

**Geochemical Expressions in Deep-sea
Sediments and Corals of Late Quaternary Climate
Signals in Australia**

Der Fakultät für Physik und Geowissenschaften
der Universität Leipzig
eingereichte
Habilitationsschrift
zur Erlangung des akademischen Grades

Doctor habitatus

Dr. habil.

vorgelegt

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geboren am 25. ~~März~~ 1968 in Halle (Saale)

Leipzig, den 7. ~~März~~ 2004.

The data, interpretations and conclusions presented
in this thesis are my own unless stated otherwise.

Brisbane, February 2004

Acknowledgments

Bradley N. Opdyke gave access to sediment cores and provided financial support for geochemical analyses. Michael K. Gagan gave access to coral cores and geochemical analyses and gave assistance during mass spectrometry. I am grateful to Janice Lough for advise on coral ecology and climatology and for making density measurements possible. I am also grateful for scientific discussions, which led to the publication of articles in Paleoceanography (Müller & Opdyke, Vol. 15. No. 1, Pages 85-94, February 2000) and Geophysical Research Letters (Müller, Gagan & McCulloch, Vol. 28. No. 23, Pages 4471-4474, December 2001) and Global Biogeochemical Cycles (Müller, Gagan & Lough, 2004, in press). Furthermore, some results of this thesis, as published in the above articles, were presented at a number of conferences in co-authorship with Bradley N. Opdyke, Michael K. Gagan, Malcolm McCulloch and Janice M. Lough.

Barry Tobin gave assistance during density measurements, and David Barnes gave scientific input. Gary Meyers and Stuart Godfrey provided scientific advise on oceanography. Alan Pearce and Nick D'Adamo helped with regional knowledge on Ningaloo Reef ecology and oceanography. Rob Allen gave information on climatological topics. I am grateful to Joan Kleypas for providing data of surface-ocean saturation state and to Chris Langdon for providing data on expected future decrease in calcification. I also thank Jean-Pierre Gattuso and Nicolas Leclercq for providing data and helpful comments. Discussions with

Ignacio Martinez on micropaleontological topics improved the quality of the work presented here. Malcolm McCulloch gave access to thermal ionization mass spectrometry. I am also grateful for technical assistance during geochemical analyses from Joe Cali, Heather Scott-Gagan, Joan Cowley, Graham Mortimer and John Vickers. Ullrich Senff carried out XRF analyses. Gail Craswell gave assistance in academic writing.

I am grateful to the UFZ Center for Environmental Research Halle-Leipzig Ltd. for a visiting research fellow grant in 2003, which enabled me to complete this thesis.

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ABSTRACT

Geochemical records (TOC, N, CaCO₃, K, Ba, Al, δ¹⁵N, δ¹³C_{TOC}, δ¹⁸O) of two marine sediment cores from the southern Timor Trough are presented for the past 80,000 years. These records reflect an El Niño-like mean oceanographic and climatic state during isotope stage 2 and, in particular, during the LGM. A comparison of the paleoceanography inferred from the paleodata with the modern-day analogue of an El Niño event suggests that, during the LGM, the Indonesian Throughflow (ITF) was restricted. The above results reinforce recent suggestions in the literature of an El Niño-Southern Oscillation (ENSO)-like equatorial climate mechanism operating at glacial-interglacial time scales in the tropical eastern Indian Ocean.

Improved understanding of the operation of the above mentioned equatorial climate mechanism in the tropical Indian Ocean in the past would greatly have benefited from a coral-based study of the operation of any modern equatorial climate mechanisms in the eastern Indian Ocean over the past few centuries. However, the scale of such a project would be such that it cannot be completed within the confines of a study of this type. Consequently, one goal of this thesis was to find a suitable site for pursuing the necessary coral-based high-resolution reconstructions in subsequent studies. Based on the results from measurements of growth characteristics and geochemical tracers of a number of coral cores from different sites, it was found that only one coral core from Ningaloo Reef was suitable for paleoceanographic reconstructions for the

region. Another core from the same reef was found to be unsuitable because of postdepositional alteration at the base of the core. The results of this thesis show that within Ningaloo Reef, Tantabiddi Bay appears to be a suitable site for the collection of coral-based paleoceanographic records.

The results of this thesis also contribute to the solution of some of the controversies currently found in paleodata bases. Differences found among the reconstructions of sea surface temperatures from different paleoproxies for adjacent sites can be explained by potential misinterpretations of values measured on coral material that may have been influenced by postdepositional alteration. The results also show that corals for which reconstructions of sea surface temperatures have been cross-checked with several tracers (e.g. $\delta^{18}\text{O}$, Sr/Ca) may not be reliable indicators of paleoceanographic conditions. They suggest that coral-based reconstructions of sea surface temperatures may have overestimated cooling of the tropical Indian Ocean in the past. Furthermore, the $\delta^{13}\text{C}$ values and the growth characteristics (density, growth rates, calcification rates) measured on pristine and altered coral material, help clarify the reasons for opposing findings in the current literature of past and recent changes in calcification in the tropical surface ocean in response to changes in atmospheric CO₂ levels. For example, a decrease in calcification seen in many coral records during the 20th century may not have been caused by changes in the carbonate saturation state of the tropical surface ocean. Instead, postdepositional addition of secondary aragonite has caused an apparent decrease in calcification rates

towards the present because of higher density values measured by coral densitometry at the base of the coral cores.

CHAPTER I

Introduction

Paleoceanographic and paleoclimate reconstructions in the eastern Indian Ocean

The eastern Indian Ocean is a key region for paleoclimate research (Thunell et al. 1994, Linsley 1996, Beaufort et al. 2001). Data on paleoceanography and paleoclimate are still lacking, however, for some of the significant parts of the region such as the Timor Sea off northwestern Australia and Ningaloo Reef Marine Park in Western Australia. Yet knowledge of paleoclimate variability in the region is of great importance for understanding the mechanisms behind tropical and global climate variability (e.g. Beaufort et al. 2001).

The region is influenced by the Indonesian Throughflow (ITF), which carries warm, low salinity water from the western Pacific into the eastern Indian Ocean (Godfrey and Golding 1981, Godfrey and Ridgway 1985). Because of this transport of warm water masses from the Western Pacific Warm Pool (WPWP), climate signals from the Pacific are transferred into the eastern Indian Ocean (Meyers 1996). As the warm water determines the degree of convection, the ocean currents strongly influence atmospheric circulation and precipitation patterns in the region (Nicholls 1989, Frederiksen and Balgovind 1994).

Recent studies have suggested that the eastern Indian Ocean is likely to be affected by an equatorial climate mechanism (Beaufort et al. 2001, De Garidel-Thoron et al. 2001). Such a mechanism has previously been suggested by Beaufort et al. (1997) for the western equatorial Indian Ocean, but its influence in the eastern Indian Ocean still needs further investigation. In the eastern Indian Ocean, this equatorial climate mechanism is believed to be directly related to insolation and to resemble the dynamics of the Southern Oscillation. It is thought to be independent of global ice volume variations and thus allows study of equatorial climate dynamics (Beaufort et al. 2001).

The hypothesis proposed by Beaufort et al. (2001) of the operation of an equatorial climate mechanism and resemblance of this climate mechanism to dynamics of the Southern Oscillation is quite revolutionary and represents considerable progress in the field of tropical paleoclimatology. No explanation of this mechanism, however, was offered in their paper. The authors merely state in their paper that contrasts in paleoceanographic features between interglacial and glacial times resemble the features typical of a contrast of the opposing phases of the El Niño-Southern Oscillation (ENSO), i.e. El Niño and La Niña. This statement is based solely on the observations of primary productivity in the surface ocean for areas of the Indian Ocean north of and close to the equator. Thus, the hypothesis of Beaufort et al. (2001) needs further proof from studies based on other proxies, covering different time scales and, in particular, for regions adjacent to the study area of Beaufort et al. (2001) in the eastern Indian

Ocean. The data of Beaufort et al. (2001) alone do not allow derivation of the character and the driving of their proposed climate mechanism.

Currently, the data base for the region with respect to this hypothesis is so sparse that no attempt can be made within a thesis project to prove the hypothesis by Beaufort et al. (2001). The existing data base needs to be considerably expanded to allow clear identification of a climate mechanism behind these large-scale oscillations over glacial and interglacial time scales.

Most of the data of Beaufort et al. (2001) from the eastern Indian Ocean have been collected north of or very close to the equator. Collection of data from regions located south of the equator in the eastern Indian Ocean is essential to fill the vacuum in the data base. The region of the eastern Indian Ocean stretching from the Timor Trough off the coast of northwestern Australia to Ningaloo Reef off the coast of Western Australia is one of the regions clearly understudied as scarce data exist. Along with data sets to be produced by other researchers, the new data presented in this study for this region may eventually contribute to a justification of the hypothesis proposed by Beaufort et al. (2001).

Expansion of the available data sets based on marine sediments in a key area south of the study area of Beaufort et al. (2001), i.e. the area of the southern Timor Trough in the eastern Indian Ocean south of the equator, was then a major goal of this project.

A second, original goal was to provide for the past 150 years a high-resolution oceanographic data set from coral for several relatively small time windows covering about 15 years. This goal was defined because the identification of past climate mechanisms clearly requires identification of and cross-checking with the modern mechanisms.

The majority of studies of modern climate variability in the Indian Ocean have focused on the forcing of such variability by ENSO occurring in the tropical Pacific Ocean. One recent study of sea-level variability in the Indian Ocean provided further evidence that interannual warming occurs in the Indian Ocean with a frequency similar to that of El Niño in the Pacific Ocean (Chambers et al. 1999). Furthermore, recent results from a 194-year annual record of skeletal $\delta^{18}\text{O}$ from a coral growing at Malindi, Kenya, suggest that the tropical Pacific Ocean imparts substantial decadal climate variability to the western Indian Ocean and, by implication, may force decadal variability in other regions with strong ENSO teleconnections (Cole et al. 2000).

The original intention of providing a small high-resolution oceanographic data set, as mentioned above, was to discriminate modern ENSO signals for the region for the past few centuries. It was during this work that, unexpectedly, it became evident that the studied region of the eastern Indian Ocean, reaching from the southern Timor Trough to Ningaloo Reef, appears in modern times to have not only been affected by the ENSO signals but possibly also by the Indian Ocean Dipole. The possible effect of the Indian Ocean Dipole in the

region was inferred because for some of the data variability in the coral studied by Kuhnert et al. (2000), no relation to ENSO was found and no sound explanation could be given.

The extent of the separate or combined influence of the two modern equatorial climate mechanisms believed to be operating in the eastern Indian Ocean, i.e. ENSO (Kuhnert et al. 2000) and the Indian Ocean Dipole (Saji et al. 1999) are currently not understood. Instrumental records, however, suggest that in 1994 both ENSO and Indian Ocean Dipole events may have occurred simultaneously in the equatorial eastern Indian Ocean north of Ningaloo Reef (cf Meyers 1996, Saji et al. 1999).

At present, the instrumental Indian Ocean dipole records available (cf Saji et al. 1999) are too short to allow identification of the degree and kinds of interference of the two mechanisms over the past 150 years. Also, no high-resolution coral-based data sets are available to allow extension of these instrumental records into the past. To date, the only high-resolution coral-based reconstruction including the Indian Ocean dipole has been done on coral from Christmas Island in the tropical Indian Ocean (Marshall and McCulloch 2001). However, this reconstruction is restricted to a 24-year period for which also blended ship and satellite data from the region are available. The results record unusual oceanographic conditions set up by the Indian Ocean Dipole, but do not extend far enough into the past to allow explanation of the driving forces of the

mechanism or comparative analysis of the overall impact of the Indian Ocean Dipole and ENSO signals.

