the Southern Ocean and coupled with a high sea-level pulse is likely to destabilise the Antarctic ice sheet as well. Radiocarbon and Th-U results obtained in the present work constitute a direct confirmation of severe and abrupt climate oscillations observed in Greenland ice cores and deep sea sediments. They provide the first direct evidence for the start-stop behaviour of the North Atlantic conveyor belt circulation during the last glacial as put forward mainly by Wallace S. Broecker (1998), and the
increasingly evident global influence of these events, beyond the boundaries of North Atlantic.

A by-product of TIMS U-series dating is high precision values of the $^{234}\text{U}/^{238}\text{U}$ ratio in sea water at the time of coral growth. There was some evidence from previous work that $^{234}\text{U}/^{238}\text{U}$ of the Last Interglacial ocean was higher than present by about $4\%$, while sea-levels were 3-4 m higher. The present data show 1% lower values of $^{234}\text{U}/^{238}\text{U}$ during the last glacial period, during MIS 2 and MIS 3. There is evidence for a trend from lower to higher values during deglaciation both for termination I (Bard et al. 1990) and termination II (Esat et al. 1999), loosely correlated with sea-level change. It appears that chemical weathering and meteoric terrestrial to ocean flux was higher during interglacials than glacial periods. A similar behaviour was previously observed for Os isotopes (Oxburgh, (1998).

Locations, geographically far away from former ice sheets, are the best areas for observations to constrain historic ice volumes. In the present study, two locations were selected for this purpose: tectonically uplifted Huon Peninsula and tectonically stable North Western continental shelf. Radiocarbon dated samples from an uplifted Holocene reef at Madang appear to provide evidence for meter-scale co-seismic uplift. Although further investigation is required, the Th-U dated corals from Huon peninsula, together with previously determined uplift rates yield an equivalent sea-level history in general agreement with deep sea isotope ($^{18}\text{O}$) derived sea-levels.
Sea-level work in North Western Australia was focused on the Last Glacial Maximum period. Sedimentological, and micropalaeontological data from gravity-core samples, combined with more than 50 AMS radiocarbon dates show details of equivalent sea level (esl), the timing of the termination of Last Glacial Maximum, and the maximum volume attained by ice sheets. Isostatically corrected esl value at ca. 22,000 years BP was 134 m and was observed as a sea-level low-stand of ~3000 year duration, followed by a ~15 m rapid sea-level rise starting at ~ 19000 years BP. These observations are in remarkably good agreement with previously reported values from the same region (van Andel and Veevers, 1969), and Barbados (Fairbanks 1989; Bard et al., 1990). Further work will be necessary to identify the source of additional melt-water at the LGM. Most previous studies have derived smaller values of esl during the LGM, and the current ice models for the Northern Hemisphere are insufficient to provide the esl difference of 5-8 m between the previous and present reconstructions. Geological and glaciological studies of the Antarctic ice sheet suggest minimal changes over the last ~22000 years; hence, contributions from secondary ice sheets, such as Tibetan, Patagonian, Himalayan, Siberian ice sheets, may need to be considered as part of the improvement in ice models.
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Appendix

§A-1 Step-wise dissolution technique for $^{14}$C measurements

In the present study, samples in age range 30 – 60 ka were collected from Reef II and Reef III of Huon Peninsula. Textures in both longitudinal and latitudinal thin sections were investigated under a petrographic microscope. Calcite content in coral skeleton was measured by XRD as secondary carbonate may affect $^{14}$C dating. In addition, all samples were partially dissolved and aliquots radiocarbon dated as was previously attempted by Burr et al. (1993), but in a much more severe fashion. Partial dissolution was firstly attempted by Bard et al. (1990c) and more systematically by Burr et al. (1993). The latter study used corals older than 70 ka from both Barbados and Huon Peninsula. They performed XRD measurements, bulk sample $^{14}$C dating, and $^{14}$C dating following step-wise leaching. They concluded that the first 50% of acid etching effectively removed secondary younger age carbon (Burr et al. 1993). In the present study, the first 50% of the coral was etched and discarded, the rest of the sample was collected, in up to three aliquots, until 100% dissolution. Each aliquot was AMS dated so that at least 3 AMS $^{14}$C ages were produced from each sample (Table A.1).

