

Geochemically tracing
the intermediate and surface waters
in the Tasman Sea, southwest Pacific

HELEN C. BOSTOCK

A thesis submitted for the degree of
Doctor of Philosophy
of The Australian National University.

Except where otherwise indicated in the text, the research described in this thesis is my own original work.

Helen C. Bostock
30th October 2004
(Corrected October 2005)

Chemical oceanography is at a crossroads connecting almost all branches of marine sciences. Therefore, chemical oceanographers must learn more or less all the disciplines of oceanography. Furthermore, taking into account the fact that chemical substances are four dimensionally cycling on the Earth, chemical oceanographers must investigate not only the present ocean, but also the atmosphere, biosphere and geosphere, including the past and future of the Earth.

Tsunogai (2002)

Acknowledgements

Firstly thanks and gratitude goes to everyone who has helped in the preparation and processing of samples and data that are presented in this thesis. Primarily to Bradley Opdyke for initiating the project and encouraging me to come to Australia. I am very grateful for the free range I have had during this project to explore the aspects I found most interesting. Thanks to John Marshall, who helped me get the project off the ground in the first six months, and who has been a reality check and encouraging friend over the last three and half years. Mike Gagan, who allowed me the use of the stable isotope mass spectrometer at the Research School of Earth Sciences and for his thorough and constructive criticism that he provided for papers that have been submitted from this thesis. Thanks to Joe Cali and Heather Scott-Gagan who patiently talked me through using the mass spectrometer, and corrected the data. Patrick De Deckker, who also sat on my advisory panel and was always willing to lend books and journals and answer questions. Keith Fifield who provided the use of the AMS for radiocarbon dates, and to Vladimir Levchenko for the many hours spent preparing the AMS samples. To Ulrike Troitzsch for helping with the XRD analyses. A special thankyou also goes to Brian Harrold for his ever cheery help with fixing computers problems and making printers work.

Acknowledgements also to the students and crew that were on the Research Vessel Franklin 1/97 cruise that collected all the cores used in this study. Also all the people that collected and have worked on the data during the World Ocean Circulation Experiment (WOCE) Pacific Ocean cruises for providing such a great data set to work with. Thanks to Alexa Troedson for allowing the use of her data set for comparison.

There were many discussions with different people about the content and ideas within this thesis. Thanks to the Earth and Environment Group for sitting through my attempts to explain wild ideas during group meetings and always providing feedback - especially on colour schemes!! Specific people were a great help for bouncing ideas off; Mary Elliot, Will Howard, Gavin Dunbar, Graham Hughes, Tim Barrows, Ed Rhodes and and also for the helpful reviews of the AAIW paper from Howie Spero and an anonymous reviewer. Andrew Kiss had great patience with me in explaining physical oceanography concepts, and for his “thesis style” and “witty humour”.

I have thoroughly enjoyed my time in the department, there are some great people who have a wealth of knowledge and are always ready to provide ideas and support. Thankyou.

My fellow PhD students, especially those who I shared an office with over the years;



Figure 1: The fabulous paint job on my car, who are you Michelangelo?

Helen Degeling, Karla Olvera, Annette MacKintosh, Jessica Reeves, Lynne Bean. Others who have kept me entertained and amused; Andrew McPherson, Thomas Berly, Andy Tomkins, Luke Foster, Marty Young, Siwan Rees, Greg Shirtliff, Julia Mullarney, Julie Brown, Frances Jenner, Martin Smith (aka Chucky), Matthew Lenahan (aka Butch), Alistair Usher (aka Beaker), Bridget Ayling, Sam Burgess, Stewart Fishwick, Silvano Sommacal and many more!!

To all of those, including many from the above list, who have participated in crazy sports (mountain biking, climbing, canoe polo etc..) and ridiculous events (24 hour races and triple triathlons), but also Louisa Roberts, Alison Skinner, Bec Thomson, Susie Kluth, Patrick Kluth, Dave Osmond, Dan Mackay, Uli Faul, Hugh Webb. I apologise to all those people who I enjoyed beating on the squash court - sorry Prof Rainer Grun! But also thanks to Kerry Jackson (my doubles partner), Steve Eggins, Mike Double and all the other people I've played in squash teams with over the past three years. The RSES soccer boys for letting me play in the highly competitive "purple shin" competition.

