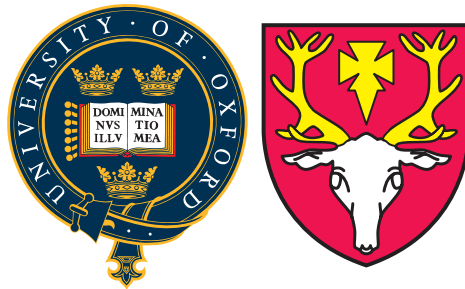


Variations in Past and Present Ocean Circulation Assessed with U-Series Nuclides

by

Alexander L. Thomas

Thesis submitted to the University of Oxford
for the degree of Doctor of Philosophy
in
Geology and Mineralogy



Department of Earth Sciences
and
Hertford College
University of Oxford

Hilary, 2006

Supervised by Dr Gideon M. Henderson

*Eternal Father, strong to save,
Whose arm hath bound the restless wave;
Who bidd'st the mighty ocean deep
Its own appointed limits keep
Oh hear us when we cry to thee
For those in peril on the sea.*

William Whiting(1825-1878)

Declaration

I declare that the work presented in this thesis is my own.

Alexander L. Thomas

Abstract

Variations in Past and Present Ocean Circulation Assessed with U-Series Nuclides

Alexander L. Thomas
Hertford College, Oxford
Hilary Term, 2006

This thesis considers the use of two U-series nuclides – ^{231}Pa and ^{230}Th – as proxies for studying ocean circulation. A total of six water-column profiles of ^{231}Pa , ^{230}Th , and ^{232}Th have been measured from two regions of the southwestern Indian Ocean: the Madagascar and Mascarene Basins; and the southeastern continental margin of South Africa. Measurement by MC-ICP-MS of 10 litre water samples is possible for samples with as little as 4 and 2 fg of ^{231}Pa and ^{230}Th and yields typical uncertainties of 6% and 14% respectively. These profiles show that the scavenging and advection histories of water masses can affect their ^{231}Pa concentration, with distinct variations superimposed on a general increase in concentration with depth due to reversible scavenging. A 1D particle scavenging model is used to show that sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is most representative of the $(^{231}\text{Pa}/^{230}\text{Th})$ of the bottom most water mass at any one locality, although in turn this water mass $(^{231}\text{Pa}/^{230}\text{Th})$ will be dependent not only on its advection and scavenging history but also the ^{231}Pa and ^{230}Th concentrations of the overlying water masses during advection. Acknowledgment that sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is “set” by the bottommost water mass is important for interpretation of scenarios where changes in depth of circulation, as well as circulation strength, may have occurred.

A record of sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ has been recovered from a 6 m Kasten core from the Mascarene Basin covering the past 140 ka, in order to reconstruct flow of AABW into the basin. The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ measured is below the production ratio of 0.093 and shows no significant variation. This indicates that $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is sensitive to changes in particle productivity and circulation at this location and that there has been little or no change in either environmental variable over the last full interglacial-glacial cycle. This finding is in contrast to other ocean basins, particularly the North Atlantic, where large changes in circulation are observed.

Extended Abstract

Variations in Past and Present Ocean Circulation Assessed with U-Series Nuclides

Alexander L. Thomas

Hertford College, Oxford

Hilary Term, 2006

This thesis deals with the development of a proxy for past ocean circulation. This proxy makes use of the difference in removal rate from seawater of two naturally occurring radioisotopes, ^{231}Pa and ^{230}Th . Firstly, Chapter 1 introduces ocean circulation, specifically in the Indian Ocean where my research has been focused, and why it is an important part of the climate system. Chapter 1 also introduces the concept of radioactive decay, and specifically the U-series decay chains and nuclides of interest to this study. Secondly, this thesis covers the development of methods for the measurements of ^{231}Pa and ^{230}Th in both seawater and in deep sea sediments. Thirdly, three studies of ^{231}Pa and ^{230}Th from the Indian Ocean are presented which investigate the behaviour of ^{231}Pa and ^{230}Th in the water column and the use of a sedimentary record of $^{231}\text{Pa}/^{230}\text{Th}$ to investigate the flow of bottom water into the Indian Ocean over the past 140 ka.

Both ^{231}Pa and ^{230}Th are produced from decay of U in the water column at a constant ($^{231}\text{Pa}/^{230}\text{Th}$) of 0.093. ^{231}Pa and ^{230}Th are highly particle reactive in seawater, being scavenged onto the surface of particles which then settle to the seabed. ^{230}Th is more particle reactive than ^{231}Pa and hence has a shorter residence time in the ocean (20 years compared to 120 for ^{231}Pa). Thus, as ^{230}Th is preferentially removed from the ocean, the water becomes enriched in ^{231}Pa relative to ^{230}Th . As a water mass circulates around the oceans the ($^{231}\text{Pa}/^{230}\text{Th}$) of the water therefore

increases with time as ^{230}Th is preferentially removed. This allows the ($^{231}\text{Pa}/^{230}\text{Th}$) preserved in sediments to be used to investigate past circulation.

^{231}Pa and ^{230}Th were measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) utilising multiple-ion counting channels. A multi-step approach was used for the measurement of Th isotopes, collecting both ^{229}Th and ^{230}Th in the same ion counter. Pa and U were each measured in a single step, Pa utilising ion counters for ^{231}Pa and ^{233}Pa , and U using a single ion counter for ^{234}U and Faraday collectors for the other isotopes (^{235}U , ^{236}U , ^{238}U and ^{232}Th). A standard bracketing approach was used for all measurements to assess mass discrimination, ion counter gain, abundance sensitivity and molecular interferences. Sedimentary measurements of ^{231}Pa and ^{230}Th are corrected for any ^{231}Pa and ^{230}Th supported by detrital and authigenic U, to give the excess that is produced from the water column ($^{231}\text{Pa}_{\text{xs}}$ and $^{230}\text{Th}_{\text{xs}}$). These values are then converted to activities and decay corrected to the time of deposition to give $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ ($(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ being the activity ratio of ^{231}Pa to ^{230}Th in sediment that is derived from the water column and corrected for decay since deposition at $t = 0$).

A rigorous chemical separation of U, Th, and Pa from seawater and sediment sample has been developed. The chemistry, following dissolution and co-precipitation with Fe, is a three column anion exchange using AG1-X8 resin. The separation of Pa is crucial because the measurement of Pa is hampered by abundance sensitivity arising from large U and Th beams and by the molecular interference of ^{232}ThH on the ^{233}Pa beam. Total uncertainties for ^{230}Th , ^{232}Th , and ^{231}Pa in seawater samples are 6%, 8%, and 14% respectively. These uncertainties are large due to the low concentrations in seawater samples, especially near the surface. The detection limits for ^{230}Th and ^{231}Pa are determined by the total procedural blanks, which are 1.4 and 0.6 fg respectively, leading to detection limits of 4 and 2 fg for ^{230}Th and ^{231}Pa .

A study of water column profiles along a transect at approximately 50°E in the

Madagascar and Mascarene Basins (Chapter 3) has increased the global data set of water column ^{231}Pa and ^{230}Th in a previously understudied region. Profiles of ^{231}Pa suggest water masses can have distinct ^{231}Pa concentrations, depending on their circulation and scavenging histories. This is important when using $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in settings where the water column comprises many water masses with differing histories. A simple 1D particle scavenging model was developed which indicates that the ^{231}Pa and ^{230}Th scavenged to the seafloor last equilibrated within 1000 m of the seabed. Thus, in the Mascarene Basin the sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ record can be used to investigate the flow of the deepest water mass, AABW, into the Indian Ocean. This finding also has implications for the interpretation of records of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in other regions, such as the North Atlantic, where a shoaling of overturning circulation and the influx of southern sourced bottom water could change sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to give the same values expected for a total shutdown of overturning circulation.

A 140 ka record of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ from the Mascarene Basin in the western Indian Ocean has been measured (Chapter 4). This is the first time the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy for circulation has been used over such a long record, and is one of only very few downcore records of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ as yet measured. The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy is shown to be sensitive to changes in the circulation or scavenging history of AABW as it flows to this locality, because the ratio is < 0.093 , the production ratio. No change in $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is observed, however, indicating that there has been no change in bottom water flow into the Indian Ocean over the past 140 ka. This is a surprising result considering the changes in circulation on glacial-interglacial, and millennial timescales that have been inferred for the North Atlantic and the changes in deep Pacific inflow of AABW on glacial-interglacial timescales observed with the sortable silt proxy. The lack of any variation of AABW inflow into the Indian Ocean suggests that any increase in Southern Ocean deep water formation associated with

any interhemispheric bipolar see-saw may be AAIW rather than AABW. Inferred increases in AABW flow into the Pacific may reflect increased production of AABW around the margins of East Antarctica, such as at the Adelie Shelf, rather than in the Weddell Sea where it would influence flow into the Indian Ocean.

Byproducts of the measurement of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ are the $(\text{U}/\text{Th})_{\text{detrital}}$ and a record of authigenic U. The measurement of $(\text{U}/\text{Th})_{\text{detrital}}$ is an improvement on previous methods in the Indian Ocean and thus reduces the uncertainty in corrections for detritally supported ^{231}Pa and ^{230}Th in this region. The authigenic U record shows two periods of authigenic U production at 30 and 140 ka indicating oxygen depleted bottom water in the Mascarene basin during glacial maxima, most likely due to globally reduced deep water oxygenation brought about by sluggish deep circulation in the North Atlantic.

A further, high resolution, water-column profile has been measured from the southwestern Indian Ocean, close to the South African continental margin (Chapter 5). Measurement of U concentration and isotopic composition has confirmed the conservative behaviour of U in the ocean. The concentration of U, normalised to a salinity of 35, is found to be 3.184 ± 0.004 ppm. Confirmation of the ability of ^{231}Pa to ‘trace’ water masses through their advection and scavenging history is seen in this water column profile. Intermingling of Red Sea Water with Antarctic Intermediate Water is associated with ^{231}Pa variation, and NADW and AAIW are observed to have high and low ^{231}Pa concentrations respectively as observed at lower resolution in Chapter 3. A diluted nepheloid layer extending up to 1700 m from the seafloor, observed through elevated total ^{232}Th concentrations, may be significant in controlling the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ preserved in sediments. Selective dissolution on the seafloor of phases such as carbonate, which favourably scavenges ^{230}Th over ^{231}Pa , and resuspension of the remaining material (which may fractionate ^{231}Pa and ^{230}Th less) will change the bulk particle composition in the bottom water, which will

influence the ($^{231}\text{Pa}/^{230}\text{Th}$) exported to sediments.

This thesis has developed improved measurement of ^{231}Pa and ^{230}Th in water and sediment matrices. It has also improved our understanding of how ^{231}Pa and ^{230}Th behave in the water column and how that behaviour is recorded in the sedimentary record. This improved understanding of the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy has implications for the interpretation of records from regions other than the Indian Ocean, such as the North Atlantic. Understanding how the scavenging and advection histories of bottom water controls sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$, has enabled the interpretation of a new record from the Mascarene Basin. This record of AABW flow, indicates that there has been little or no change in flow rate, of AABW into the Indian Ocean, over the last 140 ka.

Acknowledgements

I should firstly thank my supervisor Gideon Henderson, as he has been an invaluable source of scientific inspiration and guidance. My undergraduate supervisor at the University of Bristol Tim Elliott is also deserving of thanks for my induction into isotope geochemistry, and brief foray into the mantle.

My initiation on the MC-ICP-MS was made all the easier with the help of Mona Becker, Laura Robinson, and Nick Belshaw. I thank them all for their tolerance of often obvious questions and my ability to cause breakage of almost every part of a mass spectrometer. I also wish to thank all of the Oxford geochemists, both for Fridays at the Rose & Crown and for discussions of a more scientific nature.

For provision, and assistance in the production, of ^{233}Pa spike I would also like to thank Marcel Regelous, Julia Shaw, Julie Prytulak, and Sylvain Pichat.

Both Steve Wyatt and Don Porcelli were both very accommodating of my use of all available space in the clean lab for water samples, and were invaluable in providing advice on matters chemical.

I am grateful to the crew and scientific staff of the *RRS Charles Darwin* (Cruises CD 129 & CD 154). In particular I should thank: the chief scientists of CD154 Ian Hall and Rainer Zahn, for providing exemplary service at Christmas lunch and for all the croissants; and Laura Robinson for collecting the samples from cruise CD 129 used in this thesis.

There are also those in the Department of Earth Science of whom a special mention is merited: Alice Thomas, Laura Robinson, Lisa Hall, and Deb Foster for introducing me to “The Camel”, and Lebanese food; Andy Needham and Julie Ferguson for games of sardines in various offices around the department; Gareth Funning and Ben Kilner for the seamless transitions from }{appy }{our to the Octagon on many a Friday night; Ali Gemmel for the occasional light game of table tennis to boost

office moral; and to Kit Chambers for proving three years is long enough.

I would like to thank my examiners, Ros Rickaby and Jerry McManus, for being the only people to continue reading past this point and for a thoroughly satisfying three and a half hours. Finally I should like to acknowledge the help of support of my family, and especially Anna, without whom this thesis would not have been possible.

This work has been supported by a Natural Environmental Research Council studentship.

Contents

Declaration	i
Abstract	ii
Extended Abstract	iii
Acknowledgements	viii
Contents	xii
List of Figures	xiv
List of Tables	xv
List of Abbreviations	xvi
1 Introduction	1
1.1 Overview	1
1.2 Basic principles of ocean circulation	1
1.2.1 Wind-driven currents	4
1.2.2 Geostrophic currents	6
1.2.3 Thermohaline circulation	8
1.3 The role of ocean circulation in heat transport	16
1.4 The role of ocean circulation in the carbon cycle	19
1.5 The Indian Ocean	22
1.5.1 Indian Ocean hydrography	22
1.6 Uranium Series Nuclides	24
1.6.1 Radioactive decay	24
1.6.2 Radioactive decay series	28
1.6.3 Secular equilibrium	30
1.6.4 Uranium series nuclides in the ocean	31
1.6.5 ^{231}Pa and ^{230}Th as paleoceanographic proxies	38
1.7 Summary	44
2 Methods	47
2.1 Introduction	47
2.2 Sampling	48
2.2.1 Water samples	48
2.2.2 Sediment samples	50
2.3 Chemistry	53
2.3.1 Laboratory conditions	53
2.3.2 Cleaning procedures	54
2.3.3 Reagents	55

2.3.4	Weighing	56
2.3.5	Sample pre-treatment	57
2.3.6	Elemental separation	61
2.4	Standards and spikes	74
2.4.1	Isotope dilution	74
2.4.2	^{236}U and ^{229}Th spikes	76
2.4.3	^{233}Pa spike	78
2.4.4	Standards	85
2.5	Mass spectrometry	87
2.5.1	The machine	87
2.5.2	Uranium	98
2.5.3	Thorium in sediments	103
2.5.4	Thorium in seawater	104
2.5.5	Protactinium	105
2.5.6	Blanks	106
2.5.7	Uncertainties	107
2.6	Summary	109
3	Water Column ^{231}Pa and ^{230}Th	111
3.1	Overview	111
3.2	Introduction	112
3.2.1	Aims	112
3.2.2	The ($^{231}\text{Pa}/^{230}\text{Th}$) proxy	112
3.3	Regional setting	115
3.4	Methods	118
3.5	Results	119
3.6	Controls on radionuclide concentrations in Indian Ocean waters	124
3.6.1	^{231}Pa and ^{230}Th	124
3.6.2	^{232}Th	125
3.7	Modelling of export of ^{231}Pa and ^{230}Th to sediments	126
3.7.1	Introduction	126
3.7.2	The model	127
3.7.3	Model results	129
3.7.4	Interpretation	130
3.8	Discussions	131
3.8.1	Sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ is most representative of the bottom-most water mass	131
3.8.2	Implications for interpretation of sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) records in other regions	132
3.9	Summary	133
4	Sedimentary ^{231}Pa and ^{230}Th	135
4.1	Overview	135
4.2	Introduction	135
4.3	Regional setting & samples	137

4.4	Methods	140
4.4.1	Chemistry	140
4.4.2	Mass spectrometry	141
4.5	Results	142
4.5.1	Data and corrections	142
4.5.2	Calculation of detrital (U/Th)	144
4.5.3	Calculation of sedimentation proxies	145
4.5.4	Description of results	155
4.6	Discussions	157
4.6.1	Consistency of AABW flow into the Indian Ocean	157
4.6.2	Authigenic U	160
4.6.3	Detrital provenance	161
4.6.4	Mass accumulation rate: productivity vs. dissolution	162
4.6.5	Comparison with the “sortable silt” flow-speed proxy	163
4.6.6	Modelling of water column ^{231}Pa and ^{230}Th	166
4.7	Summary	172
5	A High Resolution ^{231}Pa and ^{230}Th Water Column Profile	175
5.1	Introduction	175
5.2	Regional setting	175
5.3	Methods	178
5.3.1	Sampling strategy	178
5.3.2	Chemistry	179
5.3.3	Mass spectrometry	180
5.4	Results	181
5.5	Discussion	189
5.5.1	Oceanic behaviour of uranium	189
5.5.2	Comparison of ^{231}Pa and ^{230}Th with existing data	190
5.5.3	Deep particulate ^{232}Th	193
5.5.4	Interfingering of Red Sea Water	194
5.5.5	NADW and AABW mixing	196
5.5.6	Fractionation of Pa and Th isotopes by varying particle type	197
5.6	Summary	199
6	Conclusions	203
6.1	U-series nuclides as an ocean circulation proxy	203
6.2	Future analytical developments	204
6.3	Extending the application of ^{231}Pa and ^{230}Th	205
6.3.1	Water column ^{231}Pa and ^{230}Th measurements	205
6.3.2	Testing the bipolar seesaw hypothesis	206
6.3.3	Longer timescales and quantification	207
	Bibliography	209

List of Figures

1.1	Athanasius Kircher's map of ocean circulation	2
1.2	Stommel's 1958 schematic of abyssal circulation.	3
1.3	Map of prevailing winds and wind driven currents	4
1.4	The Coriolis force	5
1.5	Ekman spiral	7
1.6	The geostrophic balance	7
1.7	Sea surface height of the North Atlantic and geostrophic flow	9
1.8	Surface divergence and upwelling caused by cyclonic wind	10
1.9	Schematic map showing the formation of North Atlantic Deep Water	11
1.10	Southern Ocean water mass movements	12
1.11	Deep flow of AABW away from Antarctica	13
1.12	Global net radiation balance	17
1.13	Meridional heat transport	18
1.14	Heat transport in the ocean	19
1.15	CO ₂ speciation	20
1.16	Holocene carbon reservoirs	21
1.17	Bathymetry of the southwestern Indian Ocean	23
1.18	Decay series	25
1.19	Uranium concentration in seawater, and salinity	33
1.20	²³⁰ Th concentration profile	36
1.21	²³⁴ Th concentration profiles	37
2.1	CTD rosette	49
2.2	Shipboard filtration	49
2.3	Kasten core recovery	51
2.4	Kasten core processing	51
2.5	Piston core	52
2.6	Under CTD gravity core	52
2.7	Effect of static on weighing spike solution.	57
2.8	Calibration of TEVA resin	70
2.9	Calibration of AG1-X8 resin	72
2.10	Isotope dilution	75
2.11	Ingrowth of ²³³ Pa	79
2.12	Nu Instruments MC-ICP-MS	89
2.13	Schematic of an ion counter	90

2.14	Abundance sensitivity at 1 amu	94
2.15	Abundance sensitivity at -3 amu	94
2.16	Thorium standard for measuring abundance sensitivity	96
2.17	^{232}ThH	97
2.18	^{232}ThH throughout measurement run	98
2.19	Resolving ^{232}ThH from high mass abundance sensitivity	99
2.20	Breakdown of uncertainty in measurement	108
3.1	Schematic representation of $(^{231}\text{Pa}/^{230}\text{Th})$ proxy	113
3.2	Map of SW Indian Ocean	116
3.3	T-S profiles of stations measured for ^{231}Pa and ^{230}Th	117
3.4	Water column Th and Pa profiles	122
3.5	Sections through water column ^{230}Th and ^{231}Pa data	123
3.6	Schematic of 1D particle scavenging model	128
3.7	Sensitivity of model	130
3.8	Results from model	130
4.1	Hydrography of the southwest Indian Ocean	138
4.2	Map of sample localities in SW Indian Ocean	139
4.3	Results from WIND 28K	156
4.4	Sortable silt and stable isotope records from WIND 5K and 10K	164
4.5	Variation of sortable silt across a current	165
4.6	Modelled $(^{231}\text{Pa}/^{230}\text{Th})$ exported to sediments	171
4.7	The effect of varying the production rate on the export of $(^{231}\text{Pa}/^{230}\text{Th})$ to sediments	172
5.1	Locality of profile CD154-13 4C	176
5.2	T-S plot of CD 154-13 4C	179
5.3	Particulate concentration, oxygen, and temperature-salinity profiles at CD154-13 4C	182
5.4	CD 154 13 4C uranium results	183
5.5	Concentration profiles of ^{231}Pa , ^{230}Th , and ^{232}Th at CD 154 13 4C	187
5.6	$(^{231}\text{Pa}/^{230}\text{Th})$ profile at CD 154 13 4C, and F factors.	188
5.7	Comparison of ^{238}U concentration measurements	190
5.8	Comparison of ^{230}Th ^{231}Pa data from CD 129 and CD 154	192
5.9	Proportion of ^{230}Th , ^{232}Th , and ^{231}Pa associated with particles	194
5.10	Interfingering of Red Sea Water	195
5.11	Deep water ^{231}Pa and ^{230}Th at CD154 13 4C	197

List of Tables

1.1	Nuclides in the U-series' decay chains	26
1.2	Laboratory measurements of $K_{d,Th}$	36
2.1	Reagent blanks	56
2.2	Literature elemental separation techniques.	68
2.3	^{236}U and ^{229}Th spikes	77
2.4	Standards	85
2.5	Collector array	88
2.6	Collector configuration for measurements	102
2.7	Total procedural blanks	107
3.1	Results for WIND water samples.	121
3.2	Model parameters	129
4.1	U and Th results for surface sediment samples.	148
4.2	U and Th results for down core sediment samples.	150
4.3	^{230}Th and ^{231}Pa results for surface sediment samples.	152
4.4	^{230}Th and ^{231}Pa results for down core sediment samples.	154
4.5	Parameters used in model of water column ^{231}Pa and ^{230}Th , and ex- port to sediments.	167
5.1	CD 154 13 4C uranium results	184
5.2	CD 154 13 4C thorium and protactinium results	185
5.3	CD 154 13 4C thorium and protactinium results	186

List of Abbreviations

Abbreviation	Description
a	year
ka	10^3 years
Ma	10^6 years
ppm	parts per million (mass)
ppb	parts per billion (mass)
mg	milligram 10^{-3} g
μ g	microgram 10^{-6} g
ng	nanogram 10^{-9} g
pg	picogram 10^{-12} g
fg	femtogram 10^{-15} g
ag	attogram 10^{-18} g
s.d.	standard deviation
σ	standard error of the mean
λ	decay constant
(.../...)	activity ratio
$\delta^{234}\text{U}$	$[(^{234}\text{U}/^{238}\text{U}) - 1] \times 1000$
t	time
$t_{1/2}$	half life
$^{231}\text{Pa}^0$	initial ^{231}Pa at $t = 0$
$^{231}\text{Pa}_{\text{xs}}$	excess ^{231}Pa , derived only from within the water column
Cv	Column volume, (of resin)
cps	counts per second
d.p.m.	disintegrations per minute

Chapter 1

Introduction

1.1 Overview

This chapter introduces the nature of ocean circulation, and the formation of the principle water masses discussed in this thesis (Section 1.2). Understanding the pattern and rate of ocean circulation in the past is of great interest to paleoceanographers because the oceans are responsible for transporting heat around the planet (Section 1.3), and play a major role in the carbon cycle (Section 1.4).

The tools used to study past ocean circulation investigated in this thesis are the decay products of uranium. Uranium series nuclides and their decay chains are discussed in Section 1.6, along with the geochemical behaviour of uranium and two daughter isotopes of interest, ^{230}Th and ^{231}Pa . The use of ^{230}Th and ^{231}Pa as paleoceanographic proxies is also briefly introduced in Section 1.6.4.

1.2 Basic principles of ocean circulation

Movement of water within the oceans occurs on scales ranging from small, cm-sized eddies to the large scale circulation of the entire ocean. This thesis deals largely with the large-scale circulation of the oceans, but it is important to realise that superimposed upon this large scale circulation are a myriad of smaller scale features.

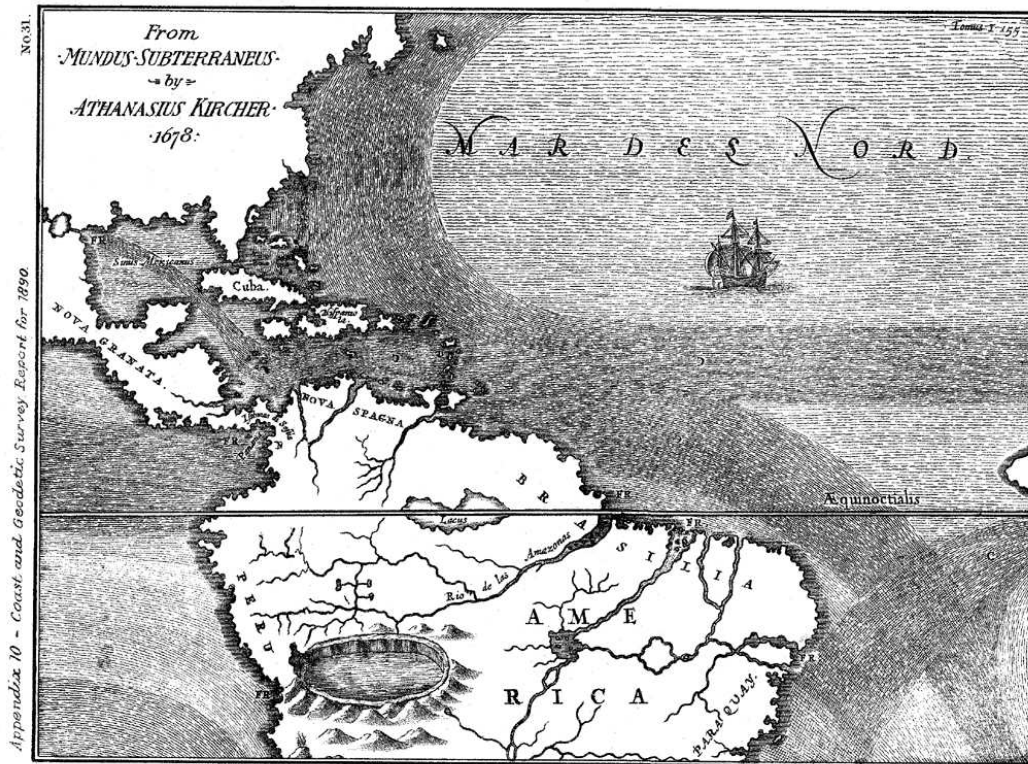


Figure 1.1: A map drawn by Athanasius Kircher, a German monk of the Society of Jesus, in ‘Mundus Subterraneus’ published in 1678. Although Kircher’s principle interests lay in geology and specifically volcanism, the position of the Gulf Stream, and the North and South Equatorial Currents are clearly marked on his map. This image is a reproduction of Kircher’s original in a U.S. Coast and Geodetic Survey report (Pillsbury), image from NOAA photo library < <http://www.photolib.noaa.gov/index.html> >

The existence of ocean currents has been known at least as far back as the 16th century, the oldest surviving chart showing ocean currents was produced sometime later by Athanasius Kircher in his book “Mundus Subterraneus”, published in 1678 (Figure 1.1). The study of the oceans focused on surface currents and circulation until the mid 20th century, when in 1958 Henry Stommel published an assessment of the abyssal circulation (Figure 1.2). Stommel noted:

“It seems likely that the low temperature of deep waters in the world ocean is maintained in the face of downward diffusion of heat from the warm surface layers by a very slow upward component of velocity in the

The image originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.2: Stommel's 1958 assessment of the abyssal ocean circulation showing schematic flow lines, derived by connecting two point sources of deep water to a diffuse upwelling into the thermocline, considering that flow is on a rotating sphere. The black circles indicate the formation of bottom water in the Weddell Sea in the southern hemisphere and North Atlantic in the northern hemisphere. From Stommel (1958)

deep water. ...

The slow upward flow over most of the ocean must be compensated for somewhere by downward flowing sources of deep water. I envisage these deep-water sources as occurring in very limited areas of weak gravitational stability where the thermocline "springs a leak". ..."

From this starting hypothesis and the distribution of sparse measurements of dissolved oxygen, Stommel hypothesised the sources of deep water were the North Atlantic and the Weddell Sea. Linking the sources of deep water to the dispersed gradual upwelling using the method of motions on a rotating sphere a generalised model of deep water circulation was produced (Figure 1.2).

The two images originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.3: (a) a map showing generalised surface wind patterns for January. (b) Schematic surface ocean currents for January, cold currents in blue and warm in red. maps are adapted from Grolier Online Atlas < <http://go.grolier.com/> >

1.2.1 Wind-driven currents

As winds blow over the surface of the ocean, friction at the boundary layer pushes the surface of the water in the direction the wind is blowing. In Figure 1.3 it can be seen that the pattern of surface ocean circulation follows roughly that of the surface winds. There are, however, some differences: there are large scale differences imposed by the positions of land masses restricting the wind driven component of circulation. There is also an offset due to the Coriolis force (Coriolis, 1835) acting at right angles to the frictional force of the wind on the surface of the water.

This offset of direction is termed “Ekman Motion” and arises because of the Coriolis force acting on the water as it moves across the surface of a rotating sphere. The Coriolis force is not a real force, rather it is an apparent deflection of an object moving in a rotational reference frame. The size of the Coriolis force is given by equation 1.1,

$$\text{Coriolisforce} = m \times 2\Omega \sin \phi \times u \quad (1.1)$$

where m is the mass of the object with angular velocity Ω , and speed u at latitude ϕ . The deflection is to the right in the Northern Hemisphere and to the left in the Southern, and the ‘force’ increases towards the poles and with the speed and mass of the object.

A conceptual example is a missile fired northwards from the equator. As the

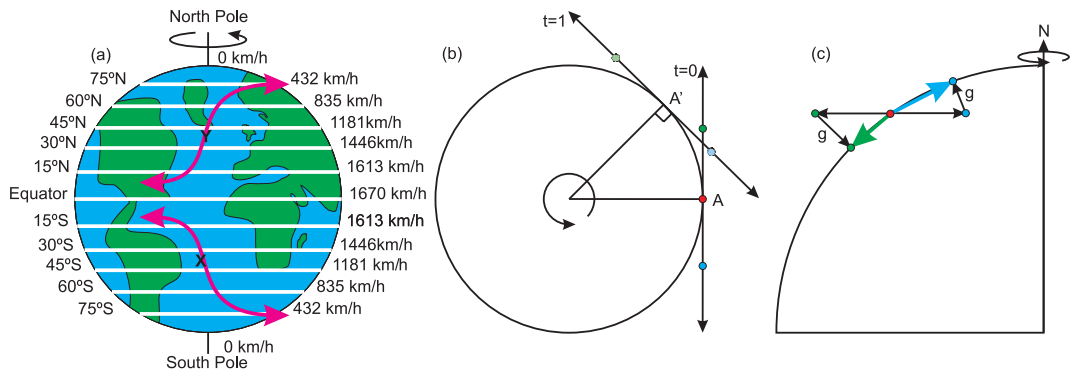


Figure 1.4: (a) A schematic of motion of two objects travelling from X in the Southern Hemisphere and Y in the Northern Hemisphere. The eastward velocity of the surface of the Earth is illustrated as it changes with latitude. Image adapted from the Australian Bureau of Meteorology < www.bom.gov.au/info/ftweather > (b) a view looking down on a the North Pole of a sphere rotating eastwards, see text for description of motions. (c) a quadrant of a north-south section through the sphere in (b) with east coming out of the page. The ball thrown east is shown in green and that west in blue. The black horizontal arrows are the deviations in trajectory due to the centrifugal ‘force’ in (b), g is the force due to gravity or the ground pushing up. the resultant south and north motions are shown by the coloured arrows.

missile is not fictionally coupled to the ground as it moves north it will maintain the eastward velocity it had at the equator. The eastward velocity of the Earth decreases towards the poles as the radius normal to the pole of rotation decreases. As the relative eastward velocity of the missile to the Earth beneath it increases northward a apparent deflection to the east is observed (Figure 1.4 a).

The deflection due to the Coriolis force is the same irrespective of the direction of travel. This may not appear obvious with the example above (Figure 1.4 a), but if another fictitious force – centrifugal force – is considered then north-south deflections are possible. Consider a ball thrown due east from A at $t=0$ (Figure 1.4 b, red), if there were no gravity the ball would continue in a straight line. If the Earth rotates such that the launch site of the ball is now at A' at $t=1$ the ball now appears to have deviated away from the pole of rotation from its expected position (light green) to its position along the straight line trajectory (dark green). A ball thrown due west would likewise appear to be deflected towards the pole of rotation. If the effect of

gravity is now considered (Figure 1.4 c), which acts only towards the center of mass of the Earth, and the effect of the ground pushing up, which acts perpendicular to the ground. The ball thrown east (green) will be pulled back towards the center of the Earth, resulting in a net force southwards (green arrow). The ball thrown west (blue) will be held up by the ground resulting in a net force upwards.

With a proper understanding of the Coriolis force the Ekman motion of wind driven currents can be explained, if the ocean is considered as a number of layers, in an infinitely wide and deep ocean, coupled to one another by the friction – or more specifically the eddy viscosity – between layers. The topmost layer is pushed by the friction of the wind blowing over it. The Coriolis force acts at right angles to the direction of movement, deflecting the current to approximately 45° to the right in the Northern Hemisphere and to the left in the Southern. This top layer then pushes the layer below which is also deflected by the Coriolis force. This continues down the water column producing a spiral of flow known as an “Ekman spiral” (Figure 1.5). The depths over which ocean currents are effected by the wind is known as the Ekman layer. The average motion of this layer, or Ekman transport, is at right angles to the direction of the prevailing winds and is a significant component of the circulation of the upper ocean.

1.2.2 Geostrophic currents

Geostrophic currents are the result of a balance between a pressure gradient force and the Coriolis force (Figure 1.6). In the ocean, pressure is a resultant of the weight of the overlying water. Pressure gradients can form due to variations in the sea surface height caused by: atmospheric pressure or water piling up in regions due to wind-driven Ekman transport. Pressure gradients can also form because of lateral variations in water mass density.

Geostrophic currents can form at all depths within the ocean, and are commonly

The image originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.5: A schematic diagram of an Ekman spiral in the Northern Hemisphere. Note the velocity of the wind driven flow decreases exponential with depth and the average flow in the Ekman layer is at right angles to the wind shear. Image from “Oceanworld” at Texas A&M University < <http://oceanworld.tamu.edu> >

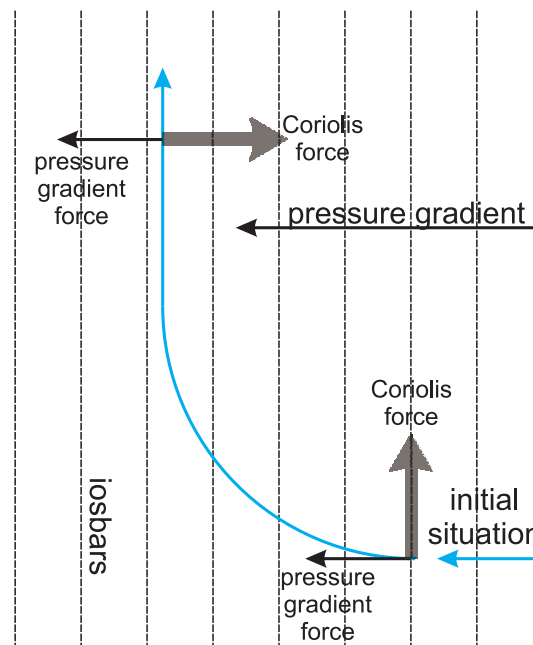


Figure 1.6: The motion of a parcel of water down a pressure gradient as it is effected by the Coriolis force until the pressure gradient force is balanced by the coriolis force and a geostrophic current is established parallel to the isobars. Adapted from Colling et al. (2001).

associated with the boundaries of basins, where flow is constrained by bathymetry. Examples of these currents are the deep western boundary currents that export North Atlantic Deep Water south out of the North Atlantic hugging the eastern continental margins of North America. Geostrophic currents can also be found away from bathymetric controls around the oceanic gyres. For example in the North Atlantic, surface winds result in a clockwise surface circulation which, through Ekman transport, moves water to the center of the basin causing an elevation of the sea surface (Figure 1.7 a). This surface elevation sets up a pressure gradient which induces a clockwise geostrophic flow (Figure 1.7 b). The center of the ‘bulge’ in sea surface height is offset to the west of the basin due to the eastwards rotation of the Earth. This causes an intensification of the pressure gradient which is responsible for the high flow rates seen in the “Gulf Stream”.

1.2.3 Thermohaline circulation

Vertical motions of the ocean are driven by the relative densities of water masses, changes in which are controlled by the temperature and salinity of the water mass, hence “thermohaline” circulation.

Vertical mixing within the oceans is normally suppressed by strong stratification in the upper water column, namely at the thermocline. Generalising a well mixed warm surface layer sits atop a colder deep ocean. The water above the thermocline is kept warm via solar heating and continual wave action distributes this heat throughout this layer. The high temperature of this mixed layer normally keeps it buoyant and prevents vertical mixing. There are however some places in the present ocean in which surface water can sink and form deep bottom water. Principle amongst these are, the North Atlantic (the Labrador, Greenland Seas and Norwegian Seas) and in the Southern Ocean near the continental margin of Antarctica (in the Weddell and Ross Seas). There are also other regions where water can sink due to thermohaline

The two images originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.7: (a) Sea surface height on the 1st October, 1995 estimated from the ECCO 2 JPL model. This is a contribution of the Consortium for Estimating the Circulation and Climate of the Ocean (ECCO) funded by the National Oceanographic Partnership Program (b) Near-surface geostrophic currents for 1st October 1995, from the Parallel Ocean Program numerical model developed at the Los Alamos National Laboratory. The length and direction of the vector is representative of the mean speed and direction in the upper 50 m of the ocean. Image from Stewart (1997)

density changes, such as the formation of intermediate waters in the Southern Ocean (Section 1.2.3), and in the eastern Mediterranean. The density changes associated with these regions are however not sufficient to cause the ventilation of water to the bottom the major ocean basins.