First we tested the effectiveness of this procedure by using corals as old as 120,000 years that grew during the Last Interglacial (LIG). Burr et al (1992), conducted step-wise leaching for a reef IV coral, from Huon Peninsula, which was dated by Th-U (72.8 ± 2.2 ka (Chappell et al. 1996)). The first 40% was of this coral was contaminated by younger carbon, the next 60% gave an age close to the analytical background (Fig 4.11a). We have used a LIG coral from Western Australia (WA-1) that was previously Th-U dated (Stirling et al., 1996) and has an age of 124.7±0.9 ka with an initial $\delta^{234}$U ratio of 152 ± 2. WA-1 appears to be pristine under the optical microscope, and no calcite was detected by XRD. The first 0-17% aliquot from WA-1 shows a considerably younger radiocarbon age compared to the analytical background (~48000 $^{14}$C years). However, the next 5 aliquots, indicate an almost uniform age of ~49000 years (Fig 4.11a).
### Table A.1 Radiocarbon results

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<tr>
<th>Lab.code* (ANUA-)</th>
<th>Sample</th>
<th>Dissolved percent</th>
<th>pM</th>
<th>$^{14}$C age* (yr BP)</th>
<th>Error$^b$ (years)</th>
<th>Error$^c$ (years)</th>
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<tr>
<td>3607</td>
<td>LIG coral 0-17</td>
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<td>39460</td>
<td>+1500</td>
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<td>48230</td>
<td>+1880</td>
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<td>OZD-535</td>
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<td>0.52±0.18</td>
<td>42300</td>
<td>+3410</td>
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<tr>
<td>10017</td>
<td>Tridacna A 0-17.2</td>
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<td>9928</td>
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### Table A.1 (continued)

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*All samples were measured at ANU except OZD- series which measured at ANSTO (Australian Nuclear Science and Technology Organisation).

* Age obtained using Libby’s half life (5568).

$^8$ Errors are quoted as two sigma.

Giant clams, *Tridacna gigas* were previously collected from Reefs IIIa and IIIb. *Tridacna* from IIIa shows a nearly constant age profile at ~47000 years which is close to the analytical background of the present system. Another *Tridacna* was treated in a similar fashion. The first 17% indicated younger carbon contamination.
However the last ~50% yielded consistent results of ~47000 years. Both *Tridacna* consist of 100% aragonite according to the XRD results (Fig.4.11b).

In summary, the above experiments illustrate the following points:

1) Necessity of strict criteria based on textural analysis, XRD and step-wise dissolution.
2) The first approximately 20% is likely to be contaminated by younger carbon for all samples.
3) After 50% dissolution, most of the contamination is eliminated.

Overall, tests using step-wise dissolution appear to be the only quantitative way to ascertain the veracity of $^{14}$C ages from corals. Our results are consistent with the experiments of Burr et al (1993) that after 50% etching, $^{14}$C age reaches analytical background levels using LIG and MIS 4 corals from Papua New Guinea and Barbados. Although their sequential dissolution experiment mainly concentrated on the first 50% fraction, they also clearly demonstrated that some leaching is necessary to ensure reliable $^{14}$C ages. In the present study, all samples were step-wise leached; the last 3 aliquots after 50% dissolution "reached an age plateau" (Fig.4.11c; A.1). Although, this appears to be the best method, so far available, to obtain reliable radiocarbon ages from corals, it does not guarantee that the sample was free from diagenesis.
Fig. A.1a  Step-wise dissolution of corals used in the present study. Shaded columns are for bulk samples that result in significantly younger ages than others.
Step-wise dissolution of corals used in the present study. Shaded columns are for bulk samples that result in significantly younger ages than others.
Fig. A.1c Step-wise dissolution of corals used in the present study. Shaded columns are for bulk samples that result in significantly younger ages than others.
SA-2 Sample verification using various methods

The important assumption in $^{14}$C and U/Th dating is that the samples remained as closed systems for the isotopes used in the measurement. In general, two sources of contamination can be expected in $^{14}$C dating. One from contamination in the laboratory during the graphitisation process and the other is from inherent diagenesis in corals.

The former can be assessed by several ways. Firstly, by using "old" carbonate which ideally contains no $^{14}$C. In our laboratory, we have used Carrara marble (IAEA C-1) which is referred to internationally, which yielded ages of 47 000 - 48 000 $^{14}$C yr BP for the analytical background value, including AMS analysis (See Chapter 2). Therefore, any dates younger than this age are reliable assuming sample integrity.
Secondly, most of the samples used in the present study have also been measured at another laboratory. Samples were sent to ANSTO (Australian Nuclear Science and Technology Organisation) for $^{14}$C dating (Hotchkis, et al., 1996). Measurement of $^{14}$C at ANSTO were done using whole coral samples without leaching. This is plotted as 0-100% dissolution in Figure 4.11 and A.1. As can be seen, all of the results obtained from ANSTO are significantly younger than our results. This and the description in the previous section clearly indicate the importance of step-wise leaching.