A huge thanks to Martin Worthy for nursing my little car through my PhD. Also to the person/people who decorated the car - great paint job! (Figure 1) Best secret ever kept from me, you can own up now!

My family, for always supporting me in everything I've done, including many crazy adventures.

Big thanks to Sarah O'Callaghan for being an incredible friend and neighbour who has helped me through various crises over the last few years. Finally to Aaron Lyman for being a wonderful partner and putting up with me through everything this last year.

Abstract

The relatively understudied intermediate waters of the world have been implicated as an important part of the global ocean circulation. This thesis discusses the intermediate waters of the Pacific over space and time. Initially, by using geochemical tracers to look at the present distribution, sources and mixing of the water masses. Secondly, by using oxygen and carbon isotopes from sediment cores to study changes in Antarctic Intermediate Waters (AAIW) over the late Quaternary in the north Tasman Sea.

The geochemical tracers highlight the presence of three separate intermediate water masses in the Pacific: North Pacific Intermediate Water (NPIW), AAIW and Equatorial Intermediate Water (EqIW). The EqIW has previously been considered an extension of intermediate water masses to the north or south. The unique geochemical characteristics of EqIW indicate, however, that it cannot be formed by direct mixing of the NPIW and AAIW. Geochemical tracers suggest instead that EqIW must also include mixing with nutrient rich, oxygen deficient, old Pacific Deep Water (PDW).

The AAIW distribution and circulation shows a primary formation region in the southeast Pacific. The high oxygen, low salinity signature of this southeast Pacific source is altered during its circulation of the subtropical gyre. This is the result of aging during circulation and mixing with other intermediate waters entering the region. A second source region is in the eastern equatorial Pacific (EEP), where mixing occurs with the old, nutrient rich EqIW. Mixing between the EqIW and AAIW is evident as far south as 30°S. The data also suggests a tongue of EqIW, overlying and mixing with the upper layers of the AAIW flows south adjacent to the South American coast. A third source of AAIW enters the south Tasman Sea directly from the Southern Ocean. This third source, has little influence on the main subtropical gyre. However, it contributes to the geochemistry of the intermediate waters in the Tasman Sea and Coral Sea. The uniformity of the AAIW in the Tasman Sea and Coral Sea advocates for a separate recirculating gyre in the southwest Pacific. The main exit of AAIW from the south Pacific is either through mixing to form the EqIW along the equator, or south to the east of the Tonga-Kermadoc Ridge following the subtropical gyre circulation. This present day distribution and chemistry of the intermediate water masses allows interpretation of past conditions.

A series of marine sediment cores were collected from a depth transect in the Capricorn Channel ($\sim 23^\circ\text{S}$), off the southern Great Barrier Reef (GBR) province. Data extracted from the cores provide a preliminary model of hemipelagic deposition within this region over the late Quaternary. The sedimentary evidence highlights the importance of bathymetry, especially the morphology of reef platforms and the continental shelf, to understand hemipelagic systems over time. Compared to the northern GBR province, the southern GBR province continues to be influenced by terrestrial sediments during the glacial lowstand. These terrestrial sediments are primarily distributed by the Fitzroy River system, which meanders across the continental shelf and flows into the Capricorn Channel.

The sediments in the Capricorn Channel appear to be focussed at intermediate water depths, possibly related to an increase in the slope gradient. This provides a high sedimentation rate core (FR1/97 GC-12) to look at relatively high resolution palaeoceanographic variations during the last deglaciation. Stable oxygen and carbon isotope compositions were analysed on a suite of planktonic foraminifera (*Globigerinoides ruber*, *Globigerinoides sacculifer*, *Globorotalia menardii* and *Globorotalia truncatulinoides*) and benthic foraminifera (*Cibicidoides* spp.), to examine changes in the water column throughout this period. Comparison of the $\delta^{13}\text{C}$ data of the different species were used to determine changes in the ocean circulation and display three distinct phases 1) Glacial, 2) Deglaciation 18-12 ka BP and 3) 12-0 ka BP.