North Atlantic Deep Water, NADW

In the North Atlantic, surface water from the tropics that has been warmed by solar heating and has lost freshwater through evaporation, travels northwards firstly in the Gulf Stream and then in the North Atlantic Current. This water is initially salty but

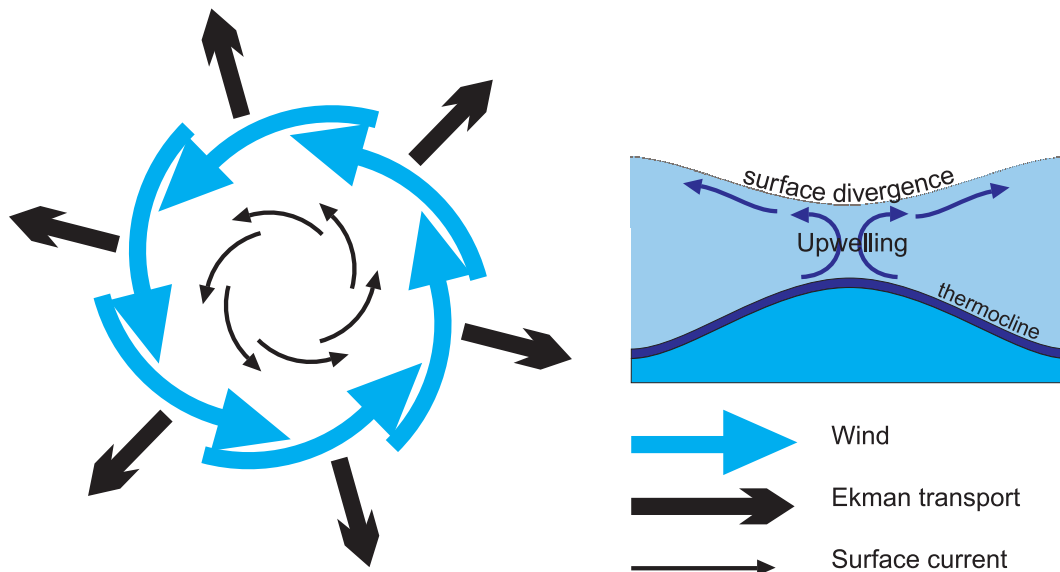


Figure 1.8: A schematic view of surface water divergence and upwelling caused by cyclonic winds (a depression) in the Northern Hemisphere. Adapted from Colling et al. (2001)

warm enough to remain buoyant. As this water moves northward, the overlying air masses become increasingly cold which promotes heat exchange into the atmosphere. There is also net evaporation, as freshwater is transferred from the Ocean to western Europe. This results in the water getting colder and more salty. Winter sea ice formation also has the effect of removing freshwater from the ocean making surface waters still more salty. These changes in the temperature and salinity of the water make the surface water dense and prone to sinking.

Although the surface water in the northern North Atlantic is both cold and salty, vertical convection is still inhibited by a strong thermocline. This stratification can be overcome during storm events which can disrupt the thermocline (Clarke and Gascard, 1983; Gascard and Clarke, 1983). Cyclonic winds, through Ekman transport, cause a surface divergence of water. This divergence causes local upwelling which draws up the thermocline (Figure 1.8). During storm events, intense wave action can penetrate deep enough to disrupt the shoaled thermocline and enable the cold salty water to sink.

The image originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.9: A schematic map showing the cyclonic gyres – in the Labrador, Greenland, Norwegian, and to a lesser extent the Irminger Seas – where deep water formation occurs. Image from Colling et al. (2001)

Vertical advection of water as described above occurs in discrete events, only when the conditions are favourable to overcome the stratification of the thermocline. In the Greenland and Norwegian Seas this newly formed deep water ‘ponds’ behind the Denmark Strait and the Iceland-Faeroe Ridge. This overflows as either Denmark Strait Overflow Water or Iceland-Faeroe Overflow Water. These water masses form a deep western boundary current and incorporate deep water formed in the Irminger and Labrador Seas to become North Atlantic Deep Water (Figure 1.9).

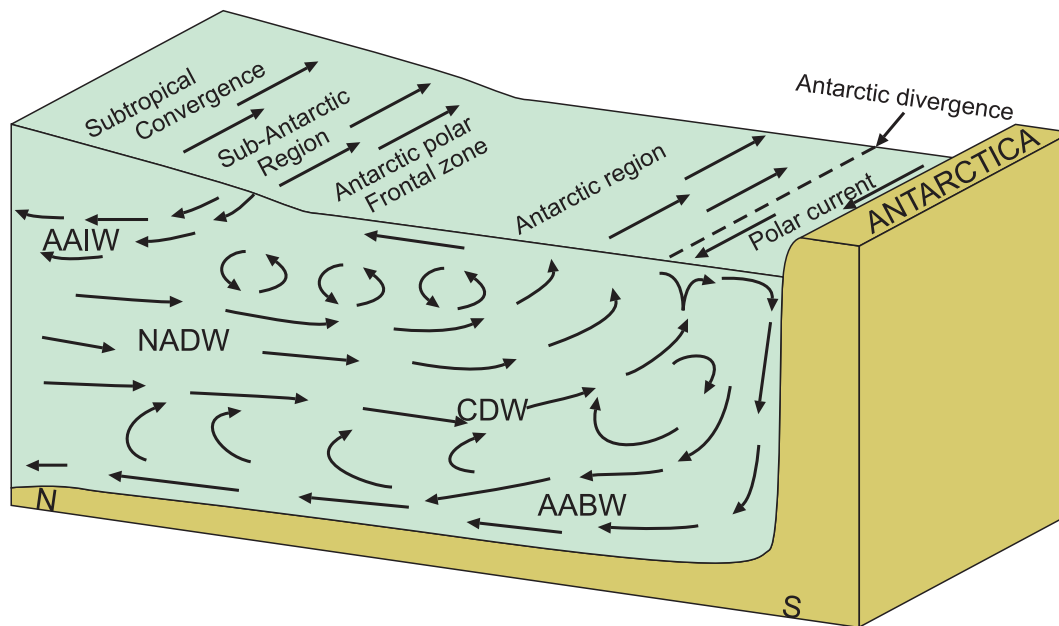


Figure 1.10: A block diagram illustrating the motions of water masses in the Southern Ocean south of about 40°S Image adapted from Sverdrup et al. (1942)

Antarctic Bottom Water, AABW

Antarctic Bottom Water is the most common deep water mass in the world's oceans, it is found in all ocean basins and is also the densest water mass, so is often the bottom most water mass in the deep ocean basins. Of particular importance to this thesis, AABW is the bottom water for the deep basins of the Indian Ocean.

Upwelling around Antarctica at the Antarctic divergence, caused by Ekman transport forced by the prevailing westerly winds, brings Circumpolar Deep Water (CDW) to the surface. CDW is the resultant of mixing NADW with AABW (Figure 1.10). At the surface, if there is no ice cover, the CDW loses heat and moisture to the dry and cold atmosphere. This effect is enhanced by cold catabatic winds blowing off the Antarctic land mass. The catabatic winds also push sea ice away from the coast, forming costal polynyas. This allows heat to be lost to the atmosphere through conduction and latent heat of freezing. Moving ice away from the coast allows more ice to form which removes freshwater from near the coast and moves it away to lower lati-

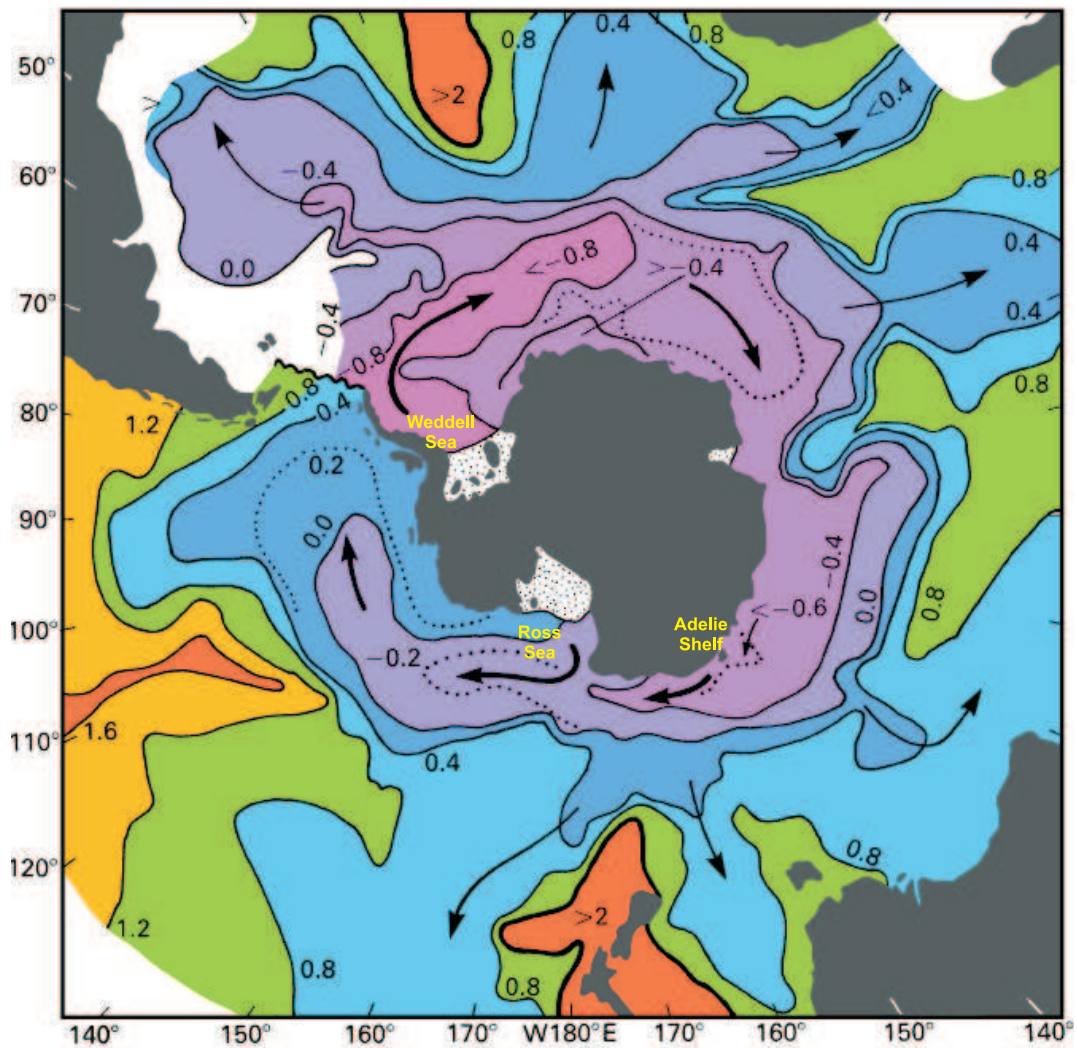


Figure 1.11: A map of sea floor potential temperature in °C, arrows indicate the direction of flow of AABW Image taken from Tomczak and Godfrey (2002), adapted from Gordon (1986)

tudes. The loss of heat from the water, and the increase in salinity, allows the surface water to become dense enough to sink (Gordon, 1982). Downwelling is enhanced by Ekman transport of surface water towards the coast caused by the westward flow of the Polar Current (Figure 1.10). As the surface water sinks down the continental rise of Antarctica it mixes with the overlying CDW to become a much thicker layer of AABW (Warren, 1981), which then moves away from Antarctica, filling the deep ocean basins (Figure 1.11).

AABW formation is limited to discrete regions around the coast of Antarctica. These are in the Weddell Sea, Ross Sea and from under the Adelie Ice Shelf. The Scotia Ridge at $\sim 69^\circ\text{W}$ has a average sill depth of 2000 m (3000 m is the deepest water can pass through), this acts as a barrier to AABW circulating Antarctica. Thus bottom water formed under the Adelie Shelf and in the Ross Sea cannot reach the Atlantic or southwest Indian Basins which are therefore only subject to bottom water derived from the Weddell Sea.

The amount of deep water formation in the Weddell Sea is not thought to be constant Gordon (1982); Visbeck et al. (2001). The amount of AABW formed is dependent on a range of near and far field controls. Within the Weddell Sea the large changes in the amount of convection to the bottom are dictated by the presence or absence of a large open ocean polynya, as was the case from 1974–1976 Colling et al. (2001). When an open ocean polynya is present the large area of open water allows upwelled CDW to loose heat to the atmosphere allowing it to sink and mix into AABW. The cooling effect on upwelled CDW, of and open ocean polynya, will also increase the formation of deep water over the continental margin as it will supply denser water to the costal polynyas which is then further densified, via heat loss and the exclusion of salt during sea ice formation. The amount upwelled water is densified is controlled by the amount of sea ice formed. Sea ice formation around the Antarctic margin is strongly linked to wind speed, as catabatic winds blow ice away from the land allowing more ice to form (Parish, 1988). These local effects on the amount of AABW formation also have far field consequences. Increases in the density of the AABW, produced by extra cooling because of an open ocean polynya or increased salinity by increased sea ice production, has the effect of increasing the penetration of AABW north into the world’s oceans (Stossel et al., 1998).

The rate of AABW formation is also influenced from outside the Southern Ocean. There are two main ‘external’ controls on AABW formation: the wind stress across

the Drake Passage; and the strength of NADW formation (Brix and Gerdes, 2003). An increase in NADW formation will translate into the Southern Ocean as a smaller meridional density gradient across the Antarctic Circumpolar Current as NADW mixes with AABW to form CDW. A decreased density contrast across the ACC will have the effect of weakening it and the Antarctic Divergence through lessened Ekman transport. Thus less CDW is supplied to the continental shelf, limiting AABW formation. A weakened ACC will also have the effect of reducing the strength of the Weddell Sea gyre which will lower the pycnocline, inhibiting further deep water formation Marshall and Schott (1999).

An increase in wind speed has the similar effect as, through Ekman transport, surface water is ‘pumped’ into the South Atlantic and eventually works its way up into the North Atlantic where it enhances deep water production, and hence through the route described above weakens AABW formation. This indirect forcing, however, takes a long (1000s of years) time to happen, and meanwhile the increased wind stress strengthens the ACC which intensifies AABW formation (Brix and Gerdes, 2003). This scenario requires strengthening and weakening of NADW and AABW to be in phase, and rather the opposite is observed in records of temperature from ice cores (Broecker, 1998). It is therefore unlikely that the primary driver of change in AABW formation is the changes in wind stress across the Drake Passage. It is also possible that the mechanism by which heat is oscillated between hemispheres (Stocker, 1998) does not directly involve the formation of AABW rather the Southern hemisphere contribution to the “bi-polar see saw” is the formation of AAIW (Marshall and Schott, 1999).

Antarctic Intermediate Water, AAIW

This is a water mass derived in the Southern Ocean which, like AABW, can be found in all of the major ocean basins, predominantly in their southern portions.

The depth to which AAIW can penetrate is, however, rather limited as it is both less saline and less cold than AABW.

AAIW is formed at the Antarctic Polar Frontal Zone (Figure 1.10) from CDW upwelled at the Antarctic divergence to the south. As surface CDW moves to the north through Ekman transport, freshwater is added from melting sea ice (and snow that fell on this sea ice). The water is also cooled through heat loss to the atmosphere. When this cooled and freshened water reaches as far north as the Antarctic Polar Frontal Zone it encounters warmer water from the north. Because the northward moving water is colder and denser it sinks beneath the warmer ‘Sub-Antarctic’ water to form AAIW.

1.3 The role of ocean circulation in heat transport

The surface of the Earth is warmed by radiative heat from the Sun. This solar heating is, however, not distributed evenly over the planet. As the planet is spherical, heat arriving at the equator is incident on a smaller area than near the poles which are angled away from the Sun so receive less energy per unit area. As the planet is warm with respect to the space around it, it loses heat as a function of its temperature. The discrepancy between the incoming and outgoing radiation is shown in Figure 1.12. The tropics receive more heat from the Sun than they radiate back out to space and the polar regions are a net exporter of heat from the planet (Bryden and Imawaki, 2001). The amount of geothermal heating ($\sim 50 \text{ mWm}^{-1}$ on abyssal plains and up to $\sim 200 \text{ mWm}^{-1}$ at mid ocean ridges (Sclater et al., 1980)) is insignificant to the amount received from the Sun, which is $>300 \text{ Wm}^{-2}$ at the equator (Stephens et al., 1981).

The excess heat from the tropics must somehow be transported towards the poles for there to be a net export of heat to space in these regions. This transport occurs as circulation within the atmosphere and oceans (Figure 1.13). Although the

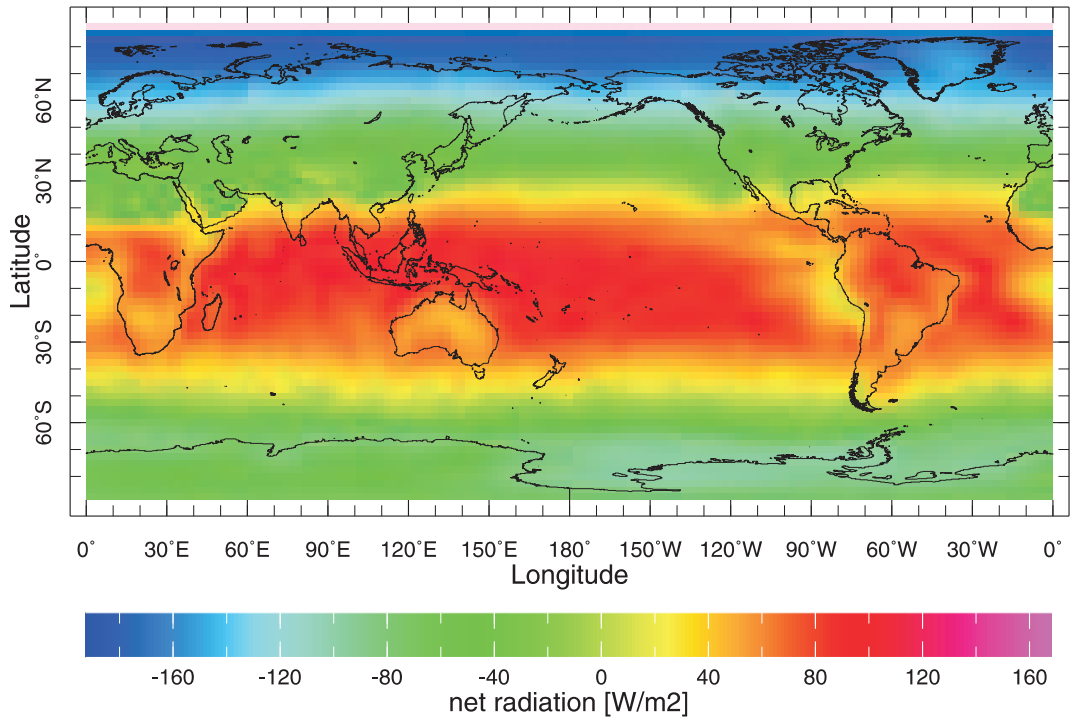


Figure 1.12: . Global net radiation balance averaged for October. From data collected for the NASA ERBE: Earth Radiation Budget Experiment, in the LDEO/IRI Data Library < <http://iridl.ldeo.columbia.edu/> >.

atmosphere has a much shorter overturning time than the oceans, and can therefore transport heat energy more quickly than the oceans, the total meridional heat transport by each is approximately the same (Figure 1.13). The oceans although circulating more slowly, are able to transport as much heat as the atmosphere because water has a much higher heat capacity ($4186 \text{ Jkg}^{-1}\text{K}^{-1}$ for water at 15°C (Osborne et al., 1937) vs. $1005\text{-}1030 \text{ Jkg}^{-1}\text{K}^{-1}$ for dry-wet air) and can thus store and transport more heat.

Heat transport by the oceans has been assessed quantitatively by Ganachaud and Wunsch (2000) (Figure 1.14). In summary, heating of surface waters in the tropics, particularly in the Pacific, creates warm buoyant waters. Surface circulation takes this water via the Indonesian Throughflow, into the Indian Ocean and then exiting, in packets of water spun off the Agulhas retroflexion at the southern tip of Africa, into the Atlantic (Gordon, 1985). A greater proportion – often ignored – of warm

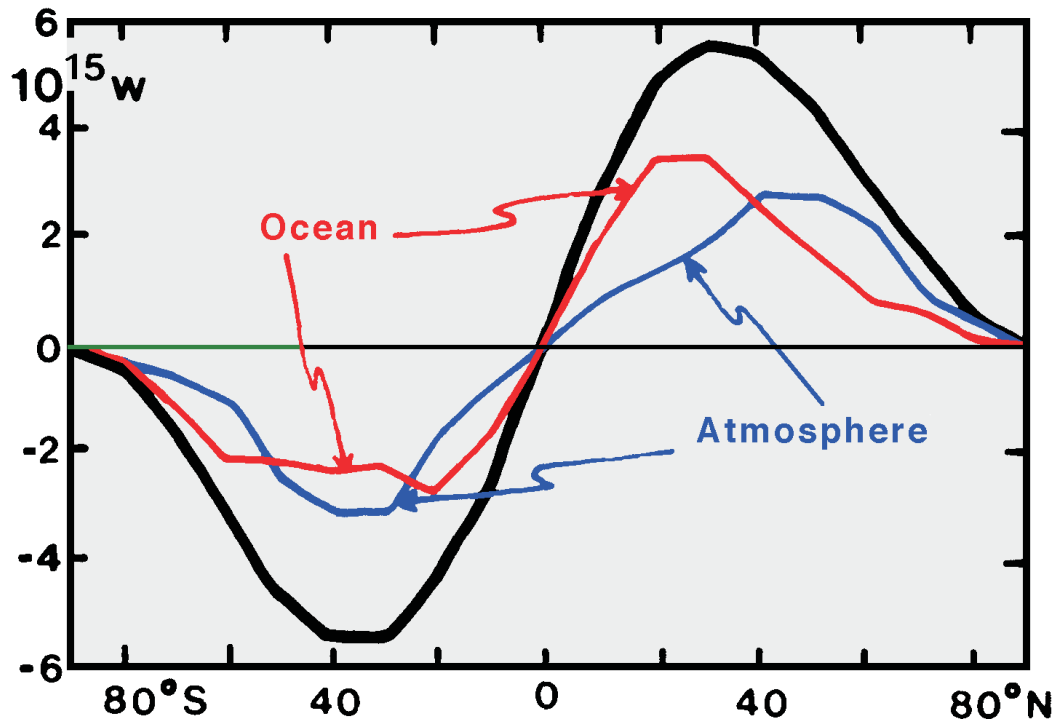


Figure 1.13: . “Annual mean meridional heat flux in the ocean and the atmosphere (thin lines), and total annual mean meridional heat flux (heavy line)”. Image from Tomczak and Godfrey (2002), adapted from Carissimo et al. (1985).

surface water from the Pacific is transferred directly to the Atlantic through the Drake Passage (Broecker, 1991). This warm water makes its way northwards in the Atlantic gaining more heat as it passes through the tropics, before being entrained into the Gulf Stream which transports the water to high latitudes where heat is lost to the atmosphere, and the water sinks as NADW (Section 1.2.3). Surface waters are replenished by gradual upwelling of deep waters initially subducted to depth at high latitudes (NADW, Section 1.2.3 and AABW, Section 1.2.3). This upwelling of deep water to the surface where it is warmed and then returned to high latitudes to form more deep water, completes the “Great Ocean Conveyor” (Broecker, 1991) that transports heat around the planet.

The image originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.14: . A map of the global transport of heat by the oceans and exchange with the atmosphere. “The resulting heat (or ‘enthalpy’, where the net mass flux is non-zero) transports are indicated by the arrows and red numbers (positive northward/eastward). The white box at the tail end of each arrow is the one-standard-deviation uncertainty. Between sections, oceanatmosphere heat transfers are indicated by the zonal length of the coloured boxes (blue for ocean cooling; red for ocean heating), with the length of the white box inside indicating the uncertainty.” Image and caption from Ganachaud and Wunsch (2000).

1.4 The role of ocean circulation in the carbon cycle

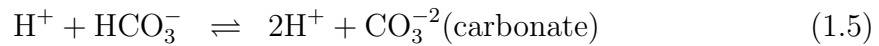
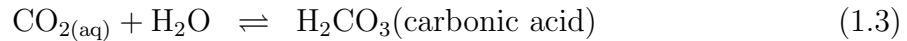
The oceans can not only store a vast quantity of heat, but they can also store and transport large quantities of carbon (Keeling and Heimann, 1986; Broecker and Peng, 1992). This is important in regulating the atmospheric concentration of CO_2 , an important greenhouse gas.

CO_2 from the atmosphere can exchange with the ocean at the air-sea interface, gaseous CO_2 dissolves in seawater to become aqueous CO_2 (Equation 1.2). Once dissolved $\text{CO}_{2(aq)}$ reacts with water to form carbonic acid (Equation 1.3) which then

The image originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.15: . The relative proportions, α , of dissolved inorganic carbon at varying pH. Image from Girard (2005).

disassociates to bicarbonate and carbonate ions (Equations 1.4 and 1.5 Bigg (2003)).



The relative abundances of the different species ($\text{CO}_{2(aq)}$, H_2CO_3 , HCO_3^{-1} , and CO_3^{-2}) that make up dissolved inorganic carbon (DIC) in seawater is dependent on a variety of variables. The pH of the water in which the CO_2 is dissolved is the primary control on speciation. At high pH the carbonate ion is the dominant species and at low pH $\text{CO}_{2(aq)}$ is more dominant, with the bicarbonate species being more abundant at intermediate pHs. Because the pH of the oceans is 8.2 ± 0.3 (Raven et al., 2005) the dominant species is HCO_3^{-1} representing approximately 91% of DIC, 8% is in the CO_3^{-2} form, leaving only 1% as $\text{CO}_{2(aq)}$ and H_2CO_3 (Raven et al., 2005).

Because only the $\text{CO}_{2(aq)}$ can exchange with the atmosphere, and this species makes up only a tiny proportion of the carbon in the ocean, the oceans can hold an enormous quantity of carbon. The amount of carbon stored in the ocean is approximately 50 times that in the atmosphere (Figure 1.16). While the amount of carbon stored in rocks is 1500 times greater again, the timescales on which carbon

The image originally presented here cannot be made freely available via ORA for copyright reasons.

Figure 1.16: A box model of the pre-industrial Holocene carbon cycle. Reservoirs thought not to effect climate on glacial-interglacial timescales are omitted. Clathrate release is also not shown due to the large uncertainties associated with rates of release. The sizes of reservoir are shown in Pg C or 10^{15} g carbon. Image from (Sigman and Boyle, 2000).

can be exchanged between such rocks and the atmosphere and oceans is too long to effect deviations on glacial-interglacial timescales.

Changes in ocean circulation can alter the exchange of carbon between the atmosphere and the oceans, thus changing the amount of CO_2 in the atmosphere and hence radiative balance. This has been demonstrated by simple box models (Siegenthaler and Wenk, 1984; Sarmiento and Toggweiler, 1984). Specifically, the stratification between the surface and deep ocean in the Antarctic Zone of the Southern Ocean controls the “leak” of CO_2 from the deep ocean to the atmosphere. In the modern ocean, CO_2 is released to the atmosphere when deep water upwells in the Southern Ocean. A reduction of the formation of Antarctic Bottom Water (Michel et al., 1995) could cause a reduction of this upwelling and increased stratification. This stratification would reduce the exchange of CO_2 from the deep ocean through the upper ocean to the atmosphere, thus reducing atmospheric CO_2 . Coupled with the increased solubility of CO_2 in sea water at cooler temperatures, and increased bio-

logical export production, changes in ocean circulation may have been responsible for lower CO₂ during Glacial times (Francois et al., 1997)

1.5 The Indian Ocean

The Indian Ocean is the smallest of the world's oceans, covering only 48×10^6 km² (Tomczak and Godfrey, 2002). This thesis deals largely with the southwestern Indian Ocean which is isolated below ~ 3000 m from the eastern Indian Ocean by the Central Indian Ridge. The southwestern Indian Ocean is divided up into smaller basins separated by a series of ridges (Figure 1.17).

1.5.1 Indian Ocean hydrography

Bottom water in the Indian Ocean is AABW which enters the eastern basins through the Australian-Antarctic Discordance. This water travels northwards constrained by the Ninety-East Ridge, which it eventually overflows filling the Central Indian Basin (Wyrtki, 1971). The western basins of the Indian Ocean (Figure 1.17) are completely separated from the rest of the Indian Ocean at depth and are filled from a separate source of AABW. Here AABW overflows the Southwest Indian Ridge, through a series of fractures at roughly 55°E, from the Southern Ocean. Once in the Madagascar Basin AABW forms a geostrophically constrained boundary current which hugs the Southwest Indian and Madagascar Ridges (Swallow and Pollard, 1988; Toole and Warren, 1993). This western boundary current transports AABW northward through the Madagascar and Mascarene Basins, and out through the Amirante Passage into the Somali Basin in the northern Indian Ocean. As this water mass moves northwards it mixes with the overlying water, becoming less dense and gradually upwelling, eventually to the surface. Overlying AABW in the south of the western Indian Ocean is a water mass derived from NADW, evident in a

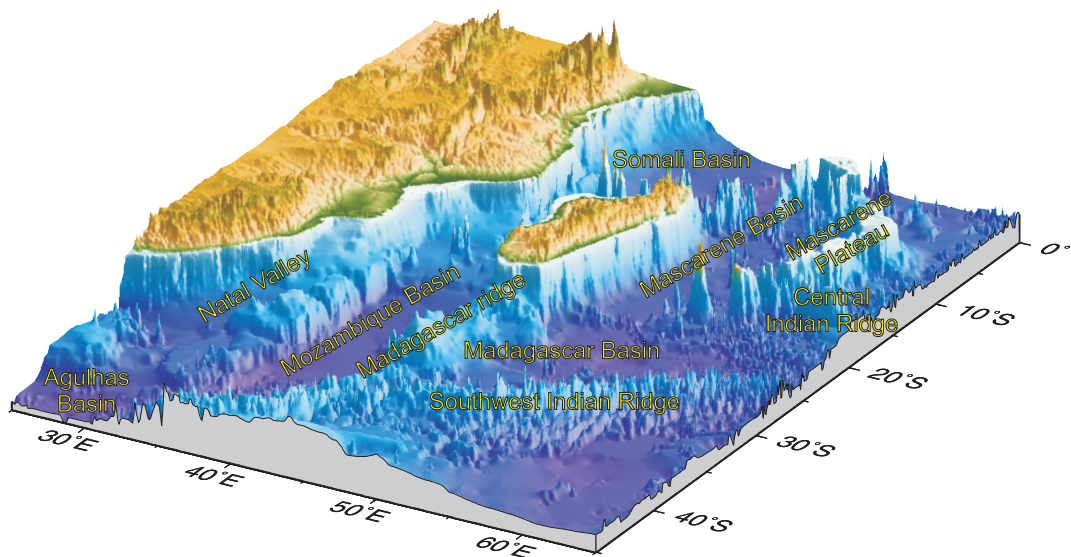


Figure 1.17: The Bathymetry of the southwestern Indian Ocean showing the major basins and ridges.

salinity maximum at about 3000 m (Figures 3.3 and 5.2). This “NADW” is less constrained by bathymetry, and enters the Indian Ocean as a geostrophic boundary current around the tip of Africa. The boundary current of “NADW” snakes through the Natal Valley and the Mozambique Basin before overflowing the Madagascar and Southwest Indian Ridges and entering the Madagascar Basin. Like AABW, this “NADW” forms a boundary current flowing northwards along the Madagascar ridge mixing gradually with the surrounding water (Toole and Warren, 1993). In the north of the western Indian Ocean this “NADW” water mass is replaced by a much older, nutrient enriched, North Indian Deep Water (NIDW) this is essentially still NADW derived water but it has mixed with AABW from the Eastern Basins and is moving south from the Somali Basin in the north (Sirinvasan et al., 2004). Overlying these water masses is typically AAIW from the Southern Ocean and, to the north, warmer waters formed within the Indian Ocean such as Red Sea Water (Gründlingh, 1985) or Persian Gulf Water, and water from the Pacific that entered through the Indonesian Throughflow.

1.6 Uranium Series Nuclides

Uranium is the 92nd element of the periodic table, and is widely considered the last of the “naturally occurring” elements. Transuranic elements with more protons than uranium do exist in nature, for instance, in supernovae and on Earth in trace quantities in uranium rich ores, where neutron bombardment produces Np, Pu, Am, and other transuranic elements. But for the purpose of this thesis and most U-series studies the transuranic elements can be assumed to be extinct. Uranium forms the parent isotope of two of the four possible alpha decay chains the $4n+2$ and the $4n+3$ series (Figure 1.18 and Table 1.1). ^{238}U decays to ^{206}Pb via the emission of 8 α particles ($^4\text{He}^{2+}$), while ^{235}U decays to ^{207}Pb via the emission of 7 α particles.

The ratio of ^{238}U to ^{235}U is a function of the ratio at which they were originally produced in an extra solar supernova prior to the formation of the solar system, and the relative decay of the two isotopes over time. Currently the $^{238}\text{U}/^{235}\text{U}$ in all natural samples is 137.88 (Stirling et al., 2005). One notable exception to this is the natural reactor at Oklo, Gabon¹. This constant ratio of 137.88 is the basis of internal standardisation of mass bias of isotopic measurements (Section 2.5.1 and equations 2.22 and 2.23), and enables direct comparison between isotope of the two different decay chains.

1.6.1 Radioactive decay

Although the decay of a radioactive parent isotope to its daughter isotope is a random process, the probability of a decay occurring in a specified time can be represented

¹In 1972 uranium ore from a mine in Gabon, western Africa, was found to have a depletion of ^{235}U (Bodu et al., 1972). This depletion is due to the ore body having a sufficiently high U concentration that sustained nuclear chain reactions took place. This occurred in the proterozoic 1.8 billion years ago, when the natural $^{238}\text{U}/^{235}\text{U}$ was higher than today. Spontaneous fission of ^{235}U produced a high enough neutron flux to sustain a fission chain reaction of ^{235}U thus reducing the $^{238}\text{U}/^{235}\text{U}$ of the ore body. The high neutron flux also ‘bred’ more nuclear fuel by bombarding ^{238}U with neutrons to produce ^{239}Pu which decayed to ^{235}U providing more fuel, sustaining the reaction.

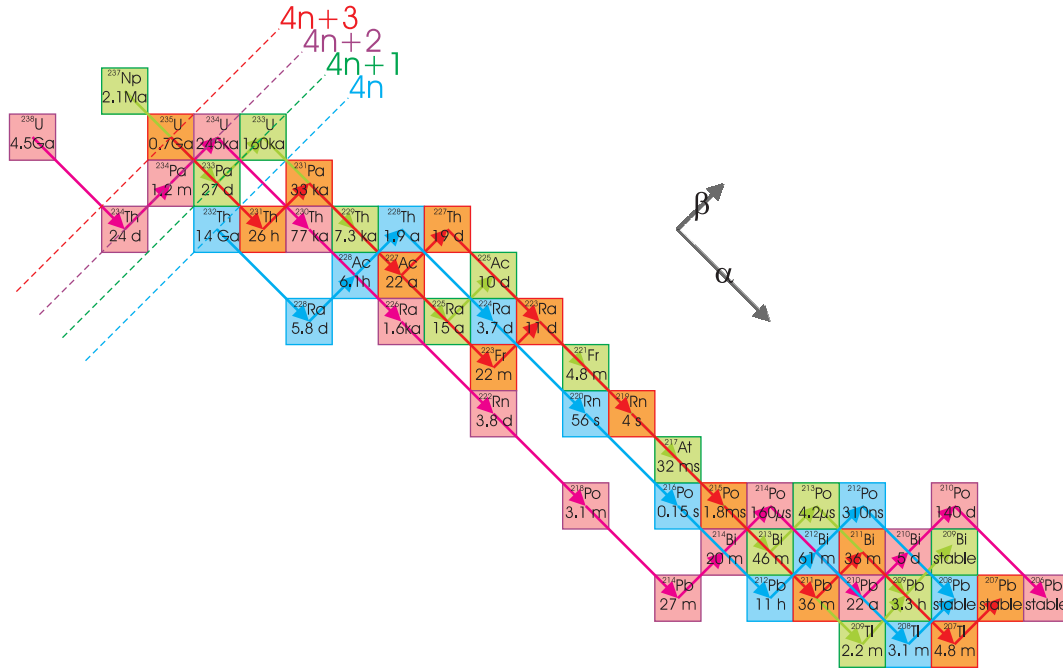


Figure 1.18: Simplified decay series for the 4 α emitting decay chains, with isotopes of mass $4n$ (^{232}Th series), $4n+1$ (^{237}Np series), $4n+2$ (^{238}U series), and $4n+3$ (^{235}U series). In this configuration the number of neutrons of nuclides increases from right to left, and the number of protons increases from bottom to top. The decay series shown are greatly simplified: there are isotopes heavier than the parent isotopes shown that add to each decay chain but these are considered extinct, and are therefore irrelevant to the study of natural systems; there are also other ‘branching’ decays similar to ^{227}Ac which are not shown because the daughters have very short half lives and decay to the same end daughter product. Decay series and half lives adapted from Argonne National Laboratory (2005a,b)

as a “decay constant” (Rutherford and Soddy, 1902). Thus the rate of decay is dependent on the number of atoms of the parent isotope and the decay constant.

$$-\frac{dN}{dt} = \lambda N \quad (1.6)$$

Rearranging and integrating with respect to N and t this becomes:

$$-\ln N = \lambda t + C \quad (1.7)$$

238U decay chain				235U decay chain			
isotope	decay mode	half-life	ref	isotope	decay mode	half-life	ref
²³⁸ U	α	4.4683 $\pm$ 0.0048	Ga 1	²³⁵ U	α	0.70381 $\pm$ 0.00096	Ga 1
²³⁴ Th	β	24.1	days 2	²³¹ Th	β	1.063	days 2
²³⁴ Pa	β	6.69	hours 2	²³¹ Pa	α	32.760 $\pm$ 0.220	ka 5
²³⁴ U	α	245.250 $\pm$ 0.490	ka 3	²²⁷ Ac	α, β	21.77 $\pm$ 0.02	a 4
²³⁰ Th	α	75.690 $\pm$ 0.230	ka 3	²²⁷ Th	α	18.72	days 2
²²⁶ Ra	α	1.599 $\pm$ 0.004	ka 4	²²³ Fr	α, β	22	min 2
²²² Rn	α	3.823 $\pm$ 0.004	days 4	²²³ Ra	α	11.435	days 2
²¹⁸ Po	α, β	3.04	min 2	²¹⁹ At	α, β	50	s 2
²¹⁸ At	α, β	1.6	s 2	²¹⁹ Rn	α	3.96	s 2
²¹⁸ Rn	α	35	ms 2	²¹⁵ Bi	β	7.7	min 2
²¹⁴ Pb	β	26.9	min 2	²¹⁵ Po	α, β	1.78	ms 2
²¹⁴ Bi	α, β	19.7	min 2	²¹⁵ At	α	0.1	ms 2
²¹⁴ Po	α	0.1637	ms 2	²¹¹ Pb	β	36.1	min 2
²¹⁰ Tl	β	1.3	min 2	²¹¹ Bi	α, β	2.14	min 2
²¹⁰ Pb	α, β	22.6 $\pm$ 0.1	a 4	²¹¹ Po	α	0.516	sec 2
²¹⁰ Bi	α, β	5.01	days 2	²⁰⁷ Tl	β	4.77	min 2
²¹⁰ Po	α	138.4 $\pm$ 0.1	days 4	²⁰⁷ Pb		stable	
²⁰⁶ Hg	β	8.2	min 2				
²⁰⁶ Tl	β	4.2	min 2				
²⁰⁶ Pb		stable					

Table 1.1: Decay modes and half-lives of all the nuclides in the two “uranium” decay chains, 4n+2 and 4n+3. Half-lives are from (1) Jaffey et al. (1971), (2) Lide (1998), (3) Cheng et al. (2000), (4) Holden (1990), and (5) Robert et al. (1969). Adapted from Bourdon et al. (2003)

and with the initial condition that the number of atoms at $t = 0$ is N_0 ,

$$C = -\ln N_0 \quad (1.8)$$

thus,

$$\begin{aligned}
-\ln N &= \lambda t - \ln N_0 \\
\ln \frac{N}{N_0} &= -\lambda t \\
\frac{N}{N_0} &= e^{-\lambda t} \\
N &= N_0 e^{-\lambda t} \quad (1.9)
\end{aligned}$$

giving the number of parent atoms remaining, from an original amount N_0 at $t = 0$, at time t . The number of daughters produced, D , is simply:

$$D = N_0 - N$$

thus,

$$D = N_0(1 - e^{-\lambda t}). \quad (1.10)$$

The rate of decay of an isotope is often referred to by a half-life, $t_{1/2}$. This is the time taken for half of the original atoms to decay. From equations 1.9:

$$\begin{aligned} \frac{N}{N_0} &= \frac{1}{2} \\ \ln \frac{1}{2} &= -\lambda t_{1/2} \\ \ln 2 &= \lambda t_{1/2} \\ t_{1/2} &= \frac{\ln 2}{\lambda} \end{aligned} \quad (1.11)$$

It is often more convenient to consider the activity of a nuclide in a decay chain, rather than the actual number of atoms. The activity, A , is simply the total number of ‘decays’, or disintegrations, per unit time and is defined as:

$$A = \lambda N. \quad (1.12)$$

and is given as units of disintegrations per minute (d.p.m.). Activities are used, as early measurements of radioactive relents was by means of counting the decay emissions, via alpha or gamma spectrometry rather than measuring directly the number of atoms of an isotope as is the case in mass spectrometry. The use of activities simplifies comparisons between isotopes within the U-series decay chains, as the activities of all of the isotopes in a decay chain should all be the same if they are in secular equilibrium (Section 1.6.3).