§A-2-1 Textural investigation and XRD analysis

To evaluate the possibility of the open system behaviour for $^{14}$C is much more difficult than for Th-U dating. However, to some extent, it is possible to check for secondary material as pristine coral consists only of aragonite. XRD (X-ray diffraction) can be used to check for secondary calcite. We have investigated textures with a petrographic microscope and XRD analyses (See Chapter 2). In most of the samples secondary fillings were observed in the voids of the coral. These were physically removed using a dental drill prior to leaching. Thus, even in cases where minor secondary replacement was observed, as detected in XRD analyses of whole samples, they were mechanically removed. All the samples had typically less than 2% calcite. The detection limit of our XRD system is ca. 2-3%. Thus calcite content of most of the samples were at the detection limit (Table A.2).
Appendix

Table A.2 XRD results

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§A-2-2 Stable isotope analysis

Stable isotopes of Oxygen and Carbon were measured in the present work. If marine carbonates preserve their original composition, both isotopes values should be around zero (see Chapter 2). Stein et al. (1993) conducted an extensive study of Huon LIG corals. Oxygen isotopes are likely to have been affected if exotic isotopes were introduced into the coral skeleton through percolation by meteoric water. However, Oxygen and Carbon isotopes appear not to have responded to small scale diagenetic alteration in corals. The present corals are significantly younger than LIG corals used by Stein et al., (1993) as such they are less likely to have detectable variations in oxygen or carbon isotopes correlated with small scale diagenesis. The test result show that carbon and oxygen isotope values are within acceptable ranges (Fig.A.2) as found by Stein et al. (1993).
Fig. A.2 Stable isotopes measurement results for corals used in the present study. All the data are within the acceptable range as used by Stein et al. (1993).
§A-2-3 Uranium concentration

$^{238}$U concentration of corals in this study are shown in Figure A.3 and they range between ~2–3.5 ppm. These values are consistent with previously reported results for younger age corals (Hamelin, et al., 1991), Holocene corals (Edwards et al., 1988; Zhu, et al., 1993), and the LIG corals (Edwards et al., 1986; Hamelin, et al., 1991; Edwards, et al., 1987; Stirling et al., 1995;1998). Species dependence of uranium content in corals has been reported previously (Zhu et al., 1993; Stirling 1995). Stirling (1995) reported that uranium content of *Acropora* was higher than other species such as *Porites* or *Favidae*, but Zhu et al (1993), pointed out that *Acropora* and *Montipora* corals have inherently higher $^{238}$U values in Holocene corals. Therefore, the variations in Uranium content might be species dependent, but generally range between 2 to 4 ppm. Thus all corals used in the present study are well within this range.

![U content](image)

Fig. A.3 $^{238}$U content of corals. All corals are within the 2-3.5 ppm range and similar to levels found in modern corals.

§A-2-4. $^{232}$Th concentration in the corals

In Figure A.4 and b, $^{232}$Th abundance is shown plotted with $\delta^{234}$U(T) and $\Delta^{14}$C. $^{232}$Th in modern corals is typically less than 0.5 ppb (Edwards et al., 1986; Chen et al., 1991). In the freshwater or marine environment, voids can be filled with externally introduced detritus material, thus if $^{232}$Th abundance departs significantly from 0.5 ppb level, it may indicate the presence of secondary contamination. Previous workers attempted to correct for $^{232}$Th in the U/Th age, though the
correction is not generally considered to be particularly reliable (e.g., Chen, et al., 1991). The effect is to shift the Th-U age to younger ages.

![Diagram](image)

**Fig. A.4** Relationship between observed (a) $^{232}$Th and $\delta^{234}$U(T), (b) $\Delta^{14}$C, and (c) actual age. No systematic variations were found.

In the present study, for most corals $^{232}$Th is well below the 0.5 ppb limit. One coral has $\approx$1.1 ppb. This coral was collected at a depth of $\approx$175 m in the GBR (Veeh and Veevers, 1970). It had not been exposed to aerial or subaerial environment. Therefore, the excess $^{232}$Th must have been added in the marine environment. There is no systematic relationship between $^{232}$Th and U/Th age, $\delta^{234}$U(T), or $\Delta^{14}$C (Fig 4.18c).
%A-2-5 δ²³⁴U(T)

Although many studies have investigated the cause and circumstances of diagenetic processes in corals (e.g., Bathurst, 1968; Lighty, 1985; Moore 1989; Strasser, et al., 1997), the nature of the mechanism is still unclear (Bar-Matthews, et al., 1993). To evaluate its effect for corals, several criteria have previously been employed, such as microscopic textural analysis, XRD measurements, stable isotope measurements, total uranium contents, the amount of ²³⁵Th in the coral, trace element analysis and, and measurement of the initial ²³⁴U/²³⁸U ratio (δ²³⁴U(T)).