Coral-based reconstruction of the Indian Ocean Dipole covering the past few centuries would require collection of a substantial amount of new data. The scale of this project is such that it cannot be completed within the confines of a single PhD thesis. One project currently being carried out at the Research School of Earth Sciences at the Australian National University is one of the first to have taken up the topic of the reconstruction of the Indian Ocean Dipole based on coral chemistry (Abram et al. 2003). The project focuses on the area off Sumatra which is a key site for a clear signal of the Indian Ocean Dipole (Stuart Godfrey, pers.comm. 2002). At present, the resolution of the above reconstruction is too low to allow identification of the degree and kinds of interference of the ENSO and Indian Ocean Dipole mechanisms in high-resolution oceanographic data sets from corals for the past 150 years.

Due to the lack of long-term data series of the Indian Ocean Dipole, the original second goal of this current project to produce reliable high-resolution paleoceanographic reconstructions based on geochemical data from coral for the area of Ningaloo Reef in the eastern Indian Ocean had to be abandoned. However, the results of the initial preliminary bulk analysis already performed on coral samples revealed another important finding. They showed that the data collected at different sites in Ningaloo Reef proved not to be representative for the entire area.

This finding led to a redefinition of the second goal of this thesis: to find a suitable site for pursuing the necessary coral-based high-resolution reconstructions in subsequent studies. Among a larger number of coral cores from different sites, only two coral cores from Ningaloo Reef initially appeared suitable for paleoceanographic reconstructions based on geochemical coral data for the region. Only for these two sites were coral growth rates found to be sufficiently large to exclude vital and kinetic effects on geochemical tracers due to a variation in growth rates. Further geochemical analysis conducted on 5-year-increments of the complete cores revealed that, of these two cores, only one was suitable for high-resolution studies. The other core proved unsuitable because, as shown in chapters III and IV, the formation of secondary aragonite after coral deposition obscured the results of measurements of growth parameters and geochemical tracers in this coral.

Recognition of the above deviations of growth parameters and geochemical values also drew attention to the potential of the results to help resolve controversies currently found in paleodata bases regarding the interpretation of sea surface temperatures, salinities and the carbonate saturation state of the ocean in the past. Consequently, the third goal of this project was to show that some of the current controversies in paleodata bases such as differences found among the reconstructions (e.g. sea surface temperature) from different paleoproxies for adjacent sites can be explained by potential misinterpretations of values measured on coral material which may have been influenced by

postdepositional alteration such as early marine diagenesis. Given the data presented in chapter III it can be inferred that fossil corals for which reconstructions of sea surface temperatures have been cross-checked with the two presumably independent tracers $\delta^{18}\text{O}$ and Sr/Ca (Guilderson et al. 1994, Beck et al. 1997) may not be reliable indicators of paleoceanographic conditions. This would imply that some of the above coral reconstructions of sea surface temperatures may have overestimated cooling of the tropical ocean in the past. Furthermore, the results and interpretations given in chapter IV clearly contribute to the solution of current controversies concerning possible effects of changes of the carbonate saturation state of the surface ocean in response to changes in atmospheric CO₂ levels. The geochemical data presented for pristine and altered material in chapter IV offer possible explanations for the opposing findings currently available in the literature of past and recent changes in calcification in the tropical surface ocean.

CHAPTER II

Glacial-interglacial changes in nutrient utilization and paleoproductivity in the Indonesian Throughflow sensitive Timor Trough

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Paleoclimatic implications for the region of the easternmost Indian Ocean

2.1. Introduction

The Western Pacific Warm Pool (WPWP, Fig.2.1) is characterized by waters with mean sea surface temperatures (SSTs) exceeding 28°C. Its importance for climate dynamics has been recognized in recent studies, as has the need to understand long-term variations of primary production in low latitudes (e.g. Thunell et al. 1994, Ahmad et al. 1995, Linsley 1996, Beaufort et al. 2001, De Garidel-Thoron et al. 2001). Knowledge of past variation in primary production and nutrient utilization may contribute to the understanding of past changes in the thermal structure in the region. In the Timor Trough (Fig.2.2), which is situated at the southern edge of the WPWP, variations of primary production are poorly documented.

At present, the study area is strongly influenced by the Indonesian Throughflow

(ITF). The ITF (Fig. 2.1) enters the Indian Ocean as a narrow band of low-salinity water, with a maximum water transport estimated in the range of 7-18 Sv (Gordon and Fine 1996). It is strongest in austral winter. The ITF represents the interocean transport of excess freshwater from the Pacific to the Indian Ocean through the Indonesian Seas (Godfrey and Golding 1981, Godfrey and Ridgway 1985). This is caused by the necessity to maintain constant pressure around islands, such as the island continent Australia (Godfrey 1989). Water that passes the ITF flows into the Indian Ocean as the west flowing South-Java and the South Equatorial Currents and as the south flowing Leeuwin Current (Godfrey and Ridgway 1985). The latter is maintained because of the lower steric height further south along the coast off Western Australia. Southward flow is accompanied by surface cooling, and surface cooling produces continuous southward flow (Tomczak and Godfrey 1994).

The dynamics of this eastern boundary current along the Western Australian coast are thus different from those of the Pacific and Atlantic Oceans. In these oceans, equatorward winds produce equatorward surface current flow, poleward undercurrents, and coastal upwelling along the eastern boundaries of the ocean basins. Along the Western Australian coast, however, annual mean winds do blow toward the equator, but at the surface a strong poleward flow runs against the wind, and the undercurrent is equatorward. The poleward flow is strong enough to override the wind-driven equatorward current, and the onshore geostrophic flow is strong enough to override the offshore Ekman flow.

Hence the upwelling that one might expect from the equatorward winds along the Western Australian coast is overwhelmed by an onshore geostrophic drift (Smith 1992, Tomczak and Godfrey 1994).

At present, no significant upwelling occurs in the study area (Tomczak and Godfrey 1994). However, because the pressure difference from the Pacific to the Indian Ocean is the driving force for through flow (Wyrtki 1987), both the volume transport of through flow and the thermal structure in the area are expected to vary during the El Niño-Southern Oscillation (ENSO) cycle. Larger than normal transport is expected during the La Niña phase, when strong easterlies along the equatorial Pacific build up a high sea level in the western Pacific (Clarke and Liu 1994). Conversely, during an El Niño event, Pacific equatorial winds are anomalously westerly, and the western Pacific sea level falls. This low sea level is transferred to the coast northwest of Australia (Clarke and Liu 1994, Potemra and Lukas 1999). As a consequence, the baroclinic pressure gradient between northwestern Australia and Java decreases (Clarke and Liu 1994), resulting in a weakening of the ITF (Clarke and Liu 1994, Potemra 1999).

The alternation of easterly and westerly wind stress anomalies during an ENSO cycle is accompanied by a weaker reversal of anomalies in the eastern Pacific and in the equatorial Indian Ocean. The winds over the equatorial Indian Ocean determine the thermal structure on the Indonesian coast. During ENSO, when Pacific wind anomaly is westerly, Indian Ocean anomaly is easterly, resulting in

a shallow thermocline along the coast of Java. This has been observed to occur simultaneously with extremely cold SST, suggesting that upwelling contributes to the formation of a "cold spot". This SST temperature anomaly is widespread during some ENSO events, extending from Timor along Java and Sumatra (Meyers 1996).

During the Last Glacial Maximum (LGM), the circulation patterns in the Indian Ocean were significantly different from those of today. It has been suggested that a northflowing West Australian Current, associated with a weaker or absent Leeuwin Current linked to a reduced WPWP (Martinez 1994) and thereby weaker ITF, led to increased productivity and coastal upwelling at higher latitudes off Western Australia (McCorkle et al. 1994, Wells et al. 1994). As well, the Westerlies may have been compressed, and thus more intense, and moved north during the LGM. Part of the West Wind Drift was deflected equatorward by Australia. Thus, in contrast to the modern pattern of weak, seasonally reversing flow, the West Australian Current was a significant eastern boundary current. This current transported cooler waters equatorward all year-round (Prell et al. 1980).

In this chapter, geochemical results are presented from two sediment cores from the continental margin off northwestern Australia to show past changes in productivity and nutrient utilization, which may be related to changes in the ITF and thermal structure in the area. The chapter focuses on Holocene/LGM contrasts because for these time periods ^{14}C dating (B.N. Opdyke, unpublished

data) is available in addition to the $\delta^{18}\text{O}$ record of *Globigerinoides ruber*. Signals observed during isotope stages 3 and 4 for which an age model based on the $\delta^{18}\text{O}$ record of *Globigerinoides ruber* has been established will be pointed out, but they will not be discussed in detail due to the lack of results from additional dating.

4.4. Procedures

Two gravity cores, GC4 ($12^{\circ}17.48\text{ S}$, $121^{\circ}56.01\text{ W}$, water depth 2069 m) and GC5 ($12^{\circ}22.3\text{ S}$, $122^{\circ}12.03\text{ W}$, water depth 1462 m), were taken during a R.V. Franklin cruise in 1996 (Fig. 2.2). Two series of 3cm^3 syringe samples were taken at 10-cm intervals for each core. To establish a foraminiferal $\delta^{18}\text{O}$ record, organic matter was removed from the samples of one series by treatment with 5% hydrogen peroxide solution (H_2O_2). The size fraction $>150\text{ }\mu\text{m}$ was separated by wet sieving. Foraminiferal specimens of *Globigerinoides ruber* were hand picked from the $>150\text{ }\mu\text{m}$ size fraction, washed in alcohol and placed in an ultrasonic cleaner for less than 5 seconds. 10-15 clean specimens (with a total weight between 150 and 200 μg) were selected for stable isotope analysis. Isotope analysis was carried out using an automated individual carbonate-reaction (Kiel) device coupled with a Finnigan-MAT 251 mass spectrometer. The $\delta^{18}\text{O}$ values were calculated as per mil (‰) deviations relative to PDB, and were calibrated via the NBS-19 standard ($\delta^{18}\text{O}=-2.20\text{‰}$). Average reproducibility for a typical 150- μg sample was 0.05‰.

The chronostratigraphy of the cores was based on the $\delta^{18}\text{O}$ records for *Globigerinoides ruber*, applying the SPECMAP time scale (Imbrie et al. 1984, Martinson et al. 1987, Fig. 2.3). An interpolation was made between $\delta^{18}\text{O}$ -age tie points, and linear sedimentation rates were derived.

For all following analyses, the samples of the second series were freeze dried, crushed and homogenized. For stable isotope analysis ($\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}$) carbonate was removed from the sediment samples by adding 2% hydrochloric acid to sediment subsamples (20 mg aliquots). This was repeated until formation of CO_2 bubbles ceased. The samples were then dried at 60 °C, and combusted with a CHN-analyzer (ANCA/SL) coupled to a 20/20 mass spectrometer (Europa Scientific Ltd, UK). Pure CO_2 and N_2 gases from tanks calibrated as a standard against carbonate (NBS-22) and atmospheric nitrogen (Mariotti 1983) respectively, were used as reference gases. Isotope ratios were calculated using the following equation,

$$\delta X (\text{\textperthousand}) = (R_{\text{sample}} / R_{\text{reference}} - 1) * 10^3.$$

where X and R are ^{13}C (or ^{15}N) and $^{13}\text{C}/^{12}\text{C}$ (or $^{15}\text{N}/^{14}\text{N}$), respectively.

Two secondary standards, flour for N and beet sugar for C, calibrated against IAEA-NI $(\text{NH}_4)_2\text{SO}_4$ and IAEA reference standard NBS-22 respectively, were included in the sample batch after every 8th sample. Values were reported relative to air nitrogen and relative to PDB. Analytical variability was checked

again using a soil, homogenized as an internal standard, as a sample after every reference standard. Throughout the analysis of sets of up to 50 samples, the test standard (flour) analysed in this way gave a standard deviation of 0.16‰ on a measured mean $\delta^{15}\text{N}$ of 3.87‰, and similar precision was obtained for the reference soil (16.56 + 0.33‰). Variation between duplicates was less than 0.2‰. The precision of $\delta^{13}\text{C}$ analysis was better than 0.22‰, and variation between duplicates was less than 0.3‰. Total organic carbon (TOC) and total nitrogen (N) values were determined simultaneously when measuring the isotope ratios, with the test standard showing a standard deviation of 0.009% for C and 0.001% for N, with duplicates having a variation less than 0.08% and 0.009% for C and N respectively.