1.6.2 Radioactive decay series

In a decay series in which N_1 decays to N_2 which in turn decays to N_3 . The rates of decay for N_1 and N_2 are given from Equation 1.6 as:

$$-\frac{dN_1}{dt} = \lambda_1 N_1 \quad (1.13)$$

$$-\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad (1.14)$$

Substituting the number of atoms of N_1 remaining at time t , from Equation 1.9, into Equation 1.14 gives:

$$\frac{dN_2}{dt} + \lambda_2 N_2 - \lambda_1 N_1^0 e^{-\lambda_1 t} = 0 \quad (1.15)$$

Solving Equation 1.15 (Bateman, 1910; Friedlander and Kennedy, 1995) where the solution is assumed to be of the form $N_2 = uv$ where u and v are functions of t .

Differentiating $N_2 = uv$ we get

$$\frac{dN_2}{dt} = u \frac{dv}{dt} + v \frac{du}{dt}$$

Substituting into Equation 1.15

$$u \frac{dv}{dt} + v \frac{du}{dt} + \lambda_2 uv - \lambda_1 N_1^0 e^{-\lambda_1 t} = 0$$

or, rearranging to

$$u \left(\frac{dv}{dt} + \lambda_2 v \right) + v \frac{du}{dt} - \lambda_1 N_1^0 e^{-\lambda_1 t} = 0 \quad (1.16)$$

If we arbitrarily choose a value of v such that

$$\begin{aligned}
 \frac{dv}{dt} + \lambda_2 v &= 0 \\
 \frac{dv}{v} &= -\lambda_2 dt \\
 \ln v &= -\lambda_2 t \\
 v &= e^{-\lambda_2 t}
 \end{aligned} \tag{1.17}$$

Substituting Equation 1.17 into Equation 1.16, when $\frac{dv}{dt} + \lambda_2 v = 0$ gives

$$\begin{aligned}
 e^{-\lambda_2 t} \frac{du}{dt} - \lambda_1 N_1^0 e^{-\lambda_1 t} &= 0 \\
 \frac{du}{dt} - \frac{\lambda_1 N_1^0 e^{-\lambda_1 t}}{e^{-\lambda_2 t}} &= 0 \\
 du &= \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t} dt
 \end{aligned}$$

Integrating with respect to t , for u

$$u = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{(\lambda_2 - \lambda_1)t} + C \tag{1.18}$$

Substituting Equations 1.17 and 1.18 into $N_2 = uv$

$$\begin{aligned}
 N_2 &= \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{(\lambda_2 - \lambda_1)t} \cdot e^{-\lambda_2 t} + C e^{-\lambda_2 t} \\
 N_2 &= \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t} + C e^{-\lambda_2 t}
 \end{aligned} \tag{1.19}$$

From Equation 1.19, when $t = 0$, we can assume $N_2 = N_2^0$ thus

$$C = N_2^0 - \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \tag{1.20}$$

Substituting Equation 1.20 into Equation 1.19 we get

$$\begin{aligned} N_2 &= \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t} + \left(N_2^0 - \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \right) e^{-\lambda_2 t} \\ N_2 &= \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \end{aligned} \quad (1.21)$$

The first term in Equation 1.21 is ingrowth of N_2 from the N_1 parent accounting for decay of the daughter N_2 . The last term in Equation 1.21 is representative of any atoms of N_2 remaining from those initially in the system. If the assumption of no initial N_2 is made then Equation 1.21 simplifies to:

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (1.22)$$

1.6.3 Secular equilibrium

Where the decay constants of N_1 and N_2 are sufficiently different, for example $\lambda_1 < \lambda_2$, further simplifications can be made. If $\lambda_1 < \lambda_2$ $e^{-\lambda_2 t}$ will tend to zero before $e^{-\lambda_1 t}$ as t increases, thus:

$$N_2 \approx \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t} \quad (1.23)$$

and substituting from Equation 1.9,

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2 - \lambda_1} = \text{constant} \quad (1.24)$$

For a decay chain where the parent isotope has a significantly longer half-life, than the other isotopes in the chain, i.e. $\lambda_1 \ll \lambda_2$ and the amount of parent isotope does not decrease significantly during many half-lives of the daughter then

$$\frac{N_2}{N_1} = \frac{\lambda_1}{\lambda_2} \text{ or } \lambda_1 N_1 = \lambda_2 N_2 \quad (1.25)$$

This is known as secular equilibrium, and the activities of all the nuclides in the chain are the same.

$$A_1 = A_2 \quad (1.26)$$

From Equation 1.21, where $N_2^0 = 0$ at $t = 0$ and $\lambda_1 \ll \lambda_2$, thus $e^{-\lambda_2 t} \approx 1$, and $\lambda_1 N_1^0$ can be replaced with $\mathbf{R}$, where $\mathbf{R}$ is the production rate of N_2 atoms, the growth of N_2 can be written

$$N_2 = \frac{\mathbf{R}}{\lambda_2}(1 - e^{-\lambda_2 t}) \quad (1.27)$$

From Equation 1.25 at secular equilibrium $\mathbf{R}/\lambda_2$ approaches a maximum thus Equation 1.27 can be rewritten

$$N_2 = (N_2)_{\max}(1 - e^{-\lambda_2 t}) \quad (1.28)$$

Thus after one half-life of the daughter nuclide the amount of daughter will be half of the maximum possible at secular equilibrium. After two half-lives 75% of the total will be reached, and after: three it will be 87.5%; 4 it will be 93.8%; 5 it will be 96.9% and so on as the decay chain moves towards secular equilibrium. Thus for decay chains in which the parent is the significantly the longest lived isotope – as is the case for both U series and the Th series decay chains – it will be the half-lives of the daughters that determine how long it takes for the system to reach secular equilibrium.

1.6.4 Uranium series nuclides in the ocean

The three principle elements of interest in this study are uranium, thorium, and protactinium. It is the differences in chemical behaviour between these three elements that provide the basis for their use as oceanographic proxies.

Uranium

Uranium is commonly found in natural systems in one of two valence states: the reduced form U(IV), or the oxidised form U(VI). Because the oceans are predominantly oxic and carbonate rich, uranium is found in the U(VI) form as either a $\text{UO}_2(\text{CO}_3)_2^{2-}$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$ uranyl-carbonate ion (dominantly $\text{UO}_2(\text{CO}_3)_3^{4-}$ in the ocean, Langmuir (1978)), both of which are very soluble. This high solubility means that uranium behaves conservatively in seawater, its concentration only varying with salinity (Figure 1.19), i.e. only the addition or removal of water effects its concentration. The concentration of ^{238}U being approximately 3.21 ppb at 35‰ salinity (Chen et al., 1986).

In reducing anoxic conditions U can also be found in the reduced uranous U(IV) form where it is found as UO_2 (Klinkhammer and Palmer, 1991). UO_2 is insoluble, thus its formation is the major sink of U from the ocean. Although reduction of U(VI) to U(IV) occurs under anoxic conditions, anoxic deep-water is dominated by the U(VI) form. This is due to a kinetic limitation of the reduction process (Anderson et al., 1989). Authigenic uranium can form in anoxic sediments where oxygen fugacity is low enough for U(VI) to be reduced to U(IV). The insolubility of UO_2 lowers pore water U concentration, initiating a concentration gradient which draws U into the sediment. In surface waters UO_2 can be found, sorbed onto the surface of particles due to localised low oxygen concentration around organic matter (Anderson, 1982).

The residence time of the two parent isotopes, ^{238}U and ^{235}U , in the ocean is long, on the order of 400 ka. The residence time of ^{234}U is somewhat shorter at approximately 190 ka, because the shorter half-life (Table 1.1) provides an additional removal term from the oceans (Henderson and Anderson, 2003). It is the long residence time of uranium with respect to the mixing time of the oceans (1500-2000 years) that ensures that the concentration and isotopic composition of uranium in seawater is constant over all the world's oceans and has remained constant over

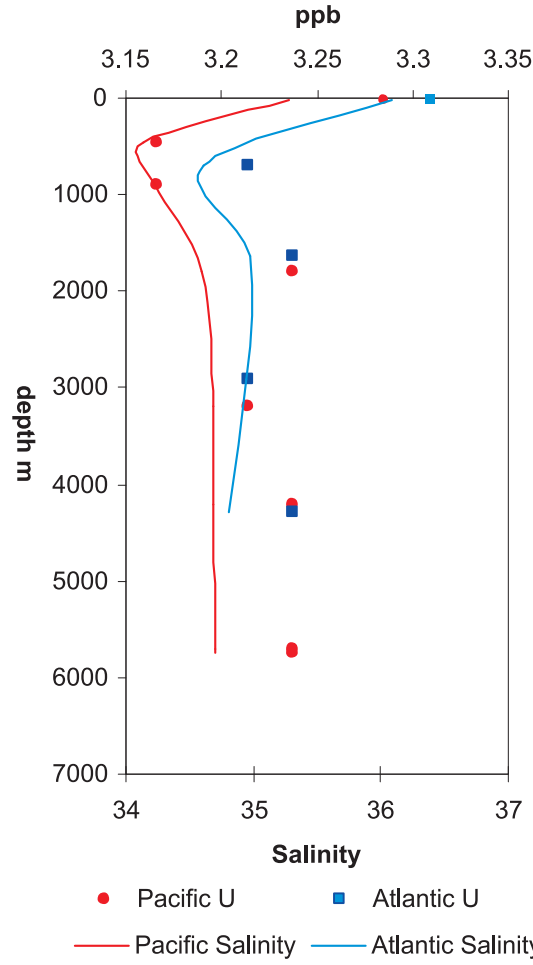


Figure 1.19: The uranium and salinity concentration profiles from two profiles, from the Pacific and the Atlantic oceans, $31^{\circ} 4' \text{ N}$, $159^{\circ} 1' \text{ W}$ and $7^{\circ} 44' \text{ N}$, $40^{\circ} 43' \text{ W}$ respectively. Data is from Chen et al. (1986)

timescales shorter than the 10^4 a. Changes in the export flux of U from the oceans due to changes in the amount of anoxic sediments available for authigenic U formation are not thought to be large enough to alter the U concentration of the oceans on glacial-interglacial timescales (Rosenthal et al., 1995; Morford and Emerson, 1999).

If seawater were in secular equilibrium with respect to uranium isotopes ^{238}U and ^{234}U (of the $4n+2$ series) the activity ratio ($^{234}\text{U}/^{238}\text{U}$) would be 1. The actual value for ($^{234}\text{U}/^{238}\text{U}$) in seawater is 1.146 (Robinson et al., 2004a) equivalent to a $\delta^{234}\text{U}$ 146‰ (where $\delta^{234}\text{U} = ((^{234}\text{U}/^{238}\text{U})_{\text{sample}} - 1) \times 1000$). This deviation from secular equilibrium is due to the addition to the ocean of ^{234}U enriched water, predominantly

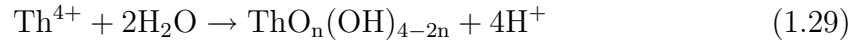
in river runoff. ^{234}U is preferentially weathered over ^{238}U and ^{235}U due to the process of alpha recoil (Moore, 1967).

Alpha recoil occurs during radioactive decay. In the case of ^{234}U , ^{238}U decays to ^{234}Th via emission of an alpha particle. The ^{234}Th decays rapidly through beta emission to a short lived isotope, ^{234}Pa , and then to ^{234}U (Figure 1.18). Because the alpha particle ejected from the nucleus has a mass of 4 amu and is energetic, the daughter nuclide is propelled in the opposite direction. This ‘recoil’ causes significant damage to the crystal lattice in which the U atom was held, and if the U atom was close enough to the edge of a mineral the daughter can be ejected from the mineral. The length scale of alpha recoil is 10^{-8} to 10^{-7} m (Kigoshi, 1971; Thompson and Goldstein, 2005) and as such ^{234}Th is only ejected if the parent U atom is very close to the mineral edge. The crystal lattice is, however, damaged by the displacement of the daughter nuclide, which creates a weakness in the mineral which can be later exploited by chemical weathering to preferentially remove ^{234}U from the damaged location in the mineral.

The $\delta^{234}\text{U}$ of seawater should be constant spatially due to the long residence times of ^{234}U with respect to the mixing time of the ocean. However, on glacial-interglacial timescales large changes in the fluxes of uranium weathered from continental margins during deglaciation has been shown to have the possibility of altering the global $\delta^{234}\text{U}$ of seawater (Robinson et al., 2004b). And local effects of enclosed basins such as the Black Sea have been shown to have small effects on the $\delta^{234}\text{U}$ of the adjoining seas (Henderson et al., Prep). On the timescales of interest in this thesis, it is reasonable to assume, the uranium composition of seawater is constant within 7‰, which is well within the precision of measurements for ^{231}Pa and ^{230}Th .

Thorium and protactinium

Thorium has only one stable valence state under natural conditions: Th(IV). In a pure aqueous scenario the solubility of Th is very low, the Th^{4+} ion being strongly hydrolysed to form polyhydroxy colloidal complexes.



The solubility of such complexes is strongly dependent on the form of the ThO_2 . Crystalline ThO_2 has been shown to have an exceptionally low solubility of 10^{-15} M, while smaller amorphous colloidal phases produced during dissolution or precipitation have increased solubility of 10^{-8} to 10^{-10} M (Fanghanel and Neck, 2002). Binding of Th(IV) to organic ligands (Guo et al., 1997) also greatly increases the solubility of Th. It should, however, be stated that the solubility, although increased by the presence of colloidal phases and organic ligands, is always very low in the oceans (^{230}Th having a residence time of ~ 20 years (Henderson and Anderson, 2003)).

Thorium is strongly sorbed to particle surfaces and, as a result, is rapidly removed from the ocean. Sorption onto particles can be represented as a partition coefficient, K_d ,

$$K_d = \frac{C_p}{C_d} \quad (1.30)$$

where C_p and C_d are the concentrations of the particulate and dissolved portions of the nuclide of interest in the water and on the particles respectively in d.p.m./g for C_p and d.p.m.m $^{-3}$ for C_d . The K_d is dependent on particle type, as demonstrated by laboratory based experiments (Table 1.2) and field studies (Luo and Ku, 1999; Chase et al., 2002). Partition coefficients for field studies typically give higher K_d due to the coating of mineral particles with organic films which have a greater affinity for Th. The K_d has also been shown to be particle concentration-dependent (Honeyman

particle type	$K_{d,Th}$	Ref
SiO ₂	$10^3 - 10^5$	1
CaCO ₃	$10^4 - 10^5$	2,3
Al ₂ O ₃ /clays	$10^{5.6}$	4
FeOOH	$10^{5.1} - 10^{5.8}$	3,5
MnO ₂	$10^{4.4}$	3,6
APS-EPS [†]	10^8	7

Table 1.2: Laboratory measurements of $K_{d,Th}$, following Santschi et al. (2005). [†] APS, Acid polysaccharides and EPS exopolymeric substances References refer to: 1, Roberts and Santschi unpublished data in, Santschi et al. (2005); 2, Cochran (1992); Edwards et al. (1987); 3, Guo and Gueguen (2002); 4, Niven and Moore (1993); 5, Guo and Gueguen (2002); Quigley et al. (1996); 6, Guo and Gueguen (2002); Hunter et al. (1988); and 7, Quigley et al. (2002)

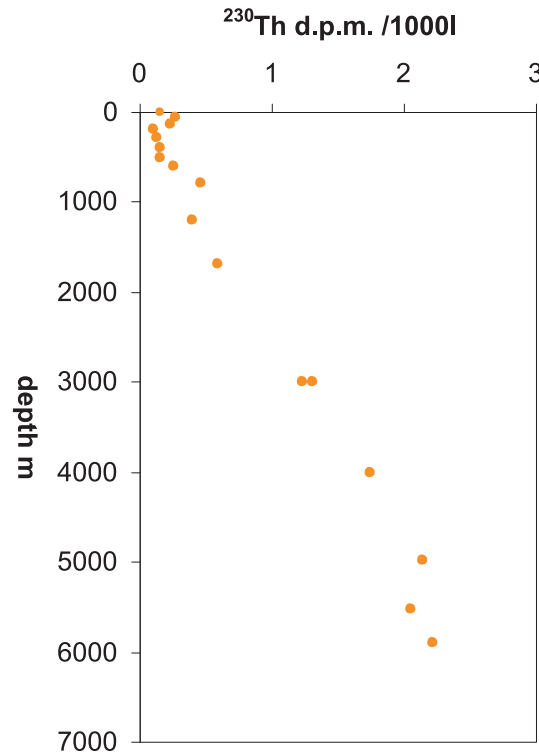


Figure 1.20: A ²³⁰Th concentration profile from the Pacific at 25° 00'N, 169° 55' E, showing the linear concentration increase with depth due to reversible scavenging. data from Nozaki and Nakanishi (1985).

et al., 1998). This is likely to be due to the high particle concentrations having associated high colloidal concentrations which can pass through filters and elevate the ‘dissolved’ concentration.

Scavenging of dissolved thorium, while strongly favouring the particulate phase,

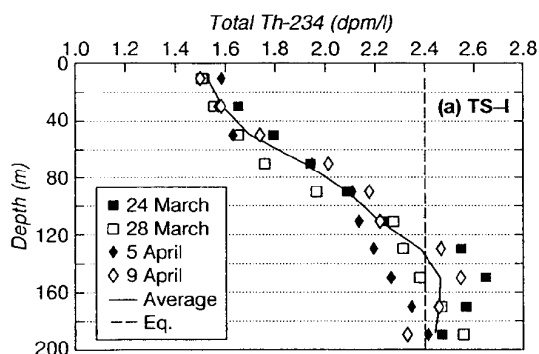


Figure 1.21: A ^{234}Th concentration profiles from the Equatorial Pacific at 0° N , 140° W , showing the depletion of ^{234}Th in surface waters due to particulate export. The dashed line is the concentration at secular equilibrium with ^{238}U . From Bacon et al. (1996).

is reversible (Bacon and Anderson, 1982). Thorium scavenged onto particles can desorb back to the dissolved phase. Thus, dissolved Th scavenged on particles in surface waters is exported to depth before being released again into the water. This results in typical ^{230}Th profiles that increase in concentration with depth (Figure 1.20). Other isotopes of Th, however, do not share this water-column profile. ^{232}Th , for example, is principally locked up in detrital material and little is dissolved, so the concentration profiles are dominated by the detrital partial load. ^{234}Th and ^{231}Th are, like ^{230}Th , both produced from the decay of U and as such are initially in the dissolved phase in seawater, they are however too short lived to develop profiles similar to ^{230}Th , and are in secular equilibrium with their parent U at depth. Surface waters do however show a depletion of ^{234}Th (and presumably ^{231}Th) as export of particles from the surface layer occurs within the timescales of the decay of these isotopes (Bacon et al., 1996) (Figure 1.21).

Protactinium exhibits a very similar oceanic chemistry to that of thorium. Protactinium, like thorium, has only one stable valence state: Pa(V) (rather than the (IV) of thorium). In seawater protactinium rapidly hydrolyses in a similar manner to thorium (Equation 1.29), and is similarly insoluble. The affinity of Pa to particles is slightly less than that of thorium resulting in a longer residence time in seawater

(120 years as opposed to 20 years for Th (Henderson and Anderson, 2003)). The particle type dependence is however different for Pa. While Pa and Th both have high affinities for organic matter (Guo and Gueguen, 2002), the relative affinities for CaCO_3 and SiO_2 are markedly different. CaCO_3 has been shown to favourable adsorb Th over Pa while SiO_2 has been shown to either favour the adsorption of Pa (Guo and Gueguen, 2002; Chase et al., 2002) or have little fractionating effect (Geibert and Usbeck, 2004; Luo and Ku, 1999). The role of other particle types in fractionating Pa and Th from seawater, such as MnO_2 , Fe_2O_3 , chitin, and some organic compounds is thought to be minimal (Guo and Gueguen, 2002). Fractionation via differential adsorption onto clays is however more controversial (Li, 2005), with Luo and Ku (2004) observing a preference for sorption of Th onto clays, and Chase et al. (2002) observing little or no fractionation. Global modelling of ($^{231}\text{Pa}/^{230}\text{Th}$) export to sediments (Siddall et al., 2005) provides a better fit to the available data when fractionation on clays is not considered, i.e. the findings of Chase et al. (2002) are supported.

1.6.5 ^{231}Pa and ^{230}Th as paleoceanographic proxies

Excess in sediments

To use of sedimentary ^{230}Th and ^{231}Pa as proxies for past processes in the oceans, the component of each nuclide scavenged from the water column must be separated from that added to the sediment from other sources. The total amount of ^{230}Th and ^{231}Pa in sediment is a sum of: the ^{230}Th and ^{231}Pa in terrestrially derived detrital material; ^{230}Th and ^{231}Pa produced from the decay of authigenic uranium formed in the sediment; and the ^{230}Th and ^{231}Pa scavenged from the water column on sinking particles.

An assessment of the contribution from detrital material can be made from the measured ^{232}Th content of the sediment and the assumptions that: all ^{232}Th is

terrestrially sourced; the ($^{238}\text{U}/^{232}\text{Th}$) of detrital material is known; and the detrital material is in secular equilibrium with respect to ^{230}Th , ^{231}Pa and their parent U. The contribution from the decay of authigenic U is assessed using the ^{238}U content of the sediment and discounting any U associated with detrital material already accounted for. The remaining U is assumed to have been added at the same time as the sediment deposition and, for the calculation of authigenic ^{230}Th , to have formed at the same $\delta^{234}\text{U}$ as seawater. For measurements of surface sediments the authigenic term is zero, because there is no time to grow in any ^{230}Th or ^{231}Pa . Excess ^{230}Th and ^{231}Pa ($^{230}\text{Th}_{\text{xs}}$ and $^{231}\text{Pa}_{\text{xs}}$) can then be corrected for decay since deposition (Equations 1.33 and 1.34).

$$^{230}\text{Th}_{\text{xs}} = ^{230}\text{Th}_{\text{meas}} - \left\{ (\text{U/Th})_{\text{detrital}} \times ^{232}\text{Th}_{\text{meas}} \right\} - \left\{ \left[\begin{aligned} &^{238}\text{U}_{\text{meas}} - (\text{U/Th})_{\text{detrital}} ^{232}\text{Th}_{\text{meas}} \\ &\left[(1 - e^{-\lambda_{230}t}) + \frac{\lambda_{230}}{\lambda_{234} - \lambda_{230}} (e^{-\lambda_{230}t} - e^{-\lambda_{234}t}) \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{init}} - 1 \right) \right] \end{aligned} \right] \times \right\} \quad (1.31)$$

$$^{231}\text{Pa}_{\text{xs}} = ^{231}\text{Pa}_{\text{meas}} - \left\{ 0.046(\text{U/Th})_{\text{detrital}} \times ^{232}\text{Th}_{\text{meas}} \right\} - \left\{ \left[\begin{aligned} &0.046^{238}\text{U}_{\text{meas}} - 0.046(\text{U/Th})_{\text{detrital}} ^{232}\text{Th}_{\text{meas}} \\ &1 - e^{-\lambda_{231}t} \end{aligned} \right] \times \right\} \quad (1.32)$$

The first term in curly brackets in Equations 1.31 and 1.32 account for the detrital component, while the second term in curly brackets in equations 1.31 and 1.32 accounts for the ^{230}Th and ^{231}Pa produced from the decay of authigenic U. The added complexity in Equation 1.31 is due to the presence of an intermediate decay chain between ^{238}U and ^{230}Th (Section 1.6.2). The factor of 0.048 in Equation 1.32 is the ($^{235}\text{U}/^{238}\text{U}$) ratio. The excess ^{230}Th and ^{231}Pa ($^{230}\text{Th}_{\text{xs}}$ and $^{231}\text{Pa}_{\text{xs}}$) must then be

corrected for decay of the excess component since deposition at time t .

$$^{230}\text{Th}_{\text{xs}}^0 = ^{230}\text{Th}_{\text{xs}} e^{\lambda_{230}t} \quad (1.33)$$

$$^{231}\text{Pa}_{\text{xs}}^0 = ^{231}\text{Pa}_{\text{xs}} e^{\lambda_{231}t} \quad (1.34)$$

The time since deposition is derived from an age model independent of ^{230}Th and ^{231}Pa measurements. This usually involves the use of radiocarbon measurements, or $\delta^{18}\text{O}$ stratigraphy.

^{230}Th constant flux proxy

Because the residence time of ^{230}Th in the ocean is very short, most of the ^{230}Th produced in the water column at any one locality is removed to sediments (Bacon and Anderson, 1982). In this case the $^{230}\text{Th}_{\text{xs}}$ in sediment should relate only to the amount of ^{234}U in the overlying water column, i.e.

$$P_{\text{Th}} = z(^{234}\text{U})\lambda^{230} \quad (1.35)$$

where P_{Th} is the production rate of ^{230}Th in the water column and z is total water depth. Measured $^{230}\text{Th}_{\text{xs}}^0$ in sediments can then be used, assuming P_{Th} is constant, to find the sedimentation rate (Bacon, 1984).

$$F_w = \frac{P_{\text{Th}}}{^{230}\text{Th}_{\text{xs}}^0} \quad (1.36)$$

Because there is a small amount of ^{230}Th dissolved in seawater, the above is an ideal case and the possibility exists for discrepancy between the production in the water column (Equation 1.35) and the flux to sediments. This is due to the lateral advection of ^{230}Th on timescales shorter than it can be removed from the ocean by scavenging. Water-column measurements in the North Atlantic (Vogler

et al., 1998; Moran et al., 1997) have confirmed the presence of ^{230}Th advection, showing depletions in ^{230}Th at depth associated with the advection of NADW out of the basin to the Southern Atlantic. Also, in the Southern Ocean, elevated ^{230}Th in intermediate waters has been shown to be the result of upwelling of ^{230}Th rich deep water (Rutgers van der Loeff and Berger, 1993). GCM modelling of the ^{230}Th flux to sediments (Henderson et al., 1999) suggests that advection of ^{230}Th is significant, although $\approx 70\%$ of the world's seafloor receives within 30% of its expected flux of ^{230}Th from the overlying water column. The regions from which the flux of ^{230}Th is not predictable from the depth of overlying water are those with extremely high or low particle fluxes such as those covered with sea ice, or at the boundaries of the oceans. Notwithstanding these complications (Lyle et al., 2005), the ^{230}Th constant flux sedimentation rate proxy is a valuable tool for paleoceanographers because ^{230}Th has the shortest residence time in the oceans of any species used as a “constant flux proxy” and is not thought to be remobilised within or from the sediment once deposited.

The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ ratio

Protactinium, like thorium is rapidly removed from the ocean by scavenging, and its concentration in sediments can be likened to that of a constant flux proxy. The residence time of protactinium in the ocean is, however, significantly longer than that of thorium (120 years as opposed to 20 years Henderson and Anderson (2003)). The enhanced relative solubility of protactinium allows advection of protactinium around the oceans basins to play a role in controlling the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ ratio preserved in sediments.

Both ^{231}Pa and ^{230}Th are produced in the water from the decay of uranium at constant rates ($2.45 \pm 0.05 \times 10^{-3}$ and $2.62 \pm 0.05 \times 10^{-2}$ d.p.m.m $^{-3}$ a $^{-1}$ for ^{231}Pa and ^{230}Th respectively), and hence also at a constant activity ratio of 0.093. Ini-

tially a water mass with no ^{231}Pa or ^{230}Th (i.e. freshly advected from the surface) will start to grow in ^{231}Pa and ^{230}Th at the production ratio. Because Th is more particle reactive than Pa, the Th is preferentially removed to sediments, resulting in $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ of the sediments <0.093 . As the water advects through the ocean its $(^{231}\text{Pa}/^{230}\text{Th})$ increases because Th is preferentially removed. In theory this enrichment of Pa will continue until the $(^{231}\text{Pa}/^{230}\text{Th})$ of the water become sufficiently high the output to the sediments is equal to the input from decay of U (i.e sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0 = 0.093$). Thus the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ of sediment beneath the water mass, between the initial low value and it reaching an equilibrium, will be some function of the rate of advection, allowing sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to be used as a paleo-proxy for ocean circulation.

The rate at which the $(^{231}\text{Pa}/^{230}\text{Th})$ of a water mass increases towards an equilibrium will, however, depend on a number of parameters other than only on ocean circulation. At high particle fluxes the scavenging efficiency of both ^{231}Pa and ^{230}Th is increased due to the higher surface area available for scavenging (Kumar et al., 1993). Thorium is, however, already effectively scavenged onto sinking particles due to its lower solubility, so the increase in particle concentration does not have as much an effect as for protactinium. For instance high particle fluxes at ocean margins and associated high scavenging has been shown to result in elevated $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ preserved in sediments due to more effective Pa scavenging (Anderson et al., 1983b). Similarly in open ocean settings a relationship between $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ of sediments, and inferred productivity has been observed Kumar et al. (1995). An increase in particle flux will cause protactinium to be more effectively scavenged and will bring the water mass to an equilibrium more quickly.

The degree to which thorium is preferential scavenged over protactinium is also dependent on the composition of the particles involved in the scavenging. The greater the difference in efficiency of scavenging between thorium and protactinium, the

longer it will take for the water mass to reach an equilibrium at any given particle flux. The relative affinity of ^{231}Pa and ^{230}Th for a particular particle type is expressed as a fractionation factor, F (Anderson et al., 1983a).

$$F_{\frac{\text{Th}}{\text{Pa}}} = \frac{(^{231}\text{Pa}/^{230}\text{Th})_{\text{xs}}^{\text{particles}}}{(^{231}\text{Pa}/^{230}\text{Th})_{\text{xs}}^{\text{dissolved}}} \quad (1.37)$$

$$= \frac{K_{\text{dTh}}}{K_{\text{dPa}}} \quad (1.38)$$

Experimentally, pure calcite has an F of ~ 100 and silica an F of ~ 0.1 (Guo and Gueguen, 2002)(Section 1.6.4). These extreme fractionations are, however, mediated in the natural system by organic coatings on the particles which have a much higher affinity for both Pa and Th than the pure mineral grains and appear not to fractionate Pa and Th. In the open ocean, calcite has an F of ~ 42 and opal of ~ 0.3 (Chase et al., 2002). The role of Mn and Fe oxides is thought to be minimal in fractionating ^{231}Pa and ^{230}Th and they have an F close to 1 (Guo and Gueguen, 2002). Regions with particles fluxes which are dominated by phases which have low F values (i.e. silica) will have high sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ which can be higher than the production ratio if the water advecting into the region has previously had Th preferentially removed onto particles with a high F , i.e. calcite. An example of such a region is the Southern Ocean, which recives high $(^{231}\text{Pa}/^{230}\text{Th})$ water from the Atlantic and has a high opal productivity and thus typical high $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is observed in sediments (eg, Yu et al. (1996)). The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in sediments therefore also records information on the dominant particle type during scavenging from the ocean, which may differ from the sedimentary record due to dissolution on the seafloor.

The Southern Ocean is perhaps the best example of a region of the world's oceans where all of the, above mentioned, controls on sedimentary are important in controlling sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$. The high sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$

values of the Southern Ocean have been proposed to be due to: advection of high ($^{231}\text{Pa}/^{230}\text{Th}$) water from the Atlantic Yu et al. (1996); elevated total particle flux due to the high biological productivity of Southern Ocean surface waters (Kumar et al., 1995); and also due to the particle type being dominated by opal and scavenging ^{231}Pa more effectively (Chase et al., 2003). It is apparent that any sedimentary record from the Southern Ocean, or record of water that has left the Southern Ocean, will be challenging to interpret, without proper consideration of all the factors controlling the ($^{231}\text{Pa}/^{230}\text{Th}$) of the water (circulation, and scavenging history) and the fractionation from the water into the sediments (particle type and flux).

1.7 Summary

Understanding the past circulation of the oceans is of great interest not only to the paleoceanographic community, but to all those studying the climate system. Understanding how heat and carbon are stored and moved around the planet in the past can be used to put in context the many paleoclimatic records available to climate scientists.

This thesis deals with one approach to the reconstruction of ocean circulation in the past, the use of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})_0$ preserved in deep sea sediments. The main theme of this thesis is to better constrain the use of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})_0$ as a proxy for circulation and application of this proxy to investigate oceanic circulation. Through measurements of ^{231}Pa and ^{230}Th in seawater, the way in which ^{231}Pa and ^{230}Th concentrations in the water column are represented in the sedimentary record is investigated and constrained.

The methods used to attain and measure samples for U-series isotopes are covered in Chapter 2. Measurement of water column profiles from the Madagascar and Mascarene Basins are presented in Chapter 3. Chapter 3 also investigates the use of a 1D particle settling model to constrain the depths from within the water column

that the sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})_0$ is most representative. In Chapter 4, the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})_0$ proxy is applied to a sediment core in the northern Mascarene basin to assess the inflow of AABW into the Indian Ocean over the past 140 ka. Finally the behaviour of ^{231}Pa and ^{230}Th in the water column is further investigated in Chapter 5, in which a high resolution water column profile is measured with filtered and unfiltered samples to investigate the partitioning of the isotopes between the dissolved and particulate phases.

Chapter 2

Methods

2.1 Introduction

This chapter covers the methods used throughout this thesis. The bulk of this chapter concerns the chemical preparation of samples, which have been developed from work previously carried out at Oxford by Laura Robinson (Robinson, 2003). Significant advances have been made in both chemical pre-treatment and mass spectrometry. Chemical separation of U, Th and Pa has been improved, both in purity of the separations but also in sample throughput. These improvements are crucial for measurement of Pa in samples with low Pa concentrations, and/or high ^{232}Th concentrations. Advances in mass spectrometry have centered largely on the realisation that separate measurement of Pa and Th yields better results, reducing sample throughput only minimally.

The author participated in research cruise CD154 aboard the *RRS Charles Darwin*, from Durban to Cape Town, from 13th December 2003–10th January 2004. Sample collection procedures and shipboard sample processing relevant to this study are also described in this chapter.

2.2 Sampling

2.2.1 Water samples

Sample collection

Ten litre water samples were collected from throughout the water column in Niskin bottles, deployed on a CTD (Conductivity, Temperature, Depth) rosette (Figure 2.1). Samples were collected on two cruises, cruise CD 129 and cruise CD 154, both aboard the *RRS Charles Darwin*. Cruise CD 129 (Chapter 3) sailed from Durban, SA to Reunion in the Indian Ocean in 2002 (Principal Investigator I. N. McCave). Sampling proceeded along the western margins of the Madagascar and Mascarene Basins to the east of Madagascar, and water samples were collected by Laura Robinson. Cruise CD 154 (Chapter 5) sailed from Durban to Cape Town, SA in 2003-2004. Water Samples were collected and processed by the author (Alex Thomas).

As the CTD rosette was lowered through the water column the temperature and salinity were monitored, and water masses identified. The proximity to the sea floor was measured with a pinger on the bottom of the CTD and, where deployed, the gravity corer attached to a proximity sensor. The particle concentration was monitored in a qualitative manner with a “Seatech” nephelometer. As the CTD was lowered towards the bottom the cable was let out slowly so to get as close to the bottom as possible without disturbing the sediment. The Niskins were then fired on the upcast so that all water masses were sampled, with a concentration of samples biased towards greater depth rather than the surface.

Once the CTD was recovered on deck the unfiltered samples were emptied directly into acid-cleaned carboys and acidified with Romil ultra pure HNO_3 . Samples destined for filtration were kept in the Niskins and transferred to the “wet lab” for processing (Figure 2.2). Sample carboys are 10 litre, and made from high density

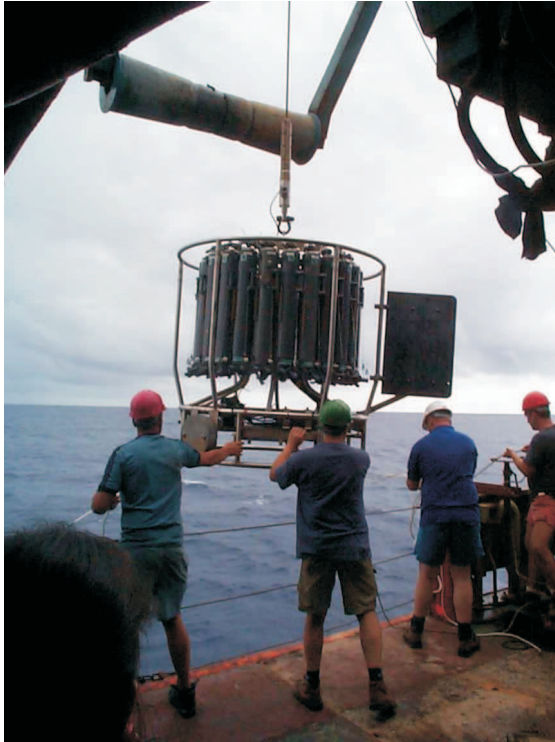


Figure 2.1: A CTD rosette with 24 10 litre Niskin bottles cocked and ready for deployment.



Figure 2.2: The “Wet Lab” aboard the *RRS Charles Darwin* with the filtration apparatus. The set up is such that water is filtered directly from the Niskin bottle, through the filter, under suction provided by a peristaltic pump. The filtered water passes directly into the sample bottle through a specially modified cap so the sample’s contact with the air and hence contamination from the lab is minimised.

polyethylene plastic. Once acidified no further processing of the sample was performed on the ship. Samples were sealed with a screw top and Parafilm to prevent contamination and evaporation. All further treatment was carried out in either a clean laboratory, or dedicated water processing laboratory, in Oxford.