1. During the glacial there is a large $\Delta\delta^{13}\text{C}$ planktonic-benthic difference of 1.1‰ , implicating a well stratified surface to intermediate depth ocean. Abundant *Gr. menardii* and *Gr. truncatulinoides* suggest that the thermocline was shallow and the intermediate waters were thick. The AAIW in the Tasman Sea appears to be dominated by the southern source, directly from the Southern Ocean, and may be mixing with the underlying nutrient rich deep waters.
2. At ~ 18 ka BP there is a collapse in the $\Delta\delta^{13}\text{C}$ planktonic-benthic offset to $\sim 0.4\text{‰}$. This is the result of a rapid ventilation event in the AAIW and a switch from the southern source to the northeast source waters in the Coral Sea. During this phase the *Gr. menardii* and *Gr. truncatulinoides* decrease in abundance and *G. ruber* and *G. sacculifer* return to prominence. The $\delta^{13}\text{C}$ planktonic minimum is evident over a wide geographical extent and the AAIW has been implicated as the driver for the release of deep-water CO_2 and the main conduit for transporting this preformed $\delta^{13}\text{C}$ signal within the southern hemisphere ocean basins. This $\delta^{13}\text{C}$ planktonic minimum correlates with the rise in atmospheric CO_2 measured in ice cores.
3. At ~ 12 ka BP the $\Delta\delta^{13}\text{C}$ planktonic-benthic offset begins to recover and reaches modern values of 0.7‰ . This is possibly related to the onset of the NADW formation and the return to present day thermohaline global ocean circulation.

The $\delta^{18}\text{O}$ data from *G. ruber* from the same core (FR1/97 GC-12) was also compared with another high sedimentation rate core RV105 GC-25 from $\sim 26^\circ\text{S}$ in the Tasman Sea.

The differences in the $\delta^{18}O$ values suggest variations in the surface current, the East Australian Current (EAC), during the last deglaciation.

The EAC is the western boundary current (WBC) of the south Pacific subtropical gyre and important for modulating the climate of eastern Australia and New Zealand. Like all WBCs it separates from the coast at a particular location and flows out to sea in an eastward jet, the Tasman Front. Recent modelling suggests the reason for the EAC separation and the formation of the Tasman Front is related to a rapid gradient in the zonally integrated wind stress curl at this latitude.

The $\delta^{18}O$ *G. ruber* data from GC-12 exhibits a 1.5‰ decrease between the last glacial maximum (LGM) and present. Taking into account ice volume and assuming no salinity changes, this represents a temperature difference of 2-3°C, comparable to the estimates from foraminiferal abundances. RV105 GC-25, a core from ~3° south of GC-12, displays a ~2.2‰ decrease since the LGM, suggesting an ~6°C difference compared with present sea surface temperatures (SST). This large temperature gradient of 3-4° in ~3° latitude is similar to the temperature gradient evident across the Tasman Front today. This suggests that during the LGM the EAC separation occurred north of RV105 GC-25 at ~26°S. Palaeo-evidence suggests that there is a considerable weakening of the trade winds as a result of a reduction in the equatorial east-west SST gradient. There is also increasing evidence to suggest a ~3-5° equatorial shift of the subtropical westerlies, combined with a strengthening of the westerlies, especially in the south. These changes in the winds would have had a considerable affect on the wind stress field, and consequently the wind stress curl of the south Pacific, potentially causing the EAC separation to shift as far north as 26°S.

A rapid convergence of the $\delta^{18}O$ *G. ruber* data from FR1/97 GC-12 and RV105 GC-25 is evident between 12-11 ka BP suggesting the EAC was forced south of 26°S at this time. This shift is synchronous with a rapid warming in tropical SSTs at the end of the Younger Dryas and the onset of a La Niña-like state in the Pacific. This change in the east-west SST gradient would have enhanced the easterly trade winds, altering the wind stress field. The EAC separation would have readjusted accordingly. This marks the onset of modern circulation in the southwest Pacific. Present EAC flow, however, was probably only achieved when complete modern conditions, including present day El Niño Southern Oscillation (ENSO) periodicities, are achieved after 5 ka BP.