Total carbon was measured on 2-mg aliquots, weighed in aluminum capsules, with a NA 1500 NC Fisons Analyzer at 1020°C. Together with the samples, urea, soil and one sediment sample were measured as internal standards after every 6th sample. From these measurements, the reproducibility appeared to be better than 0.06%. Here, mean values of duplicate measurements are reported, with the standard deviation usually better than +/-0.2%. Inorganic carbon content was derived from the difference between total carbon and organic carbon, and calcium carbonate content was calculated from inorganic carbon values by multiplying the inorganic carbon content by a factor of 8.33.

For major element determination (BaO , Al_2O_3 , K_2O) samples were prepared as glass discs following the method of Norrish and Hutton (1969), with the

exception that the flux used consisted of 12 parts lithium metaborate. These glass discs were measured on a PW2400 wavelength dispersive X-ray fluorescence (XRF) spectrometer. The precision of these measurements was better than 0.002% for BaO, 0.03% for Al₂O₃ and 0.05% for K₂O. Total barium was corrected for the nonbiogenic barium fraction using the Al content of the sediments, where Al is used as a measure of aluminosilicate contribution (Calvert 1976, Shimmield 1992). Total barium content was normalized using the equation given in Dymond et al. (1992): Baexcess = Batot - (Al x 0.0075).

The correction factor in the equation refers to the global Ba/Alaluminosilicate ratio of crustal rocks. Like in Francois et al. (1995), ranges for biogenic Ba fluxes have been estimated which refer to the extrema in the range of Ba/Al of 0.01<Ba/Al<0.005 for crustal rocks as reported by Taylor and McLennan (1985). There is, however, a measure of imprecision with this method depending on the magnitude of the terrigenous barium fraction (Dymond et al. 1992). Because much of the terrigenous barium may be contained within feldspar, Ba/K ratios were also calculated to normalize for variations in feldspar contents (Schneider et al. 1997).

2.3. Results

Linear sedimentation rates range from 3.5 to 15.3 cm/kyr (Fig. 2.4). Values are higher during the LGM than the Holocene in the shallow core GC5, but not in core GC4. It is possible that the values are influenced by syndepositional

redistribution of the sediments, which may result from changes in downslope transport, possibly related to changes in sea level.

TOC concentrations are higher in the sediments from the LGM than the Holocene (Fig. 2.4), implying higher productivity during the LGM. The LGM falls into the shaded section covering isotope stage 2 in the figure. The organic matter fraction of the sediments is predominantly of marine origin, although a minor terrigenous component may be present. Evidence for this is given by the TOC/N, $\delta^{13}\text{C}_{\text{TOC}}$ and TOC/AI and N/AI values (Fig. 2.4 and 2.5).

The TOC/N ratios in the sediments are relatively low and point toward the dominance of a marine organic matter fraction (Fig. 2.4., cf Müller 1977 and references therein). TOC/N ratios are higher during isotope stages 2 and 3. For the sediments from these stages, terrigenous input cannot be ruled out from the elemental composition alone.

Low TOC content (mostly <0.8%) associated with low TOC/N ratios (<7.5) can be seen for both cores in isotope stage 1. In contrast, relatively high TOC contents (>0.8%) can be observed together with high TOC/N ratios (>7.5) in the core section corresponding to isotope stage 2. Unlike the sediments of stage 1, the sediments of stage 2 contain an inorganic nitrogen fraction in both sediment cores. The latter is likely to be bound to illite (cf Müller 1977). The TOC/AI and N/AI ratios in core GC4 show similar trends in being highest in stage 2 and lowest in stage 1 (Fig. 2.4). These changes occur almost simultaneously with

the transition from isotope stage 1 to isotope stage 2 and indicate the presence of two distinct sedimentological or stratigraphic units rather than continuous diagenetic alteration.

Higher CaCO_3 concentrations were observed in the sediments from the LGM compared with those from the Holocene (Fig. 2.5). As with the above values, excess barium concentrations and Ba/K ratios are higher during the LGM than the Holocene (Fig. 2.5), implying higher productivity. As TOC are relatively low in the study area compared with high productivity regions, it seems unlikely that barite undergoes significant diagenetic mobilization and reprecipitation due to anoxic conditions in the surface sediments (von Breymann et al. 1992, Torres et al. 1996).

The pattern of the records of the values above and those of $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{15}\text{N}$ show similar trends along the cores. The sediments show clearly lower $\delta^{15}\text{N}$ and higher $\delta^{13}\text{C}_{\text{TOC}}$ values during the LGM than the Holocene (Fig. 2.5). The Holocene-LGM variations of TOC, $\delta^{13}\text{C}_{\text{TOC}}$, $\delta^{15}\text{N}$, Baexcess, Ba/K and CaCO_3 records show a strong relationship with the planktonic foraminiferal $\delta^{18}\text{O}$ record. As a general trend, the Holocene is characterized by low TOC, CaCO_3 , Baexcess, Ba/K, $\delta^{13}\text{C}_{\text{TOC}}$ and high $\delta^{15}\text{N}$ values, while the values from the LGM show the opposite. Apart from these general trends, the $\delta^{13}\text{C}_{\text{TOC}}$ and especially the $\delta^{15}\text{N}$ records appear to lag the $\delta^{18}\text{O}$, TOC, N, CaCO_3 and barium records, and reach maximum and minimum values a few years later. In

addition to the glacial/interglacial changes, higher-frequency fluctuations appear to be recorded in the sediment sequence. However, at this stage the resolution and the length of the data series is not sufficient to ensure that these fluctuations are not subject to noise. These high-frequency fluctuations using a longer time-series and a higher-resolution time-scale should be the subject of future studies.

2.4. Discussion

2.4.1. Glacial-interglacial changes in paleoproductivity

The combined use of paleoproductivity proxies in this chapter has proven useful in pointing out times of elevated productivity. This proxy comparison shows generally good agreement between three different paleoproductivity indicators. Given the uncertainty of any single proxy, simultaneous application of more than one tracer strengthens the interpretation of glacial/interglacial changes in paleoproductivity. However, the results also indicate that glacial productivity was increased only relative to the low productivity characteristics of this region in the modern ocean. In the following each proxy is discussed independently.

2.4.1.1. Organic carbon, TOC/N ratios and possible diagenetic imprints

Evidence of higher surface ocean productivity during the LGM is given by the TOC concentrations, which are higher in the sediments from the LGM than the Holocene (Fig. 2.4). In estimating changes in productivity from TOC values,

possible differences in organic matter preservation due to changes in the magnitude of the sedimentation rates (Heath et al. 1977, Müller and Suess 1979) have not been accounted for. They were not accounted for because TOC variations do not appear to show dependence on the sedimentation rates. In particular, higher TOC during the LGM are not always associated with higher sedimentation rates which could have supported preservation of organic matter.

As well, sediments from northwestern Australia do not appear to contain a significant input of terrigenous organic matter. This is because the $\delta^{13}\text{C}_{\text{TOC}}$ values of the sediments are high (Fig. 2.5), excluding significant input from C3 plant detritus. The only possible input of a terrigenous organic matter fraction would be from C4 plants. This cannot be excluded for the study area as palynological studies have shown that the climate was drier and grassland vegetation, characterized by C4 plants, was more prevalent during the LGM in northern Australia (van der Kaars 1991). Increased input of C4 plant detritus, associated with increased aridity during the LGM (Prell et al. 1980), could cause a shift to heavier $\delta^{13}\text{C}_{\text{TOC}}$ values in the sediments because C4 plants generally have a higher range of $\delta^{13}\text{C}$ values than C3 plants (Schidlowski et al. 1983). For example, Goñi et al. (1998) demonstrated in the Mississippi River drainage basin that when both C3 and C4 plant sources are equally important, land derived organic carbon ($\delta^{13}\text{C}_{\text{terr}} = -20$ to $-22\text{\textperthousand}$) can be isotopically indistinguishable from marine sources ($\delta^{13}\text{C}_{\text{mar}} = -19$ to $-21\text{\textperthousand}$).

However, at present the study area is not affected by large river inputs as is the case for the sites of Goñi et. al (1998). As well, dust input around Australia is smaller than during the LGM (Hesse 1994). During the Holocene, the ranges of the $\delta^{13}\text{C}_{\text{TOC}}$, TOC/N and $\delta^{15}\text{N}$ and the similar occurrence of higher C/N and lower $\delta^{13}\text{C}_{\text{TOC}}$ in GC4 than GC5 may reflect a terrigenous matter input from C3 plants, although the C/N values are too low to support the input having significant influence. Hydrodynamic transport patterns could be responsible for differences in the values between the cores from different water depths.

Due to the different geographical and climate conditions, increased input of terrigenous organic material from rivers and dust, in the form of C4 plant detritus, seems possible during the LGM. Although such an input cannot be excluded, it does not in itself appear significant enough to account for the magnitude of the shift in the TOC/N values and the isotope signals of bulk organic matter in the sediments. Therefore an increased input of C4 plants is not considered to have caused the observed shifts in the TOC/N and $\delta^{13}\text{C}_{\text{TOC}}$ values.

The cause of the glacial-interglacial variations in the TOC/N ratios may be attributed to variations in organic matter preservation rather than a source change. Variations in TOC/N ratios during diagenesis may be caused by variations in the organic matter/clay associations. This is because the sorption of organic matter to mineral surfaces (decreasing grain size meaning increasing specific surface area) in marine sediments stabilizes the component molecules

and slows remineralization rates (Keil et al. 1994). Most of the sediments from isotope stage 1 contain only small amounts of organic matter (<0.8% TOC) and consequently have low organic matter/clay mineral (TOC/Al) ratios (Fig. 2.4). In these sediments, the (mainly organic) nitrogen compounds protected within the interlayer spaces of clay minerals (e.g. Müller 1977) appear to primarily determine the lower TOC/N ratios.

In contrast, the diagenetic alteration in the sediment sequence of stage 2, with high TOC concentrations (>0.8%) and higher TOC/N, is likely to be different from that occurring in the sediment sequence corresponding to isotope stage 1. This is because the effect of clay mineral assemblages on the TOC/N ratios may vary with the amount of organic matter in the sediments. Increasing TOC/N ratios are often accompanied by an increasing organic matter content (Müller 1977, Fontugne and Calvert 1992). In the stage 2 sequence, a higher organic matter/clay mineral ratio (TOC/Al) can be observed (Fig. 2.4), allowing a relatively smaller fraction of nitrogen to be preserved. It can be concluded that changes in the TOC/N ratios in the sediments of the study area are primarily controlled by organic matter preservation.

2.4.1.2. Barium

Baexcess and Ba/K values are higher during the LGM than during the Holocene, suggesting elevated productivity. Barium is a highly refractive element in the water column, retaining a high proportion of the original

productivity signal relative to other common proxies like organic carbon and calcium carbonate (Dymond et al. 1992). It can be used as a paleoproductivity indicator because living plankton consists of a relatively large pool of labile barium, which is rapidly released during plankton decomposition. This pool of labile barium acts as the main source of barium for barite formation in supersaturated microenvironments. In addition to barite, biogenic barium occurs mainly as refractory organic barium (Ganeshram et al. 2003). Here, a comparison of biogenic (or excess) barium concentrations (Francois et al. 1997) and Ba/K ratios (Schneider et al. 1997) was done to obtain a reliable picture of productivity changes based on barium values. The similar glacial/interglacial trends of the Baexcess and Ba/K ratios suggest that changes in terrigenous input do not mask the productivity signal reflected by the ratios.