Filtration

To investigate the partitioning of ^{230}Th and ^{231}Pa between the dissolved and particulate phases, pairs of samples from depths of interest were sampled and one sample filtered. Filtration was conducted directly from the Niskin, through a 142 mm,

0.2 μm , cellulose nitrate filter held in a polycarbonate filter holder, under reduced pressure provided by a peristaltic pump. The filtered water was pumped directly into the acid cleaned sample carboy. This procedure minimises the samples contact with the air, and hence contamination. The only contact the sample has with the air in the wet lab is through the small air exchange holes in the top of the Niskin and in the sample carboy cap. (Figure 2.2). Acidification of both filtered and unfiltered samples was performed in semi-clean conditions in a recirculating fume hood aboard the ship but outside the wet lab used for sediment processing. Acidification was with 1.5-2 ml of concentrated (16 N) HNO_3 , which lowered the pH to < 2 . The removal and folding of used filter papers was carried out in a laminar flow hood with filtered air, as was the cleaning of the filter holder between samples.

2.2.2 Sediment samples

Promising localities for coring were identified by 3.5 kHz seismic profiling. Once identified a short Kasten core was deployed to test the sediment suitability for coring. If the penetration is good with the short Kasten, progressively longer cores were deployed to get maximum core length. This was then repeated with piston cores. All cores retrieved have a small amount of sediment, which was scraped from their uppermost surface of all cores and kept separately as a core top sample.

Kasten core

Kasten corers have a square section coring “barrel”, approximately 15 cm wide, with a 1 tonne weight (“bomb”) which drives the corer into the mud (Figure 2.3). The sediment is retained in the corer by a core catcher consisting of two door like flaps which only open inwards.

Once the cores were recovered on deck the barrel was removed from the bomb and transferred to the wet lab, where they were laid down for processing (Figure



Figure 2.3: A Kasten core being recovered aboard *RRS Charles Darwin*.



Figure 2.4: A Kasten core with the upper 'side' removed exposing the sediment. The screws for jacking up the false bottom are visible protruding from the underside of the core.

2.4). The Kasten core barrel has a removable side which exposes the core and a false bottom which is used to jack-up the mud for processing. The top surface of the mud was scraped off to remove any smearing along the sides of the corer. The cores were logged for any sedimentary features and colour scanned. 33 cm plastic trays were then pressed into the mud, the core jacked up and the mud in the trays removed. Three layers of samples were taken in this way: One working, one to be X-Rayed, and one to be archived. The remaining mud was also sub-sampled for water content.

Piston core

Piston cores (Figure 2.5) deployed on the two cruises were narrower than the Kasten cores and had a circular cross section, about 7 cm across. The piston core also



Figure 2.5: A piston core being recovered aboard *RRS Charles Darwin*. This core bent while penetrating the sediment.

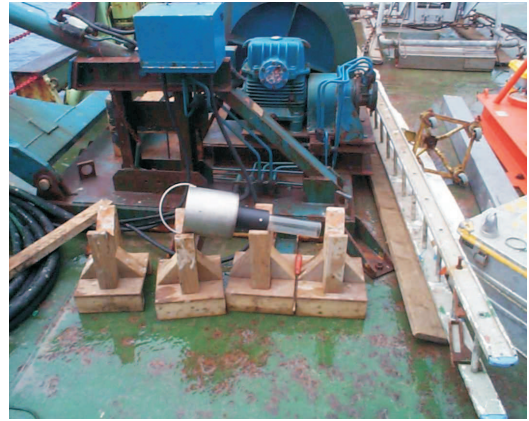


Figure 2.6: A small gravity core, to be suspended from the proximity sensor on the bottom of the CTD.

differs in that it is not lowered onto the sea floor but it is dropped, resulting in greater penetration. The corer is suspended from a quick release mechanism linked to a trigger weight. When the trigger weight hits the bottom the main corer falls to the bottom. The corer is attached to the main coring cable by an extra length of cable that is exactly the same length as the cable supporting the trigger weight. This cable is attached to the “piston”, a slug initially at the bottom of the coring barrel. When the corer is dropped and hits the seafloor the piston should remain at the sediment water interface and suck the mud up into the barrel as it penetrates down into the mud.

The coring barrel is lined with polycarbonate which was removed when the corer is retrieved on deck. The core liner, with its sediment fill is cut into pieces, the ends of the tubes capped, before storage for processing ashore.

Under CTD gravity core

In an attempt to gain surface sediments from beneath water column profiles a small gravity corer (Figure 2.6) was deployed from beneath the CTD. The success of this corer was however, limited by rough weather. The roll of the ship resulted in the

corer being repeatedly bounced on the seabed which knocked all of the mud out of the corer.

2.3 Chemistry

2.3.1 Laboratory conditions

All water and sediment chemistry was performed at the Earth Sciences department and the University of Oxford. Due to the low concentration of ^{230}Th and ^{231}Pa in seawater samples, most chemistry was carried out under clean lab conditions. The laboratory used was over-pressured with class 1000 hepa-filtered air. Column chemistry was performed in a clean box, also over-pressured with filtered air. At all times latex gloves and Tyvek clean suits were worn and over shoes worn to reduce contamination of the lab.

The use of ^{233}Pa spike along with the very low sample concentrations, necessitate the use of a clean lab separated from that usually used for U-series sample preparation of carbonate. This was to remove the, possibility of ^{233}Pa and ^{233}U spikes cross contaminating, and also due to the large amounts of uranium in seawater which could contaminate the established U-series lab.

Much of the sample processing for the water samples was impractical to perform in a clean lab due to the space requirements associated with 10 l samples. Sample weighing, acidification (If not already done aboard the ship, as was the case for samples from cruise CD 129), spiking, and co-precipitation were performed in a laminar flow hood, with class 100 filtered air, in a “non-clean” lab. Latex gloves and Tyvek sleeves were worn to reduce sample contamination. When it was necessary to look into water samples, a cleaned mirror was employed to see into the sample (rather than stand over the sample and risk contamination).

2.3.2 Cleaning procedures

All Teflonware was cleaned thoroughly before use, and that used for seawater samples was either new or only used previously for seawater measurements. The principle of the cleaning procedures is to dissolve and dilute the contaminants rather than to “scrub” the beakers which would damage the smooth surface of the Teflon.

The cleaning procedure for beakers used for sample preparation is as follows:

- Beakers are initially rinsed with Milli-Q, before being left overnight filled with 2N HCl. The HCl is then poured out and the beakers rinsed in Milli-Q. This first cleaning step removes the bulk of any sample left in the beaker from previous uses.
- The inside of the beaker is gently wiped with a clean lab wipe to remove any remaining solids and rinsed once more with Milli-Q.
- Any markings on the outside of the beakers are removed with acetone and the open beakers are submerged in hot 7.5N HNO₃, in a Teflon bucket, overnight. Once cooled the bucket of beakers is rinsed three times with Milli-Q, and each individual beaker is rinsed with Milli-Q such that all liquid is removed from the inside of the beaker.
- For the final cleaning step, quartz-distilled 6N HCl is added to the beakers and they are capped and heated overnight on the hotplate at ~140°C to leach any remaining U or Th from the beaker. If Pa is to be measured 0.05N HF is added as well to mobilise any Pa. This last cleaning step is repeated just prior to the use of each beaker to ensure the blank is as low as possible. A final rinse with Milli-Q before leaving to dry upturned on a clean lab wipe removes any contaminants in the acid wash.

Bottles used for storing acids are precleaned by leaching in the acid they will be

used to store, on a hotplate overnight. All non Teflon plasticware, including seawater sample containers, is leached in 10% HNO_3 and rinsed in Milli-Q before use.

2.3.3 Reagents

All acids used are quartz distilled from reagent grade, blanks have been assessed and are summarised in Table 2.1. Water used for chemistry is 18 M Ω Milli-Q. NH_4 is isothermally distilled in an acid-cleaned Teflon container, or high purity NH_4 is purchased. Fe carrier is either made up from Specpure Fe powder or is purified from reagent grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ by liquid-liquid extraction using the procedure described below.

Liquid–liquid extraction of Fe

Fe is purified by extracting Fe into isopropyl ether from HCl. Fe has a greater solubility than the actinides in isopropyl ether and water, and Fe also partitions into isopropyl ether from strong HCl and into water from isopropyl ether. Thus the actinides may be separated from Fe by mixing of suitable immiscible liquids and subsequent physical separation. The isopropyl ether was cleaned by mixing with H_2O and separating the water off using a glass separating funnel. 50 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 g of Fe) was dissolved in 500 ml of 6N HCl. This was then added to the ether, shaken, allowed to separate and the acid then separated off. Clean Fe was extracted from the ether with H_2O in a similar manner. The entire process was repeated to provide a cleaner separation. The resulting solution was dried down and dissolved in 200 ml of 2N HCl to make an approximately 50 mg/ml solution.

Reagent blanks

Concentrations of ^{230}Th , ^{231}Pa , ^{232}Th , and ^{238}U were measured in the reagents used in chemical procedures (Table 2.1). This was achieved by drying down up to 270 ml

Reagent	^{230}Th ag/g	^{231}Pa ag/g	^{232}Th fg/g	^{238}U fg/g	Mass Dried Down g
HNO_3 (AAR)	128	b.d.l.	4732	2290	27.5405
$\pm$	74		2912	22	0.0001
MilliQ	14	6	b.d.l.	19	192.3
$\pm$	3	4		1	0.1
15N HNO_3	11	b.d.l.	38	24	271.2
$\pm$	5		25	2	0.1
7.5N HCl	4	25	23	8	246.3
$\pm$	4	21	23	0	0.1
	fg	fg	pg	pg	
beaker only	1.4	1.4	2.0	2.7	
$\pm$	0.6	1.5	6.1	3.4	

Table 2.1: U-series concentrations in reagents used in chemical procedures, and amounts of nuclides measured with no reagent in the beaker (ie. the ambient contribution from the lab). This extra blank is not accounted for in the measurements of the reagent nuclide concentrations due to the random nature of the “lab” blank. These concentrations thus represent large overestimates of the actual concentrations. Uncertainties are presented as 2σ

of reagent, spiking with a mixed ^{229}Th – ^{236}U spike, and then measuring the 230/229, 231/229, 232/229, and 238/236 ratios by MC–ICP–MS. As the concentrations of other elements should be very low in these reagents, no elemental separation was used so the Th, Pa and U were all measured together.

2.3.4 Weighing

Weighing of sediments and spike solutions was performed on an analytical balance readable to 0.00001 g, with a precision of better than ± 0.0001 g. All weighing was into Savilex Teflon beakers with the exception of water samples which were far too large to be weighed on an analytical balance. In the case of water samples, each sample is weighed on a top pan balance with a capacity of 30 kg and a precision of ± 5 g. The mass of the spike added was assessed by weighing the spike bottle, adding spike to the sample, and then reweighing the spike. Loss through evaporation from the mixed U–Th spikes is prevented through the use of a spike bottle with a pin hole

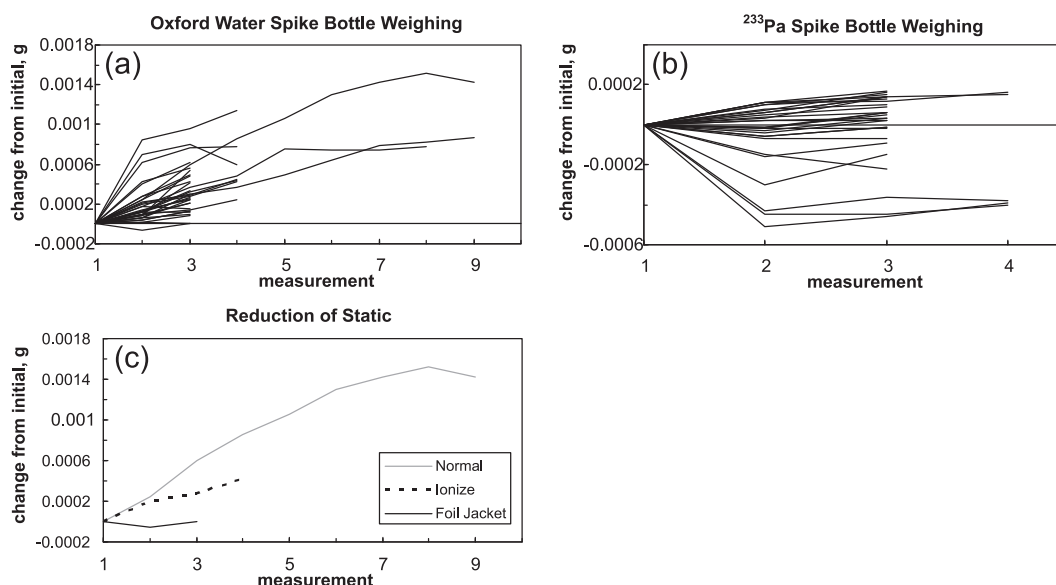


Figure 2.7: Graphs illustrating the apparent drift in mass as Oxford Water Spike, (a), and ^{233}Pa spike, (b), bottles are repeatedly weighed. Measures to minimise the static and drift are shown in, (c). Here, repeated weighings of the Oxford Water Spike bottle after: an internal calibration of the balance and deionisation of the bottle between measurements; and covering the spike bottle with aluminium foil, are compared to the repeated weighing under “normal” conditions where no steps are taken to reduce static.

sized opening to dispatch the spike.

To ensure a reliable mass each bottle and beaker was weighed at least three times until a reproducible number was attained. As both the spike bottle and the beakers are made from Teflon, there is considerable build up of static which inhibits accurate weighing (Figure 2.7 a and b). To reduce this effect, the spike bottle and beakers are deionised with either an external “Stat-Attack” static removal device or by the internal deionisation facility of the “Sartorius Genius ME” balance.

2.3.5 Sample pre-treatment

Water samples

Ten litre water samples were weighed to ± 5 g and samples from CD 129 were also acidified to $\text{pH} < 2$ with 7.5N HNO_3 . The CD 129 samples were then left for at least 24 hours to allow Th and Pa to desorb from the walls of the container.

Samples were spiked with ^{233}Pa (Section 2.4.3) and Oxford Water Spike (Section 2.4.2). 50 mg of Fe was added to each sample to act as a carrier for the lanthanides and actinides. The sample was shaken and left, at least, overnight to allow sample-spike equilibration, extra shaking is also employed during the equilibration period.

The samples were neutralised with NH_4 to pH 8. Care was taken during this stage, due to the variable concentration of the NH_4 caused by the distillation process, so as not to raise the pH above 9 which would lead to the formation of insoluble hydroxides. This is made easier by a subtle colour change in the samples during neutralisation as $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. Samples were then shaken and left for approximately 2 hours to allow any slow buffering in the water to act and the pH was rechecked. Samples were left for up to 2 days for the Fe precipitate to settle and form an observable orange layer on the bottom of the container. After ~ 6 hours the precipitate had started to collect on the bottom of the container. To increase recovery, this was resuspended by vigorous shaking to give the Fe another chance to scavenge more actinides. The overlying water was then siphoned off, leaving as little liquid as possible without disturbing the precipitate layer. The precipitate was then centrifuged to remove the remaining liquid, and rinsed with H_2O to remove water-soluble salts. The precipitate was then transferred into a Teflon beaker and taken up in 1 ml of 7.5N HNO_3 , dried down and redissolved in 0.5 ml 7.5N HNO_3 ready for column chemistry.

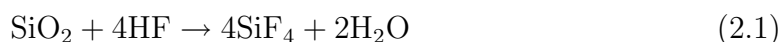
Sediment samples

Sediments were dried in an oven at 110°C overnight to remove any moisture. 0.1 g of sediment was weighed into a Teflon beaker, and a few drops of Milli-Q H_2O added to wet the sample. The sample was then sonicated to disassociate the sediment.

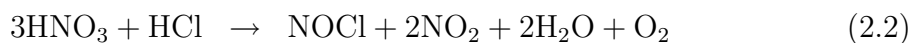
A separate beaker was spiked with ^{233}Pa (Section 2.4.3) and Oxford Carbonate Spike (Section 2.4.2). This spiked beaker was also used to hold each acid used in the digestion prior to their addition to the sample (excluding HF, which is added

directly to the sample beaker), thus transferring the spike to the sample. The spikes are not added directly to the samples as the acids in the spike solutions will react with the sample, and any nitrates formed before the addition of HF may inhibit the total digestion of the sample.

The digestion procedure is taken from a method developed by S. Wyatt (pers. corr) at Oxford. Two millilitres of HF conc was added drop wise (care was taken as the sample fizzes violently). The beaker was capped and heated overnight so the HF could attack any silicates. The cap was removed and the samples dried down to a white residue. A further 2 ml of HF was added and allowed to dry down to ensure all Si was driven off as SiF_4 . The HF was added in two steps rather than one because when HF reacts with silicates, water is produced which reduces the molarity of the acid.

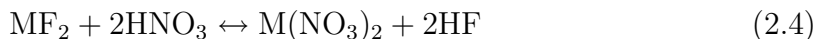


The dried sample was then redissolved in 2 ml of 15N HNO_3 taken from the spiked beaker. The sample was then dried down again, and redissolved in 2 ml reverse aqua regia ($3\text{HNO}_3 : 1\text{HCl}$), adding the HNO_3 and then the HCl , using the acids to rinse the spike beaker before they were added to the sample. The aqua regia acts as a strong oxidising agent, due to the Nitrosyl Chloride (NOCl) produced, which removes organic matter from the solution.



The sample was again dried down, redissolved in 2 ml 15N HNO_3 and dried down. Due to repeated addition of HNO_3 during the dissolution any remaining fluorides

are converted to nitrates:



To ensure that all the HF is driven off, forcing the reaction to completion, the temperature must be elevated above 140°C. Finally the sample was dissolved in 4 ml 7.5N HNO₃ and heated overnight with the cap on. Total dissolution was only achieved once the total volume of the solution was increased, due to the partial insolubility of some nitrates.

Once the sample was completely dissolved it was transferred to a 50 ml centrifuge tube and made up to 25 ml with Milli-Q. Ten milligrams of Fe was added to the sample to act as a scavenger of the actinides. The sample was shaken to ensure the Fe was well mixed, and then NH₄ was added dropwise to raise the pH of the solution to 8. This allowed the actinides to co-precipitate with the Fe, while leaving the more soluble components (principally Ca, Mg and Na) behind in solution. The suspension was left for 24 hours to increase the effectiveness of the scavenging, and was then centrifuged and the liquid decanted off. The precipitate was then washed with Milli-Q, centrifuged and decanted. 0.5 ml of 7.5 N HNO₃ was added to the sample to resuspend the precipitate, and then transferred back to beaker. This was dried down and redissolved in 0.5 ml 7.5 N HNO₃ ready for column chemistry.

This elaborate dissolution procedure is required to ensure complete dissolution of samples that contain both silicates and carbonates, and hence sample spike equilibrium. Silicates require HF to break down Si-O bonds while the addition of HF to a solution containing Ca leads to the formation of very insoluble CaF₂. A method involving the use of HClO₄, to prevent the formation of fluorides, was considered but the hazards associated with the use of HClO₄, particularly with samples that may contain significant organic mater, necessitated the use of the above procedure.

2.3.6 Elemental separation

Aims of elemental separation

It is important to separate the Pa, Th and U from other elements as well as from each other. Separation from the matrix, particularly Fe which is the most abundant cation in most samples, allows us to introduce the sample to the mass spectrometer at a sufficiently high concentration that it may be measured accurately, without introducing a solution with such a high total dissolved solids that would clog the nebuliser or effect the stability of the plasma. Separation of Pa, Th and U from each other is essential as the concentration of U compared to that of Th and Pa is so high that measurement of Th and Pa with U is hindered by the limited dynamic range of the mass spectrometer. Running Pa, Th and U separately also lessens interferences from abundance sensitivity, and hydrides.

The most important reason for ensuring good U separation is, however, to separate the ^{233}Pa spike (Section 2.4.3) from any ^{233}U (produced from decay of ^{233}Pa) so when mass 233 is measured it represents only the concentration of ^{233}Pa in the spiked sample at the time of separation.

It is also desirable to develop a separation procedure that has a low blank and high yields, so that low concentration samples may be measured. A procedure that is as fast as possible will aid sample throughput because column chemistry is typically a time consuming part of sample preparation. To develop a procedure that achieves good separation, with low blank and fast sample throughput, two approaches were investigated: one using Eichrom TEVA resin; and another using anion exchange resin, AG1-X8. A summary of literature protocols for U, Th and Pa separation, which was used as a starting point for the development of the two procedures is shown in Table 2.2.

Table 2.2

Author	Elements Separated	Col No	Resin	load in	wash	elute	elute	yield	blank
Nour et al. (2002)	Th	1, 2 ml	TEVA	2.5N HNO ₃	20 ml 2.5N HNO ₃ (contains U)	Th in 5 ml 1M H ₃ PO ₄			
Samples are leached from sediments using a “hot block”. H ₃ PO ₄ is used as an eluting agent because it is favourable for the liquid scintillation counting used. HCl + trace HF could be an alternative to elute Th and Pa. No information is available for behaviour of Fe or Pa on TEVA resin.									
Eikenberg et al. (2001)	Th, U	1	U/TEVA	10 ml, 2×4 ml 3N HNO ₃	Th in 5M HCl	Th in 2×10 ml 0.02M HCl			
Liquid samples (urine) actinides are extracted using U/TEVA (similar to co-precipitation rather than using a column)									
Goldstein et al. (1997)	Th, U, Pu	1, 2ml	U/TEVA	6N HNO ₃	6N HNO ₃	Th in 5N HCl	U & Pu in 0.01N HCl		24 ng ²³⁸ U
Goldstein et al. (1997)	U	2	AG1 X8	7N HNO ₃	7N HNO ₃	Pu sticks to the column		70-86%	
		Co-precipitation for liquids and dissolution for solid samples.							
Goldstein et al. (1997)	U	1	AG1 X8	8N HCl	HCl and dil H ₂ SO ₄	U in 0.01N HCl		70-86%	
		Co-precipitation for liquids and dissolution for solid samples. 8N HCl removes major elements except Fe and U, Fe is removed with HCl/ H ₂ SO ₄ mix. U is not separated from Np.							
Robinson et al. (2004a)	Th, U, Pa	1, 2ml	AG1 X8	4 ml, 2×2 ml, 7.5N HNO ₃	Th in 6M HCl (Pa with HF trace)	Th in 1+4 ml U in 2×1 ml, 2×4 ml H ₂ O			

Continued on next page...

Table 2.2 continued from previous page...

Author	Elements Separated	Col No	Resin	load in	wash	elute	elute	yield	blank
Chen et al. (1986)	U	2, 170ml	AG1 X8	150	ml 2×255 ml 7.5N HNO ₃	U in 170 ml + 850 ml H ₂ O then 170 ml + 850 ml HCl			100 pg 238U
				7.5N HNO ₃					
	Th	3, 170ml	AG1 X8	200	ml 2×170 ml + 1020 ml 7.5N HNO ₃	Th in 2×170 ml + 1020 ml 1N HNO ₃			9 fg 231Pa, 48 pg 232Th, 2 fg 230Th
				7.5N HNO ₃					
Chen et al. (1986)	U	1, 2, smaller	AG1 X8	7N HNO ₃	7N HNO ₃	U in 1N HBr		>95%	4 pg 238U
	Th	1	AG1 X8	7N HNO ₃	7N HNO ₃	Th in 6N HCl		>95%	2 pg 232Th
Pickett et al. (1994)	Th, U	1, 3.5 ml	AG MP-1 (Cl-) 100-200 mesh	7N HNO ₃	7N HNO ₃	U and Th with H ₂ O and HBr			
		2, 0.5 ml	AG MP-1 (Cl-) 100-200 mesh	7N HNO ₃	7N HNO ₃	U and Th with H ₂ O and HBr			~5 pg U , ~15 pg Th,
Pickett et al. (1994)	Pa	3×7 ml	10M HCl +sat	10 ml 10N HCl	Pa in 3×7 ml 10N HCl + 0.5N HF			>95%	
		isobutyl Ketone extraction	DIBK H ₃ BO ₃						

Continued on next page...

Table 2.2 continued from previous page. . .

Author	Elements	Col No	Resin	load in	wash	elute	elute	yield	blank
Separated									
Layne and Sims (2000)	Pa purification	1, 1 ml	AG MP-1 (Cl-) 100-200 mesh	0.5M H ₂ SO ₄ + 2.5 Cv	0.5M H ₂ SO ₄ , Pa in 3 Cv	8M HCl + 0.05M HF		>95%	
		2, 0.5 ml	AG MP-1 (Cl-) 200-400 mesh	1 Cv 10M HCL + drop rated H ₃ BO ₃	2 Cv 10M HCl, 4 Cv 8M HCl, 2 Cv 6N HCl	Pa in 3.5 Cv + 0.05M HF		>99%	Pa BDL
		Measurement by TIMS need ~100 fg for good analysis of Pa. Boric acid prevents formation of insoluble fluorides (important for Pa). The second Pa purification column completely separates Pa from U.							
	Th	1, 2-5 ml	TRU-Spec	Up to 40 ml 10M HCl		Th from U, Pa, Ra + trace elements			
	Th purification	2, 1 ml	anion	HNO ₃					
	Th purification	3, 0.5 ml	anion	HNO ₃				5 pg ²³² Th	
Poor detail given for separation technique but Th is separated from Pa U and Ra. No detail on how U is purified, but U chemical blank is <0.01 pmol (Th = Chem. blank)									
Bourdon et al. (1999)	Pa	1, 20 ml	AG1 200-400 mesh	X8 2 Cv	9N HCl	Pa in 2 Cv	9N HCl +0.1N HF (U, Fe stick)		
		2, 2 ml	TRU-Spec	Dry to half volume from col1	2 Cv 9N HCl, 6 Cv 8N HCl	Pa in 2 Cv	2N HF		

Continued on next page. . .

Table 2.2 continued from previous page...

Author	Elements Separated	Col No	Resin	load in	wash	elute	yield	blank	
		3, 1 ml	AG1 X8 200-400 mesh	2 Cv 9N HCl	6 Cv 9N HCl,	Pa in 9N HCl + 0.1N HF			
						13 Cv 8N HCl,			
						2.5 Cv 7.5N HNO ₃			
		4, 1 ml	TRU-Spec	From col 3	4 Cv 4N HCl	Pa in 2 Cv 2N HF			
		By not fully drying down products of each column and loading directly onto the next column no Pa is lost to hydrolysis.							
		Choi et al. (2001)	Th, Pa, U	1, 4 ml	AG1 X8 100-200 mesh	10-20 ml 9N HCl (Th in the wash)	Pa in 12 ml 9N HCl + 0.14N HF		
				Th purification	2 AG1 X8 100-200 mesh	Th split in 8N HNO ₃			
Pa purification	3 AG1 X8 100-200 mesh			9N HCl	Pa in 12 ml 9N HCl + 0.14N HF				
U and Fe retained on 1st column after Pa elution. U left on column after 3rd column. If there is not perfect U Pa separation U is washed off the column after Pa with 1N HCl and its ²³³ U concentration measured to correct for ²³³ Pa mass. Typically <0.01% of added ²³⁶ U spike is found in the Pa split.									
Timm et al. (2002)	Pa Th	1	TRU spec	20 ml Pu in 20 ml 4M HCL + Np in 15 ml 8M HNO ₃ + 0.5 ml TiCl ₃	2M HCl + 0.015M oxalic acid				
				1M Al(NO ₃) ₃					

Continued on next page...

Table 2.2 continued from previous page. . .

Author	Elements Separated	Col No	Resin	load in	wash	elute	elute	yield	blank
Lundstrom et al. (1998)	Pa	1, 10 ml	AG1 X8	8-10 ml 12M HCl	16 ml 12M HCl	Pa in 2 Cv 9M HCl + 0.05M HF	Th in 10 ml Pa in 20 ml Pa 95% 1M HCL 0.1M HCl + 0.1M HF		
		2, 1 ml	AG1 X8	Dry down, Saturated, 0.5 ml 12M HCl	2 Cv 12M HCl, 4 Cv 6 M HCl	2 Cv Pa in 3 Cv 9M HCl + 0.05M HF			
		3, 0.15 ml	AG1 X8	Dry down, Saturated, 0.5 ml 12M HCl	2 Cv 12M HCl, 4 Cv 6 M HCl	2 Cv Pa in 3 Cv 9M HCl + 0.05M HF			
		4, 0.15 ml	TEVA	0.05 ml 2M HNO ₃	5 Cv 2M HNO ₃	Pa in 9N HCl + 0.05M HF			BDL
		Samples are dissolved basalts. After spiking the samples were fumed twice in HClO ₄ to ensure equilibration. Measurement is by TIMS so the purity of the final solutions must be very high hence the 4 columns. It is noted that the TEVA column gives good separation from Zr and Nb. 30-40fg of ²³¹ Pa is required for each measurement.							
Lundstrom et al. (1998)	Th, U, Ra	1, 10 ml	AG1 X8	10 ml 6N HCl	3×2 ml 6N HCl	U, Fe in H ₂ O			
			100-200 mesh						

Continued on next page. . .

Table 2.2 continued from previous page...

Author	Elements Separated	Col No	Resin	load in	wash	elute	elute	yield	blank
		2, 8 ml	AG50 X12	Load + wash	2×1 ml 6N HCl, 16 ml	Ra in 2 ml Th in 16 ml			
			200-400 mesh	from coll drip	6N HCl	4M HNO ₃ , 16 ml	4M HNO ₃		
				directly onto		4M NO ₃	+0.5M HF		
				col 2					
	U purification	1	AG1 X8	8M HNO ₃	8M HNO ₃	8M HNO ₃			15 pg
	Th purification	1. 0.5 ml	TEVA	Dry	down, 8 Cv 2N HNO ₃	Th in 5 Cv 6N HCl			
				Drop	Saturated				
				boric acid, 0.5ml 4M HNO ₃					
		2, 0.15 ml	AG1 X8	Dry	down, 12 Cv 8M HNO ₃	6M HCl			40 pg
				0.05 ml					
				8M HNO ₃					
	Ra purification	1, 0.7 ml	AG50 X12	0.1 ml 4N HCl	99% of Ba in 10 ml 4N HCl	Ra in 4 ml			
					4N HCl	4M HNO ₃			
		2, 0.15 ml	Sr spec	0.05	ml 0.2 ml 3M HNO ₃	Ra in 0.45 ml			BDL
				3M HNO ₃		3M HNO ₃			
Burnett and Yeh (1995)	U Th Pa	1,	TRU-	20-30	ml 10 ml 2N HNO ₃ ,	Th in 15 ml 1N HCl	U and Pa in		
		6×0.9 cm,	Spec	2N HNO ₃			20 ml 0.1N HCl +		
							0.1N HF		
		0.7 g resin			2 ml 9N HCl,				
					10 ml 4N HCl,				

Continued on next page...

Table 2.2 continued from previous page. . .

Author	Elements Separated	Col No	Resin	load in	wash	elute	elute	yield	blank
	U Pa	2,	AG 50W- 11	ml	10 ml 0.1N HCl	Pa in	10 ml 10 ml 0.1N HCl, U Pa	80%,	
		6×0.9 cm, x8	0.1N HCl+			0.1N HCl + 0.1N	in 20 ml HCl	Th 80%, U	
			1N HClO ₄			HF		90%	
		1 g resin							
		Samples are phosphatic crusts and thus load volume is adjusted to ensure phosphoric acid is less than 0.1M to not introduce matrix effect. The U–Pa split from the first column is fumed in HClO ₄ to remove any F [−] , the sample is never dried down thus some HClO ₄ remains.							
Morgenstern et al. (2002)	Pa	1, 0.5 ml (3 mm di- ameter)	Silica Gel 8N HNO ₃	U, Np, Th in 6 ml	Pa in 4ml 0.4M ox- alic acid			90-95%	
		2, 0.25 ml (3 mm di- ameter)	Silica Gel 8 ml 0.2M oxalic acid + 7.2N HNO ₃	Residual U in 4ml 8N HNO ₃	Pa in 600 μl 5% H ₂ O ₂ + 3N HNO ₃			95%	
		Method for separation of Pa from U ₃ O ₈ samples from the nuclear industry. Elute from 1st column is put directly onto the 2nd column in conc nitric. H ₂ O ₂ is decomposed with Pt after Pa separation.							

Table 2.2: A compilation of literature elemental separation techniques. Each method is summarised with: the elements that are to be measured; the number and size of the columns used; the type of resin; the load, wash and eluting solutions, with the elements which are washed off the column; and where information is given, the yield and blank of the procedure. Notes on selected techniques are given below each record.

Method of column calibration

A uraninite standard, JU-1 (Section 2.4.4) was used to test two separation recipes based loosely on those of Nour et al. (2002) and Robinson et al. (2004a) (Table 2.2). In each case JU-1 is treated as a sample and passed through the column. Rather than simply collecting the Th, Pa, and U splits, many fractions were collected separately to investigate in greater detail when each element is eluted from the column. Once the procedure was shown to work for the JU-1 standard, a solution mimicking a sample (by adding 50 mg Fe) was calibrated to ensure the procedure worked under realistic chemical conditions.

TEVA resin

A separation using the Eichrom resin “TEVA” was investigated following the method of Nour et al. (2002) (Table 2.2). The principle of this approach is that TEVA resin should retain both Th and Pa in 2.5N HNO₃ while U is washed off, while in 6N HCl Th is not retained by the resin and Pa will also elute from the column if HF is present. A 200 μ l Teflon column was used, loading the “sample” in 2.5N HNO₃, which should wash off any U. The Pa and Th were then eluted from the column with 6N HCl + 0.05N HF, the HF was used to mobilise Pa from the column along with the Th. A calibration with only U and Th (Figure 2.8, a and b) found that excellent separation of Th from U could be achieved with a single column. Presumably Pa would also follow Th and enable good separation from U, with the added possibility that delaying the addition of HF to the 6N HCl elution would allow the separation of Th from Pa. When Fe was added to a JU-1 solution to mimic a sample, however, this TEVA procedure fails (Figure 2.8, c,d and e). Fe elutes from the column with the load solution and subsequent washes with so that separation of Fe from U is very poor. Furthermore the Th and Pa are not retained on the column with 2.5N HNO₃ but instead ‘bleed’ through with the Fe and U.

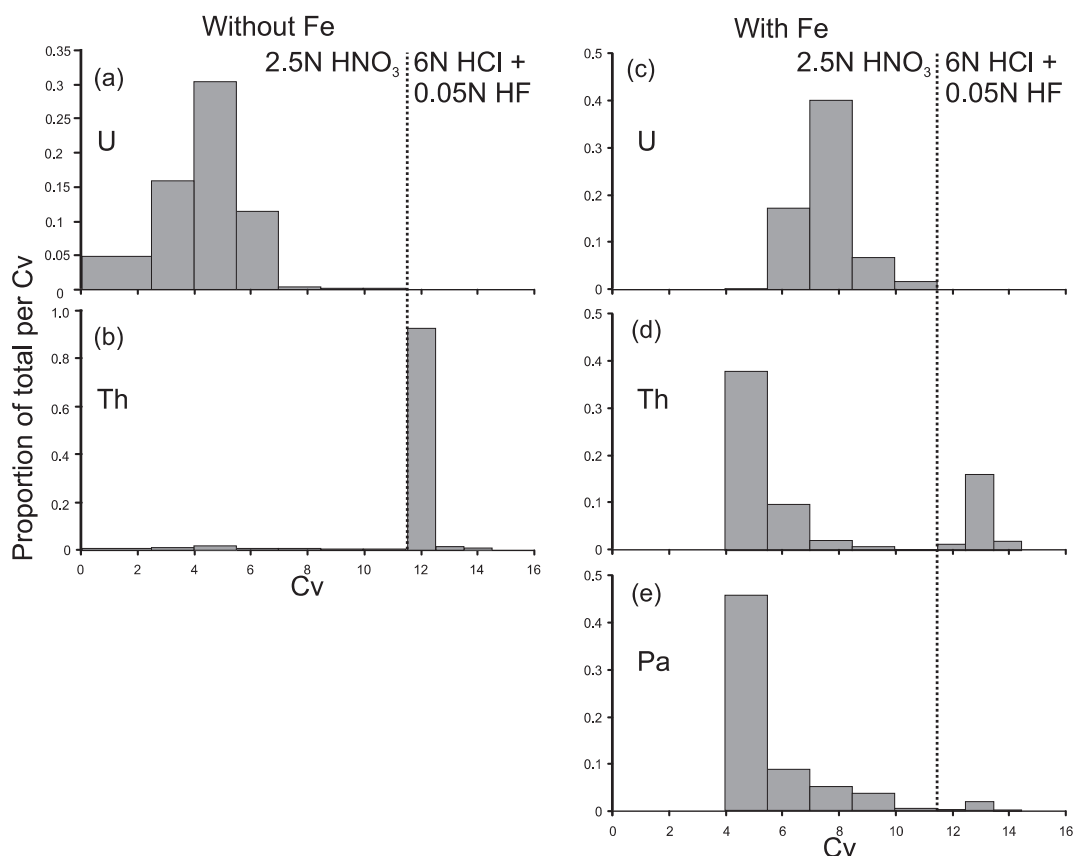


Figure 2.8: Histograms showing the elution behaviour of TEVA resin. (a and b) shows how just a uraninite standard, HU-1, doped with Th elutes from the column, while (c,d and e) illustrate how the addition of Fe to a uraninite standard, JU-1, alters the elution behaviour of U, Th and Pa. No Pa elution is shown for the “without Fe” scenario because the HU-1 did not have sufficient ^{231}Pa to use for calibration. It would be expected, however, that Pa followed a similar elution to Th if HF is used with 6N HCl to elute it.

The TEVA resin is therefore unsuitable for use as the principle separation for U, Th and Pa for load solutions that contain a lot of Fe, although it may be of use as a ‘clean-up’ column. Scaling up the chemistry may negate the effect of Fe on the retention of Th and Pa on the column but would add extra blank to the procedure and would prove a costly modification due to the high cost of Eichrom resins, therefore the TEVA method was abandoned.

AG1-X8 Resin

The column procedure using Dowex “Biorad AG1-X8” resin is a modification of the procedure used in Robinson et al. (2004a) which is in turn based on the method of Chen et al. (1986). The principle of this approach is that both Th and Pa have a high affinity for the resin in 7.5N HNO₃, while Fe is washed off easily and U is moderately adhered to the resin. In 6N HCl both Th and Pa are washed off the column (the latter only if HF is present) and U is strongly retained on the column. The remaining U is then stripped from the column with Milli-Q giving a pure U split free from Fe and Th (Figure 2.9). This approach is possible with samples such as seawater and deep-sea sediments where low yields are not a problem for U but the recovery of Th and Pa are important.