Contents

Acknowledgements	vii
Abstract	xi
1 Introduction	1
1.1 Scientific Objective	1
1.2 Carbon Cycle and Geochemistry	2
1.2.1 Ice Core Records and Atmospheric CO_2	3
1.2.2 Carbon Chemistry of the Oceans	4
1.2.3 Stable and Radioactive Isotopes	6
1.3 Oceanography	12
1.3.1 Oceanography of the Pacific Ocean	12
1.3.2 Oceanography of the Southwest Pacific	17
2 Methods	21
2.1 Part I - Modern Oceanography	21
2.2 Part II - Palaeoceanography	22
2.2.1 Sampling and Sieving	22
2.2.2 Stable Isotopes	22
2.2.3 Radiocarbon Dating	23
2.2.4 $CaCO_3\%$	24
2.2.5 X-ray Diffraction	25
I Modern Oceanography	27
3 Pacific Intermediate Waters	29
3.1 Abstract	29
3.2 Introduction	29
3.3 Intermediate Waters of the Pacific	29
3.3.1 North Pacific Intermediate Water (NPIW)	30
3.3.2 Antarctic Intermediate Waters (AAIW)	30
3.3.3 Equatorial Intermediate Waters (EqIW)	31

3.4	Geochemical Tracers	32
3.5	Data and Results	33
3.5.1	Salinity (Figure 3.4A)	33
3.5.2	Oxygen (Figure 3.4B)	37
3.5.3	Phosphate and Nitrate (Figures 3.6C and D)	39
3.5.4	Silicate (Figure 3.7E)	40
3.6	Carbon data	40
3.6.1	$\delta^{13}C$ (Figure 3.8F)	43
3.6.2	$\Delta^{14}C$ (Figure 3.8G)	43
3.6.3	Total Inorganic Carbon and Alkalinity (Figures 3.11H and J)	45
3.7	Discussion	47
3.7.1	Sources of the Equatorial Intermediate Waters	47
3.7.2	Other Derived Geochemical Tracers	53
3.8	Summary and Conclusions	59
4	Antarctic Intermediate Waters	61
4.1	Abstract	61
4.2	Introduction	62
4.3	AAIW Formation, Sources and Circulation	62
4.4	AAIW Geochemical Characteristics	63
4.5	Data and Results	63
4.5.1	Salinity (Figure 4.2)	66
4.5.2	Oxygen (Figure 4.3)	68
4.5.3	Nitrate (Figure 4.4)	68
4.5.4	Silicate (Figure 4.5)	68
4.5.5	$\delta^{13}C$ (Figure 4.6)	71
4.5.6	$\Delta^{14}C$ (Figure 4.7)	71
4.5.7	Total Inorganic Carbon (TIC) (Figure 4.8)	71
4.5.8	Alkalinity v TIC (Figure 4.9)	75
4.6	Discussion	75
4.7	Summary and Conclusions	80
II	Palaeoceanography	83
5	Siliciclastic/carbonate sedimentation model for the Capricorn Channel	85
5.1	Abstract	85
5.2	Introduction	86
5.2.1	Previous work on the east coast of Australia	87
5.2.2	Regional Setting	90
5.2.3	Regional Climatology and Oceanography	91
5.3	Methods and Samples	92

5.4	Results	96
5.4.1	GC-09	96
5.4.2	GC-10	97
5.4.3	GC-11	98
5.4.4	GC-12	100
5.4.5	GC-13	103
5.4.6	GC-14	103
5.4.7	GC-15	105
5.5	Discussion	105
5.5.1	Sedimentary Model	105
5.5.2	Comparisons with other siliciclastic/carbonate regions	112
5.6	Conclusions	114
6	Changes in the AAIW Circulation	115
6.1	Abstract	115
6.2	Introduction	116
6.2.1	Oceanography	117
6.2.2	Stable Isotopes	118
6.2.3	Foraminifera	120
6.3	Methods and Samples	121
6.4	Results	121
6.5	Model	124
6.6	Discussion	130
6.7	Summary and Conclusions	131
7	Changes in the East Australian Current	133
7.1	Abstract	133
7.2	Introduction	134
7.2.1	The EAC and Western Boundary Current Dynamics	134
7.2.2	Previous Research	138
7.3	Methods and Samples	138
7.4	Results	141
7.5	Discussion	144
7.5.1	Glacial Conditions	145
7.5.2	Onset of the EAC at 11 ka BP	148
7.5.3	Other western boundary currents	149
7.6	Conclusions	150
8	Conclusions and Future Work	151
8.1	Summary and Conclusions	151
8.2	Future Work	153