2.4.1.3. Calcium carbonate

The CaCO_3 concentrations imply higher productivity during the LGM. Glacial-interglacial changes in CaCO_3 values have been interpreted in terms of variations in both CaCO_3 supply and dissolution intensity (Lyle et al. 1988, Farrell and Prell 1989, Archer and Maier-Reimer 1994). Carbonate dissolution varies as a function of water depth, bottom water chemistry and carbonate flux (Archer 1991). The possibility that the lower carbonate values in the Holocene section of the sediments reflect dissolution rather than low carbonate supply cannot be ruled out. However, the similarity of the CaCO_3 trends with those of TOC and barium (Fig. 2.4 and 2.5) suggests that changes in the rate of CaCO_3

supply, due to variations in productivity, drive the glacial/interglacial changes in CaCO_3 concentrations. All productivity proxies in this chapter show elevated values during the LGM, although the degree to which they are subject to dissolution or alteration may differ between proxies.

2.4.2. Glacial-interglacial changes in $[\text{CO}_2(\text{aq})]$ in surface waters

The changes in the $\delta^{13}\text{C}_{\text{TOC}}$ values in the sediments occur chronologically parallel to paleoproductivity changes documented by the organic carbon, calcium carbonate and barium data. The $\delta^{13}\text{C}_{\text{TOC}}$ values suggest CO_2 depletion in the surface waters, possibly as a result of enhanced productivity, during stage 2 and during the second half of stage 3. As has been shown, phytoplankton blooms can cause rapid lowering of surface water PCO_2 (e.g. Watson et al. 1991). Diagenetic alteration does not appear to have caused the change in the $\delta^{13}\text{C}_{\text{TOC}}$ values. The likelihood that a terrigenous organic matter fraction has influenced the $\delta^{13}\text{C}_{\text{TOC}}$ values of the sediment has also been excluded. Based on the assumption that changes in inorganic carbon $\delta^{13}\text{C}$ did not occur it was concluded that the shift from higher to lower marine sedimentary $\delta^{13}\text{C}_{\text{TOC}}$ across the Pleistocene/Holocene transition has resulted from an increase in ^{13}C discrimination by Holocene phytoplankton. This was associated with a widespread increase in relative $\text{CO}_2(\text{aq})$ availability and/or a decrease in phytoplankton carbon demand (cf Descolas-Gros and Fontugne 1985, Falkowski 1991, Rau et al. 1992). Alternatively, the elevated glacial

$\delta^{13}\text{C}_{\text{TOC}}$ values could reflect increased phytoplankton utilization of ^{13}C -rich HCO_3^- (relative to $\text{CO}_2(\text{aq})$) during that time, which could also be the result of increased productivity in the surface waters (Degens et al. 1968, Descolas-Gros and Fontugne 1985, Falkowski 1991).

This study documents past glacial/interglacial variations in plankton $\delta^{13}\text{C}_{\text{TOC}}$, and suggests that these variations have been caused by changes in surface water CO_2 concentrations as a result of variations in surface ocean productivity. In addition, the magnitude of change is in agreement with those reported in association with glacial/interglacial changes in surface ocean PCO_2 (cf Rau 1994). However, no empirical relationship between plankton $\delta^{13}\text{C}_{\text{TOC}}$ and $[\text{CO}_2(\text{aq})]$, and no detailed and sound paleo-SST estimates have been provided for the study area so far. That is why it is difficult to delineate local from global signals within the sedimentary record (cf Rau 1994), which may have been caused by lower atmospheric CO_2 levels during the LGM (Barnola et al. 1987).

2.4.3. Changes in nutrient utilization in the surface waters

Sedimentary nitrogen isotope ($\delta^{15}\text{N}$) records from a number of regions have been interpreted as reflecting changes in relative nitrate utilization (e.g. Farrell et al. 1995, Francois et al. 1997, Holmes et al. 1997). Thereby isotopically light particulate organic matter is produced during conditions of relative nutrient depletion (low relative nutrient utilization), whereas the opposite applies for

isotopically heavy organic matter (high relative nutrient utilization). As well, from several studies it is apparent that glacial/interglacial cycles have a strong effect on $\delta^{15}\text{N}$ values in many regions when climate induced changes in hydrography and/or upwelling intensity occur (e.g. Altabet et al. 1995, Farrell et al. 1995, Ganeshram et al. 1995).

$\delta^{15}\text{N}$ values in the sediments of the study area were measured in order to investigate changes in nutrient availability and productivity (Fig. 2.5). The following discussion shows that the values do reflect these specific changes rather than having been influenced by the factors of a terrigenous organic matter input, the degradation of sedimentary organic matter and the occurrence of denitrification in the water column of the study area.

The TOC/N and $\delta^{13}\text{C}_{\text{TOC}}$ data suggest that the input of terrigenous organic matter into the sediments was not significant. Therefore, a $\delta^{15}\text{N}$ signature of terrestrial matter in the sediments would be clearly overprinted by the signal of relative nitrate utilization. As well, it is assumed that the $\delta^{15}\text{N}$ signal has not been influenced by offsets between isotope ratios of particulate organic matter sinking through the water column and underlying sediments due to particle decomposition and trophic exchange of nitrogen. Although such offsets have been observed in similar settings with low TOC concentrations in sediments deposited under oxic conditions, their effects are usually constant and therefore not considered to be significant relative to the signals observed (Altabet and Francois 1994a).

In addition, the $\delta^{15}\text{N}$ values do not appear to be affected by the occurrence of denitrification in the water column of the study area. Evidence for this comes from several sources. First, the $\delta^{15}\text{N}$ values in the sediments do not exhibit a general elevation which would indicate the occurrence of denitrification (Cline and Kaplan 1975). As well, O_2 concentrations today do not drop below 0.2 ml/l (Wyrtki 1988), the value that has been described for modern upwelling areas off Peru as being the threshold necessary for denitrification to occur (Packard et al. 1983). Moreover, if denitrification was an important factor affecting the $\delta^{15}\text{N}$ values in this area in the past, high sedimentary organic matter content should be associated with high sedimentary $\delta^{15}\text{N}$ values (e.g. Schäfer and Ittekkot 1993, Ganeshram et al. 1995). The highest $\delta^{15}\text{N}$ values are observed during the Holocene when TOC concentrations are low, and denitrification does not occur today. This indicates that denitrification has not occurred in the past either.

The results indicate that the sedimentary isotopic signal is primarily controlled by the degree of nutrient utilization in the surface waters and that, in this region, changes in relative nutrient utilization between the LGM and the Holocene determine the variation in the $\delta^{15}\text{N}$ signal in the sediments. During the Holocene, lower paleoproductivity was concurrent with higher $\delta^{15}\text{N}$ values, which suggests higher relative nitrate utilization. In contrast, the low $\delta^{15}\text{N}$ values suggest that nitrate was less depleted during the LGM when productivity

was high. Thus, although productivity was higher, relatively less of the available nitrate pool was utilized by the phytoplankton. Absolute nitrate concentrations must have been elevated to support the high rates of productivity.

Given the present day oceanography, one plausible explanation for the higher nutrient levels during the LGM involves nutrient supply to the surface waters being more efficient. This is because of a shallower thermocline, the restriction or the absence of the low-salinity cap of the ITF, and the occurrence of upwelling in the area. Upwelled water provides a large pool of nitrate which is available for uptake during photosynthesis, leading to lower planktonic $\delta^{15}\text{N}$ values than when nitrate is more limiting (Altabet and Francois 1994b, Holmes et al. 1996). Moreover, increased productivity, associated with the presence of upwelled nutrients, has been found to correlate with low $\delta^{15}\text{N}$ values in both sinking organic matter and sediments (Schäfer and Ittekkot 1993, Altabet and Francois 1994b). However, glacial productivity in the Timor Trough was high relative only to the low productivity characteristics of this region in the modern ocean. There is no evidence of strong upwelling of the magnitude of that observed in the modern ocean off the western coasts of Africa and South America.

In addition to the above interpretation for the LGM decline in the $\delta^{15}\text{N}$ values, other factors must have affected the sediment $\delta^{15}\text{N}$ record. This is because the $\delta^{15}\text{N}$ values of the sediment in the study area are very low compared to those from other study areas with similar settings for which total nitrate utilization and

diagenetic enrichment by ~3-4‰ has been considered. Similar to the study area, the latter areas are characterized by low TOC in the sediments as well as high O₂ in the water column (Altabet and Francois 1994a, Francois et al. 1997). If the values presented in this chapter showed such a diagenetic offset, they would reflect extremely low nitrate utilization.

Alternatively, the values could be explained by the removal of nitrate, not utilized by phytoplankton, from the surface waters, by physical processes like advection or mixing (Francois et al. 1997). At present there is strong evidence for tidal mixing in the study area (Godfrey and Mansbridge 2000). Another explanation could be that nitrogen (N₂) fixation was of importance. The δ¹⁵N signature of newly fixed nitrogen is ~0‰, close to the isotopic composition of N₂ in air (Wada and Hattori 1979). N₂ fixing cyanobacteria of the genus *Trichodesmium* occur off northwestern Australia (Capone et al. 1997). N₂ fixation provides fixed N to compensate for the deficit in nitrate relative to phosphate that results from denitrification (Falkowski 1997).

The δ¹⁵N values indicate that if N₂ fixation was of importance, it was more intense during the LGM than the Holocene. This could be for two reasons. First, the inflow of nitrate depleted surface waters from semi-enclosed basins of the Indonesian Seas into the study area may have occurred during the LGM. Inflow of oxygen-depleted waters has been reported for the Indonesian Throughflow sensitive northern Indian Ocean (Vénec-Peyré et al. 1995). At that time sea level was lower and denitrification was likely to occur in those semi-enclosed

basins in the Indonesian Seas, which were characterized by high productivity during the LGM (Linsley 1996, Ahmad et al. 1995). Haug et al. (1998) showed for the Cariaco Basin that denitrification resulted in the removal of nitrate from thermocline depths. This encouraged the growth of N₂-fixing cyanobacteria when this nitrate deficit was transferred into the surface layer by mixing. A N₂ fixation response (Haug et al. 1998) to glacial/interglacial variations in denitrification on a global scale in the open ocean (Altabet et al. 1995, Ganeshram et al. 1995) is not likely to have occurred in the study area. The trend seen in the data does not accord with global trends of a glacial decrease in denitrification, accompanied by an increase in the oceanic nitrate reservoir, as the values suggest that N₂ fixation would have been more likely to occur during glacials in the Timor Trough.

Second, apart from the reported evidence for changes in the nutrient supply due to variations in the strength of the ITF, it cannot be excluded that changes in N₂ fixation may have been influenced by other factors. Besides phosphorus, N₂-fixing cyanobacteria need trace elements, in particular iron and molybdenum (e.g. Capone et al. 1997). Given the lower sea level and the increase in dust flux to the study area during the LGM, metal input is likely to have been higher at that time and would not have inhibited higher levels of N₂ fixation. Further studies will be necessary to show the importance of N₂ fixation in the region.

There is still not enough information to unambiguously interpret these $\delta^{15}\text{N}$ records in more detail. However, the interpretation of upwelling in the region

during the LGM is derived from a combination of factors. Primarily, the increased productivity during the LGM suggests increased nutrient supply. Previous studies have also shown that during the LGM, the WPWP was reduced in size. Moreover, the present day oceanography favors the occurrence of a shallow thermocline and weak upwelling during El Niño events (Meyers 1996), when the WPWP is reduced in size (Yan et al. 1992).

2.4.4. Fluctuations and lags in proxy records

The TOC, CaCO₃ and δ¹³C_{TOC} records and their correlation with the δ¹⁸O record suggest that sea level variations have driven changes in the fertility of the surface waters of the study area. This is because variations in environmental parameters such as SSTs and surface ocean stratification can be expected to be linked to glaciation and sea level history. The parallel trend of the bulk sediment δ¹⁵N variations suggests coincident changes in the nutrient cycling. However, the lag between δ¹⁵N and sea level suggests that other factors were important.