The separation procedure used is as follows:

- The AG1-X8 100-200 mesh resin was first prepared by cleaning a batch with Milli-Q, decanting the Milli-Q off and cleaning with 2N HNO₃. This pre-cleaning was repeated three times before the resin is used.
- The columns used were 0.5 ml Teflon columns made with shrink-fit Teflon tubing, cleaned by heating in 7.5N HNO₃ overnight. The frits were punched out of sheet polyethylene frit material, and cleaned and stored in 2N HNO₃.
- 0.5 ml of resin was loaded into each column and washed with 2 ml Milli-Q. The column was then washed with 2 ml 6N HCl, and 4 ml Milli-Q, to remove any U and Th from the column. No HF was used as any HF remaining on the column may hamper the performance of the resin in retaining Pa, and the procedural blank for ²³¹Pa was very low anyway. The column was then converted from Cl⁻ to NO₃⁻ with 4 ml of 7.5N HNO₃.
- The sample was loaded onto the column in 0.5 ml of 7.5N HNO₃, and washed

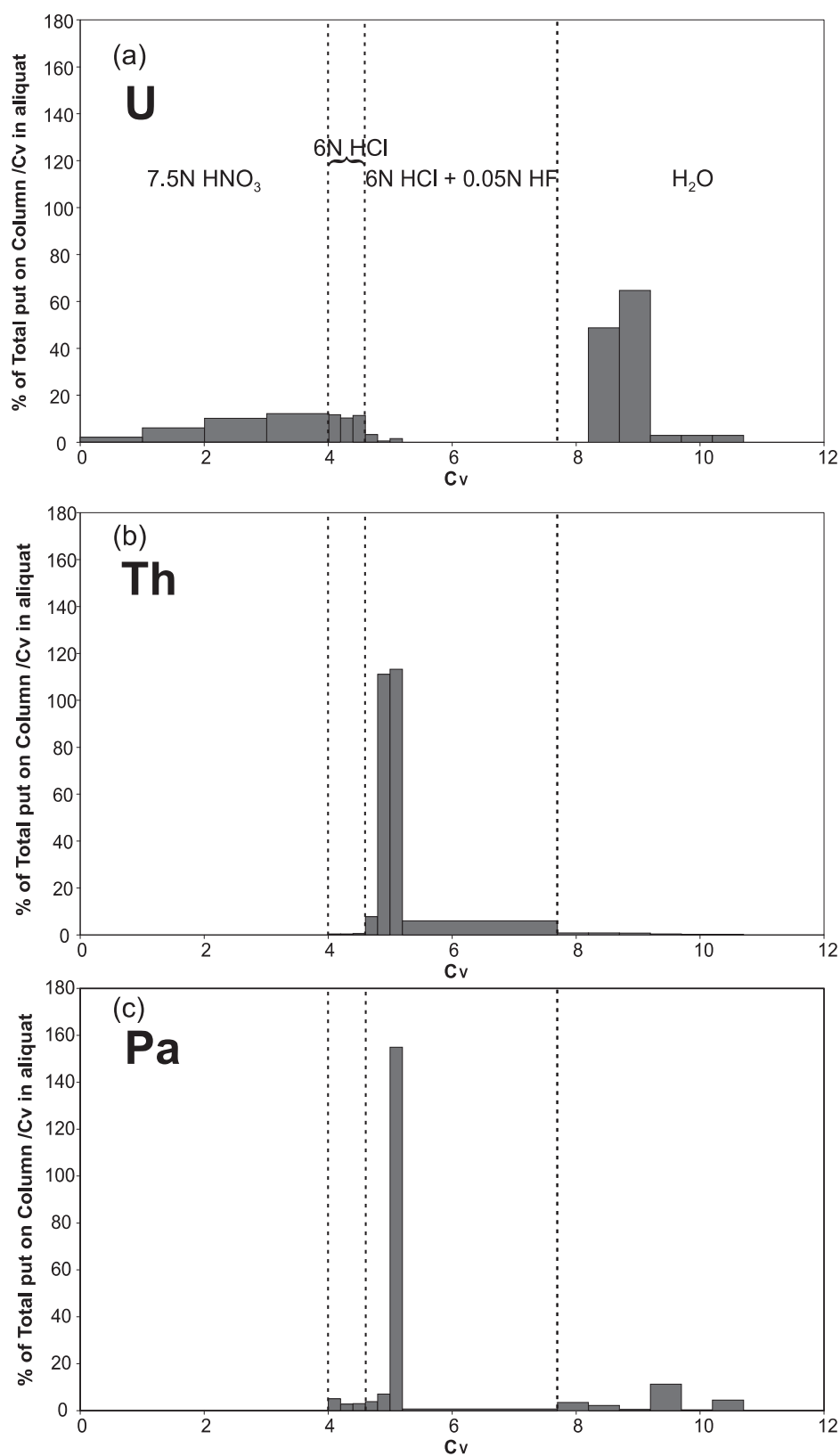


Figure 2.9: Histograms showing the elution behaviour of AG1-X8 resin. The calibration was carried out with a JU-1 standard doped with Fe to simulate a sample. The elution of Pa is dependent on the presence of trace HF in the 6N HCl. Elution of Th with 6N HCl only, enables the separation of Pa from Th. 72

in with a further 1.5ml 7.5N HNO_3 . This washed off all of the Fe and about half of the U.

- The eluting acid was switched to 6N HCl to convert the resin to Cl^- , allowing Th and Pa to be mobilised and U to stick to the resin. The conversion of the column takes 300 μl so the Th and Pa were not collected until after at least 300 μl has been eluted, ensuring good separation from U.
- If Pa and Th were to be eluted together then the eluting acid was changed to 6N HCl + 0.05N HF and Pa and Th were collected in 2 ml. If Pa was to be separated from Th the eluting acid remained 6N HCl and Th collected in 2.5 ml and then Pa collected in 2 ml 6N HCl + 0.05N HF.
- To achieve good separation of all three elements of interest, three column passes were required. A first column to separate U from Th and Pa which were collected together. Then a second column, loaded with the Th-Pa split from the first, to further separate Th and Pa from any remaining U, and to separate Pa from Th. A third column loaded with the Pa split from the second was used to further clean Pa for Th contamination. The same column was reused for each column pass as the only extra blank added will be from the sample itself, and the new reagents used. Between each column pass the resin must have all traces of HF washed off with Milli-Q, and be converted back to NO_3^- with 4 ml of 7.5N HNO_3 . The splits taken from the first and second columns to be loaded onto the second and third must also be converted from Cl^- to NO_3^- . This was achieved by drying the solution down to a drop < 1 mm across then making up to 200 μl and repeating twice before making up to 500 μl . Care must be taken so as not to dry completely which would lead to Pa being lost to the beaker walls.

2.4 Standards and spikes

2.4.1 Isotope dilution

When using a multi-collector mass spectrometer to measure more than one isotope the uncertainty in a measurement of a ratio of two isotopes is far less than the intensity of each isotope. This is due to the ability of the mass spectrometer to measure both isotopes at the same time. While the intensity varies with plasma or filament condition, this variation should be similar for both isotopes, leading to more precise ratios than absolute intensity measurements.

To make use of this feature of mass spectrometry to measure concentrations of a single isotope, a sample must be spiked. A spike is either an almost mono-isotopic solution of a different isotope to the isotope of interest (but still of the same element), or a mixture of isotopes whose proportions are markedly different than from natural samples (Figure 2.10). An example of the former would be the addition of pure ^{233}Pa to a sample to measure ^{231}Pa , and example of the latter is the addition of an enriched ^6Li spike with a $^6\text{Li}/^7\text{Li}$ of 22.007 (IRMM-015) to a sample of natural composition with a $^6\text{Li}/^7\text{Li}$ of ≈ 0.0821 .

In the simple case of a pure mono-isotopic spike the derivation of concentrations is simple. A known mass of well-calibrated spike solution is added to the sample and equilibrated. The ratio of spike isotope to sample isotope is measured and from this the amount of sample isotope can be calculated.

Where the spike isotope is not pure, but contains some of the sample isotope of interest then this must be taken into account when calculating the amount of sample isotope coming from the sample.

The measured ratio of the mixture of sample and spike, R_M , can be described as

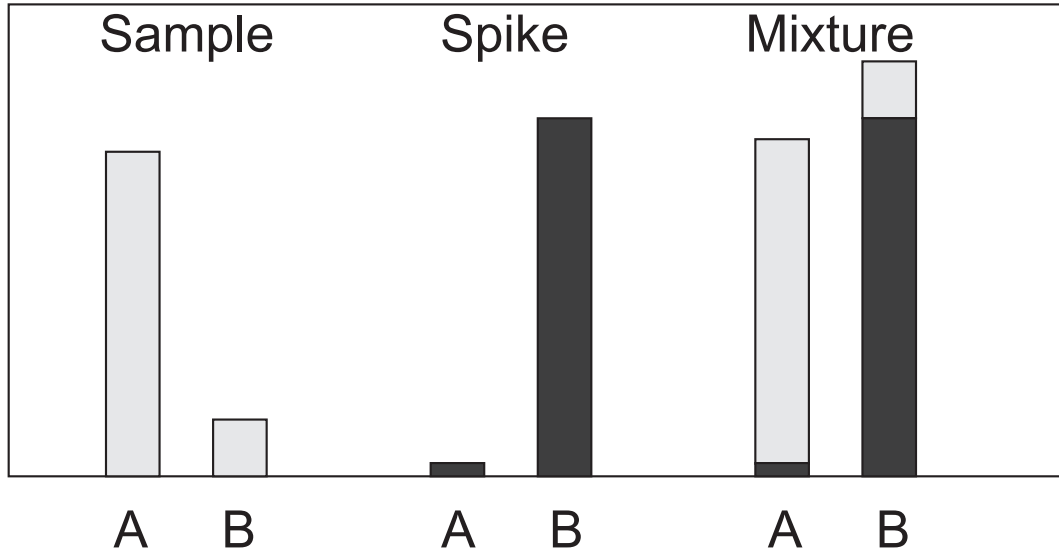


Figure 2.10: A schematic representation of isotope dilution of a sample with two isotopes, A and B.

the addition of the spike, S, and natural, N, ratios.

$$\left[\frac{A}{B} \right]_M = R_M = \frac{A_N + A_S}{B_N + B_S} \quad (2.5)$$

Where A and B are the number of moles of each isotope. As the number of moles of an isotope is the same as the number of moles of the element, M, multiplied by the abundance of the isotope, %:

$$R_M = \frac{M_N \times \%A_N + M_S \times \%A_S}{M_N \times \%B_N + M_S \times \%B_S} \quad (2.6)$$

or,

$$M_N = M_S \times \frac{\%A_S - R_M \times \%B_S}{R_M \times \%B_N - \%A_N} \quad (2.7)$$

As mass = number of moles $\times$ atomic weight,

$$P_N = \frac{P_S \times W_N}{W_S} \times \frac{\%A_S - R_M \times \%B_S}{R_M \times \%B_N - \%A_N} \quad (2.8)$$

Where P is the mass of the sample or spike and W is the atomic weight. The mass of the spike is determined from its concentration (by calibration) and from the weight of spike solution added to the sample.

2.4.2 ^{236}U and ^{229}Th spikes

Two mixed spikes are used to make measurements of U and Th concentrations in water and sediment samples. Because U and Th are commonly measured in the same samples, a spike containing both ^{236}U and ^{229}Th reduces the labour involved in spiking samples, and cancels the weighing errors from some calculations.

It is important to add approximately the same mass of spike isotope to a sample as there is of the isotope of interest in the sample. This is due to the amplification of the uncertainty where the isotope ratio of the sample and spike mixture deviates from the average of the isotopic compositions of the spike and sample (DeBievre and Debus, 1965). Thus it is necessary to have two mixed spikes so that the concentrations ^{236}U and ^{229}Th can be best matched to the ratio of U and Th in typical samples for both seawater and for sediments. The compositions of both mixed spikes, “Oxford Water Spike” and “Oxford Carbonate Spike” are summarised in Table 2.3.

Calibration of U and Th spikes

The concentration of ^{236}U in both Oxford Water Spike and Oxford Carbonate Spike was determined by Robinson (2003)(Table 2.3). This was achieved by measuring mixtures of each spike with the gravimetric standard CRM-145 (Section 2.4.4 and Table 2.4). Mass bias is corrected for internally using the $^{238}\text{U}/^{235}\text{U}$ ratio. The isotope dilution approach (Section 2.4.1) is required to account for any ^{238}U in the spike, determined through analysis of the pure spike isotope ratio.

Calibration of the ^{229}Th concentrations was also performed by Robinson (2003) (Table 2.3), but the calibration of Oxford Water Spike was repeated by Thomas

	²²⁹ Th	²³⁰ Th	²³² Th	²³³ U	²³³ Pa	²³⁴ U	²³⁵ U	²³⁶ U	²³⁸ U	atomic Th	wt	atomic U	wt
mass, amu	229.031755	230.033127	232.038054	233.039628	233.0402	234.040946	235.043924	236.045562	238.050784				
$t_{1/2}$, ^a	7,900 ^a	75,690 ^b	1.40100×10 ⁺¹⁰ _c	1.59×10 ⁺⁵ _d	7.657×10 ⁻² _e	245,250 ^b	7.0381×10 ⁺⁸ _f	2.34×10 ⁺⁷ _d	4.4683×10 ⁺⁹ _f				
λ , a ⁻¹	8.77×10 ⁻⁵	9.158×10 ⁻⁶	4.94752×10 ⁻¹¹	4.359×10 ⁻⁶	9.052	2.8263×10 ⁻⁶	9.8485×10 ⁻¹⁰	2.96×10 ⁻⁸	1.5513×10 ⁻¹⁰				
Natural U	Atom % 0	4.1632×10 ⁻⁶	0.9999958	0	0	5.4887×10 ⁻⁵	7.2527×10 ⁻³	0	0.99269	232.038046		238.028756	
Oxford Carbonate Spike	Atom % 0.99598 Conc. 2.43494×10 ⁻¹⁰ g/g 2.4	0.00006	0.00396	0	0	3.865×10 ⁻¹¹	4.20573×10 ⁻⁵	0.999727537 9.09591×10 ⁻⁸	0.000230406	229.043725		236.045982	
Oxford Water Spike	Atom % 0.32742 Conc. 5.128×10 ⁻¹³ g/g (5.083×10 ⁻¹³) 2 σ % 15.7 (16.8)	0.00075	0.67182	0	0	7.232×10 ⁻¹¹	4.23487×10 ⁻⁵	0.999717777 5.77174×10 ⁻⁸	0.000239874	231.052215		236.046001	

Table 2.3: The half lives and decay constants of all isotopes of interest (^a Goldstein et al. (1989), ^b Cheng et al. (2000), ^c Holden (1990), ^d Holden (1989), ^e Usman and MacMahon (2000), ^f Jaffey et al. (1971)), and the atomic abundances in natural materials, and the two mixed ²³⁶U and ²²⁹Th spikes: Oxford Carbonate Spike; and Oxford Water Spike. The spike concentrations and associated uncertainties as calibrated by Robinson (2003) are also shown, values in brackets are as calibrated by Thomas.

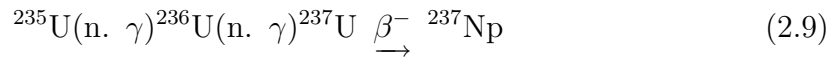
in an attempt to reduce the uncertainty. Here the spike was mixed with a secular equilibrium standard HU-1 (Section 2.4.4) with a known $^{238}\text{U}/^{230}\text{Th}$ ratio (Cheng et al., 2000). The concentration of ^{238}U in the mix of HU-1 and spike is derived from the spike ^{236}U previously calibrated. The ^{230}Th concentration can then be calculated from the $^{238}\text{U}/^{230}\text{Th}$ of HU-1. The $^{229}\text{Th}/^{230}\text{Th}$ measured then gives the concentration of ^{229}Th in the spike.

2.4.3 ^{233}Pa spike

Because Pa has only one “long lived” isotope, ^{231}Pa ($t_{1/2} = 3.276 \times 10^5$ a, the next longest being ^{234}Pa $t_{1/2} = 6.69$ hours) a short-lived radioisotope must be used as the spike isotope. The longest lived such isotope available to act as a spike for ^{231}Pa is ^{233}Pa which has a half life of 26.967 days (Usman and MacMahon, 2000). ^{233}Pa can be produced by two methods: by milking ^{237}Np ; or by irradiation of ^{232}Th . Both approaches were tested and used during this research.

^{233}Pa production from ^{237}Np milking

^{237}Np ($t_{1/2} = 2.14 \times 10^6$ a) is not found naturally but is formed as a waste product of the nuclear industry, through either the capture of thermal neutrons by ^{235}U ,



or by the interaction of fast neutrons with ^{238}U .



^{237}Np then decays to ^{233}Pa via alpha emission.



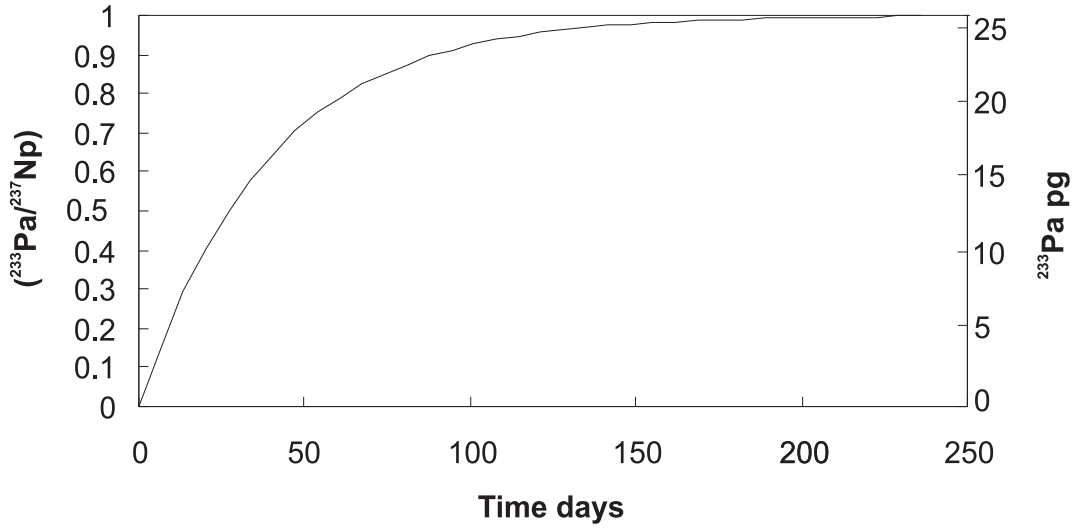


Figure 2.11: The ingrowth to secular equilibrium of a ^{237}Np solution, with zero initial ^{233}Pa , showing the increase in the ($^{233}\text{Pa}/^{237}\text{Np}$) ratio, also shown is the amount of ^{233}Pa produced from a ^{237}Np solution containing $750\ \mu\text{g}$ of ^{237}Np .

A solution of ^{237}Np will grow in daughter ^{233}Pa as it decays. The concentration of ^{233}Pa will increase until secular equilibrium is reached between the two isotopes. The rate at which this equilibrium is reached is dependent on the decay constant of ^{233}Pa as:

$$^{233}\text{Pa} = \left(\frac{\lambda_{\text{Np}}}{\lambda_{\text{Pa}} - \lambda_{\text{Np}}} \right) ^{237}\text{Np}_0 (e^{-\lambda_{\text{Np}}t} - e^{-\lambda_{\text{Pa}}t}) + ^{233}\text{Pa}_0 e^{-\lambda_{\text{Pa}}t} \quad (2.12)$$

and as $\lambda_{\text{Pa}} \gg \lambda_{\text{Np}}$,

$$\left[\left(\frac{^{233}\text{Pa}}{^{237}\text{Np}} \right) - 1 \right] = \left[\left(\frac{^{233}\text{Pa}}{^{237}\text{Np}} \right)_i - 1 \right] e^{-\lambda_{\text{Pa}}t} \quad (2.13)$$

This means that after leaving the spike for one half life (26.967 days) the activity of the ^{233}Pa will be half the activity of ^{237}Np and after three half lives (80.901 days) the activity of ^{233}Pa will have reached 87.5% (Figure 2.11).

The ^{237}Np solution at Bristol University used for production of ^{233}Pa in this study contains approximately $750\ \mu\text{g}$ of ^{237}Np . The ^{237}Np solution is stored in a mixed acid

of 7N HNO_3 + 0.05N HF. A few drops of H_2SO_4 were added to the ^{237}Np solution before it was acquired by Bristol to prevent accidental complete evaporation of the solution. After milking ^{233}Pa from the ^{237}Np solution, the ^{237}Np solution must be left for at least 3 months to allow enough ^{233}Pa to grow in before another milking is performed. Three months of ^{237}Np decay will produce approximately 20-25 pg of ^{233}Pa , sufficient for spike calibrations and measurement of samples with ~ 100 fg of ^{231}Pa .

Due to the toxicity and radioactive hazard of ^{237}Np , care must be taken while preparing the ^{233}Pa spike. All apparatus used is monitored for ^{233}Pa via gamma spectrometry after use and kept for at least three months and monitored again to ensure the absence of ^{237}Np contamination (through monitoring ingrowth of ^{233}Pa). All batches of ^{233}Pa were prepared at the Department of Earth Sciences, University of Bristol, UK.

The separation procedure is that of Regelous et al. (2004), and is based on the high affinity of Pa to silica in 7N HNO_3 while Np, U, and Th are washed from the column and the ability of trace HF to solubilise Pa. A silica gel column is prepared by loading 5 ml of MERCK “Silica Gel 60”, 60–230 mesh, in a 7 cm Bio–Rad column. This is then washed with Milli–Q water and 10 ml 7N HNO_3 . The Np solution, stored in 7N HNO_3 + trace HF, is dried down with a few drops of HClO_4 , and fumed to drive off the HF. The Np is loaded onto the column in ~ 2 ml of 7N HNO_3 and washed on with a further 5 ml 7N HNO_3 . The load and wash solutions are collected from the column and monitored for ^{233}Pa by gamma spectrometry. If no ^{233}Pa is found in the wash then the column is washed with a further 2×35 ml 7N HNO_3 to remove all the Np, U, and Th from the column. The ^{233}Pa is then collected with 2×30 ml 7N HNO_3 + 0.05N HF. The strength of the HF used is critical: too low and the Pa remains on the column; too high and the HF starts to dissolve the silica gel which blocks the column resulting in very long elution times and introduces Si into the Pa

fraction which must be removed by fuming with HF. All washes and the column are monitored for ^{233}Pa to ensure good recovery. To achieve good separation of Pa and Np the separation is repeated up to 4 times with new columns, ensuring all HF is driven off between each column by fuming with HClO_4 . Aliquots containing Np are combined and evaporated to a smaller volume, before being brought up in 7N HNO_3 + 0.05N HF and stored for the next milking separation.

Good separation of Pa from Np is crucial as any Np left in the Pa spike will continue to form ^{233}Pa and hence the concentration of ^{233}Pa will not be a simple function of the decay constant of ^{233}Pa .

$$^{233}\text{Pa}_t = ^{233}\text{Pa}_0 e^{(-\lambda_{233}t)} + ^{237}\text{Np}_0(1 - e^{(-\lambda_{237}t)}) \quad (2.14)$$

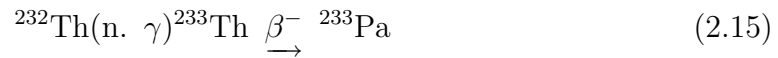
It has been shown by Regelous et al. (2004) that an atom $^{237}\text{Np}/^{233}\text{Pa}$ ratio <30 in the spike is sufficient to only require one calibration of ^{233}Pa concentration following milking. After 3 passes through silica gel columns the $^{237}\text{Np}/^{233}\text{Pa}$ atom ratio is typically about 30–100 and a fourth column can bring the ratio down to ~ 1 . The $^{237}\text{Np}/^{233}\text{Pa}$ atom ratio is measured by MC-ICP-MS by scanning across masses 229.5–238.5, and comparing peak intensities. This check of $^{237}\text{Np} - ^{233}\text{Pa}$ separation is performed on a $\times 150$ dilution of the Pa cut from the column, so as to reduce the amount of ^{237}Np introduced to the mass spectrometer if separation was poor. Separation of U from Pa is also important as calibration of the spike assumes zero initial ^{233}U , the immediate decay product of ^{233}Pa . U–Pa separation is monitored by measuring ^{238}U in the Np solution and in the final Pa spike. The Pa/U separation has been measured as $\sim 2 \times 10^6$ which is easily sufficient to assume zero initial ^{233}U in the spike.

This method of ^{233}Pa spike production has the advantage that it can be performed in a standard clean laboratory with designated area for ‘hot’ chemistry, with suitable precautions for the radioactivity of ^{237}Np and its high toxicity. Spike produced

from ^{237}Np milking will have a very low ^{231}Pa content as previous milking will have removed it, this is significant for very low concentration measurements where the contribution from ^{231}Pa in the spike may be significant. The ^{232}Th content is also likely to be lower than for production via neutron capture as large quantities of ^{232}Th are not used in the production process. Disadvantages of this method are: the total amount of ^{233}Pa that can be produced is limited by the amount of Np available, which is small due to the radioactive hazard; and contaminant U and Th build up in the Np solution over time as after each milking all of the washes and Np cuts are combined together.

^{233}Pa production from ^{232}Th irradiation

^{233}Pa has also been produced through the thermal neutron irradiation of ^{232}Th producing ^{233}Th , and subsequent beta decay to ^{233}Pa .



Due to the possibility of producing undesired, potentially highly active, nuclides from any impurities, a high purity ThO_2 is used.

18 mg of ThO_2 powder was weighed out into a polypropylene capsule and sent for irradiation at the Imperial College reactor at Ascot, UK for 21 hours. Short lived fission products were allowed to decay away for one week before the capsule was released for chemical separation.

Separation of Pa from Th and U was undertaken at the Department of Earth Sciences, University of Bristol, UK, to make use of the radiochemical laboratory facilities and gamma spectrometer.

The capsule was carefully cut open in a 60 ml Teflon beaker, under HCl, with a scalpel. Using a scalpel blade with acid added a significant amount of Fe to the solution, but using acid rather than water significantly reduced the amount of

time required for the separation as one fewer drying down was required. The pieces of capsule were then carefully removed with tweezers and rinsed with HCl into the beaker. The pieces of capsule and the solution in the beaker were then monitored with the gamma spectrometer for ^{233}Pa to check the Pa had been transferred successfully into the beaker. It should be noted that no direct calculation of yield can be made due to the differing geometries and shielding of the capsule and the solution in the Teflon beaker. The 60 ml beaker is then placed on a hotplate with the cap on at $\sim 150^\circ\text{C}$ for 1 hour to dissolve the ThO_2 . It was found that wafting HF vapour over the solution ensured Pa remained in solution without providing enough F^- to allow insoluble ThF_4 to form which would inhibit Pa recovery.

Once dissolved and allowed to cool, the solution (in 9N HCl) is loaded onto a 2 ml Dowex Bio-Rad AG1-X8 column. Separation then follows that of Anderson and Fleer (1982). The Th–Pa solution is loaded in 6 ml and then washed with 2 ml 9N HCl, used previously to wash the beaker the Th was dissolved in. This rinsing is repeated 4 times to wash off the Th. All the elutant is retained and monitored for ^{233}Pa , along with the beaker used for dissolution, on the gamma spectrometer. The eluting acid is then changed to 24 ml 9N HCl + 0.1N HF which washes off the Pa for collection and monitoring on the gamma spectrometer. The used column is also checked for ^{233}Pa to ensure all of the ^{233}Pa is collected. U and Fe are retained on the column throughout this procedure. The Pa solution is then repeatedly dried down to near dryness and taken back up in 9N HCl to drive off any remaining HF. This Pa solution is then heated with HF vapour to ensure complete dissolution of Pa and then the column separation is repeated, with a new column, to get better separation of Pa from Th and U. After final separation the ^{233}Pa is made up in 3N HCl + trace HF and transferred into a Teflon bottle for use as a spike.

Production of ^{233}Pa via neutron bombardment has the advantage over ^{237}Np milking that the amount of spike produced is limited by the amount of ^{232}Th , and

the intensity and duration of neutron bombardment that can safely be carried out in a nuclear reactor, rather than the amount of ^{237}Np . Thus more ^{233}Pa can be produced, which is required for samples with high ^{231}Pa contents such as ocean sediments. The purity of the spike is however poorer than for ^{237}Np milking due to the large amounts of Th used and the bombardment of ^{230}Th to produce ^{231}Pa . This method also requires access to a nuclear reactor as well as designated ‘hot’ space in a clean lab to perform the chemical separation.

^{233}Pa spike calibration

Good characterisation of the ^{233}Pa spike is crucial to making good ^{231}Pa measurements because a large fraction of the uncertainty arises from uncertainty in the spike concentration. Because the concentration of ^{233}Pa decreases over time due to decay (Equation 2.14), it is essential that the time of calibration and the time of final separation of U from Pa during sample preparation is recorded. This allows the concentration of the spike at the time of chemistry to be calculated. ^{233}Pa decays to ^{233}U - an isotope of similar mass with a considerably longer half life (159 ka). The concentration of ($^{233}\text{Pa} + ^{233}\text{U}$) can therefore be assumed to be constant once the final separation of Pa and U is performed.

Calibration of ^{233}Pa in reported studies has been calibrated against a secular equilibrium U-series standard, because no gravimetric ^{231}Pa standard is available. Many authors make use of the widely unavailable TML (Table Mountain Latite) silicate standard (Regelous et al., 2004; Pickett et al., 1994; Pichat et al.), while others use in house standards with matrices closer to their samples (rhyolitic glass, Bourdon et al. (1999) and speleothem, Mortlock et al. (2005)). Secular equilibrium calibration requires the ^{233}Pa spike to be added to the secular equilibrium standard - usually powdered - which is also spiked with ^{236}U spike. The spiked standard is fully dissolved and spike sample equilibration is ensured. The standard is then passed

Standard	$^{238}\text{U}/^{235}\text{U}$	$^{235}\text{U}/^{234}\text{U}$	$^{232}\text{Th}/^{230}\text{Th}$	$^{238}\text{U}/^{230}\text{Th}$	$^{232}\text{Th}/^{229}\text{Th}$	$^{230}\text{Th}/^{229}\text{Th}$	$^{238}\text{U}/^{231}\text{Pa}$
CRM-145	137.88	137.19					
ABC2			718.056		399.114	0.556	
HU-1	137.88	132.161		5.884×10^4			
JU-1	137.88	75	0.11	9×10^4			5×10^6
MIAOW	137.88	137.19	5.0×10^3	5.2×10^3	2.5×10^3	0.5	Trace Pa

Table 2.4: A Table of standards used in this study, showing the isotope ratios. Values in *italics* are approximate and not calibrated.

through a separation procedure to separate U and Pa. The measured $^{236}\text{U}/^{238}\text{U}$ gives the amount of ^{238}U in the standard using equation 2.8, and hence also the ^{231}Pa because ($^{231}\text{Pa}/^{238}\text{U}$) should be 1. The $^{233}\text{Pa}/^{231}\text{Pa}$ ratio then gives the concentration of the spike.

As no TML or other suitable secular equilibrium standard was available, a different approach was taken. Calibration of ^{233}Pa was performed against a ^{236}U spike. To ensure that any fractionation, due to differences in ionisation energy, between Pa and U does not effect the measured 233/236 ratio, the ^{233}Pa solution was spiked with ^{236}U and then left for 4-5 months until $\sim 95\%$ of the ^{233}Pa had decayed. The time of the initial separation of U from Pa during spike preparation was taken as the calibration “time”. The measured $^{233}\text{U,P a}/^{236}\text{U}$ ratio then gives the ^{233}Pa concentration when the spike was prepared. This method has the advantage that no assumption of secular equilibrium is required, and involves the propagation of fewer errors. It does assume that there is no initial ^{233}U in the spike, but this can be assessed during spike chemistry (Section 2.4.3)

2.4.4 Standards

A variety of standards are used while calibrating columns, optimising the mass spectrometer and making measurements, they are summarised in Table 2.4, and detailed here.

CRM-145, uranium, Certified Reference Material

CRM-145 is a gravimetric uranium standard made from a high purity metal, available from the New Brunswick Laboratory, NJ, USA. The $^{238}\text{U}/^{235}\text{U}$ is natural at 137.88 and the $^{235}\text{U}/^{234}\text{U}$ is also close to natural at 137.19 (Table 2.4). The $^{235}\text{U}/^{234}\text{U}$ ratio has been measured by Gideon Henderson using a standard-sample bracketing technique with HU-1 (which is in secular equilibrium (Cheng et al., 2000)), and by TIMS (Robinson, 2003; Cheng et al., 2000).

ABC2, thorium, Artificial Bahamas Carbonate

ABC2 (successor to ABC1) is a thorium standard, containing ^{232}Th , ^{230}Th and ^{229}Th , and was mixed and calibrated by Laura Robinson (Robinson, 2003). The isotope ratios in ABC2 are similar to that in spiked carbonate sediment samples so it can be used to externally correct samples for machine biases during standard-sample bracketing measurement.

HU-1, uranium, Harwell Uraninite

HU-1 is a uraninite standard which has been shown by Ludwig et al. (1992) and more recently Cheng et al. (2000) to be in secular equilibrium with respect to ($^{238}\text{U}/^{234}\text{U}$) and to be within 1.3 ‰ of secular equilibrium for ($^{238}\text{U}/^{230}\text{Th}$) (Cheng et al., 2000).

JU-1, uranium, Joachimsthal Uraninite

A uraninite standard containing ^{238}U , ^{230}Th , and ^{232}Pa used for column calibration. The standard was prepared from a dissolution of uraninite from a mine in St Joachimsthal¹, now in the Czech Republic. Dissolution was performed by the author on 07/01/03, by taking ~15 mg of uraninite (not crushed or powdered) in a Teflon

¹The mine in St Joachimsthal (Lieber and Leyerpapf, 1986) was the source of the “waggon loads” of pitchblende residue that Marie and Pierre Curie used in their experiments to produce radium (Sklodowska-Curie, 1903).

beaker and heating in HNO_3 conc for two days. The solution was separated from the residue by centrifuging and made up to 50 ml with 3N HNO_3 .

MIAOW, Uranium & Thorium, Mean Indian Atlantic Ocean Water

MIAOW is a mixture of uranium and thorium with isotopes that span the whole mass range of isotopes of interest. It has a composition similar to the combined Th and Pa fractions of typical sea-water samples (Table 2.4). This standard is used while optimizing the mass spectrometer, ensuring all peaks are centered in collectors.

2.5 Mass spectrometry

2.5.1 The machine

The mass spectrometer used throughout this study is a multi-collector inductively coupled plasma mass spectrometer, MC-ICP-MS,² manufactured by Nu Instruments (Figure 2.12). The Nu Instruments MC-ICP-MS (Belshaw et al., 1998) is a double focusing mass spectrometer, using a 350 mm ESA and a 250 mm magnet. Variable dispersion “zoom” optics focus the ions into an array of fixed collectors. The collector array (Table 2.5) consists of twelve Faraday collectors and three ion counting channels. The Faraday collectors have a dynamic range from $\sim 10^{-18}$ A to $\sim 10^{-10}$ A – this is measured as a voltage ~ 0.1 mV to 10 V, across a $10^{11}\Omega$ resistor (The current produced by the arrival of ions is not directly measured as a voltage across the $10^{11}\Omega$ resistor. The signal is amplified by a high impedance operational amplifier using the resistor). The ion counters have the sensitivity to register the arrival of a single ion and are used to measure up to 500,000 cps (8 mV).

²An alternative acronym is PIMMS (not PIMM’s) for Plasma Ionisation Multi-collector Mass Spectrometer.

F(+8)	F(+6)	F(+4)	F(+3)	F(+2)	F(+1)	AXIAL	F(-1)	F(-2)	IC(-3)	F(-4)	IC(-5)	F(-6)	IC(-7)	F(-8)
DVM ₀	DVM ₁	DVM ₂	DVM ₃	DVM ₄	DVM ₅	DVM ₆	DVM ₇	DVM ₈	IC ₀	DVM ₉	IC ₁	DVM ₁₀	IC ₂	DVM ₁₁

Table 2.5: A table showing the array of collectors in the Nu Instruments MC-ICP-MS. The top row is the nomenclature used in the text (following Robinson (2003)), F referring to Faraday collector and IC to ion counting channel. The number in brackets is the effective mass between each collector and the axial faraday collector. The effective difference is with respect to Pb isotopes. For lower/higher mass isotopes the collectors are less/more than one mass unit apart, requiring the zoom optics to focus the different isotopes into the collectors. The bottom row refers to the nomenclature used in the software that controls the mass spectrometer

Ion counters

The ion counters are ETP discrete dynode multipliers (Figure 2.13). Each dynode plate is made from an electron emissive material, which in this case is an “active layer” of an aluminium oxide material. When an ion strikes the first dynode electrons are emitted and drawn to the second dynode by the cascading voltage. Electrons hitting subsequent dynodes release more electrons, amplifying the signal by approximately 10^7 at the detector where a pulse is detected. The advantages of a discrete dynode configuration as opposed to a continuous one, is that as the cascade passes a plate it can start replenishing the lost electrons immediately. Thus the dead time is reduced as a new cascade can begin before an earlier one has finished, this also increases the maximum count rate that can be measured to over 5×10^7 cps. Such a high count rate is however not usually measured as the large number of ions would damage the detector, and to prevent this the Nu Instruments MC-ICP-MS has deflecting lenses which protect the ion counters at high count rates.

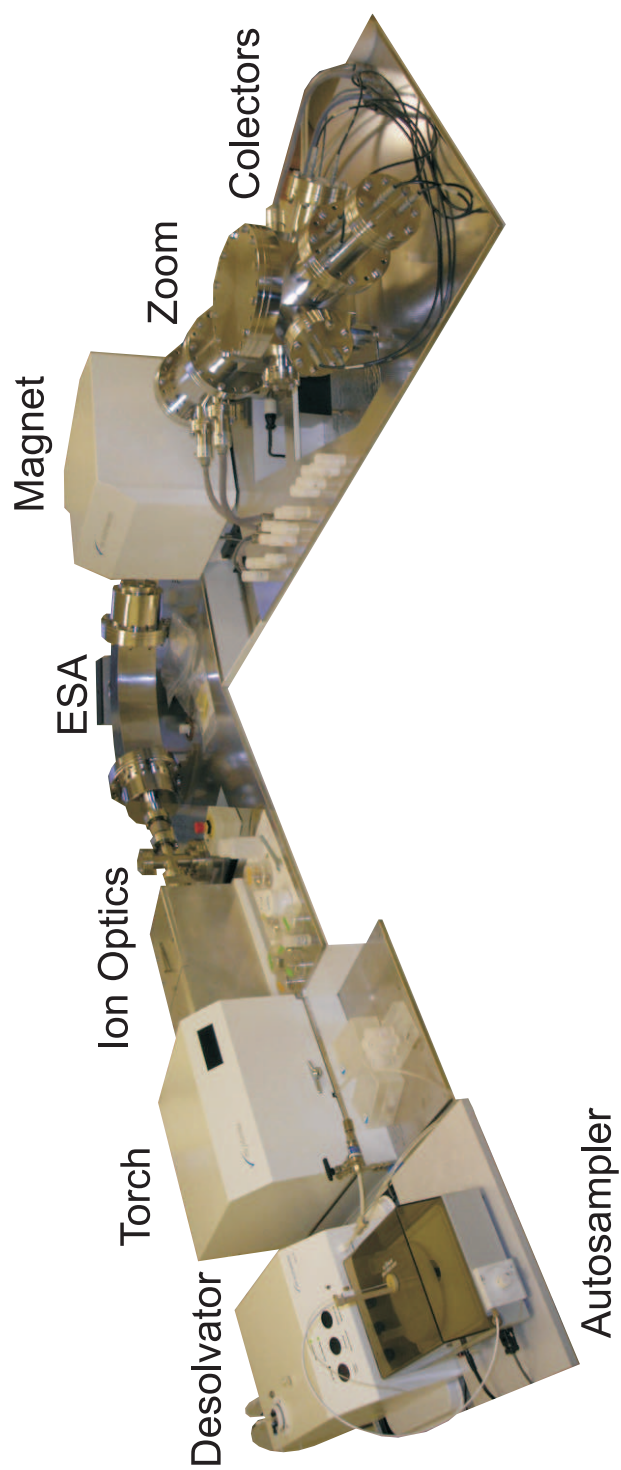


Figure 2.12: The Nu Instruments MC-ICP-MS, “Plasma 2” at Oxford. The principle components are labelled.