A	Studying the Carbonate System	155
A.1	Alkalinity	155
A.2	TIC - Total Inorganic Carbon	155
A.3	pH	157
A.4	Fugacity of CO_2	157
A.5	Carbonate Saturation - Calculating the Lysocline	157
B	Radiocarbon Analyses and Corrections	159
C	The International Equation of State for Seawater, 1980, UNESCO	161
D	Oxygen Solubility in Seawater	163
E	Foraminifera	165
E.1	Planktic Foraminiferids	165
E.1.1	<i>Globigerinoides ruber</i> (d'Orbigny, 1839)	165
E.1.2	<i>Globigerinoides sacculifer</i> (Brady, 1877)	167
E.1.3	<i>Globorotalia menardii</i> (Parker, Jones and Brady, 1865)	168
E.1.4	<i>Globorotalia truncatulinoides</i> , (d'Orbigny 1839)	169
E.2	Benthic Foraminiferids	170
E.2.1	<i>Cibicidoides sp.</i> (Phleger and Parker 1951)	170
F	Wind Stress Curl and EAC Circulation	173
F.1	Surface Winds	173
F.2	Ocean currents	173
G	Abbreviations	175
	Bibliography	179

List of Figures

1	My car!	viii
1.1	The carbon cycle and reservoirs	2
1.2	Vostok ice core CO_2 , CH_4 and temperature records	4
1.3	Atmospheric CO_2 concentrations for the last 150kyr	4
1.4	$\delta^{13}C$ in the atmosphere, biosphere and oceans	7
1.5	Factors affecting the spatial $\delta^{13}C$ in the oceans	8
1.6	SPECMAP $\delta^{18}O$ curve, after <i>Martinson et al.</i> (1987)	11
1.7	The topography and bottom waters of the Pacific Ocean	13
1.8	Surface currents of the Pacific Ocean	14
1.9	Wind driven ocean circulation, after <i>Munk</i> (1950)	14
1.10	Vertical cross section of the Southern Ocean	18
1.11	The topography and ocean circulation of the Tasman Sea and Coral Sea . .	19
1.12	Vertical water profiles from the Coral Sea and Tasman Sea	20
3.1	Intermediate water distribution in the worlds oceans, after <i>Talley</i> (1999) . .	31
3.2	WOCE cruises used in Chapter 3	35
3.3	Temperature, salinity and oxygen against depth for transect P17	36
3.4	(A)T-Salinity and (B)T-Oxygen diagrams for the cruise transects	38
3.5	The distribution of intermediate waters of the Pacific	39
3.6	(C)T-Nitrate and (D)T-Phosphate diagrams for the cruise transects	41
3.7	(E)T-Silicate diagrams for the cruise transects	42
3.8	(F)T- $\delta^{13}C$ and (G)T- $\Delta^{14}C$ diagrams for the cruise transects	44
3.9	$\delta^{13}C$, $\Delta^{14}C$, TIC and alkalinity against depth for transect P17.	46
3.10	TIC v Alkalinity, after <i>Broecker and Peng</i> (1982)	47
3.11	(H)T-TIC and (J)T-Alkalinity diagrams for the cruise transects	48
3.12	TIC v Alkalinity diagrams for the cruise transects	49
3.13	Potential density and salinity for the salinity minima along 135°W, after <i>Tsuchiya and Talley</i> (1996)	50
3.14	Salinity and oxygen along the P17 transect (courtesy of R. Schlitzer) and a simplified diagram to suggest the formation of the EqIW	52