The lag of the δ¹⁵N record compared to the δ¹⁸O record is of the magnitude of a few thousand years. Similar lags have been observed in other regions and were attributed to a significant [NO₃]/[PO₄] change in the global ocean, which would take several thousand years, whereas changes on a regional scale would require less time (e.g. Haug et al. 1998). However, at present there is no proof of a global driving force for the δ¹⁵N signals.

In addition to the glacial/interglacial changes, higher-frequency fluctuations appear to be recorded in the sediment sequence. Although the resolution and the length of the present data series is not sufficient to ensure that these fluctuations are not subject to noise, similar fluctuations have been observed in other areas of the northern Indian Ocean. Vénec-Peyré et al. (1995), based on correspondence analysis of foraminiferal and radiolarian assemblages, suggested short-term events (with a duration of <5 kyr); for example temporary deepenings of the mixed layer. These authors related these events to the rapid inflow of oxygen-depleted water through the Indonesian straits, as a result of the highest sea level rise during deglaciation. They suggested that the events reflected the reorganization of the oceanographic circulation, before the establishment of the regular interglacial Throughflow. Similar explanations of variable inflow by the ITF could apply in the study area.

The strong contrasts observed at isotope transition 2/1 can be considered to be the oceanic signature of the most rapid sea level rise, which caused an increased outflow of surface waters from the Indonesian basins. Similar contrasts were observed in the Indonesian Throughflow sensitive northern Indian Ocean (e.g. Vénec-Peyré et al. 1997). Evidence for highest sea level rise at that time has been given by reef terraces, which are presently emerged in the region of the Indo-Pacific Ocean (Chappell and Shackleton 1986). The results found in these reef terraces have recently been confirmed by investigations of

the siliciclastic system on the tectonically stable Sunda Shelf in Southeast Asia (Hanebuth et al. 2000).

The high $\delta^{13}\text{C}_{\text{TOC}}$, TOC and CaCO_3 in stage 3 prior to the clearly elevated values in stage 2 may indicate that a phytoplankton community was already established and then fertilized further. This was previously observed for the northern Indian Ocean, and was thought to be related to water stratification (Vénec-Peyré et al. 1995). The more elevated values in stage 2 are linked to lowest sea level which contributed further to shallow water, mixing and more efficient nutrient supply to the surface waters. This is reflected by the minima seen in the $\delta^{15}\text{N}$. Although a detailed interpretation cannot be offered here, the data suggest that the enhanced barium levels in stage 2, which do not occur in stages 3 and 4, are also linked to lowest sea level.

2.5. Conclusions

Glacial-interglacial changes in productivity and nutrient utilization in the Timor Trough in the eastern Indian Ocean appear to reflect changes in the activity of the ITF and sea level. Productivity appears to be inversely proportional to the strength of the ITF. On the basis of the present day oceanography it is inferred that during the Holocene, productivity has been inhibited by stratification of the water column, suppressed vertical mixing and low nutrient concentrations in surface waters. This is because of the narrow band of low salinity water that

moves through the Indonesian Archipelago and spreads out over the equatorial portions of the eastern Indian Ocean.

However, higher surface ocean productivity during the LGM than the Holocene can be inferred for this area; the surface waters being depleted in CO₂ and relative nitrate utilization lower. Covariation of the paleo- $\delta^{15}\text{N}$ signal with changes in paleoproductivity indicates the presence of a higher flux of nutrient-rich water to the surface during the LGM. This higher flux is the result of a shallower thermocline and weak upwelling in the region. The findings reflect the restriction or the absence of this low salinity "cap" of the ITF, which would be in agreement with previous suggestions of a considerably weaker ITF during the LGM. In addition, thermal structure appears to have been influenced by sea level changes in the region.

Apart from the reported evidence for changes in the nutrient supply due to variations in the depth of the thermocline, there is the suggestion that N₂ fixation may have contributed to the N nutrition of the surface waters. Further studies will be necessary, however, to show the importance of N₂ fixation in the region. The paleo-records do not appear to be influenced by changes in the nutrient reservoir in the global ocean, but reflect local changes in nutrient supply. The latter are likely to be caused by changes in sea level and the strength of the ITF.

While the paleorecords give a good indication of past climate change and the mechanisms behind this change, high-resolution studies are needed to fully understand the nature of the climate mechanism in the region of the eastern Indian Ocean. High-resolution studies can be performed using massive coral. However, the potential of massive coral from the region of the eastern Indian Ocean to act as paleoclimate proxies still needs extensive testing. The following two chapters test the potential of corals from Ningaloo Reef in Western Australia for paleoceanographic and paleoclimate studies for the region of the eastern Indian Ocean in the more recent past.

CHAPTER III

Validity of paleoceanographic reconstructions from massive corals

Implications for sea surface temperature reconstructions for the Last Glacial Maximum and the Holocene

3.1. Introduction

Sea surface temperatures (SSTs) are an important quantity for understanding past climate dynamics, and estimates of SSTs are an essential boundary condition used in general circulation models of past and future climate (Graham 1995, Bush 1999). Large negative SST anomalies of 4 to 6.5°C have been reconstructed for the last deglaciation and the Last Glacial Maximum (LGM) using $\delta^{18}\text{O}$ and Sr/Ca measurements in scleractinian corals (Guilderson et al. 1994, Beck et al. 1997). The tropical SSTs recorded from fossil coral for the LGM (Guilderson et al. 1994), however, are much lower than those recorded from other marine proxies. These proxies, which include foraminifera speciation (CLIMAP 1981, Mix et al. 1986), foraminiferal oxygen isotopes (Broecker 1986, Birchfield 1987) and alkenone results (Lyle et al. 1992, Rostek et al. 1993,

Sikes and Keigwin 1994), suggest a cooling of no more than 3°C. At present, it is not clear if this difference reflects regional differences in the extent of cooling, or if one group of proxies is misleading (Broecker 1996). Another surprising finding is the large warming and/or freshening trends for the ocean surface over the last 200 years indicated by many recent coral $\delta^{18}\text{O}$ records (reviewed by Gagan et al. 2000). These long-term trends generally exceed those of 20th century instrumental records (Cane et al. 1997) and suggest that tracers in corals may overestimate cooling of the ocean in the past.

Recent studies indicate that anomalously low SST estimates given by Sr/Ca thermometry may be produced by early marine diagenesis including recrystallization and secondary aragonite precipitation in live coral. Secondary inorganic aragonite has a significantly higher Sr/Ca ratio than primary coral aragonite (Enmar et al. 2000). Marine aragonite is more difficult to detect in coral skeletons than calcite but it may be common in corals that are only decades old. Few studies have investigated the geochemical implications of early marine diagenesis; thus the understanding of these for paleoenvironmental and paleoclimate reconstructions is limited.

A common approach used to address the issue of diagenesis is independent geochemical tracers to cross-check the results of coral records. For example, the large cooling for the LGM and the mid-stages of the last deglaciation has been justified because SST reconstructed from both coral $\delta^{18}\text{O}$ and Sr/Ca showed the same large negative temperature anomalies (Guilderson et al.

1994, Beck et al. 1997, McCulloch et al. 1999). In this chapter, it is shown that cool artefacts in coral records can be produced by early marine diagenesis because secondary aragonite is enriched in $\delta^{18}\text{O}$ and Sr/Ca relative to the coral skeleton. In the study area, the enrichment of $\delta^{18}\text{O}$ and Sr/Ca in the secondary aragonite is such that the cool artefacts given by $\delta^{18}\text{O}$ and Sr/Ca are identical in magnitude.

3.2. Procedures

Cores were drilled from live coral colonies at two different locations in Ningaloo Reef Marine Park, Western Australia. One was located in Tantabiddi Lagoon ($21^{\circ}54.3'\text{S}$, $113^{\circ}57.9'\text{E}$) and the other off South Muiron Island ($21^{\circ}41.9'\text{S}$, $114^{\circ}18.8'\text{E}$) (Fig. 3.1). During sampling, water depth to the top of the colony was 3 m and 1 m respectively.

The cores were mounted and sawn to remove slices that were 6-7 mm thick. X-ray diffraction was carried out to detect any secondary calcite with a Siemens D501 diffractor, using Cu K α radiation (40 kV, 40 mA), equipped with a curved graphite monochromator and a scintillation detector. The diffraction data were recorded over a range of 20 to 70 degrees 2θ using a step width of 0.02 degrees per minute at a scan speed of 0.5° per minute. The detection limit was 1%. Thin sections were prepared for different parts of the cores and investigated for the presence of early marine diagenesis, particularly aragonite.

Five-year sample increments were chosen using X-ray prints, gamma densitometry data and UV fluorescence light. Peaks in the density profiles were successively counted backwards from the last (outermost or youngest) peak. Surfaces of slabs were cleaned before sampling by removing 1 mm deep and 2 mm wide grooves cut continuously along the maximum growth axis. Five-year increments 2 mm wide and 2 mm deep were then milled within this groove using a 2 mm diameter end-mill bit rotating at 170 RPM. Every second increment was analyzed. Aliquots of powder were analyzed, some in duplicate, for $\delta^{18}\text{O}$ and Sr/Ca. Isotope analysis was carried out using an automated individual carbonate-reaction (Kiel) device coupled with a Finnigan-MAT 251 mass spectrometer. The $\delta^{18}\text{O}$ values were calculated as per mil (‰) deviations relative to VPDB, and were calibrated via the NBS-19 standard ($\delta^{18}\text{O} = -2.20\text{\textperthousand}$). Average reproducibility for a typical 150- μg sample was $+/-0.04\text{\textperthousand}$ (2σ , $n=14$), which is equivalent to about $+/-0.2^\circ\text{C}$ if $\delta^{18}\text{O}$ is controlled by temperature alone. Sr/Ca ratios were measured by isotope dilution on a Finnigan MAT 261 thermal ionisation mass spectrometer (TIMS), following the method described in Alibert and McCulloch (1997). About 80 to 150 μg of powdered coral was diluted in 0.775 ml of 0.5 N HCl. The volume equivalent of 4 μg Ca and one drop phosphoric acid were added to 4-5 drops of a ^{43}Ca - ^{84}Sr -spike solution. The solution was loaded onto a Ta filament and analysed. A power law was used to correct for the instrumental fractionation relative to $^{43}\text{Ca}/^{42}\text{Ca} = 0.960269$ (the spike composition) and $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Mixed solutions of the spike and a gravimetrically known standard were measured at regular intervals to monitor

spike concentration. The reproducibility of Sr/Ca was 0.00005 (2σ) which is equivalent to $<0.2^{\circ}\text{C}$.

3.3. Results

While the results of the XRD analysis show that the coral cores do not contain any detectable amounts of calcite, petrographic investigations indicate that secondary aragonite is present within the coral skeleton toward the base of core NWC02A (South Muiron Island) (Fig. 3.2.A). Abundant secondary aragonite fibres were observed in skeletal pores exposed in thin section. Secondary aragonite could not be seen in core NWC03A (Tantabiddi) (Fig. 3.2.B).

The formation of secondary aragonite fibers in coral, as seen in Fig. 3.2, has previously been suggested to occur under marine conditions (Sansone et al. 1988, Tribble et al. 1990). Generally, as with the coral of this project, cementation in shallow marine subtidal environments is believed to result from turbulent current conditions associated with the discontinuous flow of CaCO_3 saturated seawater through the coral skeletons (Tucker 1991).