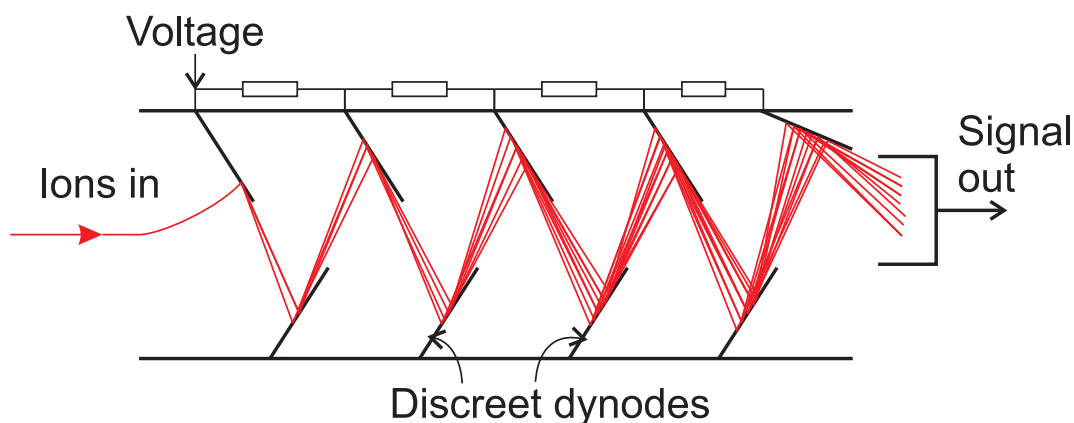


Figure 2.13: A schematic diagram of a discrete dynode ion counter showing the discrete dynodes, connected by chain of resistors so that there is a cascade of potential along the array towards the detector. the total amplification is approximately 10^7 .

Mass bias

The transfer of ions from the ion source in a plasma ionisation mass spectrometer is significantly dependent on the mass of the ions. Heavy ions are preferentially transferred into the mass spectrometer. This mass bias is primarily caused by the space charge effect (Gillson et al., 1988), where charged ions pass through a confined space their proximity and +ve charge repel one another out of the central ion beam. As the lighter ions are more easily moved out of the central ion beam the resulting beam transferred into the mass spectrometer is biased towards heavier ions. There is also a secondary effect caused by nozzle dispersion (Heumann et al., 1998), produced when a supersonic jet of gas exits the plasma torch or either of the cones and expands due to the reduced pressure. As the gas enters the region of lower pressure the lighter ions are more favourably “pumped” out, thus enriching the central beam in heavier isotopes. It should be noted that while the space charge effect is thought to have the greatest effect (Gillson et al., 1988) and acts only on charged species, nozzle dispersion can effect both charged and uncharged species. Thus although mass bias may be considered to be similar for U, Th and Pa, small discrepancies may occur due to uncharged nozzle dispersion being dependent on the chemistry of the element

in question.

To account for mass bias, a correction must be made. This is either by internal (or external) standardisation to a pair of isotopes with a known ratio, or by bracketing samples with a standard with a known isotopic ratio and normalising the samples to this to correct for all biases and interferences. To correct for mass bias a mass discrimination law must be chosen. These are typically either: linear (Equation 2.16), power (Equation 2.17), or exponential (Equation 2.18), although other laws are also used eg the “Russell” equation (Russell et al. (1978), Equation 2.19).

$$R_{\text{meas}} = R_{\text{real}}(1 + \varepsilon_{\text{linear}}\Delta M) \quad (2.16)$$

$$R_{\text{meas}} = R_{\text{real}}(1 + \varepsilon_{\text{power}})^{\Delta M} \quad (2.17)$$

$$R_{\text{meas}} = R_{\text{real}} \cdot \varepsilon_{\text{exp}}^{\Delta} \quad (2.18)$$

$$R_{\text{meas}} = R_{\text{real}} \cdot \left(\frac{m_2}{m_1}\right)^f \quad (2.19)$$

Where R_{meas} and R_{real} are the measured and real isotope ratios of isotopes m_1 and m_2 , ΔM mass units apart, f , is the mass bias factor and ε is the mass bias per unit mass. The mass discrimination law chosen for the analysis of U, Th, and Pa is the linear law (Equation 2.16) because, at the high mass end of the periodic table the relative mass difference between the isotopes is small, and to a good approximation the mass bias is linear. If precisions better than 0.01‰ are to be archived then a different law may be required, but this is not an issue for this study.

Ion counter dead time

When using the Faraday collectors to measure the beam intensity the machine measures a voltage across a resistor produced by the current produced from the beam of ions hitting the dynode of the collector. The ion counting channels measure the arrival of individual ions. Having measured an arrival, however, there is a time gap

during which the ion counter can not register the arrival of another ion. This “dead time” is caused by the mechanism by which the ion counter measures an individual ion. The arrival of a single ion on the collector dynode causes the emission of an electron which then causes a cascade of electrons, amplifying the signal such that it can be detected. While this cascade of electrons is occurring the ion counter is essentially dead to the arrival of another ion. The dead time becomes increasingly significant at high count rates where it is more likely an ion will arrive during the “dead time” period.

The dead time for ETP multipliers is expected to be approximately 18 ns. This has been quantified by Gideon Henderson as 23 ns for IC(-3). This was achieved by measuring the $^{235}\text{U}/^{234}\text{U}$ ratio of U-500 ($^{238}\text{U}/^{235}\text{U} = 1$) at varying intensities of ^{234}U . This known $^{235}\text{U}/^{234}\text{U}$ ratio of U-500 can then be used to calculate the ‘expected ^{234}U intensity for measurements with high count rates and hence the dead time from equation 2.20.

$$I_{\text{real}} = \frac{I_{\text{meas}}}{1 - I_{\text{meas}} \cdot dt} \quad (2.20)$$

Where I_{real} and I_{meas} are the true and measured intensities respectively in cps, and dt is the dead time in s. With a good characterisation of the dead time, and the assumption that the response of the ion counter is linear, measurements made in the ion counters can be corrected for dead time with equation 2.20.

The dead time is not significant for measurements of ^{230}Th and ^{231}Pa in this study as the count rates are sufficiently low for both sea water and sediment samples that the loss of signal due to dead time is tiny. Measurements of ^{234}U made at high concentrations will, however, be affected as count rates will approach 100 000’s where loss to dead time are approximately 1% of the signal.

Ion counter gain

The response of an ion counter can vary with tuning settings relative to the measurement of the same beam in a Faraday collector. This difference is referred to as the “gain” of the ion counter (Equation 2.21).

$$\text{gain} = \frac{I_{\text{IC}}}{I_{\text{Faraday}}} \quad (2.21)$$

As with mass bias, the gain of an ion counter can either be measured and corrected for, or samples can be bracketed with standards of known isotopic ratio and the gain accounted for along with mass bias and interferences by a single normalisation of the samples to the standards. External measurements of the gain can be made by measuring the $^{238}\text{U}/^{235}\text{U}$ ratio sequentially with ^{235}U centered in each ion counter and then a Faraday collector (Table 2.5).

The ion counters can be tuned to a range of gains by altering the voltage the ion counter is set to and by adjusting the level of discrimination. The gain is optimised at approximately 90% so as to register as large as signal as possible without creating any “false” signal greater than caused by genuine ion arrival. There is considerable electrical noise associated with an ion counting system so a discriminating voltage is set above which a signal is counted as a pulse. This discriminator is set by closing the line of sight valve so no ions can reach the collector array, and then finding the threshold for the discriminator where a signal is registered. The value for the discriminator is set just above this threshold level, so that no spurious ion arrivals are registered. The voltage the ion counter is set to determines how many ions are drawn into the collector and hence is efficiency. The more negative the voltage the more ions are drawn in to improve the gain, but setting the voltage too low effectively wears out the ion counter reducing its useful lifetime, so a balance must be found. Each ion counter also has a deflector which focuses the ions into the collector, which

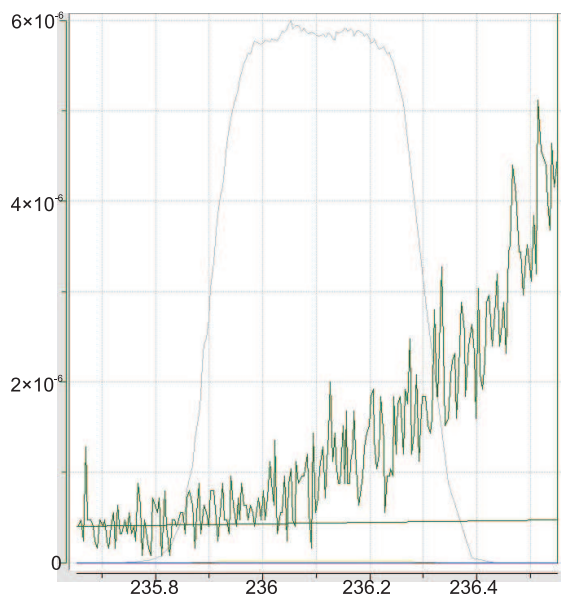


Figure 2.14: A plot showing the abundance sensitivity in IC(-5) (green) from a ^{232}Th peak of 3.1 V at +1 amu (grey). The tail from the ^{232}Th at 1 amu is 1×10^{-6} V, giving an abundance sensitivity of 0.32 ppm. This low abundance sensitivity is due to the energy filter in IC(-5). The mass scale on the abscissa is that at the AXIAL collector.

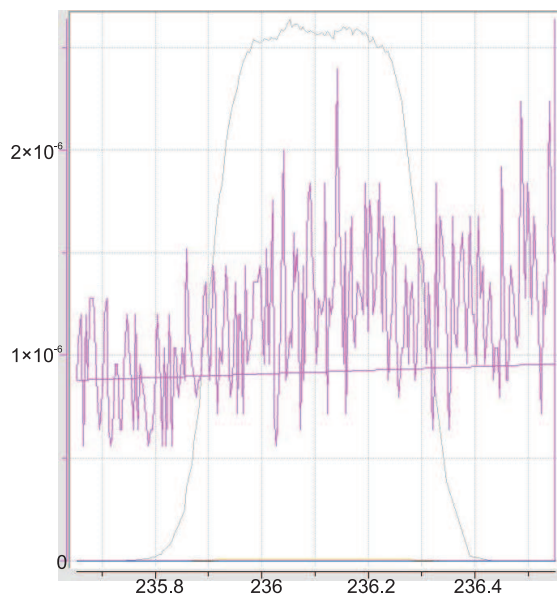


Figure 2.15: A graph showing the peak tail (pink) from a 3.1 V ^{232}Th peak (grey) at -3 amu. Note that although here the tail is at -3 amu from the ^{232}Th peak it is the same magnitude as at -1 amu (Figure 2.14). This is due to the energy filter reducing the abundance sensitivity at -1 amu measured in IC(-5).

must be tuned so that the ion beam is centered in the collector, to achieve a good gain.

Abundance sensitivity

As a beam of ions travels through the mass spectrometer a small proportion of the ions interact with gaseous atoms due to the imperfect vacuum. Most of this scattering results in the ions hitting the sides of the flight tube where they are “caught” in baffles. Some ions are slowed by these interactions and hence when the beam is deflected by the magnet are deflected more than unhindered ions of the same mass. This extra deflection due to the reduced energy of the ions causes a “tail” on the low mass side of the peak, extending many mass units (Figures 2.14 and 2.15).

Abundance sensitivity becomes a significant contribution to measurements while measuring small concentrations in the same solution as an isotope of relatively much greater concentration and slightly greater mass. For such measurements, an assessment of the abundance sensitivity must be made. An approach where the intensity at $\frac{1}{2}$ amu either side of the mass of interest is measured, and the desired abundance sensitivity is extrapolated, is desirable as it gives an accurate assessment of the abundance sensitivity. At the high mass range that the isotopes of U, Th and Pa are found the spacing of the collectors, on the Nu Instrument MC-ICP-MS, is such that measuring at $\frac{1}{2}$ amu distances is impracticable. In this case a standard is used to assess the abundance sensitivity before and after each analysis (Section 2.5.1).

IC(-5) is equipped with an energy filter to reduce the abundance sensitivity. Ions responsible for abundance sensitivity have reduced energies from the main ion beam. The filter reduces abundance sensitivity by only allowing through, to the detector, ions that have the same energy as those accelerated by the high voltage applied at the front of the machine (~ 4 kV). This is achieved with two filter plates. The first, set to ~ 4 kV, allows through only ions with energies comparable to the accelerating voltage. A second filter refocuses ions from the first filter into the collector.

Measurement of abundance sensitivity and molecular interference

As separation of U from both Th and Pa is very good, the principle source of abundance sensitivity on Th and Pa measurements is the ^{232}Th beam. Abundance sensitivity is assessed by measuring a ^{232}Th standard solution as a sample and measuring the contributions at the masses, away from 232, of interest. At mass 230 there will be a contribution from ^{230}Th as well as abundance sensitivity from ^{232}Th . The $^{230}\text{Th}/^{232}\text{Th}$ of the standard was determined by measuring the abundance sensitivity over a long time period (26 hours) at mass 230 and 231 (Figure 2.16).

As abundance sensitivity at -1 amu and -2 amu should co-vary, the abundance

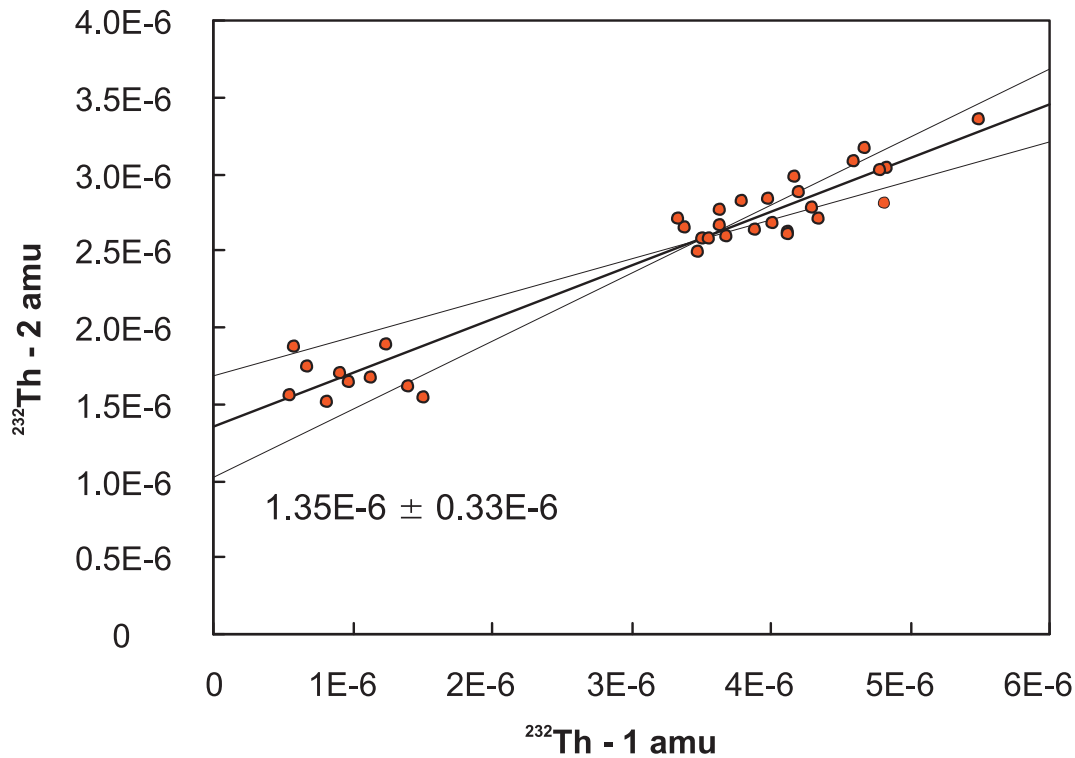


Figure 2.16: The abundance sensitivity from ^{232}Th , at -1 and -2 amu, measured over a period of 26 hours, using a “specpure” Th standard. The thick line is a best fit through the data and the thin lines are the standard errors of the regression. The intercept at 1.3×10^{-6} gives the $^{230}\text{Th}/^{232}\text{Th}$ when the abundance sensitivity is zero, thus giving the $^{230}\text{Th}/^{232}\text{Th}$ of the standard.

sensitivity at -2 amu is extrapolated to where there is no abundance sensitivity at -1 amu. Assuming that there is no ^{231}Pa in the ^{232}Th standard then this will represent the contribution to mass 230 due only to the ^{230}Th in the standard. The $^{230}\text{Th}/^{232}\text{Th}$ of the “Specpure” Th standard to be is found to be $1.35 \times 10^{-6} \pm 0.33 \times 10^{-6}$. The abundance sensitivity at -2 amu can then be measured, with the ^{232}Th standard, between samples by accounting for any ^{230}Th in the standard. Monitoring the ^{232}Th in each samples allows a correction for abundance sensitivity to be made.

Molecular interferences

Molecules formed during sample introduction into the plasma, having the same mass as an isotope of interest, can add to the beam size measured and thus need to be

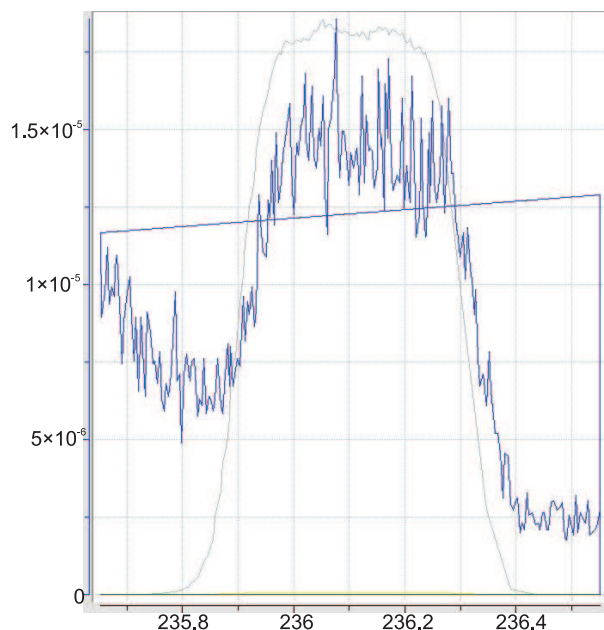


Figure 2.17: A plot showing the high mass abundance sensitivity and hydride peak from a 3.1 V ^{232}Th beam (faint gray) at +1 amu (blue). Abundance sensitivity is 1.6 ppm and hydride formation is 3.2 ppm of the ^{232}Th beam. The mass scale on the abscissa is that at the AXIAL collector.

accounted for. The most significant molecular interference is ^{232}ThH (Figure 2.17), due to the potential large ^{232}Th beam size for some samples (particularly sediments) and the small relative size of the $^{233}\text{Pa,U}$ peak.

Other molecular interferences, such as molecules of, U, Th, and Pa combined with O, N, and OH, are not important as they fall outside the range of masses of interest. An assessment of hydride formation is made by running a ^{232}Th beam in F(−4) and measuring the signal in IC(−3). The ^{232}Th beam is then monitored during sample measurement and the contribution of ^{232}ThH on mass 233 is accounted for (this correction will also correct for any high mass abundance sensitivity from ^{232}Th).

Making use of a Cetac “Aridus” de-solvating spray chamber not only increases the sensitivity of the mass spectrometer, but by drying the aerosol from the nebuliser the amount of water entering the plasma is reduced. A reduction of the amount of water (and HNO_3) in the plasma reduces the available H^+ to form hydrides.

Measurement of the ThH over time (Figures 2.18 and 2.19) shows what appears to be an exponential decay of ThH over time. The cause of this decrease is thought to relate to the gradual drying out of the sample introduction system as the machine

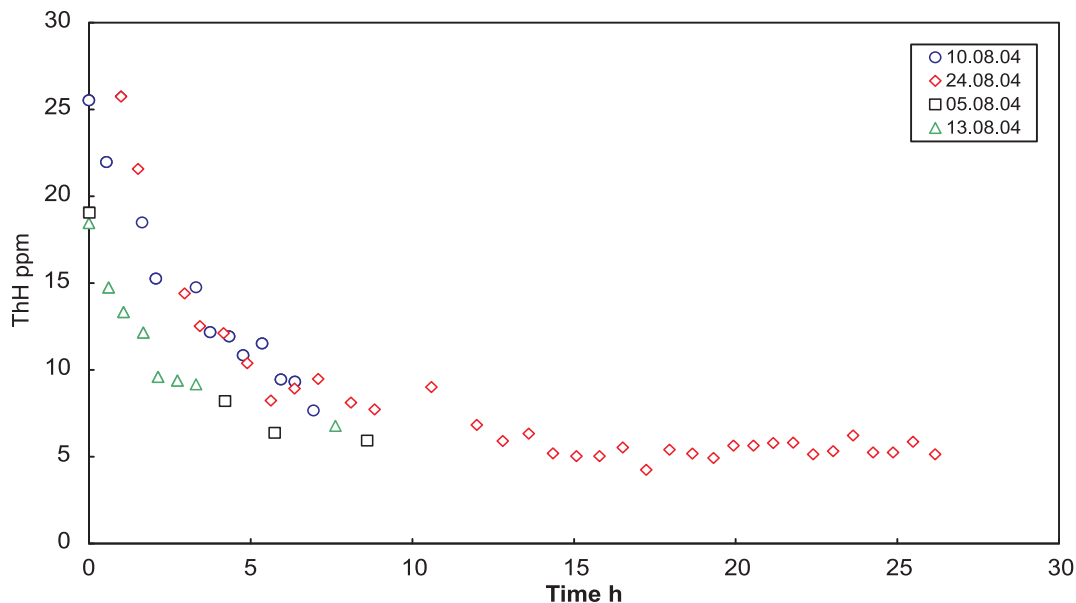


Figure 2.18: The contribution at mass 233 due to ^{232}ThH only, excluding any high mass abundance sensitivity. The measurement of ^{232}ThH is shown for four runs. Resolution of ThH from high mass abundance sensitivity is demonstrated in figure 2.19.

is run. It is unlikely that the de-solvating nebuliser is the primary cause as it is heated and any drying would occur relatively rapidly. It is more likely that moisture within the tubing leading from the de-solvator to the plasma torch is the source of this H^+ . This effect is not seen if the machine is left running for ~ 5 hours before analysis.

2.5.2 Uranium

Seawater and sediment samples are measured for uranium both using the same method. The measurements are made in a static mode with ^{238}U , ^{236}U , and ^{235}U focused in Faraday collectors, and ^{234}U in IC(-3) (Table 2.6). Samples are bracketed by CRM-145 standards to correct for: mass bias, abundance sensitivity, and ion counter gain. A CRM-145 standard is run between samples as a dummy sample to assess the reproducibility of the measurements.

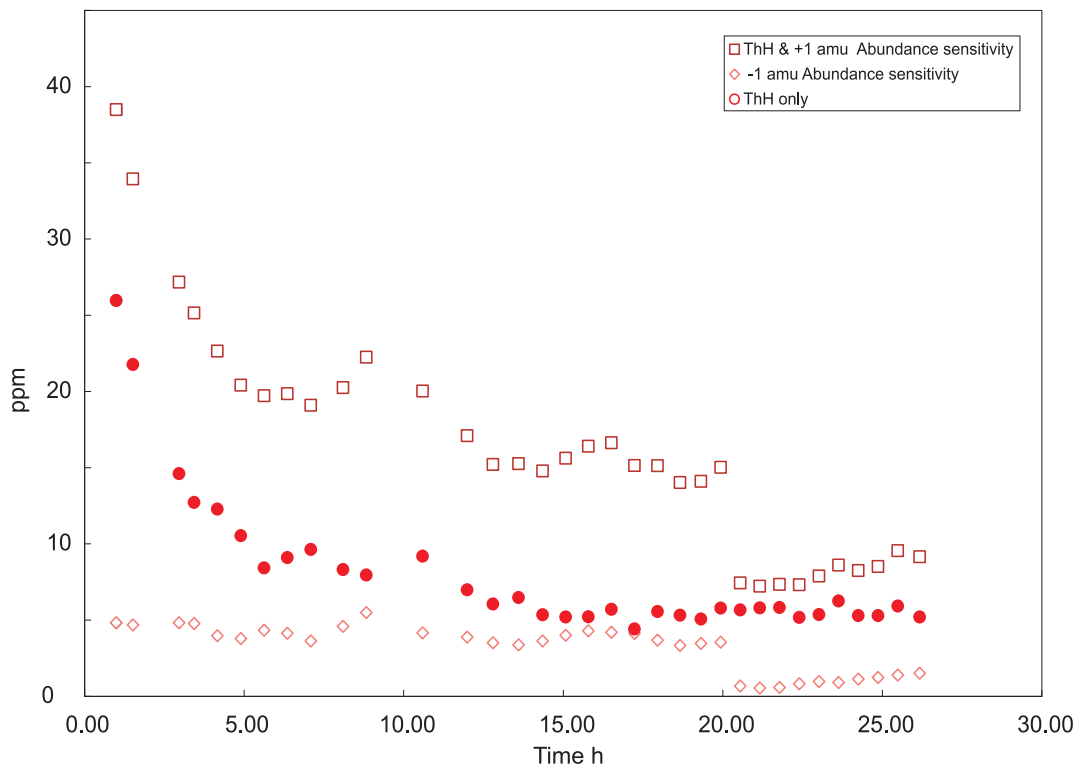


Figure 2.19: The abundance sensitivity is semi-quantitatively separated from hydride interference by scaling the abundance sensitivity at -1 amu to $+1$ amu and subtracting from the 233 signal to yield the ^{232}ThH . The scaling factor was assessed by considering where the abundance sensitivity co-varied with the ^{232}ThH + high mass abundance sensitivity. A scaling factor where this co-variance was minimised was chosen to best represent the contribution of high mass abundance sensitivity to the 233 mass. The scaling factor used was 2.6, implying that the high mass abundance sensitivity is larger than the low mass. This is unexpected and is probably the result of the energy filter on IC(-5) reducing the abundance sensitivity at -1 amu.

- 1 CRM-145
- 2 CRM-145 dummy sample
- 3 CRM-145
- 4 Sample
- 5 CRM-145
- 6 CRM-145 dummy sample
- 7 CRM-145
- 8 Sample
- ...

With this approach it is important that the concentrations of the samples and standards are well matched, so as to remove any biases which are beam-size dependent. The $^{235}\text{U}/^{234}\text{U}$ ratios of samples and standards are all normalised to the mean $^{235}\text{U}/^{234}\text{U}$ ratio of all standards to correct for machine drift. The samples (including the dummy samples) are then normalised to the drift-corrected samples' expected ratio, which is certified at 137.19 (Table 2.4). By normalising the samples, to the known ratio of the standard, they will have undergone external correction of mass bias, ion counter gain, and abundance sensitivity. An internal correction for mass bias using the $^{238}\text{U}/^{235}\text{U}$ ratio of the samples and standards, which should be 137.88, can be made rather than including mass bias in the external corrections. Typically both approaches are investigated and the method producing the best reproducibility is used. The “dummy samples” should have a mean corrected ratio of 137.19 and the scatter around this value provides a measure of external reproducibility of the measurements.

The $^{238}\text{U}/^{236}\text{U}$ ratio is internally corrected for mass bias with the $^{238}\text{U}/^{235}\text{U}$ ratio which should be 137.88. From equation 2.16:

$$\varepsilon_{\text{linear}} = \left(\frac{^{238}\text{U}/^{235}\text{U}_{\text{meas}}}{137.88} - 1 \right) / 3 \quad (2.22)$$

and

$$^{238}\text{U}/^{236}\text{U}_{\text{real}} = \frac{^{238}\text{U}/^{236}\text{U}_{\text{meas}}}{1 + \varepsilon_{\text{linear}} \times 2}. \quad (2.23)$$

The ^{238}U concentration is then calculated according to the isotope dilution equations (Section 2.4.1), and the $^{235}\text{U}/^{234}\text{U}$ ratio corrected for the ^{235}U and ^{234}U in the spike. The ratio is then expressed in $\delta^{234}\text{U}$ notation (Equation 2.24).

$$\delta^{234}\text{U} = \left[\frac{(^{238}\text{U}/^{234}\text{U})_{\text{sample}}}{(^{238}\text{U}/^{234}\text{U})_{\text{secular}}} - 1 \right] \times 10^3 \quad (2.24)$$

Where $(^{238}\text{U}/^{234}\text{U})_{\text{secular}}$ is the activity ratio at secular equilibrium (i.e. 1).

As no correction is made for machine memory it is important to ensure that all of the sample (or standard) is washed out before measurement of the next solution begins. Washing out the sample involves repeated aspiration of 10% HNO_3 and 2% HNO_3 . A balance must be made between washing out for long periods of time, and switching between samples and standards quickly to minimise drift between measurements. As the time taken to washout depends on the sipper used and gas flow rates in the nebuliser, a test is carried out to estimate washout time. The time taken for a beam to reduce to 1% of its original intensity is assessed, after the sipper is taken from a CRM-145 standard and into 2% HNO_3 . The total washout time used is then approximately three times this.

To improve the precision, samples are run at as high a concentration as possible. This allows the greatest number of ions to be measured and hence improve the counting statistics (Equation 2.26). The samples are measured in a block of ~ 30 10 s integrations. The maximum concentration that samples can be run at is limited by the size of the ^{238}U beam as this is the most abundant isotope present in the samples. The maximum voltage that can be recorded on one of the Faraday collectors, without changing the resistors on the collectors, is 10 V. If beams exceed this then not only the measurements for that isotope are invalid but readings from the other collectors also become unreliable. To increase the size of beam that can be measured, the baseline of one faraday collector can be offset to -9 V allowing beams of up to 19 V to be measured.

The uncertainty for $\delta^{234}\text{U}$ measurements can approach 0.7‰ if run at high concentrations, and the machine has good medium term stability. Depending on the sensitivity achieved (typically 50–100 V/ppm of ^{238}U), 100–200 ng of uranium is required for each measurement.

step	F(+8)	F(+6)	F(+4)	F(+3)	F(+2)	F(+1)	AXIAL	F(-1)	F(-2)	IC(-3)	F(-4)	IC(-5)	F(-6)	IC(-7)	F(-8)
<i>Uranium</i>															
<i>Ion counter gain and mass bias</i>															
A1							238U			235U		234U			
A2								238U		235U		235U			
A3									238U		238U				235U
A4							238U		235U						
B1								238U			235U		234U		
<i>Thorium</i>															
1			238U				235U		232Th	X			229Th		
2				238U				235U		X			230Th		
<i>Protactinium & thorium</i>															
1				236U					232Th			230Th			
2					238U			236U	235U		232Th	233Pa	231Pa		229Th

Table 2.6: The measurement configurations for measuring different solutions.

2.5.3 Thorium in sediments

As the spike isotope, ^{229}Th , is only one mass unit from ^{230}Th - and the spacing of the ion counters on the Nu Instruments MC-ICP-MS is two mass units at this mass range - a multi step routine is used (Table 2.6). The high concentration of ^{232}Th in sediment samples requires the Th cut to be diluted before it is run on the mass spectrometer such that the ^{232}Th beam does not exceed 9 V, and that the ^{232}Th concentration is matched in all samples and standards.

A noise correction must be made to the $^{230}\text{Th}/^{229}\text{Th}$ ratio as because the two nuclides are measured in different steps, this is achieved by normalising the $^{229+}$ beam in the two steps against ^{235}U . ^{235}U is used rather than ^{238}U , because the ^{238}U beam is sufficiently distant from the beams that are used to optimise the measurement routine that it may not be properly focused. If separation of U from Th is so good there is not enough ^{235}U to noise correct between steps, a small amount of CRM-145 is added to provide the necessary U for the correction. It would be favourable to use ^{232}Th for the noise correction as it is of the same element as the isotopes of interest, but the ^{232}Th beam falls in an ion counter during one of the measurement steps and, as such, can't be measured.

Because both ^{229}Th and ^{230}Th are measured in the same ion counter, no correction for ion counter gain is required. If, however, ^{232}Th is of interest - which is required to make a correction of any detrital component in sediments - then a gain correction must be made to produce an accurate $^{232}\text{Th}/^{229}\text{Th}$ ratio. A single step measurement of the gain (Table 2.6, method B) is used for IC(-5). Each sample is bracketed with CRM-145 uranium standards to measure the ion counter gain and mass bias. Mass bias is accounted for externally in this way. The use of the $^{238}\text{U}/^{235}\text{U}$ ratio in a standard to correct for mass bias of the $^{232}\text{Th}/^{229}\text{Th}$ and $^{230}\text{Th}/^{229}\text{Th}$ ratios makes the assumption that mass bias is not element specific. In this case it is sufficient to assume this as the uncertainty of the measurements, typically 3-4%, is larger than

any possible elemental dependence of the mass bias ($< 1\%$, Robinson et al. (2004a)).

As with uranium no correction is made for machine memory; because washout of Th is sufficient between samples. Monitoring of the machine memory through measurement of a 2% HNO_3 solution between samples indicated the background ^{232}Th beam due to machine memory is $\sim 10^{-5}$ of the sample beams.

2.5.4 Thorium in seawater

Because the concentration of ^{230}Th is very low in seawater (10-150 fg per 10 l sample), all the Th from each sample is measured in as small as volume as possible to maximise the beam sizes of ^{230}Th and ^{229}Th . To increase the amount of ^{230}Th measured the integration times are altered such that step 1 (Table 2.6 *Thorium*) is measured for 5 s and step 2 for 10 s. The reduction in amount of ^{229}Th collected is offset by spiking the samples at sufficient level that the contribution to the uncertainty of the $^{230}\text{Th}/^{229}\text{Th}$ ratio from the ^{230}Th beam still dominates the error. Because the samples are run in a small volume the solution occasionally runs out before the measurement is complete. In these cases the unprocessed data for each integration is downloaded into a spreadsheet, and data is excluded if an integration has been measured while the sample solution is running out.

As with measurements of sediment samples corrections for ion counter gain and mass bias are made externally with a uranium standard run with ^{234}U focused into IC(-5).

Due to the small beam sizes machine memory can be significant. To account for such memory a measurement of a 2% HNO_3 solution is made before each sample. Rather than simply using the intensities of the ^{230}Th and ^{229}Th beams to correct for the memory, the $^{230}\text{Th}/^{229}\text{Th}$ ratio of the memory is measured and the correction

made using a mass balance approach (Equation 2.25).

$$\frac{{}^{230}\text{Th}}{{}^{229}\text{Th}_{\text{real}}} = \frac{\frac{{}^{230}\text{Th}}{{}^{229}\text{Th}_{\text{meas}}} \times I_{\text{meas}} - \frac{{}^{230}\text{Th}}{{}^{229}\text{Th}_{\text{mem}}} \times I_{\text{mem}}}{I_{\text{meas}} - I_{\text{mem}}} \quad (2.25)$$

This allows the ability of the MC-ICP-MS to measure ratios precisely to be used, which reduces the uncertainty in the correction, as the intensity of only one isotope is used in the calculation.

2.5.5 Protactinium

As with ${}^{230}\text{Th}$, concentrations of ${}^{231}\text{Pa}$ are very low in seawater. Concentrations in sediments is also relatively low. Due to these low concentrations of ${}^{231}\text{Pa}$ available for measurement samples are run as concentrated as possible, i.e. all of the available ${}^{231}\text{Pa}$ dissolved in 0.5 ml. Spiking to give a ${}^{233}\text{Pa}/{}^{231}\text{Pa} \gg 1$ is not a realistic option because a limited amount of ${}^{233}\text{Pa}$ is available from each spike preparation, so that such spiking would reduce the total number of samples that can be measured.

Measurement of the ${}^{231}^+ / {}^{233}^+$ ratio is performed in a single step with ${}^{231}\text{Pa}$ and ${}^{233}\text{Pa}, \text{U}$ measured in IC(−3) and IC(−5) respectively (Table 2.6 *Protactinium & thorium* step 2). Ion counter gain is assessed along with mass bias by bracketing samples with measurements of CRM-145 uranium standard, setting ${}^{235}\text{U}$ sequentially into each ion counter and then a Faraday collector (Table 2.6, method A). Mass bias could be measured internally for each sample from the ${}^{238}\text{U}/{}^{235}\text{U}$, but the chemical separation is too good to leave enough U in the Pa cut for this to be possible. An assessment of abundance sensitivity on ${}^{231}\text{Pa}$ and ${}^{233}\text{Pa}, \text{U}$ as well as molecular interference from ${}^{232}\text{Th}$, is made by monitoring ${}^{232}\text{Th}$ in each sample and bracketing every sample (or every two samples) with a measurement of a ${}^{232}\text{Th}$ solution.

Early attempts, by the author, to measure both ${}^{230}\text{Th}$ and ${}^{231}\text{Pa}$ together in the same aliquot (Table 2.6), were hampered by the interferences caused by large ${}^{232}\text{Th}$

beams (even with water samples). The increases in sample throughput gained by simultaneous measurements are outweighed by the increased uncertainty resulting from larger corrections due to molecular interferences, so separate measurement of ^{231}Pa and ^{230}Th is most appropriate.

The spike isotope, ^{233}Pa , has a short (26.967 days) half life. To use a measured $^{231+}/^{233+}$ ratio to find the amount of ^{231}Pa in a sample, it is important to record the time when Pa was last separated from U. This time is taken as the time of the final column pass. Once separated from U, the ^{233}Pa spike will continue to decay and produce daughter ^{233}U (159 ka half life). Fortunately this daughter has the same mass as ^{233}Pa , so the $^{231+}/^{233+}$ ratio of the sample shouldn't change after separation. Although the ionisation efficiency, by ICP, of U and Pa has been shown to be essentially the same (Choi et al., 2001), samples are measured as soon as possible after chemical separation to minimise any potential fractionation of ^{233}U and ^{233}Pa during ionisation.

2.5.6 Blanks

Total procedural blanks processed and run alongside samples are summarised in Table 2.7. For water samples a ~ 100 ml polypropylene bottle of Milli-Q was processed as a sample and for sediments an empty Teflon beaker was used.