3.15	$\delta^{13}C_{as}$ for P17 transect calculated directly from AOU and from <i>Broecker</i> and <i>Maier-Reimer</i> (1992) equation	56
3.16	Plots of Redfield ratios using AOU, phosphate, nitrate and $\delta^{13}C$	57
4.1	South Pacific cruises used in Chapter 4	64
4.2	T-Salinity plots for AAIW	67
4.3	T-Oxygen plots for AAIW	69
4.4	T-Nitrate plots for AAIW	70
4.5	T-Silicate plots for AAIW	72
4.6	T- $\delta^{13}C$ plots for AAIW	73
4.7	T- $\Delta^{14}C$ plots for AAIW	74
4.8	T-TIC plots for AAIW	76
4.9	Alkalinity v TIC plots for AAIW	77
4.10	Adjusted absolute steric height of 1000 dbar in dynamic metres from the Pacific circulation scheme, after <i>Reid</i> (1997)	78
4.11	Summary of AAIW formation region, sources and circulation in the south Pacific.	80
5.1	Classic sedimentation models for mixed carbonate and siliciclastic systems .	86
5.2	Sealevel fluctuations over the last glacial cycle.	87
5.3	Map to show the location of the Capricorn Channel, southern GBR.	88
5.4	Sedimentation models for the mixed carbonate and siliciclastic systems of the northern GBR.	89
5.5	Bathymetry of the Capricorn Channel	93
5.6	Calculated calcite and aragonite saturation in the Tasman Sea	94
5.7	XRD results from samples in the Capricorn Channel cores.	95
5.8	FR1/97 GC-09 results	97
5.9	FR1/97 GC-10 results	99
5.10	FR1/97 GC-11 results	101
5.11	FR1/97 GC-12 results	102
5.12	FR1/97 GC-13 results	104
5.13	FR1/97 GC-14 results	106
5.14	Sedimentation model for the Capricorn Channel	109
5.15	Palaeochannel evident in the bathymetry data	110
5.16	Comparison of sedimentation models for the northern GBR, subtropical east coast of Australia and the Capricorn Channel.	113
6.1	AAIW circulation in the southwest Pacific and the location of GC-12	118
6.2	Water column data for the Tasman Sea and Coral Sea.	119
6.3	$\delta^{18}O$ for a suite of foraminifera from core GC-12	122
6.4	Abundance of <i>Gr. menardii</i> and <i>Gr. truncatulinoides</i> in core GC-12	122
6.5	$\delta^{13}C$ and $\Delta\delta^{13}C$ planktonic-benthic for a suite of foraminifera in core GC-12	123

6.6	Model of AAIW circulation in the southwest Pacific LGM to Holocene . . .	125
6.7	Comparison of foraminiferal $\delta^{13}C$ from GC-12 with atmospheric CO_2 and $\delta^{13}C_{CO_2}$ measured in Antarctic ice cores	129
7.1	EAC circulation in the Coral Sea and Tasman Sea	136
7.2	Simplified diagram of the wind stress curl τ in the Coral Sea and Tasman Sea	137
7.3	$\delta^{18}O$ <i>G. ruber</i> results for GC-12 compared with GC-25, GC-9 and PC-27a .	141
7.4	$\delta^{18}O$ <i>G. ruber</i> from core tops and LGM plotted against latitude in the Coral Sea and Tasman Sea.	143
7.5	A potential scenario for the EAC circulation during LGM	147
E.1	Vertical distributions of foraminifera used in this thesis.	166
E.2	<i>Globigerinoides ruber</i>	166
E.3	<i>Globigerinoides sacculifer</i>	168
E.4	<i>Globorotalia menardii</i>	169
E.5	<i>Globorotalia truncatulinoides</i>	170
E.6	<i>Cibicidoides pseudoungeriana</i>	171
E.7	<i>Cibicidoides kullenbergi</i>	171
E.8	<i>Cibicidoides wuellerstorfi</i>	171

List of Tables

1.1	Oceanography Acronyms	12
3.1	WOCE Cruises used Chapter 3	34
3.2	Geochemical data for intermediate water masses	35
3.3	Latitudinal range of the different intermediate waters in the Pacific Ocean .	39
4.1	Geochemical characteristics of AAIW	64
4.2	WOCE Cruises used in Chapter 4	65
4.3	Longitudinal limits of cruise data P21 to P06	66
4.4	Latitudinal limits of cruise data P11s, P14c, P15s, P16s, P18, P19	66
5.1	Location of gravity cores	93
5.2	Radiocarbon dates for GC-10 and GC-12	96
5.3	XRD results from clay fraction	98
6.1	Stable isotope corrections for different species of planktonic foraminifera. . .	120
7.1	List of cores used in Chapter 7	139
7.2	Radiocarbon ages and calibrated ages for core PC-27a, GC-12, GC-25 and GC-9	139
7.3	Latitudinal variations in Holocene and glacial $\delta^{18}O$ and $\Delta\delta^{18}O_{glacial-Holocene}$ for <i>G. ruber</i>	140