The presence of the secondary aragonite is reflected by the dramatic shift in the $\delta^{18}\text{O}$ and Sr/Ca values toward the base of the core. The $\delta^{18}\text{O}$ and Sr/Ca values for the pristine coral show little change over time (Fig. 3.3.A). However, higher $\delta^{18}\text{O}$ and Sr/Ca values can be seen in the cemented bottom part of core NWC02A (South Muiron Island) and are linked to the presence of the

secondary aragonite (Fig. 3.4.A). The findings for Sr/Ca are in agreement with those of Enmar et al. (2000), who also reported higher Sr/Ca in early marine inorganic aragonite cements than in pristine *Porites* skeletons. Consequently, in the altered core, there is a trend to lower $\delta^{18}\text{O}$ and Sr/Ca values toward the present, due to the presence of decreasing amounts of this cement which is characterized by high $\delta^{18}\text{O}$ and Sr/Ca values. A change in growth rate does not account for the anomalous skeletal chemistry at the basal part of this core because extension rates were the same at the base of the core as those elsewhere. The results suggest that, in this case, the $\delta^{18}\text{O}$ and Sr/Ca values do not reflect the true SSTs for the altered coral core. SSTs were calculated from $\delta^{18}\text{O}$ using the mean slope of five established equations for the temperature dependence of oxygen isotope fractionation in coral aragonite (Fig. 3.3.B and 3.4.B): $T=(4.854 \pm 0.773)\delta^{18}\text{O}$ (McConaughey 1989, Leder et al. 1996, Quinn et al. 1996, Wellington et al. 1996, Gagan et al. 1998). Similarly, the mean slope of five published Sr/Ca-SST relationships was used, which were established using TIMS measurements of Sr/Ca to calculate a change in degree Celsius ($^{\circ}\text{C}$) per unit change in Sr/Ca (Fig. 3.3.B and 3.4.B): $T=(17242 \pm 3506)\text{Sr/Ca}$ (Beck et al. 1992, Min et al. 1995, Shen et al. 1996, Alibert and McCulloch 1997, Gagan et al. 1998). To simplify these calculations and since only the slope of the relationship of each tracer to temperature is of interest, only the mean slope of the five equations considered for each tracer was used, and the offset was ignored. Consequently, rather than true SSTs, the relative SST changes per unit in $\delta^{18}\text{O}$ and Sr/Ca respectively were calculated. This

simplification is possible because the least-square approximation for these linear equations shows that the slope would be the same whether the offset was included or not (Fig. 3.5).

For both cores, the means of the reconstructed $\delta^{18}\text{O}$ -SST and Sr/Ca-SST unit values have been aligned with the mean value of the GOSTA instrumental SST data (Parker et al. 1995) for the period 1900-1994 AD (Fig. 3.3.B and 3.4.B). A comparison of the SST unit data with the GOSTA data shows that the $\delta^{18}\text{O}$ and Sr/Ca based SST trends in the pristine coral core correspond reasonably well with those of the GOSTA instrumental SST data set (Fig. 3.3.B). A comparison of the aligned SST unit data from the pristine and the altered core, however, indicates a large difference of 4-5°C in the data from the basal parts of the two cores (Fig. 3.4.B). Both the $\delta^{18}\text{O}$ and Sr/Ca based values record cooler temperatures for the altered core. Interestingly, the coral shows a similar magnitude of decrease in SSTs for $\delta^{18}\text{O}$ and Sr/Ca based reconstructions. The trend for $\delta^{18}\text{O}$ to rise from older to younger regions of the core resembles that of other records that were interpreted to reflect warming/freshening trends of the ocean (Gagan et al. 2000). In contrast, no such trend of decreasing $\delta^{18}\text{O}$ can be seen in the pristine core. There is a strong correlation of $\delta^{18}\text{O}$ and Sr/Ca in the altered core NWC02A off South Muiron Island ($r=0.94$, $n=16$) (insert in Fig. 3.4.A). This indicates simultaneous enrichment of $\delta^{18}\text{O}$ and Sr/Ca, as determined by kinetic behaviour, with the addition of secondary aragonite. The relationship between $\delta^{18}\text{O}$ and Sr/Ca in this core is such that it

yields nearly equal SST changes for both tracers regardless of the degree of diagenesis. The slope of the regression line shows that a change in $\delta^{18}\text{O}$ of 0.2‰ (equal to a change of 1°C) would be accompanied by a change in Sr/Ca of 0.8 (equal to a change of 1.3°C). The correlation coefficient in the unaltered upper half of the core is lower ($r=0.57$, $n=8$) than in the altered lower half ($r=0.95$, $n=8$). This suggests that the kinetic behaviour in the coral skeleton is moderately masked by environmental conditions, such as changes in environmental temperature and composition, which can modify $\delta^{18}\text{O}$ (McConaughey 1989) and Sr/Ca values (Alibert and McCulloch 1997). In contrast, $\delta^{18}\text{O}$ and Sr/Ca values in the unaltered core from Tantabiddi show poor correlation ($r= 0.34$, $n=14$), most likely due to changes in isotopic composition of sea water because of high rates of evaporation in the lagoon.

3.4. Discussion and conclusions

Both the skeletal aragonite and the secondary aragonite compositions deviate from equilibrium in that they show depleted compositions in ^{18}O (McConaughey 1989) and Sr (cf Kinsman and Holland 1969). The cement shows values closest to what would represent equilibrium carbonate precipitation. The correlation in the altered coral core, and particularly in its basal part, suggests a simultaneous depletion of $\delta^{18}\text{O}$ and Sr/Ca for the cement. The simultaneous depletion of ^{18}O and Sr/Ca relative to equilibrium reflects the kinetic effects which have been previously credited with much of the

^{13}C depletion and all of the ^{18}O depletion, relative to isotopic equilibrium (McConaughey 1989).

As expected, the same temperatures were reconstructed from $\delta^{18}\text{O}$ and Sr/Ca values at the top of the core (Fig. 3.4.B). This was because the $\delta^{18}\text{O}$ and Sr/Ca equations were used which have been set up for pristine coral from known seawater temperatures and isotopic compositions. These calibrations consider the specific departure of coral from equilibrium (McConaughey 1989).

It was not, however, expected that both tracers would show the same temperature at the base of the core, which proved to be the case (Fig. 3.4.B). In the coral both tracers show a downcore change in the status of kinetic disequilibrium with seawater, with the cement having a different kinetic disequilibrium status than the coral skeleton. The difference in kinetic disequilibrium can be caused by differences in the composition of the solution from which the aragonite crystals of the coral and the cement were precipitated. Another reason for the difference could be a difference in precipitation rate of the aragonite crystals. It might be expected from this difference in kinetic disequilibrium that the temperature equations would not be applicable to the cement and that temperature reconstructions based on these equations would result in different temperatures being reconstructed from each tracer.

The offset between the pristine top and the altered base of the core in Fig. 3.4.B is 4-5°C SST units for both $\delta^{18}\text{O}$ and Sr/Ca. This simultaneous anomaly can be

explained by mechanisms of crystal growth. Contrary to what would be expected, in the secondary aragonite of the coral, both distribution coefficient of Sr and isotope fractionation of ^{18}O are a function of the rate of crystal growth as well as the composition of the layer of solution in the vicinity of the crystal surface. It has previously been shown experimentally that the distribution coefficient of Sr can be a function of the composition of this layer of solution (Kinsman and Holland 1969). This study showed that coprecipitation of Sr^{2+} with aragonite can depend upon surface phenomena rather than upon equilibrium between the solution and the interior of aragonite crystals. The value of the distribution coefficient for Sr would depend upon surface phenomena under certain conditions. One such condition is a high rate of crystal growth. The rate of crystal growth needs to be greater than the rate of diffusion of Sr^{2+} and Ca^{2+} between the solution and the interior of growing aragonite crystals. A second condition is that the rate of crystal growth is sufficiently slow to allow the Sr/Ca ratio in the younger regions of the crystal to adjust itself accordingly by reaction with the solution. In this situation the growth region of the crystal is moved away from older regions before the older regions have time to equilibrate with the precipitating solution. The younger regions have time to equilibrate with the solution. It then follows that the offset is similar for both $\delta^{18}\text{O}$ and Sr/Ca because their distribution in both the coral skeleton and the secondary aragonite is largely controlled by kinetic effects, which are determined by similar mechanisms of crystal growth controlled by surface phenomena.

The covariation in $\delta^{18}\text{O}$ and Sr/Ca in the coral shows that these two measurements do not give an independent evaluation of SSTs and that they cannot reliably be used as cross checks. This implies that chemical cross checks with two tracers may not be sufficient to verify coral records and that textural studies using petrographic observations or scanning electron microscopy must be included to detect potential secondary overgrowths.

The finding of cold Sr/Ca artefacts produced by diagenesis adds to previous suggestions of potential misinterpretations of SST reconstructions from coral Sr/Ca. For example, it has also been shown that increases in the Sr/Ca ratio of seawater due to large shelf recrystallization fluxes during glacial maxima would produce up to 1.5° errors in paleotemperatures calculated from Sr/Ca ratios in *Porites* since the LGM (Stoll and Schrag 1998).

The magnitude of the "temperature" drop observed in the altered coral is nearly 5°C. This cold artefact is larger than that observed in previous investigations of diagenetic effects on Sr/Ca (Enmar et al. 2000). The magnitude of the decrease in temperature in the coral exceeds that of some observed differences in reconstructed SSTs among different paleo-proxies, as pointed out earlier. Consequently, secondary aragonite in fossil corals must be carefully considered for records suggesting SSTs are cooler than today. Diagenesis can also potentially cause other misinterpretations. When seasonal variations are identifiable (e.g. Guilderson et al. 1994), there would appear to be no diagenetic

bias in the geochemical values. However, diagenesis can change the amplitude even when a seasonal signal is evident (Enmar et al. 2000), thus giving false temperature. As well, interpretation of warming or freshening trends in coral records can be affected by early marine diagenesis. Nearly all published coral $\delta^{18}\text{O}$ records show warming/freshening trends toward the present over the last 200 years. It is possible that many of these trends are in fact related to secondary aragonite accumulating over 10s of years, beginning at the older base of the corals. Clearly, these trends have to be critically assessed, and care taken in drawing conclusions from $\delta^{18}\text{O}$ trends on the role of the tropical oceans in the hydrological cycle.

Other trends important involve changes in surface-ocean $^{13}\text{C}/^{12}\text{C}$, surface-ocean carbonate saturation state and coral reef growth as a response to global climate change. The reconstruction of these changes from massive coral is addressed in the following chapter.

CHAPTER IV

Coral reconstructions of 20th century changes in surface-ocean

$^{13}\text{C}/^{12}\text{C}$ and carbonate saturation state

Important tracers and potential errors

4.1. Introduction

The combustion of fossil fuels, deforestation, and the reduction of soil carbon reservoirs through agricultural practices release CO₂ with $\delta^{13}\text{C}$ values ~20‰ lower than the $\delta^{13}\text{C}$ of atmospheric CO₂ (Quay et al. 1992). This decrease in the $\delta^{13}\text{C}$ of atmospheric CO₂, the so-called ‘Suess effect’, has been observed in tree rings (Stuiver 1978) and CO₂ trapped in ice cores (Friedli et al. 1986, Francey et al. 1999) following the industrial revolution. The global ocean presently increases its storage of CO₂ by $1.7 \pm 0.9 \text{ Pg C yr}^{-1}$ (Keeling et al. 1996). The consequent change in the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in the surface-ocean brought about by air-sea equilibration of CO₂ has been recorded by corals (Nozaki et al. 1978, Druffel and Griffin 1999) and sclerosponges (Druffel and Benavides 1986, Bohm et al. 1996). The addition of fossil fuel CO₂ decreases surface-ocean pH and thus the carbonate ion concentration [CO₃²⁻] in seawater. The resulting decrease in [CO₃²⁻] reduces the aragonite saturation state in seawater ([Ca²⁺] [CO₃²⁻] / K_{sp}, where K_{sp} is the

equilibrium constant of CaCO_3) because $[\text{Ca}^{2+}]$ is near conservative in seawater (Broecker and Peng 1982).