Unsurprisingly the blank for ^{230}Th , ^{231}Pa , and ^{232}Th is significantly lower for water samples than for sediments and the opposite is true for ^{238}U . This difference in composition of the blanks is reflected in the typical samples with which they were processed, seawater having a very high U concentration and very low Th and Pa concentrations, while sediments are relatively rich in Th and to a certain extent Pa. Thus most of the blank appears to be arising from cross contamination from samples. Reduction of blanks could therefore be improved through better physical separation of samples during preparation. A portion of the higher ^{230}Th , ^{231}Pa , and

Blank #	Type	^{230}Th		^{231}Pa		^{232}Th		^{238}U	
		fg	2σ	fg	2σ	pg	2σ	pg	2σ
1	water	<i>8.6</i>	1.0	<i>0.04</i>	0.1	159	18		
2	water	0.4	0.3	0.7	0.1	61	2	436	37
3	water	0.5	0.3	1.0	0.1	65	3	478	80
4	water	2.4	0.3	0.6	0.1	22	0.0003	8029	552
5	water	1.5	0.3	<i>6.8</i>	0.4	22	0.0003	147	55
6	water	5.1	1.2	0.5	0.04	26	0.001	185	8
13	water	-0.08	-0.04	0.9	0.2	17	0.4	439	120
14	water	0.03	0.03	0.3	0.01	16	1	2937	1
8	seeds	11.1	0.5	2.3	0.8	240	6	84	147
11	seeds	10.6	0.8	0.4	1.1	354	12	37	36
12	seeds	11.0	0.7	0.8	0.3	212	6	148	213
		mean	s.d.	s.d.	s.d.	s.d.	s.d.	s.d.	s.d.
	water	1.4	1.8	0.6	0.3	49	49	1807	2913
	seeds	10.9	0.3	1.2	1.0	269	75	90	56

Table 2.7: Table showing the total procedural blanks run alongside both water samples and sediment samples. Values in *italics* are excluded subjectively from the sample type means.

^{232}Th blanks for sediments can be attributed to the initial sample processing not being performed in clean lab conditions due to their powdered form.

2.5.7 Uncertainties

Breakdowns for the uncertainties of measurements of ^{230}Th , ^{232}Th , and ^{231}Pa in seawater are summarised in Figure 2.20. Typical uncertainties are: 6% for ^{230}Th ; 8% for ^{232}Th ; and 14% for ^{231}Th , for water samples. These uncertainties are the mean uncertainty of the measurements in Chapter 5, and are a significant improvement on those measured earlier (Chapter 3).

The large portion of the uncertainty due to blank is due to the very low concentrations of Th and Pa in seawater. Although the blanks are small for water samples (Table 2.7) the uncertainty relative to sample concentration is still significant. The next largest contributor is the uncertainty in the raw measured ratio. This is large in part due to the low concentration of the solutions measured, limiting the total number of ions that are collected, and hence leading to a limited maximum precision

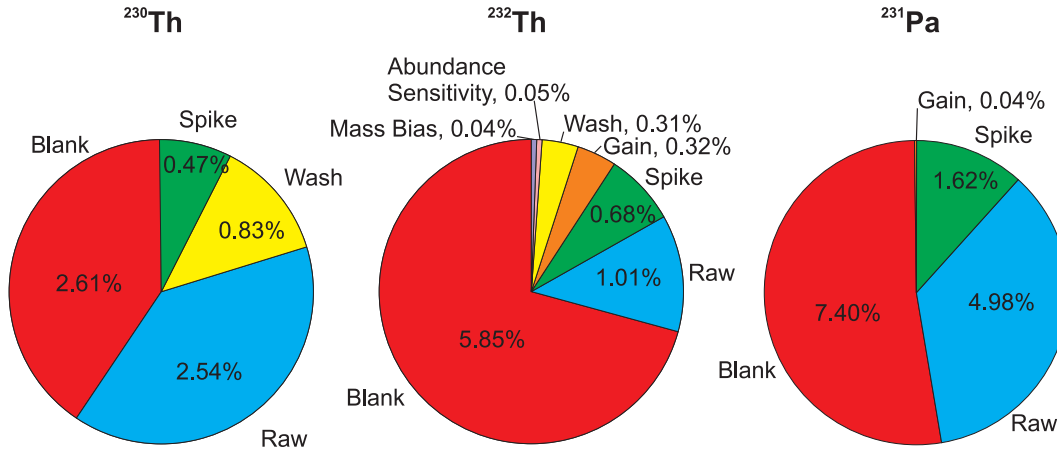


Figure 2.20: The contribution to the final uncertainty of measurements of ^{230}Th , ^{232}Th , and ^{231}Pa from the raw ratio measured and all corrections made. Contributions are assessed from the average uncertainties of 23 water samples as each correction is made. The average total uncertainties (2σ) for ^{230}Th , ^{232}Th , and ^{231}Pa are, 6%, 8%, and 14% respectively. For ^{230}Th the contributions from, weighing, abundance sensitivity, ion counter gain, and mass bias, are all less than 0.01%. For ^{232}Th the contribution from weighing is less than 0.01%. For ^{231}Pa contributions from, weighing, ^{232}Th and abundance sensitivity, and mass bias, are all less than 0.01%.

due to counting statistics, given by:

$$\text{s.d.} = \frac{1}{\sqrt{N}} \quad (2.26)$$

The uncertainties expected purely from counting statistics for ^{230}Th , ^{232}Th , and ^{231}Pa are 0.67%, 0.30% and 1.79% respectively, based on measurements of seawater samples. Because these counting statistics are much smaller than the uncertainty due to raw measured ratio, extra uncertainty must be arising due to machine instability.

Propagation of uncertainties through corrections is based on the assumption that the uncertainties in each correction are independent of each other, and as such the uncertainties can be summed quadratically using the general equation:

$$\sigma_y^2 = \left(\frac{\partial y}{\partial a} \right) \sigma_a^2 + \left(\frac{\partial y}{\partial b} \right) \sigma_b^2 + \dots \quad (2.27)$$

where a and b are independent measured variables, of which y is a function,

$$y = f(a, b) \quad (2.28)$$

Equation 2.27 can be simplified for simple operations to:

$$\sigma_y = \sqrt{\sigma_a^2 + \sigma_b^2 + \dots} \quad (2.29)$$

for additions and subtractions and,

$$\sigma_y = \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \dots} \quad (2.30)$$

for multiplication and division.

Where a correction is very small, such as the mass bias correction, and the fractional error is large, it would be unreasonable to propagate such a large uncertainty. In such a case the uncertainty in the correction is multiplied by the fractional change in the variable due to that correction.

2.6 Summary

Methods for the measurement of ^{231}Pa , ^{230}Th , ^{232}Th , and U isotopes in seawater and ocean sediments have been developed.

A low blank chemical separation is used to isolate Pa, Th and U. Clean separation of Pa from both U and Th is sufficient that molecular interferences and abundance sensitivity do not hamper accurate measurement. The separation utilises repetition of the same column, thus reducing complexity and lowering the blank.

Measurement of each element separately is necessary to eliminate interferences, while the use of multiple ion counting channels of MC-ICP-MS allows greater ion collection efficiency. Measurements of blanks suggest detection limits of ~ 3 fg for

^{230}Th and ~ 2 fg for ^{231}Pa (based on 3 s.d. of the uncertainty). Accuracy of measurements are typically 6%, and 14% for ^{230}Th and ^{231}Pa respectively (water samples), however uncertainties for samples containing greater amounts of ^{230}Th and ^{231}Pa , such as deep-sea seawater and sediments uncertainties are much lower, approaching 2-3% for both isotopes.

Chapter 3

Water Column ^{231}Pa and ^{230}Th

This chapter appears in a slightly modified form as:

“Thomas, A. L., Henderson, G. M., and Robinson, L. F. (2006). The interpretation of a paleo-circulation proxy: $^{231}\text{Pa}/^{230}\text{Th}$ measurements in the south-western Indian Ocean. *Earth and Planetary Science Letters*. 241(3-4):493-504”

3.1 Overview

This chapter covers the measurement of water column profiles from the previously little studied region of the south-western Indian Ocean. Measurements are made on five profiles each of 5-8 samples, significantly increasing the global seawater data coverage of ^{231}Pa and ^{230}Th . The profiles of ^{231}Pa show that ^{231}Pa concentration is characteristic of water masses. Low ^{231}Pa concentrations, relative for depth, are observed in Antarctic Bottom and Intermediate Waters due to preferential scavenging of Pa onto opal particles as these water masses left the Southern Ocean. A simple one-dimensional model is used to demonstrate that the ^{230}Th and ^{231}Pa exported to seafloor sediments last equilibrates with waters close to the seafloor (within ~ 1000 m), rather than averaging the whole water column. The implications for the ($^{231}\text{Pa}/^{230}\text{Th}$) proxy of this finding are then discussed.

3.2 Introduction

3.2.1 Aims

The global thermohaline circulation (THC) plays a crucial role in the climate system through its transport of heat and carbon (Broecker, 1991). Tracers used to investigate the past behaviour of the THC have often been those that label a particular water mass, such as $\delta^{13}\text{C}$ (Duplessy et al., 1984), Cd/Ca (Boyle, 1986), or Nd isotopes (Rutberg et al., 1998). Tracers that provide information about the rate of flow of these water masses have also been applied, including $\Delta^{14}\text{C}$ (Adkins et al., 1998; Goldstein et al., 2001), sortable silt (McCave and Tucholke, 1986; Bianchi et al., 1999) and $(^{231}\text{Pa}/^{230}\text{Th})$ (Scholten et al., 1995; Yu et al., 1996; Marchal et al., 2000; McManus et al., 2002, 2004). The use of $(^{231}\text{Pa}/^{230}\text{Th})$ for this purpose has only previously been assessed in the Atlantic basin.

Here we investigate the controls on $(^{231}\text{Pa}/^{230}\text{Th})$ recorded in deep-sea sediments in a region of more complex oceanography than the North Atlantic. If $(^{231}\text{Pa}/^{230}\text{Th})$ is to be more widely applied, a better understanding of the proxy is required. Specifically, in this study, the feasibility of using $(^{231}\text{Pa}/^{230}\text{Th})$ to learn about past deep-water inflow to the Indian Ocean, is assessed.

3.2.2 The $(^{231}\text{Pa}/^{230}\text{Th})$ proxy

The $(^{231}\text{Pa}/^{230}\text{Th})$ proxy relies on decay of uranium dissolved in the oceans. The high solubility of uranyl carbonate makes U a conservative element with a residence times of ~ 400 ka (Henderson and Anderson, 2003). The concentration and isotope composition of U in the oceans is therefore constant, both spatially (Ku et al., 1977; Chen et al., 1986) and temporally (Henderson, 2002b). The production of ^{230}Th and ^{231}Pa , from decay of ^{234}U and ^{235}U respectively, is thus constant at every point in the oceans (at $2.62 \pm 0.05 \times 10^{-2}$ and $2.45 \pm 0.05 \times 10^{-3}$ d.p.m.m $^{-3}$ a $^{-1}$). The

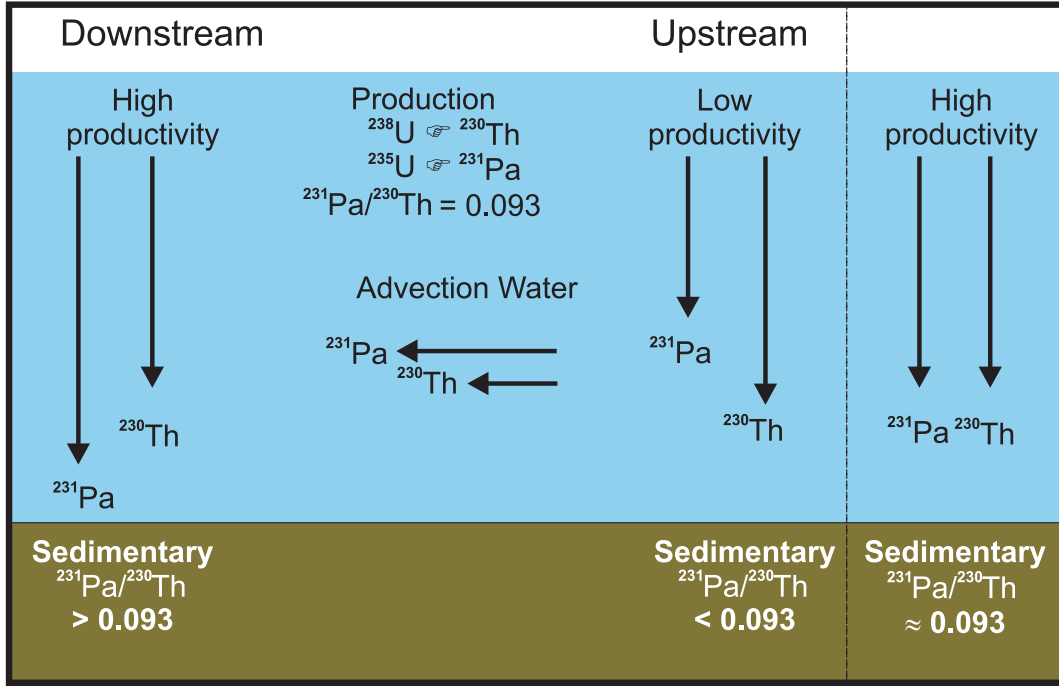


Figure 3.1: A schematic representation of the ($^{231}\text{Pa}/^{230}\text{Th}$) proxy modified from (Henderson, 2002a). Produced at a constant ($^{231}\text{Pa}/^{230}\text{Th}$) of 0.093 ^{230}Th is preferential scavenged, leaving the remaining water with relatively elevated ^{231}Pa . The ($^{231}\text{Pa}/^{230}\text{Th}$) of water increases as scavenging continues and the water advects until the output to sediments is equal to the input production ratio. High particle fluxes cause effective scavenging of both ^{230}Th and ^{231}Pa so sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) reflects the ratio of the water.

production activity-ratio of ($^{231}\text{Pa}/^{230}\text{Th}$) is therefore also constant at a value of 0.093. Once produced, both Th and Pa are scavenged to the seafloor through sorption onto particles which subsequently settle. This scavenging of Th and Pa is thought to be reversible (Bacon and Anderson, 1982), which explains the approximately linear increase of concentration typically seen with water depth for both nuclides. ^{230}Th and ^{231}Pa are removed from the upper water column, and a portion released by reversible exchange at greater depth. A newly-ventilated water mass therefore typically has low concentrations of both nuclides, similar to surface waters, and the concentrations increase with time spent at depth in the oceans. Eventually, deep waters reach equilibrium, with the rate of addition of Th or Pa from above balanced by removal to the seafloor.

^{230}Th is, typically, removed more rapidly than ^{231}Pa , and thus has a shorter oceanic residence time of about 20 years, compared to 130 years for ^{231}Pa (Henderson and Anderson, 2003). As a deep water mass ages, the concentration of ^{230}Th rapidly reaches a steady state value while ^{231}Pa takes longer and is therefore expected to be at low concentration for greater distances as deep-waters moves away from their site of formation. In these areas, the $(^{231}\text{Pa}/^{230}\text{Th})$ of particles settling to the sediment is expected to be below the production ratio of 0.093, while in regions far from the water source, the ^{231}Pa will have increased to steady state and the $(^{231}\text{Pa}/^{230}\text{Th})$ exported to the sediment is 0.093 (Figure 3.1). The effective “age” of the water since ventilation is therefore reflected by the $(^{231}\text{Pa}/^{230}\text{Th})$ removed to sediment, providing a tool to assess the rate of flow of waters in past times. Maps of sediment $(^{231}\text{Pa}/^{230}\text{Th})$ have been used in this way to indicate little change in overall meridional overturning in the Atlantic between the Last Glacial Maximum and the Holocene (Yu et al., 1996; Marchal et al., 2000). More recently, a time series study by McManus et al. (2004) has been used to investigate changes in overturning circulation rate in the North Atlantic accompanying millennial climate changes.

The $(^{231}\text{Pa}/^{230}\text{Th})$ preserved in sediments is also affected by other factors. The degree to which Pa and Th are fractionated onto particles has been shown to vary for different particle types (Luo and Ku, 1999; Chase et al., 2002; Geibert and Usbeck, 2004). Although controversy still remains as to the precise nature of this particle type dependence (Siddall et al., 2005; Li, 2005), it is clear that changes in the particle type will have a role in controlling sedimentary $(^{231}\text{Pa}/^{230}\text{Th})$. Scavenging intensity is also a factor controlling the $(^{231}\text{Pa}/^{230}\text{Th})$ preserved (Figure 3.1), because in regions of high particle flux, ^{231}Pa will be more efficiently scavenged, hence increasing sedimentary $(^{231}\text{Pa}/^{230}\text{Th})$. Boundary scavenging - the process of diffusion of nuclides to ocean margins to be preferentially scavenged there - may also play a role in setting sedimentary $(^{231}\text{Pa}/^{230}\text{Th})$ (Anderson et al., 1983b).

3.3 Regional setting

The movement of deep and bottom water in the SW Indian Ocean features three main water masses moving broadly northward (Figure 3.2): Antarctic Bottom Water (AABW); a water mass derived from North Atlantic Deep Water, referred to herein as “NADW”; and Antarctic Intermediate water (AAIW). AABW enters from the southeast through fracture zones in the Southwest Indian Ridge (Toole and Warren, 1993), flowing through the Madagascar and Mascarene Basins and exiting northward through the Amirante Passage.

Above this, water derived from NADW flows around the continental margin of southern Africa with characteristics close to that of NADW (salinity 34.8 and potential temperature 2-2.5°C). This “NADW” continues around the Madagascar ridge and then northwards as a geostrophically-constrained boundary current (Donohue and Toole, 2003)(Figure 3.2), the salinity decreasing through mixing to 34.78 by the time it has reached 25°S. The flow of “NADW” and AAIW, however, is impeded by southward movement (Sirinivasan et al., 2004) of two other water masses, North Indian Deep Water and, to a lesser extent, Red Sea Water (Tomczak and Godfrey, 2002). The influence of both AAIW and “NADW” therefore decreases northward, as shown in the temperature and salinity profiles measured for this study (Figure 3.3). Overlying these deeper water masses is Indian Central Water (ICW) formed in the subtropical gyres of the Indian Ocean. An overview of the basins’ oceanography can be found in McCave et al. (2004).

To investigate the behaviour of ^{231}Pa and ^{230}Th in this region of complex oceanography, five water-column profiles (Figure 3.2) were sampled along the western margins of the Mascarene and Madagascar Basins during the Charles Darwin Cruise 129 (McCave, 2002 [unpublished cruise report]). Five to seven unfiltered water samples

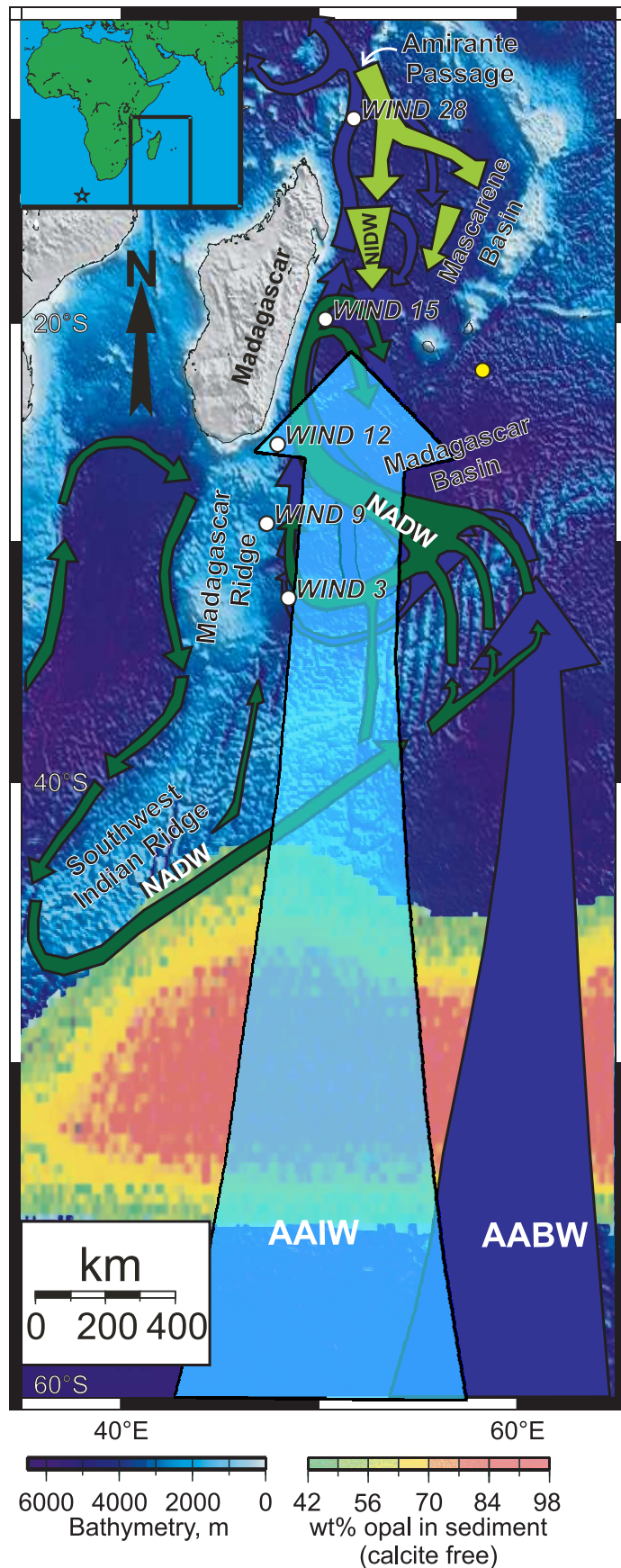


Figure 3.2: A map showing the localities of the water column profiles measured in this study (white circles). The yellow circle indicates the position of previous literature data (Ku, 1966). Also shown, schematically, are the principle water masses of the region and their flow through the Madagascar and Mascarene Basins. The position of the opal belt, illustrated by the wt% opal in sediments, taken from a Si cycle model (Ragueneau et al., 2000), is also shown. Note, the transit of AABW (dark blue) and AAIW (light blue) from the Southern Ocean takes it through the opal belt, while water sources from the Atlantic (referred to here as “NADW”, although its salinity is somewhat modified from true NADW values) are confined as a boundary current and avoid high opal productivity on its way to the Madagascar Basin. North Indian Deep water, NIDW, is also shown (light green) and impacts the most northerly of the studied sites. Inset locating the study area shows, as a star, the position of the closest existing water column profile (Rutgers van der Loeff and Berger, 1993) used for comparison in the text.

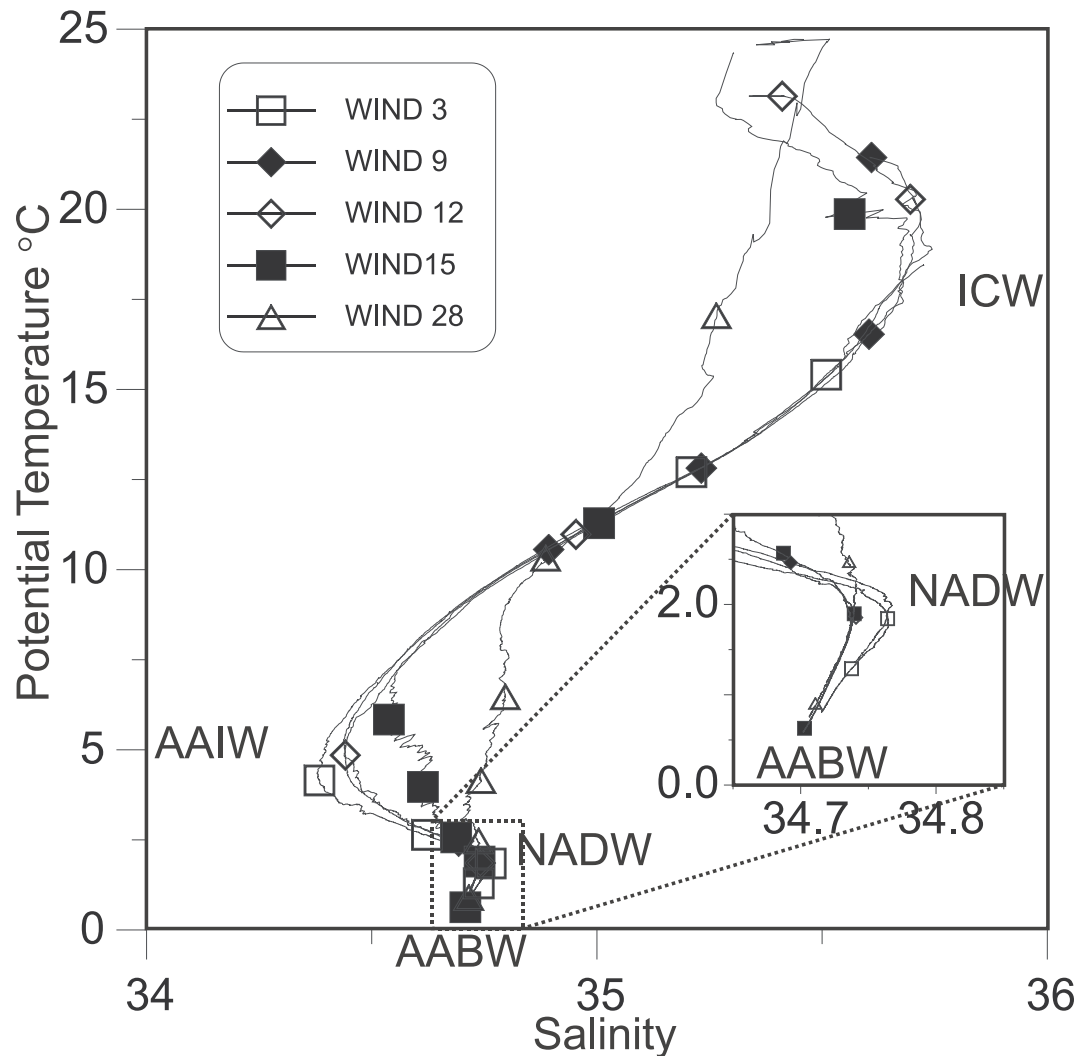


Figure 3.3: A plot of potential temperature ($^{\circ}\text{C}$) against salinity (‰) for CTD casts at stations shown in Figure 3.2 (listed in the key from south to north). The approximate position of water masses are shown: ICW, Indian Central Water; AAIW, Antarctic Intermediate Water; “NADW”, modified North Atlantic Deep Water; and AABW, Antarctic Bottom Water. Depths corresponding to these water masses are also indicated on Figure 3.4. The inset shows an expansion of the lower section of the profiles. Symbols show positions of samples analysed in this study and the station number as indicated in the key.

were collected per profile – in acid rinsed cubitainers – making a total of 31 samples. The 10 litre samples were collected with a rosette of 12 10 litre Niskins fired on the up cast (sample mass was determined once ashore). In addition, two samples from one profile were filtered using a $2\text{ }\mu\text{m}$ inline filter. Filtration was performed in the “wet-lab” aboard the Charles Darwin into a glass bottle, before being transferred

to the cubitainer. Shipboard sampling was performed by Laura Robinson. Most of these profiles are sampling northward flowing water masses from the seafloor up to depths of about 1000 m whereas the most northerly profile (WIND 28) samples a mixture of northward flowing bottom water and southward flowing intermediate water.

3.4 Methods

Methods used to sample and measure seawater samples are comprehensively covered in Chapter 2. Briefly, acidified water samples are spiked with ^{229}Th and ^{323}Pa (Section 2.4), left to equilibrate and then co-precipitated with Fe. Chemical separation via anion exchange chromatography followed (Section 2.3.6), before measurement by MC-ICP-MS (Section 2.5).

^{233}Pa spike was milked from ^{237}Np by Marcel Regelous at Bristol (Regelous et al., 2004). Calibration of the ^{233}Pa spike was performed at Oxford by addition of ^{236}U spike and measurement of $^{236}\text{U}/^{233}\text{U}$ after all the ^{233}Pa had decayed to ^{233}U . The precision achieved was 1.2% based on two aliquots, and the resulting concentration is consistent with a calibration of the same spike against a secular equilibrium standard performed at Bristol by m. Regelous.

Total yields, assessed by the comparative voltage of the spike isotopes against a uranium standard of known concentration, were poor at only $\sim 20\%$ (Pa) and $\sim 40\%$ (Th). Loss is thought to occur during co-precipitation rather than anion exchange, as yields for blanks, which were precipitated from a smaller volume of liquid, were significantly higher. The yield could be improved in future by increasing the amount of Fe added to aid co-precipitation. The separation of U from Pa is good with only 0.01% of the initial U in the final Pa fraction (assessed from ^{236}U measurements in the Pa fraction). This is important because a portion of the ^{233}Pa will have decayed

to ^{233}U since milking of the spike and this ^{233}U must be quantitatively removed.

3.5 Results

All five ^{230}Th profiles show a broadly linear increase in concentration with depth, from ~ 0.04 d.p.m./1000 litres in surface waters to ~ 1 d.p.m./1000 litres at 4000 m (Table 3.1, Figure 3.4). Note that, although nuclides were measured as fg/kg, they are converted, for the purposes of discussion, to d.p.m./1000 litres to aid comparison with literature data. These ^{230}Th profiles are similar to the average global profile (Henderson and Anderson, 2003), and to that observed in the Southern Ocean at 44.48°S 10.46°E (Rutgers van der Loeff and Berger, 1993) (Figure 3.4). ^{231}Pa profiles show an increase of concentration in the upper half of the water column, from 0.03 d.p.m./1000 litres at the surface to ~ 0.3 d.p.m./1000 litres at 2500 m, followed by a constant or slightly decreasing concentration in deeper water (Figure 3.4).

The maximum ^{231}Pa concentration coincides with the presence of “NADW”, as recognised from T-S characteristics (Figure 3.3) and a phosphate minimum (Figure 3.5). Above and below this ^{231}Pa maximum, values are somewhat lower than those found in the Southern Ocean, although these waters have recently flowed from this region.

^{232}Th concentrations are typically ~ 0.01 d.p.m./1000 litres but show significant variation. In particular, three of the deeper samples show much higher concentrations, up to 0.06 d.p.m./1000 litres and, even excepting these samples, there is a slight tendency towards higher concentration at depth.

Table 3.1

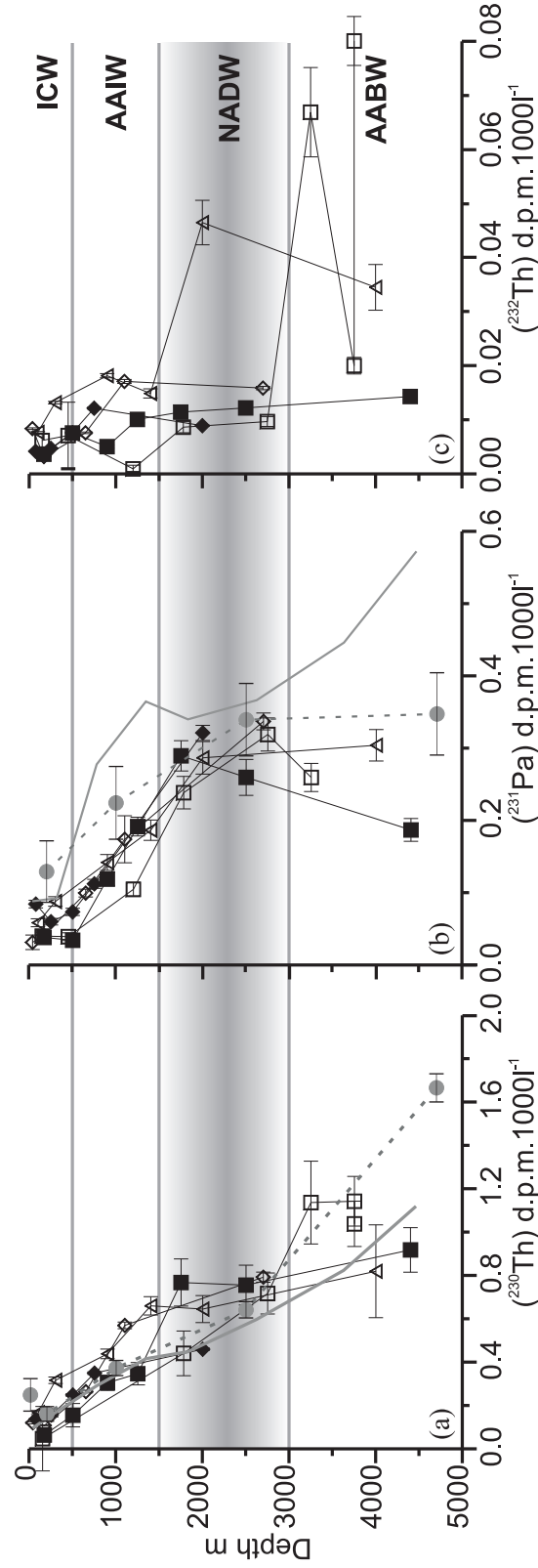
Sample	Latitude		Longitude		Water		Depth		^{230}Th		^{231}Pa		^{232}Th		2σ		$(^{231}\text{Pa}/^{230}\text{Th})$		$(^{230}\text{Th}/^{232}\text{Th})$		2σ	
	$^{\circ}\text{S}$		$^{\circ}\text{E}$		Depth m		m		d.p.m./1000l	2σ	d.p.m./1000l	2σ	d.p.m./1000l	2σ	2σ		d.p.m./1000l	2σ	d.p.m./1000l	2σ	2σ	
WIND 3-11+12	32.39.05		48.28.16		3728		150		0.04	0.15	0.04	0.006	0.006096	0.000003	1	4	6	6	24			
WIND 3-10							450		-0.59 ^a	-0.4	0.039	0.005	0.007003	0.000005	-0.07 ^a	-0.04	-86 ^a	-57				
WIND 3-9							1200		8.7 ^a	1.9	0.1	0.01	0.00084	0.00001	0.01 ^a	0.003	10000 ^a	2500				
WIND 3-8							1780		0.43	0.1	0.24	0.03	0.008533	0.000005	0.56	0.15	50	12				
WIND 3-7							2750		0.71	0.1	0.32	0.04	0.009591	0.000005	0.45	0.08	74	10				
WIND 3-5f							3250		1.13	0.19	0.26	0.03	0.06673	0.00004	0.23	0.05	17	3				
WIND 3-4							3753		1.13	0.12			0.01991	0.00001			57	6				
WIND 3-2f							3753		1.03	0.11			0.07988	0.00005			13	1				
WIND 9-10	29.24.27		47.22.25		3334		75		0.136	0.004	0.08	0.01	0.00417	0.00006	0.62	0.11	33	5				
WIND 9-8							250		0.156	0.009	0.06	0.01	0.00471	0.00008	0.38	0.11	33	8				
WIND 9-7							500		0.249	0.006	0.07	0.01	0.0076	0.00009	0.29	0.06	33	6				
WIND 9-6							750		0.349	0.006	0.11	0.02	0.012	0.002	0.32	0.07	29	6				
WIND 9-4							2000		0.46	0.005	0.32	0.04	0.009	0.001	0.7	0.08	52	7				
WIND 12-11+12	25.50.53		47.55.17		4186		37.5		0.12	0.005	0.03	0.02	0.008	0.002	0.26	0.15	14	4				
WIND 12-9							170		0.108	0.003	0.04	0.01	0.00319	0.00007	0.38	0.11	34	8				
WIND 12-7							650		0.264	0.006	0.1	0.02	0.008	0.001	0.38	0.08	35	6				
WIND 12-6							1100		0.57	0.02	0.17	0.06	0.017	0.005	0.31	0.12	33	12				
WIND 12-5							2700		0.79	0.02	0.34	0.09	0.016	0.004	0.43	0.14	50	16				

Continued on next page...

Table 3.1 continued from previous page...

Sample	Latitude		Longitude		Water		Depth		^{230}Th		^{231}Pa		^{232}Th		2σ		$^{231}\text{Pa}/^{230}\text{Th}$		$^{230}\text{Th}/^{232}\text{Th}$	
	$^{\circ}\text{S}$	$^{\circ}\text{E}$	Depth m	m	Depth m	m	d.p.m./1000l	2σ	d.p.m./1000l	2σ	d.p.m./1000l	2σ	d.p.m./1000l	2σ	d.p.m./1000l	2σ	d.p.m./1000l	2σ	d.p.m./1000l	2σ
WIND 15-12	20.00.01	50.19.93	4629	170			0.07	0.03	0.038	0.005	0.003665	0.000002	0.54	0.22	19	7				
WIND 15-11				500			0.16	0.05	0.03	0.01	0.007585	0.000004	0.21	0.09	21	7				
WIND 15-10				900			0.31	0.04	0.12	0.01	0.005072	0.000003	0.38	0.06	62	7				
WIND 15-9				1250			0.35	0.05	0.19	0.02	0.010093	0.000005	0.54	0.1	35	5				
WIND 15-8				1750			0.77	0.11	0.29	0.03	0.011439	0.000006	0.37	0.07	68	10				
WIND 15-7				2500			0.76	0.09	0.26	0.03	0.012211	0.000007	0.34	0.06	62	8				
WIND 15-4				4400			0.93	0.1	0.19	0.02	0.014323	0.000007	0.2	0.03	65	7				
WIND 28-9	10.09.85	51.45.74	4137	100			0.167	0.009	0.07	0.009	0.007713	0.000004	0.4	0.06	22	1				
WIND 28-8				300			0.32	0.02	0.09	0.01	0.013193	0.000007	0.28	0.04	24	1				
WIND 28-7				900			0.44	0.02	0.14	0.02	0.01817	0.00001	0.32	0.04	24	1				
WIND 28-6				1400			0.66	0.04	0.19	0.02	0.014902	0.000009	0.28	0.04	45	3				
WIND 28-5				2000			0.65	0.06	0.29	0.03	0.04646	0.00002	0.44	0.07	14	1				
WIND 28-2				4000			0.82	0.21	0.3	0.03	0.03449	0.00002	0.37	0.11	24	6				

Table 3.1: ^{231}Pa and ^{230}Th concentrations and isotope ratios. Concentrations have been converted to d.p.m./1000 l assuming 1 fg/kg $^{230}\text{Th} = 0.0456$ d.p.m./1000 l and 1 fg/kg $^{231}\text{Pa} = 0.105$ d.p.m./1000 l. $^{231}\text{Pa}/^{230}\text{Th}$ and $^{230}\text{Th}/^{232}\text{Th}$ are expressed as activity ratios. Half lives used throughout this study are 32.76 ka, 75.690 ka for ^{231}Pa and ^{230}Th respectively (Robert et al., 1969; Cheng et al., 2000) and 14.0100 Ga for ^{232}Th (Holden, 1990). All errors are 2σ and incorporate uncertainty due to: uncertainty in the raw measured ratios; ion counter gain; mass discrimination; peak tailing and molecular interference; machine memory; and procedural blank. f, denotes a filtered water sample. ^a, These measurements are discounted, as they fall outside the range of sensible values for natural samples.



□ WIND 3, ♦ WIND 9, ◆ WIND 12, ■ WIND 15, ▲ WIND 28, ● 1751, — global average

Figure 3.4: Concentration profiles through the water column for: (a) ^{230}Th ; (b) ^{231}Pa ; (c) ^{232}Th . Grey filled circles with dashed lines are a profile from station 1751 in Rutgers van der Loeff and Berger (1993); the thick grey line is globally averaged data from Henderson and Anderson (2003). Approximate depths of water masses are shown according to T-S data (Figure 3.3). All errors are 2σ .