Behaviour of trace chemical elements with diagenesis was studied for the Caribbean corals by Bar-Matthews, et al., (1993). These authors investigated both textural structures with optical microscope and scanning electron microscope, and then conducted chemical analyses. They concluded that textural analysis is necessary, yet it is not quantitative or reliable in evaluating the degree of diagenesis. Most of the alteration was observed in the voids of corals as secondary filling and calcium carbonate deposition. However, cementation in these corals was not always by calcite, but in many cases through secondary aragonite (Bar-Matthews et al., 1993). Therefore, they were altered in the marine environment, quite likely at the intertidal or supertidal zone as indicated by other studies (e.g., Bar-Mathews et al., 1993; Lighty, 1985).

Many studies have detailed the shift of δ²³⁴U(T) through diagenesis (Edwards, 1988; Ku et al., 1990, Banner et al., 1991, Bard et al., 1991, Chen et al., 1991; Stein et al., 1993; Gallup et al., 1994; Stirling et al., 1995). The value tends to be elevated as the degree of diagenesis increases (Fig. 4.21). Gallup et al (1994) and Bard et al. (1992) demonstrated this trend for corals from Barbados and the Bahamas. Similarly, Stirling (1995) also observed a similar increase in δ²³⁴U(T) with age for corals from Western Australia. We have used a similar acceptance criterion: δ²³⁴U(T)=149±10‰ as used in previous studies (eg., Stirling et al., 1998).
§A-3 Ice equivalent sea-level and eustatic sea-level

The sea-level equation for a tectonically stable area is (Farell and Clark, 1976; Nakada and Lambeck, 1987)

\[ \Delta \zeta_{\text{rsl}} = \Delta \zeta_{e} + \Delta \zeta_{i} + \Delta \zeta_{w} \]

where \( \Delta \zeta_{\text{rsl}} \) (\( \varphi, t \)) is the position of the palaeo sea surface relative to present sea level and is a function of position \( \varphi \) and time \( t \). \( \Delta \zeta_{e}(t) \) is the "ice-volume-equivalent sea-level change" associated with the change in ocean volume resulting from the melting or growth of land-based ice sheets and is defined as

\[ \Delta \zeta_{e}(t) = \frac{\rho_{i}}{\rho_{w}} \int_{t}^{t_{f}} \frac{1}{A_{w}(t)} \frac{dV_{i}}{dt} dt \]

where \( A_{w}(t) \) is the ocean surface area and \( \rho_{i}, \rho_{w} \) are the average densities of ice and ocean water respectively. The ocean surface area is a function of time because of the advance or retreat of shorelines as the relative position of land and sea is modified and because of the retreat or advance of grounded ice over shallow continental shelves and seas. The \( \Delta \zeta_{i} \) and \( \Delta \zeta_{w} \) are the glacio- and hydro-isostatic contributions to sea-level change from the isostatic crustal displacement and associated planetary gravity-field or geoid change. Both \( \Delta \zeta_{i} \) and \( \Delta \zeta_{w} \) are functions of position and time and of the earth rheology including the mantle viscosity. The evolution of \( A_{w}(t) \) is a function of the isostatic terms and of the extent of the ice sheets onto the shelves. The relationship between ice volume \( V_{i} \) and equivalent sea level \( \Delta \zeta_{e} \) is therefore model dependent.

If both the ice distribution through time and the earth's response to loading are known, then the ice-volume-equivalent sea level follows from observed sea levels \( \Delta \zeta_{\text{rsl}}^{\text{obs}} \) according to

\[ \Delta \zeta_{e} = \Delta \zeta_{\text{rsl}}^{\text{obs}} - (\Delta \zeta_{i} + \Delta \zeta_{w}) \]

Because of the changing shape of the ocean basins, even when melting has ceased and the ocean volume has stabilised, the \( \Delta \zeta_{i} \) and \( \Delta \zeta_{w} \) are non-zero when averaged over the oceans at any time \( t \) (Farell and Clark, 1976; Nakada and Lambeck, 1987). Writing
\[ \Delta \zeta_i (\varphi, t) = \langle \Delta \zeta_i (\varphi, t) \rangle_{A_0} + \delta \zeta_i (\varphi, t) \]

\[ \Delta \zeta_w (\varphi, t) = \langle \Delta \zeta_w (\varphi, t) \rangle_{A_0} + \delta \zeta_w (\varphi, t) \]

where \( \langle \rangle_{A_0} \) denotes the average value over the ocean surface \( A_0 \) at time \( t \) and \( \delta \zeta_{i,w} \) denote the spatial dependence of the two isostatic terms, then the eustatic sea level is

\[ \Delta \zeta_{eus} (t) = \Delta \zeta_e (t) + \langle \Delta \zeta_i (\varphi, t) \rangle_{A_0} + \langle \Delta \zeta_w (\varphi, t) \rangle_{A_0} \]