Experimental and modeling studies suggest that rates of calcification should have already declined in response to the 20th century build-up of atmospheric CO_2 (Gattuso et al. 1999, Langdon et al. 2000, Leclercq et al. 2000, Marubini et al. 2001). It is estimated that aragonite saturation in the tropical surface ocean will decrease by ~14-40% due to the rising partial pressure of CO_2 and temperature of seawater under a doubling of the pre-industrial atmospheric CO_2 (Kleypas et al. 1999, Langdon et al. 2000). Gattuso et al. (1998) provided experimental evidence for non-linear changes in calcification rate as a function of aragonite saturation state. Given that a significant acclimation of coral to a reduced saturation state is not expected, it is likely that a decreased saturation state will result in reduced coral calcification rates, a shift toward calcite secretors, or a competitive advantage for non-calcifying reef organisms (Smith and Buddemeier 1992, Buddemeier 1994).

Studies of calcification parameters in massive coral skeletons have provided evidence for changes in coral reef growth over the past few centuries. A composite record from 35 *Porites* sp. coral cores from the Australian Great Barrier Reef showed a significant decline in skeletal density and calcification over the period 1934-1982 (Lough and Barnes 1997). Analyses of several multi-century coral cores from the Great Barrier Reef, however, shows a significant increase in calcification in the late 20th century relative to the previous two

centuries (Lough and Barnes 2000). Analysis of a long coral core from French Polynesia also shows increased calcification through time (Bessat and Buiges 2001). Both these studies attributed the rise in calcification rate to increased sea water temperatures. Lough and Barnes (1997) did, however, note a tendency for skeletal density in Great Barrier Reef *Porites* to decline through time. The average skeletal density in 60% of the long coral cores was significantly higher in the oldest 30 years compared with the youngest 30 years.

In this chapter, it is shown that there may be a tendency for early addition of secondary marine aragonite to the basal portions of massive *Porites* to create an apparent reduction in skeletal density and calcification rate toward the younger portions of coral records. This tendency could lead to errors in the interpretation of past trends in coral calcification and reef growth. Consequently, evidence for reduced coral calcification in recent decades must be supported by evidence that early marine aragonite cements are not present in the coral cores. Furthermore, high $\delta^{13}\text{C}$ values in coral records can be produced by early marine diagenesis because inorganic aragonite is enriched in ^{13}C relative to coralline aragonite. Together, these signals could lead to the misidentification of an oceanic Suess effect and synchronous reduction in coral calcification deemed to be caused by an anthropogenic change in surface-ocean aragonite saturation state.

4.2. Procedures

The two coral cores from Ningaloo Reef Marine Park in Western Australia (Fig. 3.1) were further investigated in this chapter. Density was measured directly on coral slices using gamma-ray densitometry (Chalker and Barnes 1990). Peaks in density defining annual growth increments were successively counted backwards from the outermost (youngest) peak. The following time series were obtained from the density measurements for each core: (1) mean annual density (g cm^{-3}); (2) annual extension rate (cm yr^{-1}) as the distance between high-density peaks; and (3) annual calcification rate as the product of mean annual density and annual extension rate ($\text{g cm}^{-2} \text{yr}^{-1}$).

As described in chapter III, five-year sample increments were chosen for the analysis of skeletal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ using X-ray prints, gamma densitometry data and coral fluorescence observed under UV light. Surfaces of coral slabs were cleaned before sampling by removing 1 mm deep by 2 mm wide grooves cut continuously along the maximum growth axis. Five-year increments 2 mm wide and 2 mm deep were then milled within this groove using a 2 mm diameter end-mill bit rotating at 170 RPM. Aliquots of coral powder were analyzed, some in duplicate, for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Isotope analysis was carried out using an automated individual carbonate-reaction (Kiel) device coupled with a Finnigan-MAT 251 mass spectrometer. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were calculated as per mil (‰) deviations relative to the Vienna PeeDee belemnite (VPDB), and were calibrated via the NBS-19 standard ($\delta^{18}\text{O} = -2.20\text{\textperthousand}$, $\delta^{13}\text{C} = 1.95\text{\textperthousand}$). Average

reproducibility for duplicate 150- μg samples was $\pm 0.04\%$ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (2σ , $n=14$).

4.3. Results

4.3.1. Early marine diagenesis

While no secondary aragonite was evident in core NWC03A from Tantabiddi lagoon, abundant secondary aragonite needles were observed in skeletal pores exposed in thin section of core NWC02A from South Muiron Island (Fig. 3.2). These needles filled the skeletal pores almost completely in some areas near the base of the core and accounted for ~30% of the total aragonite (primary and secondary aragonite).

4.3.2. Coral calcification

The record of mean annual density for pristine coral NWC03A remained relatively constant at ~1.1 g cm⁻³ (Fig. 4.1). In contrast, the mean annual density for the altered coral NWC02A was ~1.3 g cm⁻³ from 1830-1910 AD, where secondary aragonite filled pores in the coral skeleton. The effect of this infilling was to produce a significant decrease in skeletal density toward the top of the core. Pristine coral NWC03A showed a decline in extension rate from ~1.5 cm yr⁻¹ to ~1.3 cm yr⁻¹ toward the present (Fig. 4.1), whereas extension rates in the altered coral were slightly slower and relatively constant at ~1.2 cm yr⁻¹. Since calcification rates are a product of mean density and linear extension

rate, trends of decreasing calcification rate toward the present occurred in both coral cores (Fig. 4.1).

4.3.3. Carbon and oxygen isotopes

As for mean annual density, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for pristine coral NWC03A did not show significant change over time (Fig. 4.2) and averaged $-1.3\text{\textperthousand}$ and $-4.3\text{\textperthousand}$, respectively. In contrast, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the altered coral showed declining trends toward the youngest part of the coral core (Fig. 4.2). The $\delta^{13}\text{C}$ values declined from $0.2\text{\textperthousand}$ to $-1.5\text{\textperthousand}$, a shift of $-1.7\text{\textperthousand}$, while $\delta^{18}\text{O}$ shifted by about one-half that amount ($\sim 0.8\text{\textperthousand}$). The difference of $\sim 0.5\text{\textperthousand}$ between the $\delta^{18}\text{O}$ values for the pristine, upper portions of the cores is probably due primarily to differences in seawater $\delta^{18}\text{O}$ between Tantabiddi Lagoon and South Muiron Island. Circulation in Tantabiddi Lagoon is restricted in the lee of the Ningaloo Reef tract at low-tide, whereas South Muiron Island is an open-ocean fringing reef. Therefore, the higher $\delta^{18}\text{O}$ value for coral NWC03A probably reflects evaporative enrichment of ^{18}O in the seawater of Tantabiddi Lagoon.

4.4. Discussion

4.4.1. Geochemistry of marine inorganic aragonite

There was no significant correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the pristine core NWC03A. In contrast, changes in $\delta^{13}\text{C}$ of the altered core NWC02A

correlated significantly with $\delta^{18}\text{O}$ ($r = 0.93$, $n=33$, Fig. 4.3). Covariation of the carbon and oxygen isotopic compositions has been shown in previous investigations of Holocene reef carbonates (González and Lohmann 1985). Such a covariation has also been observed in a Permian Reef complex (Given and Lohmann 1985). The findings in this present study of higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the secondary aragonite are in agreement with the observations of González and Lohmann (1985), who reported higher $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in marine inorganic aragonite cements than in pristine *Porites* skeletons.

Mass balance calculations suggest that the covariation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the altered coral reflects the mixing of isotopically enriched inorganic aragonite, precipitated close to equilibrium with ambient seawater, and isotopically depleted coral aragonite. Aragonitic skeletons of *Porites* are always depleted in ^{18}O and ^{13}C relative to inorganic aragonite precipitated in equilibrium with ambient seawater because of biological and kinetic controls on isotopic fractionation during biomineralization of hermatypic coral skeletons (McConaughey 1989). The 25% addition of secondary aragonite to the base of the altered coral has shifted the "bulk" $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to those at the top of the coral by 0.8‰ and 1.6‰, respectively. The calculated $\delta^{18}\text{O}$ value of secondary aragonite required to produce the 0.8‰ shift in $\delta^{18}\text{O}$ is -1.6‰. Such a value is consistent with the $\delta^{18}\text{O}$ value of -0.2‰ predicted for inorganic aragonite precipitated in equilibrium with ambient seawater (25°C, $\delta^{18}\text{O}$ water ~0.5‰_{SMOW}) at Ningaloo Reef (O'Neil et al. 1969, Tarutani, 1969).

Likewise, the calculated $\delta^{13}\text{C}$ value of secondary aragonite required to produce the 1.6‰ shift in $\delta^{13}\text{C}$ is 4.1‰. If the change in $\delta^{13}\text{C}$ of seawater produced by the post-industrial revolution Suess effect in subtropical mixed layer water is considered (~0.8‰; Gruber et al. 1999), then the $\delta^{13}\text{C}$ value of secondary aragonite required to produce the 1.6‰ shift in $\delta^{13}\text{C}$ is 1.7‰. Both values are in good agreement with the $\delta^{13}\text{C}$ value of 3.4‰ predicted for inorganic aragonite precipitated in equilibrium with ambient seawater (25°C, $\delta^{13}\text{C}$ water ~0.7‰_{PDB}) at Ningaloo Reef (Turner 1982).

4.4.2 Diagenesis and reconstruction of the oceanic Suess effect

Based on the observations of this study, it is clear that early marine diagenesis of coral skeletons has the potential to seriously confound paleoceanographic reconstructions. For example, there are several possible interpretations of the trend in $\delta^{13}\text{C}$ in the altered coral (Fig. 4.2) if diagenesis remains undetected. First, a decline in skeletal $\delta^{13}\text{C}$ toward the present could reflect a lower ratio of zooxanthellar photosynthesis to coral respiration (P/R) in the younger part of the coral. Photosynthesis causes enrichment of ^{13}C in the DIC of the internal calcification reservoir (Swart 1983, McConaughey 1989, Grottoli 2002). In contrast, respiration lowers the $\delta^{13}\text{C}$ of the calcification reservoir because respired CO₂ is depleted in ^{13}C . Therefore a low P/R ratio results in low skeletal $\delta^{13}\text{C}$ because of the excess of respired CO₂ that is incorporated into the

skeleton (McConaughey 1989). However, the effect of respiratory CO₂ on skeletal δ¹³C in corals is believed to be small compared to the effect of photosynthesis (McConaughey 1989). Thus it is conceivable that the decrease in the δ¹³C values toward the present could be interpreted as a change in the rate of photosynthesis. If the effects of early marine diagenesis are not considered, in general, such an interpretation could lead to the conclusion that coral reef photosynthesis has slowed during the 20th century.

A second potential interpretation of the post-industrial revolution decline in skeletal δ¹³C in the altered coral is that it reflects changes in the δ¹³C of surface seawater DIC due to the oceanic Suess effect. The secondary inorganic aragonite is enriched in ¹³C, relative to coral aragonite, resulting in a 1.6% decrease in δ¹³C toward the present. While this shift is twice as large as that expected in the subtropical surface ocean (~0.8%; Gruber et al. 1999), the trend is similar to that observed for the δ¹³C of atmospheric CO₂ (Fig. 4.4). Once again, if the potential geochemical effects of early marine diagenesis are not considered, such a trend could lead to conclusions about air-sea exchange of atmospheric CO₂ and the dynamics of ocean mixing.

It is noteworthy that the changes in calcification rate produced by diagenesis in the altered coral appear to track changes in pCO₂ of the atmosphere (Fig. 4.5). The pCO₂ data have been compiled from measurements of air trapped in ice from Law Dome in East Antarctica (Etheridge et al. 1998) and, for the last 40 years, instrumental measurements at Mauna Loa, Hawaii (Keeling et al. 1995).

The similar trends in coral calcification rate, skeletal $\delta^{13}\text{C}$, and atmospheric CO₂ levels could be misinterpreted to reflect a reduction in coral calcification due to the effect of atmospheric CO₂ on the aragonite saturation state of the surface ocean. This concept is explored in the next section.

4.4.3. Coral diagenesis and reconstruction of aragonite saturation state

DIC occurs in three basic forms in seawater: CO₂⁺ (CO₂(aq) + H₂CO₃), HCO₃⁻, and CO₃²⁻. When CO₂ dissolves in seawater, most dissociates into HCO₃⁻ and CO₃²⁻, and less than 1% remains as CO₂⁺. The seawater-mediated interaction of CO₂ and calcium carbonate is described by the equation: CO₂ + H₂O + CaCO₃ \rightleftharpoons 2 HCO₃⁻ + Ca²⁺. The acid formed by dissolution of CO₂ in seawater lowers the pH, so that some CO₃²⁻ will combine with H⁺ to form HCO₃⁻ to achieve a new equilibrium. Thus the addition of fossil fuel CO₂ to seawater decreases [CO₃²⁻] in seawater. The resulting decrease in [CO₃²⁻] reduces the aragonite saturation state ([Ca²⁺] [CO₃²⁻] / K_{sp}, where K_{sp} is the equilibrium constant of CaCO₃) in seawater.

Experimental and modeling studies suggest that rates of CaCO₃ deposition of various marine photosynthetic and calcifying organisms should have already declined in response to the 20th century build-up of atmospheric CO₂ and accompanying reduction in the aragonite saturation state of the surface ocean (Gattuso et al. 1999, Langdon et al. 2000, Leclercq et al. 2000, Marubini et al. 2001, Broecker et al. 2001). A comparison of the decline in coral calcification

indicated by the diagenetically altered coral with that predicted by experimental and modeling studies is shown in figure 4.6. The trend of the calcification rates calculated for the altered coral core appears to confirm the predicted declining trends. The figure shows the trends calculated for the CO₂ scenarios considered by the International Panel on Climate Change (IPCC) (Houghton et al. 1996). The calculations of Kleypas et al. (1999) were based on the revised mid IPCC scenario (IS92a), and the calculations of Gattuso et al. (1999) were based on the high (IS92e), mid (IS92a) and low (IS92c) scenarios respectively. The slope of the trend agrees most closely with the experimental study of Langdon et al. (2000), who suggest a decline in coral reef calcification of ~40% between 1880 and 2065 A.D. However, the results of this study demonstrate that a long-term decline in skeletal calcification rate over the life of a coral colony may be purely an artefact of early marine diagenesis in the older part of the coral skeleton.

4.5. Conclusions

Early marine diagenesis in coral skeletons can cause significant changes in coral growth and isotopic and geochemical tracers that are unrelated to large-scale environmental signals. If undetected, such diagenesis can lead to erroneous conclusions concerning the oceanic Suess effect as the increased cementation in the older part of a coral can result in an apparent decrease in ¹³C towards the present. If undetected, such diagenesis can also lead to erroneous conclusions concerning changing aragonite saturation state due to increasing atmospheric CO₂ as the increased cementation in the older part of a

coral can result in an apparent decrease in coral calcification rate towards the present.

Early marine diagenesis can be detected through thin section analysis, comparisons of the magnitude of density and geochemical changes and/or comparisons of calcification rates and $\delta^{13}\text{C}$ values. Examination of the relationships between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and between linear extension, density and calcification are useful diagnostic tools.

Correct interpretation of long-term trends in coral growth, isotopic and geochemical (cf chapter III) tracers must be supported by evidence that the coral skeleton has not been diagenetically altered. With this proviso the records contained in massive coral skeletons can make a significant contribution to understanding and detecting environmental change due to human activities.

CHAPTER V

Conclusions

Late Quaternary paleoceanography of the eastern Indian Ocean, implications for past climate reconstructions, and recommendations for future studies

The geochemical data of marine sediments and corals presented in this thesis fill an important gap in the observational paleoceanographic data base for the region of the eastern Indian Ocean. The data are essential for the reinforcement of an earlier observation and a first suggestion (Beaufort et al. 2001) of ENSO-like climate variability in the tropical Indian Ocean. They also provide a sound basis for directions of future work aimed at further improvement of the data base. Studies identifying the mechanisms behind ENSO-like climate variability at different time scales in the region depend on such improvement.

As shown in Chapter II, two marine sediment cores from the Indonesian Throughflow sensitive Timor Trough indicate distinct glacial-interglacial contrasts in paleoceanography and paleoclimatology. Elevated biogenic barium, organic carbon, calcium carbonate and $\delta^{13}\text{C}_{\text{TOC}}$ values reflect increased surface ocean productivity during the Last Glacial Maximum (LGM) in the

region. Low $\delta^{15}\text{N}$ values at this time show that such productivity was due to the occurrence of upwelling in the Timor Sea.

The geochemical data records of the sediment cores evidence an El Niño-like mean oceanographic and climatic state during isotope stage 2 and, in particular, during the LGM. A comparison with the modern-day analogue of an El Niño event suggests that, during the LGM, the Indonesian Throughflow (ITF) was suppressed.

Since $\delta^{18}\text{O}$ records are a function of both salinity and temperature, elevated foraminiferal $\delta^{18}\text{O}$ values in the sediment cores point towards lower sea surface temperatures (SSTs) during the LGM as a consequence of upwelling and/or towards higher salinity. Both of these possible interpretations reflect a suppressed ITF. Consequently, both interpretations would confirm the conclusions given above on a suppressed ITF. In order to establish the amount of cooling observed during the LGM, other temperature proxies such as Mg/Ca values of planktonic foraminifera will need to be considered in future research.

An El Niño-like climate state during the LGM would have considerable consequences for precipitation and hydrological balance in the area. As with modern El Niño events, the climate would have been affected by reduced precipitation and stronger winds over the mainland of Australia. New results from modeling studies (P.Hope, pers. comm, 2004) suggest that precipitation was indeed reduced and that stronger zonal (e.g. East-West) winds were

prevalent over Australia during the LGM. While this study allowed reconstruction of the paleoceanography, such as the variability of the ITF over the past 80,000 years, the variability of wind and precipitation patterns over this time period needs further investigation.

The results of analysis of sediments from the eastern Indian Ocean south of the equator reinforce recent suggestions derived from studies of marine sediments in the Indian Ocean north and close to the equator of an El Niño-Southern Oscillation (ENSO)-like equatorial climate mechanism operating at glacial-interglacial time scales in the tropical eastern Indian Ocean.

The contrast observed in this thesis between isotope stages 1 and 2 in the strength of the ITF is clearly an expression of contrasts in mean climate states that occurred during each isotope stage and have been transferred into the eastern Indian Ocean from the equatorial Pacific. Although the data discussed in this thesis evidence contrasts in mean climate stages similar to those of the mean climate states occurring during the opposite phases of ENSO, they do not allow for analysis of oscillations in climate similar to the analysis of Beaufort et al. (2001). In order to determine a possible resemblance of the dynamics of past climate variations in the eastern Indian Ocean south of the equator and those of the Southern Oscillation, the approach of this study needs to be extended further into the past, i.e. beyond the past 80,000 years currently covered in this thesis.

A focus of future studies should not only be the expansion in time and the frequency analysis of existing and future data series for the study area of this thesis. New data series should also extend beyond the time period of the past 250,000 years of Beaufort et al. (2001) both for the study area of this thesis and the study area of Beaufort et al. (2001). Ideally, these new data series should cover time periods including several glacial-interglacial cycles and they should be collected at the same or a higher resolution than those of Beaufort et al. (2001). As the studies of Beaufort et al. (2001) and De Garidel-Thoron et al. (2001) have shown, reliable frequency analysis of these new data series will depend on precise dating of the sediments. Consequently, a larger number than currently available of accelerator mass spectrometer (AMS) ^{14}C ages for the sediment cores of the study area will be required. The proposed future studies are essential for derivation of the true character and driving forces of the equatorial climate mechanism proposed to be responsible for climate variability in the eastern Indian Ocean.

A thorough understanding of an ENSO-like climate mechanism at glacial-interglacial cycles also requires a detailed understanding of the observation of this mechanism in modern times. Although recent studies offer observations of climate variability in the tropical Pacific and the eastern Indian Oceans, attempts to achieve such a detailed understanding have been restricted by the limitation of instrumental data available to study ENSO variability.

Values of $\delta^{18}\text{O}$ and Sr/Ca in massive coral of the eastern Indian Ocean have the potential to augment existing data series on sea surface temperatures and salinities for the region. However, suitable sites for paleoceanographic reconstructions in this region need to be chosen carefully as local reef morphology and environmental conditions at many sites obscure the large-scale paleoceanographic signals linked to climate variability.

The results of this study show that Tantabiddi Bay at Ningaloo Reef is a suitable site for paleoceanographic reconstructions for the region. The coral at this site appears to be a reliable recorder of ENSO variability in the eastern Indian Ocean. As demonstrated in Chapter III, long-term trends of SSTs reconstructed from $\delta^{18}\text{O}$ and Sr/Ca for a well-preserved coral at Tantabiddi Bay correlate strongly with instrumental SST records spanning the 20th century. This shows that the geochemical values of the coral at this site clearly reflect temperature trends. As Ningaloo Reef is strongly influenced by the Leeuwin Current, temperature trends seen in the coral are expected to be influenced by the ENSO dynamics in the western Pacific via the ITF, which feeds the Leeuwin Current. However, it cannot be excluded that the site is also significantly influenced by the Indian Ocean Dipole. Future studies will need to focus on identification of the separate influences of each of the two climate mechanisms and their interference at the study site. Little influence on $\delta^{18}\text{O}$ trends is to be expected from evaporation at Tantabiddi Bay, as increased evaporation occurs simultaneously to higher SSTs in the area. Consequently, evaporation may alter the magnitude of the $\delta^{18}\text{O}$ values at this site, but it does not obscure the long-

term climate trends recorded in the coral of ENSO variability in the eastern Indian Ocean.

The coral data presented in both Chapters III and IV shows that deviations in coral growth parameters and chemistry caused by local reef morphology and environmental conditions obscure reconstructions of the large-scale paleoceanographic signals linked to climate variability such as ENSO. For example, specific forms of reef morphology and local environmental conditions, such as fringing reef environments affected by turbulent water flow, may cause early marine diagenesis in corals that are only decades old. The $\delta^{18}\text{O}$ and Sr/Ca for a diagenetically altered coral from Ningaloo Reef give identical cool SST anomalies of 4-5°C, as a consequence of the addition of secondary aragonite enriched in ^{18}O and Sr. The results indicate that cross-checking of paleoclimate reconstructions with two supposedly independent paleothermometers may not be valid, and that coral records showing cooler SSTs in the past need to be interpreted with caution. Furthermore, modern coral records with long-term trends in $\delta^{18}\text{O}$ indicating recent warming and freshening of the ocean can potentially be explained by early marine diagenesis.

Moreover, taken together, the diagenetic changes in coral calcification rate and skeletal $\delta^{13}\text{C}$, which are presented in Chapter IV for one site at Ningaloo Reef, could be misinterpreted to reflect changes in surface-ocean aragonite saturation state driven by the 20th century build-up of atmospheric CO₂. If undetected, such

diagenetic changes can lead to erroneous conclusions concerning the oceanic Suess effect as the increased cementation in the older part of a coral can result in an apparent decrease in ^{13}C towards the present. If undetected, such diagenesis can also lead to erroneous conclusions concerning a changing aragonite saturation state due to increasing atmospheric CO_2 as the increased cementation in the older part of a coral can result in an apparent decrease in coral calcification rate towards the present.

The results presented in Chapters III and IV show that correct interpretation of long-term trends in coral growth, isotopic and geochemical tracers must be supported by evidence that the coral skeleton has not been diagenetically altered. With this proviso the records contained in massive coral skeletons can make a significant contribution to understanding and detecting climate change.

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