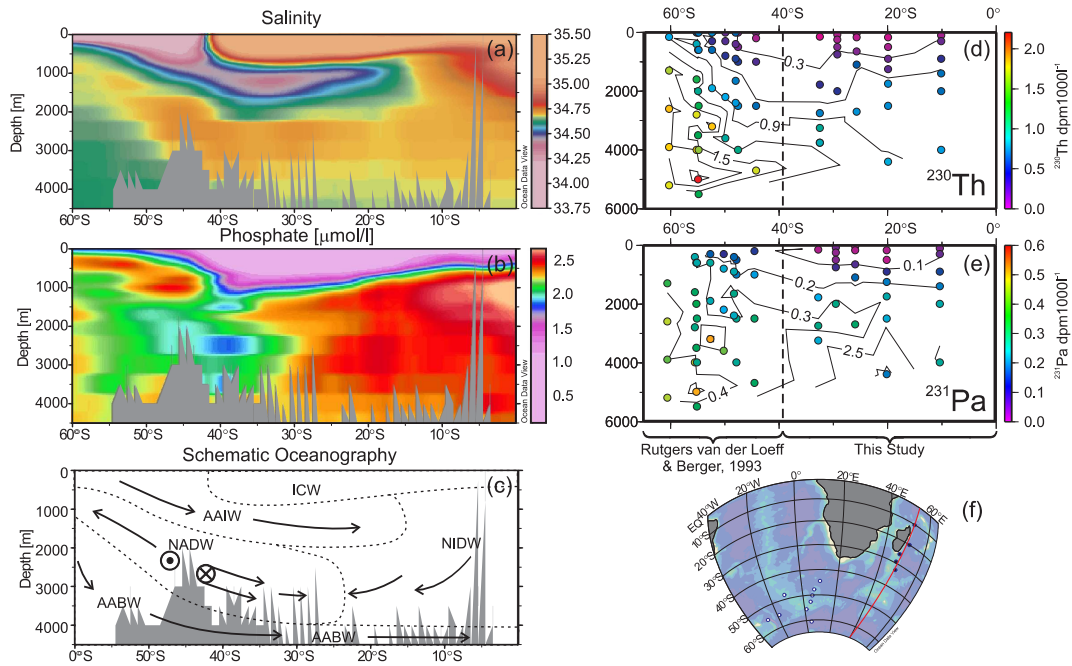


Figure 3.5: (a, b) Average salinity and phosphate sections for the western Indian Ocean (i.e. along the red line in panel f), data is taken from the World Ocean Atlas (Boyer et al., 2002; Conkright et al., 2002). (c) is a schematic representation of water masses and their movement. Note the movement of, low phosphate, “NADW” through the South West Indian Ridge at 45°S and then back west out of the section following the Madagascar Ridge. (d, e) Sections through the Southern and Indian Oceans showing the concentrations of ^{230}Th and ^{231}Pa . Note that the data in the Southern Ocean (Rutgers van der Loeff and Berger, 1993) is not at the same longitude as that in the Indian Ocean, but that comparison are valid due to similar conditions seen at any latitude in the Southern Ocean. ^{230}Th in the Indian Ocean shows a monotonous increase of concentration with depth. The ^{231}Pa profiles show more structure. Data from the Southern Ocean show no coherent variation, which may reflect larger measurement uncertainty. ^{231}Pa concentrations in the Indian Ocean, however, show elevated values at depths corresponding to “NADW”.

3.6 Controls on radionuclide concentrations in Indian Ocean waters

3.6.1 ^{231}Pa and ^{230}Th

Structure observed in the ^{231}Pa profiles measured in this study appears to be controlled by the source and history of the various water masses sampled. Correspondence between high ^{231}Pa and the high-salinity waters of “NADW” indicate that the high ^{231}Pa is a distinct feature of “NADW” in this region. This is seen in Figure 3.5, in which new data from this study are compared with data for the Atlantic sector of the Southern Ocean (Rutgers van der Loeff and Berger, 1993). Although data from the two studies are separated by ~ 40 degrees of longitude, the zonal similarity of conditions in the Southern Ocean (Sverdrup et al., 1942), due to strong west-east flow, make such comparison valid. Reasonably continuous values of ^{231}Pa are observed moving from the Southern Ocean northwards. But high ^{231}Pa concentrations are found in the section at ~ 2500 m water depth at 40° - 20°S (Figure 3.5 e).

This is the region where “NADW” is overflowing the Southwest Indian Ridge to enter the Madagascar Basin (Donohue and Toole, 2003). These high ^{231}Pa values persist northwards, demonstrating that mixing and particle settling do not obscure the differences between water masses on the timescale of transit through the Madagascar Basin.

^{231}Pa concentration in the various water masses measured in this study are likely to be controlled by their source, and by scavenging in the Southern Ocean opal belt. “NADW” enters the Madagascar and Mascarene Basins as a geostrophically constrained boundary current around the Southern African Margin and does not enter the Southern Ocean. High ^{231}Pa in these “NADW” samples must, therefore, be attributed to high ^{231}Pa water from the South Atlantic, rather than from the Antarctic Circumpolar Current (ACC). The concentrations of ^{231}Pa in the rest of

the water column are lower, and lower than seen in the Southern Ocean from where they are sourced. This is likely to be due to strong removal of Pa from the water column as the water leaves the ACC by scavenging on opal particles which has been shown to strongly favour scavenging of Pa scavenging (Walter et al., 1997; Chase et al., 2002; Dezileau et al., 2003).

3.6.2 ^{232}Th

Individual profiles typically show a slight increase in ^{232}Th concentration with depth (e.g. WIND 15; Figure 3.4) but with a large degree of scatter, especially at depths corresponding to AABW. Unlike ^{230}Th and ^{231}Pa , which are almost entirely derived from decay of U in the water column, ^{232}Th is associated with detrital material derived from aerosols or from the continental margins. The scatter in the ^{232}Th data observed here can be attributed to changing content of such detrital material, because samples in this study were not filtered. The high values and large variability of AABW ^{232}Th are likely to be caused by a dilute expanded nepheloid layer, perhaps influenced by sediment transport from the continental slope of Madagascar. Even excluding the unusually high ^{232}Th values seen in some of these AABW samples, however, a slight increase in concentration with depth persists. If insoluble ^{232}Th -bearing particles settle at a uniform speed throughout the water column such an increase is not expected. The increase can be explained, however, if some portion of the ^{232}Th is dissolving in seawater and is reversibly scavenged onto sinking particles in a similar manner to ^{230}Th .

3.7 Modelling of export of ^{231}Pa and ^{230}Th to sediments

3.7.1 Introduction

The recognition that water masses can have distinct ^{231}Pa concentrations relative to waters above and below, reflecting the differing histories of the water masses, will make interpretation of sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) ratios more complex. In contrast to ^{230}Th , which rapidly achieves an equilibrium profile, the greater solubility of ^{231}Pa allows water masses to retain a characteristic ^{231}Pa concentration for considerable distances. It is therefore to be expected that water masses with distinct ^{231}Pa concentrations will be found overlying one another in many areas of the world ocean, just as is seen in this area of the southern Indian Ocean. Before sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) ratios can be interpreted in such areas, we must understand how each water mass impacts the ($^{231}\text{Pa}/^{230}\text{Th}$) value recorded in the sediment.

A common assumption in interpretation of sediment ($^{231}\text{Pa}/^{230}\text{Th}$) ratios has been that they represent average flow conditions through the entire water column. Or, in other words, that the Pa and Th reaching the sediment has equilibrated with waters from the entire water column. If this is true, then interpretation of sediment ($^{231}\text{Pa}/^{230}\text{Th}$) in regions of complex oceanography will always be an ambiguous process. With more than one water mass overlying the sediment core, changes in ($^{231}\text{Pa}/^{230}\text{Th}$) might represent changes in the flow rate and history of one of these waters, or more than one of them. In this section, we use a simple model to test this assumption and to assess the depth at which particle Pa and Th last exchange with seawater before reaching the sediment.

3.7.2 The model

To investigate the depth at which Th and Pa are last equilibrated we use a 1D particle scavenging box model which comprises two particle classes: fine particles which do not settle and are effective scavengers because of their high surface area; and coarse particles, formed by the aggregation of the smaller particles, which are responsible for all the downward removal of ^{230}Th and ^{231}Pa from each box (Figure 3.6). No scavenging onto these coarse particles is allowed because of their low surface area to mass ratio and, particularly, because they settle too quickly to allow equilibration as they fall. The effect of eddy diffusion on redistribution of the small particle class is thought to be small (Clegg and Whitfield, 1991) and is ignored. The distribution of particles between fine and coarse in the model is governed by aggregation (r_1, y^{-1}) and disaggregation (r_{-1}, y^{-1}) constants. The distribution of the nuclides between dissolved and fine-particles is calculated from a prescribed distribution coefficient (Kd) and particle concentration. All variables in the model are listed in Table 3.2, together with values used in the control run. The value of Kd determines the distribution of nuclide between the dissolved phase and the particulate phase, so will effect the rate of removal of both nuclides to the seafloor. Kd does not, however, have any direct bearing on the depth of last equilibration which is controlled by particle cycling and settling rates. The average depth of scavenging in the model is therefore general to all nuclides undergoing reversible scavenging regardless of their Kd.

The model input is a 5500 m water-column profile of a nuclide concentration which would be expected from a 1D reversible scavenging model (Moran et al., 2001) at equilibrium. For a K value (i.e. the ratio of particulate to total concentration) of 0.14 (equal to that of Th), this would equate to a linear increase in ^{230}Th concentration with depth from zero at the surface to 2 dpm/1000 l at 5500 m. Large particles settle through the model water column (at rate, S, in m/day). As they fall, a fraction dissolves in each box, returning nuclides to the dissolved phase, and the remainder

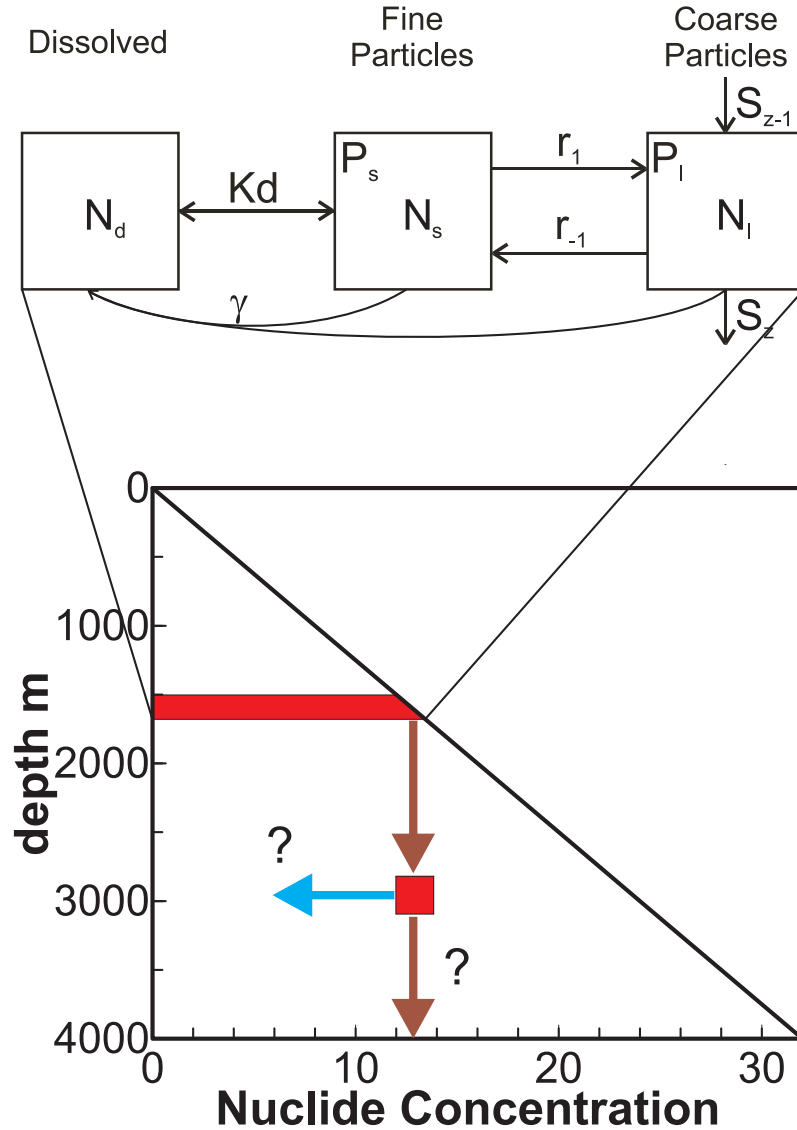


Figure 3.6: A schematic representation of the model used to assess the depth from which ^{230}Th and ^{231}Pa are scavenged to the seafloor following (Nozaki et al., 1987; Clegg and Whitfield, 1990; Huh, 1995). Dissolved isotopes are scavenged to fine particles, making up the majority of the particle mass, assuming an equilibrium K_d . These fine particles can aggregate (rate = r_1 , y^{-1}) into coarse particles which settle (rate = S , mday^{-1}) while also disaggregating (r_{-1} , y^{-1}) and dissolving (γ , y^{-1}). P_l and P_s are the concentration of large and small particles (gm^{-3}).

is allowed to disaggregate at the prescribed rate (r_{-1}). For particles settling from one box, therefore, some disaggregate in the box immediately below, while others fall further into deeper boxes or to the sediment before disaggregating. The amount of nuclide that reaches the seafloor on large particles without disaggregating or dis-

Variable	Abbreviation	Units	Values used	Reference
Nuclide concentration	N	d.p.m. 1000l^{-1}	linear increase from 0 at surface to 2.01 at 5500 m	(Moran et al., 1997)
Particle concentration	$P_s + P_l$	gm^{-3}	Particle model giving 0.015 to 0.011 below 1500 m	(Clegg and Whitfield, 1991)
Partition coefficient	Kd		10^6	
Aggregation	r_1	y^{-1}	4	(Clegg and Whitfield, 1991)
Disaggregation	r_{-1}	y^{-1}	150	(Nozaki et al., 1987; Clegg and Whitfield, 1991)
Dissolution	γ	y^{-1}	0.025-50	(Clegg and Whitfield, 1991)
Settling rate	S	mday^{-1}	150-600	(Bacon et al., 1985)

Table 3.2: Abbreviations, units and values used in the 1D model. References provide the source of these values.

solving, is calculated for each box in the water column. These amounts are then cumulatively summed to produce a curve of the fraction of the total amount of nuclide reaching the seafloor effectively scavenged from above each depth (Figure 3.8). From this the median depth of last equilibration can be found.

3.7.3 Model results

The median depth of last scavenging was found to be insensitive to the particle concentration, to the distribution coefficient, and to the aggregation rate. Only processes that directly control the transport of large particles to the seafloor affect the depth of last scavenging. The affect of varying the settling rate, S, which drives transport to the seafloor, and disaggregation rate, r_{-1} , which inhibits transport to the seafloor, are shown in Figure 3.7. Varying dissolution, γ , will have a similar effect to that of disaggregation because it prevents scavenged nuclides from sinking by returning them to the dissolved phase. A typical profile of the cumulative proportion of nuclide last scavenged at depth z is shown in Figure 3.8. Varying S and r_{-1} within reasonable limits (S is typically $\sim 100 \text{ mday}^{-1}$ (Bacon et al., 1985) and r_{-1} varies from $150\text{-}750 \text{ y}^{-1}$ (Nozaki et al., 1987)) indicates that the median depth of final scavenging is unlikely to be more than 700 m from the seabed. Shallow median final scavenging can only be achieved in the model if disaggregation is unrealistically slow ($< 50 \text{ y}^{-1}$) or the settling rate of large particles unrealistically fast ($> 600 \text{ mday}^{-1}$). Of course

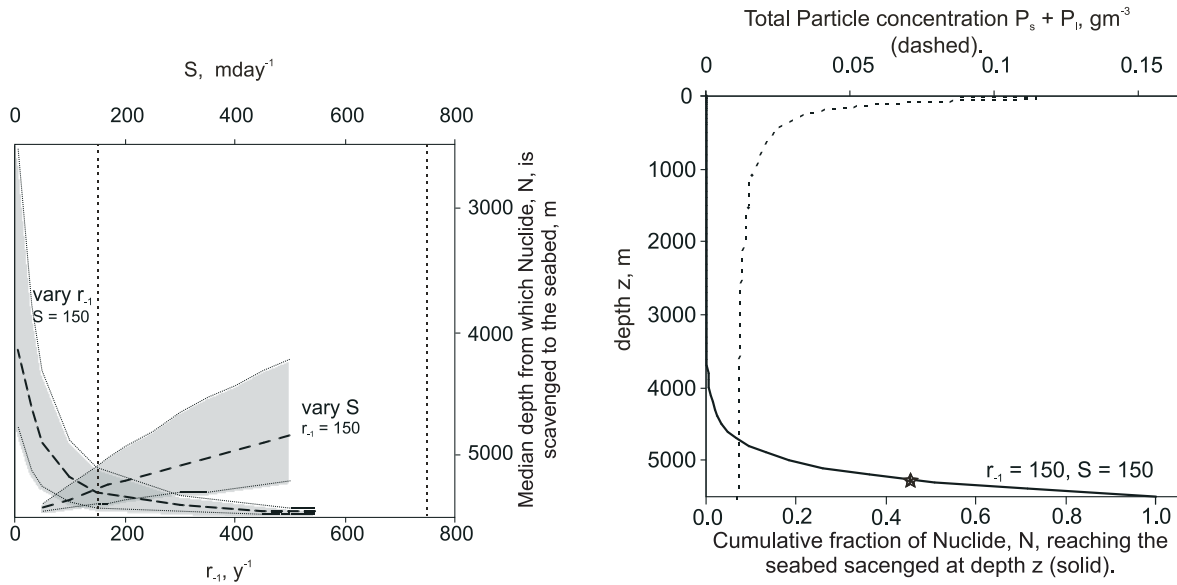


Figure 3.7: Model sensitivity tests varying the settling rate, S , and the disaggregation rate, r_{-1} . The dashed lines indicate a sensible range and disaggregation rate, $r_{-1} = 150 \text{ y}^{-1}$. Solid for r_{-1} in deep waters as determined by Nozaki et al. (1987). The shaded areas indicate the inter-quartile range for the depth of scavenging. Note that, for all reasonable values of S the particle concentration profile used for this and r_{-1} , most of nuclide, N , is scavenged within model Clegg et al. (1991). The star is the 700 m of the seafloor.

Figure 3.8: Model results for the most realistic case, where settling rate, $S = 150 \text{ mday}^{-1}$ and $r_{-1} = 150 \text{ y}^{-1}$. The dashed line indicates the total particle concentration profile used for this and r_{-1} , most of nuclide, N , is scavenged within model Clegg et al. (1991). The star is the median depth of scavenging (200 m above the seafloor).

if large particles effectively disaggregate on the seafloor and are able to exchange with seawater there, then the depth of median final scavenging is still deeper. The model therefore represents a maximum distance from the sea-bed that dissolved Th and Pa will be directly scavenged. Sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) ratios, will therefore, represent the truly bottommost waters.

3.7.4 Interpretation

Because it is the processes of particle settling and disaggregation that control the depth of final scavenging of nuclides, the results hold for both ^{230}Th and ^{231}Pa . Although large particles will have a relatively lower concentration of ^{231}Pa than

^{230}Th , leading to slower removal of ^{231}Pa , the depth in the water column from which it is last scavenged will be the same as for ^{230}Th . Thus the ($^{231}\text{Pa}/^{230}\text{Th}$) records in sediment cores can be used to investigate changes in the past chemistry and flow rate of near-bottom water masses. The chemistry of these water masses may, in turn, be influenced by water masses which overlay them, but this influence may take long enough to exert itself that waters will have travelled a significant distance. At sites where water masses have distinct ^{231}Pa concentrations, due to differing scavenging and advection histories, it is the lower-most water mass that is expected to dominate the ($^{231}\text{Pa}/^{230}\text{Th}$) signal recorded in the sediment. In the Indian Ocean, and in particular the Madagascar and Mascarene Basins, sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) will reflect the advection and scavenging history of Antarctic Bottom Water filling the basins.

3.8 Discussions

3.8.1 Sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ is most representative of the bottom-most water mass

The fact that sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) reflects only the deepest water mass may make it more difficult to provide an unambiguous interpretation of a single sedimentary record of ($^{231}\text{Pa}/^{230}\text{Th}$). Such records might be interpreted, however, by the additional use of other proxies, particularly by the information provided by a water mass tracer such as Cd/Ca or Nd isotopes. On the other hand, the fact that sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) allows reconstruction of a particular water mass is good news for its application to multiple cores. A set of ($^{231}\text{Pa}/^{230}\text{Th}$) records from varying water masses should allow the history of flow rate to be reconstructed for all water masses at that location, rather than averaging flow over the whole water column.

The findings of this study also have implications for the use of sedimentary

($^{231}\text{Pa}/^{230}\text{Th}$) as tools to investigate particle flux (Kumar et al., 1993) and particle type (Chase et al., 2002). Because the ($^{231}\text{Pa}/^{230}\text{Th}$) exported to the sediments is most representative of the bottom-most water mass, it is the particle flux and type at this depth, rather than surface conditions, that will be reflected in the sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) ratio.

3.8.2 Implications for interpretation of sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) records in other regions

The realisation that sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) values reflect only the deepest water mass has implications for previous studies of sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) in the North Atlantic (Yu et al., 1996; McManus et al., 2004). In the modern ocean, NADW represents the deepest water mass in the North Atlantic so that core-top sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) is likely to reflect the ventilation and productivity of this water mass. This situation was not necessarily always the case, however. If NADW were to shoal so that the deepest water mass was from a Southern-Ocean source, this Southern-Ocean source would control sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$). Due to the long transport distance, and hence long time to reach equilibrium, such Southern Ocean water masses would have high ($^{231}\text{Pa}/^{230}\text{Th}$), leading to values exported to the underlying sediment close to the production ratio. Such production ratio values have, for Heinrich 1 (H1) and the Younger Dryas, been proposed to represent periods of MOC shutdown or partial shut down (McManus et al., 2004). This proposal is based on the assumption that sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) is controlled by the whole water column. The modelling presented here, however, suggests that the MOC may have persisted during these intervals, but at a shallow depth. It should be stressed that this suggestion does not preclude complete cessation of MOC at H1. It just indicates that ($^{231}\text{Pa}/^{230}\text{Th}$) close to the production value may have an alternative explanation.

3.9 Summary

The first ^{230}Th and ^{231}Pa water column profiles have been presented for the south western Indian Ocean. The ^{230}Th profile is similar to that observed across the Southern Ocean at 44.48°S 10.46°E . The ^{231}Pa profiles indicate that waters flowing from the Southern Ocean (AAIW, AABW) have experienced ^{231}Pa loss due to removal by scavenging, presumably during transit through the opal belt. The high ^{231}Pa of NADW is preserved as a water mass tracer into the Indian Ocean, probably because it has not been subject to high rates of scavenging in the opal belt. The observation of water masses with distinct ^{231}Pa values in a single water column raises the question of which water mass controls the sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) values. A simple 1D model demonstrates that this sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) signal is derived from the bottom ~ 1000 m of the water column, rather than averaging the whole water column. In the region of the Indian Ocean investigated here, this indicates that sedimentary records can be used to reconstruct the past flow rate of AABW into the Indian Ocean. The importance of bottom-water for sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) records should also be considered when interpreting sedimentary ($^{231}\text{Pa}/^{230}\text{Th}$) ratios from other regions.

Chapter 4

Sedimentary ^{231}Pa and ^{230}Th

4.1 Overview

This chapter includes new sedimentary ^{231}Pa and ^{230}Th data from surface sediments from the southwest Indian Ocean, increasing the global coverage of modern sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})$. A 140 ka downcore record of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is also presented. The sensitivity of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to changes in circulation is investigated with a 1D water column model. Interpretation of the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ record indicates that there has been no change in particle productivity, or ventilation of the deep Indian Ocean from the Southern Ocean, over the past 140 ka.

4.2 Introduction

$(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is a potentially powerful tool for paleoceanographers. Studies in the Atlantic (McManus et al., 2004; Yu et al., 1996) have shown $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to be a useful proxy for circulation, and in the Southern Ocean for productivity (Kumar et al., 1995; Anderson et al., 1998), and/or particle type (Chase et al., 2003). These controls on sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ are summarised in Henderson and Anderson (2003), and in Section 1.6.5 of this thesis. In this chapter the temporal and spatial data coverage of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in the western Indian Ocean are extended,

and the potential for its use as a paleocirculation proxy for deep waters originating from the Southern Ocean assessed.

^{231}Pa and ^{230}Th are produced in seawater from the in situ decay of ^{235}U and ^{234}U , respectively. Due to the conservative behaviour and the long residence time of U the production, β , of ^{231}Pa and ^{230}Th can be assumed to be constant at $\beta_{\text{Pa}} = 2.45 \times 10^{-3}$ and $\beta_{\text{Th}} = 2.62 \times 10^{-2} \text{ d.p.m.m}^{-3}\text{yr}^{-1}$, leading to a constant production activity ratio of 0.093. Both ^{231}Pa and ^{230}Th are reversibly scavenged from the dissolved phase onto sinking particles resulting in short oceanic residence times, t_{res} , and in concentration profiles that typically increase in concentration with depth (Anderson et al., 1983a). Because $t_{\text{res,Pa}}$ is longer than $t_{\text{res,Th}}$ (120 versus 20 years) (Henderson and Anderson, 2003), marked fractionation from the production ratio can occur within the oceans. In regions of freshly formed deep water such as the North Atlantic, the concentrations of both ^{231}Pa and ^{230}Th are low due to the convection of low concentration surface water to depth in such regions. Because ^{230}Th is more readily scavenged onto sinking particles and hence removed from the ocean to the seafloor, sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is typically considerably less than the production ratio. This removal of ^{230}Th results in the water becoming more enriched in ^{231}Pa relative to ^{230}Th as the deep water mass ages. This will continue until a scenario is reached where the output of ^{231}Pa and ^{230}Th to the sediments occurs at the same ratio as the input (i.e. 0.093). It is the disequilibrium seen in regions of deep water formation and flow that provides the potential proxy for circulation. The closer to the production ratio the export from a water column is, the longer it is since that water left the surface (or had disequilibrium imposed in some other way).

$(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in sediment has been used in the North Atlantic (McManus et al., 2004) and Arctic (Moran et al., 2005) to investigate the advection out of the respective basins. In the North Atlantic surface waters with low ^{231}Pa and ^{230}Th concentrations are convected to depth, resulting in deep water which has both low

^{231}Pa and ^{230}Th concentrations and also low $(^{231}\text{Pa}/^{230}\text{Th})$. In this simple case as the water ages its $(^{231}\text{Pa}/^{230}\text{Th})$ rises, allowing $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in sediment to be used as a proxy for the North Atlantic meridional overturning circulation. It is important to investigate the use of the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy in a region where the oceanography is more complex, and the deep water is of a different source to that in the North Atlantic, if $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is to be used globally in a wide range of oceanographic settings. The southwest Indian Ocean is also a relatively understudied region with respect to ^{231}Pa and ^{230}Th , and as such, increasing data coverage will aid development of models of ^{231}Pa and ^{230}Th behaviour in the ocean (Data from this chapter has been incorporated into the global data-set used in Siddall et al. (2005)).

4.3 Regional setting & samples

The deep Madagascar and Mascarene Basins are currently filled from the south by Antarctic Bottom Water which overflows the Southwest Indian Ridge (Toole and Warren, 1993) and forms a deep western boundary current along the eastern margin of Madagascar. This boundary current flows north through the basins and exits through the Amirante Passage into the northern Indian Ocean. Directly overlying this water mass in the Madagascar Basin is water derived from the North Atlantic Deep Water with a characteristic high salinity. In the northern Mascarene Basin the overlying water mass, North Indian Deep Water, is similar to that overlying AABW to the south, except that it is more enriched in nutrients due to its greater age (Figure 4.1). Antarctic Intermediate Water enters the Indian Ocean from the south and overlies both the Atlantic and Indian Deep Waters. The uppermost water mass, Indian Central Water, is formed within the Indian Ocean's gyres and is characteristically both warm and salty.

For the spatial mapping portion of this study seven surface scrapes were selected

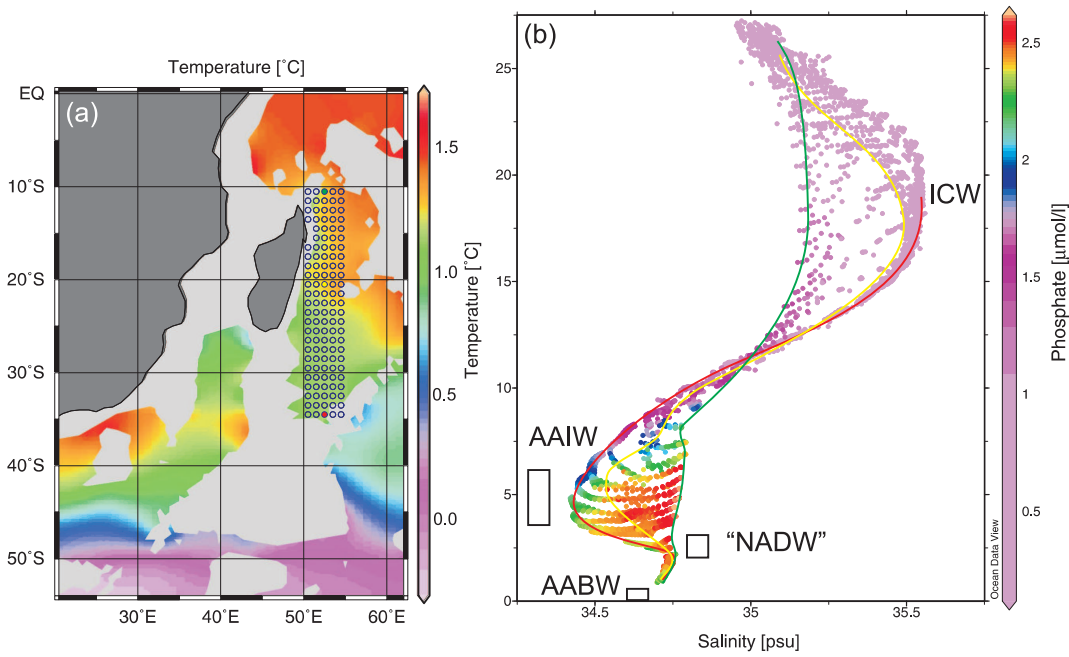


Figure 4.1: (a) A map of annual average temperature of the southwest Indian Ocean at 4000 m depth. AABW can be seen entering the Madagascar Basin through a gap in the southwest Indian Ridge and forming a boundary current of cold water along the eastern side of the Madagascar ridge. Blue circles indicate position of profiles used for the compilation (b). Red, yellow, and green dots correspond to the profiles marked on (b). (b) a temperature vs. salinity plot of all profiles from (a) showing the phosphate concentration for each profile. The Temperature and salinities of important water masses are marked: AABW, Antarctic Bottom Water; "NADW", water derived from North Atlantic Deep Water; AAIW, Antarctic Intermediate Water; and ICW, Indian Central Water. Note the reduction in influence of AAIW moving northwards. AAIW is 'replaced' by nutrient rich North Indian Deep Water, having similar temperature and salinities to NADW but higher PO_4 concentrations.

from cores taken on the *RRS Charles Darwin* (cruises CD129 (I. N. McCave), and CD154 (I. Hall & R. Zahn)) (Figure (4.2)). To collect a downcore record of past changes in conditions, a 6 m Kasten core, collected during CD129 was sampled to provide a temporal record of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$. This core, WIND 28K was taken at $51^\circ 46'\text{E } 10^\circ 9'\text{S}$, in 4157 m water depth. The core sits in a boundary current of northward flowing AABW, overlain by southward flowing NIDW with minimal influence of AAIW. The sediment is dominantly clay-rich carbonate mud.

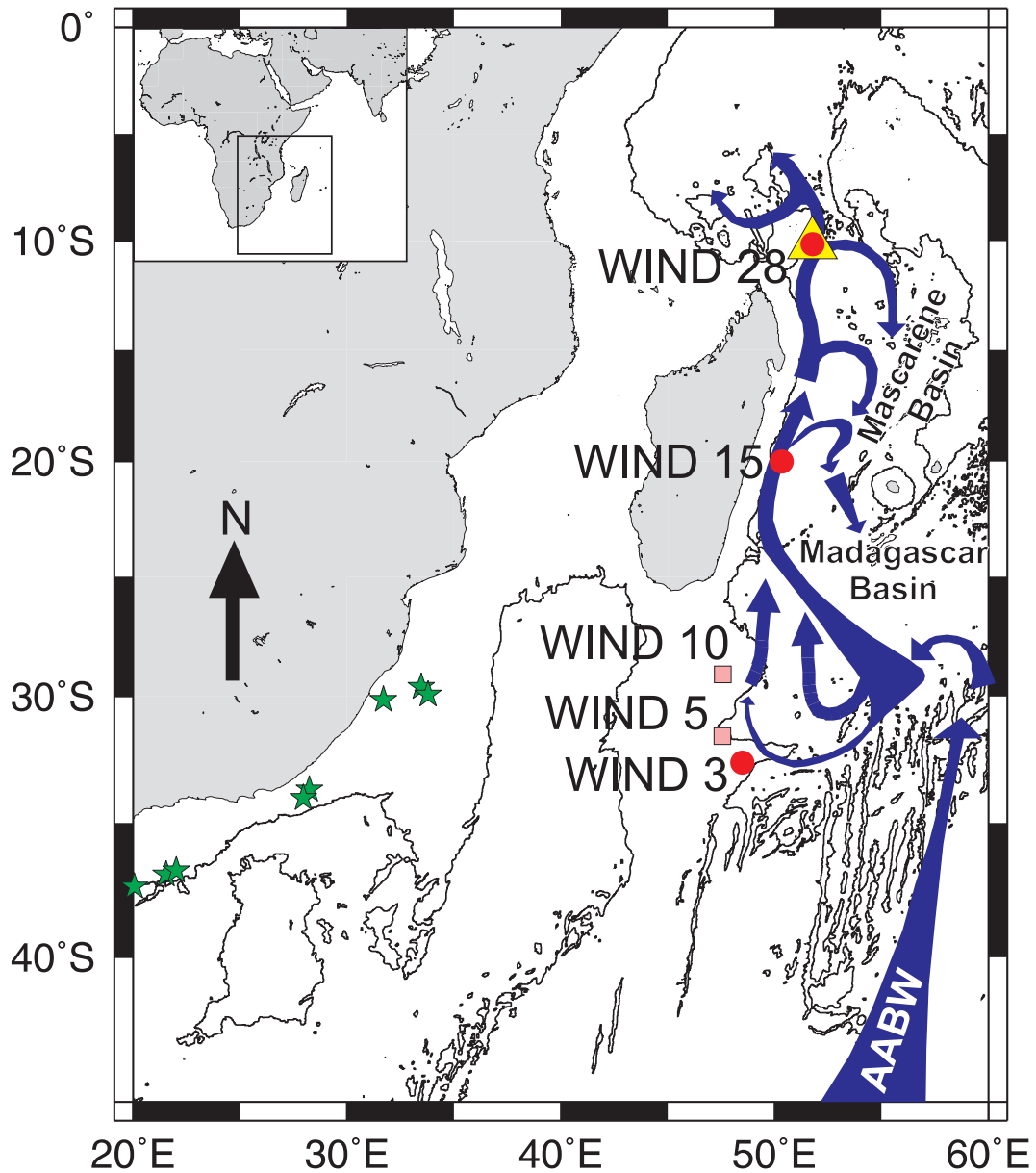


Figure 4.2: A map showing the localities of sediment samples in this study. Box-core sediment surface scrapes from *RRS Charles Darwin* cruise CD 129 (red circles), and Kasten core WIND 28K (yellow triangle), are shown along with core top scrapes from *RRS Charles Darwin* cruise CD 154 (green stars). Localities WIND 5 and 10 from Figure 4.4 are shown a pink squares. The path of Antarctic Bottom Water adapted from McCave et al. (2004) is illustrated in blue. The 4000 m isobath is also shown to illustrate the isolation at depth of the Madagascar and Mascarene Basins.

4.4 Methods

General sample preparation, elemental separation, and measurement by MC-ICP-MS are covered comprehensively in Chapter 2. The methods used which are specific to sediment samples are briefly covered here.

4.4.1 Chemistry

Sample weighing and digestion

Sediment samples were dried overnight at 110°C to remove water before weighing out approximately 0.1 g of sediment into TeflonTM beakers. The sediment was wetted with a few drops of water to prevent loss of powder from the beaker and ultra-sounded to disaggregate the sediment. Samples were then dissolved with conc HF, heated, and dried down. This step is repeated to ensure all silicates are removed. The samples were then spiked with: a mixed, ^{229}Th and ^{236}U spike (Oxford Carbonate Spike (Henderson et al., 2001)); and ^{233}Pa spike. The spikes were mixed together and made up with 2 ml of 15N HNO_3 , which was added to each sample and heated to dryness. The mixed $^{229}\text{Th}/^{236}\text{U}$ spike (Henderson et al., 2001) was added such that the $^{230}\text{Th}/^{229}\text{Th}$ is between 0.1 and 1. Samples were redissolved in 2 ml aqua regia, to remove organic matter, and dried down. The samples were then redissolved and dried twice in 2 ml 15N HNO_3 , to convert any remaining fluorides and chlorides to nitrates, before final dissolution in 4 ml 7.5N HNO_3 and heating overnight with the cap on. The dissolved sample was then transferred to an acid-cleaned, centrifuge tube, made up to 25 ml with water, and 10 mg of Fe added. NH_4 was added to co-precipitate the actinides with Fe. Care is taken so as not to raise the pH above 8, which would lead to the precipitation of $\text{Ca}(\text{OH})_2$. The precipitate is centrifuged and washed with Milli-Q before being transferred back into the TeflonTM beaker and dissolved in 0.5 ml 7.5N HNO_3 ready for anion exchange chromatography.

Elemental separation

Th, Pa and U were separated using Dowex Bio-Rad AG1-X8 100-200 mesh anion exchange resin, held in a 0.5 ml Teflon column, following an adapted procedure from Robinson et al. (2002). Each sample was loaded onto a pre-cleaned and conditioned column in 0.5 ml 7.5N HNO₃, and washed in with a further 1.5 ml of 7.5N HNO₃, this washed off the Fe and some U. The column was then converted to Cl⁻ with a few drops of 6N HCl. Elution was continued up to 300 μ l before the Pa-Th split was taken, eluted with 2ml of 6N HCl + 0.05N HF. Then the column was washed with 1.5 ml H₂O and the U split taken. The Pa-Th split was dried down and redissolved in 0.5 ml 7.5N HNO₃ and the column procedure repeated to further remove U. This second column also separates Th from Pa by elution with 2 ml 6N HCl, rather than 6N HCl +0.05N HF, to elute the Th. Pa is then eluted as before with 2 ml 6N HCl +0.05N HF. A final third column, repeating the second, was required to further purify the Pa split for Th, which is especially important for sediment samples with high Th contents. The splits for Th, Pa, and U were prepared for measurement by drying down and dissolving in a small amount of 7.5N HNO₃, such that when they were required H₂O could be added to make up to the desired volume of 2% HNO₃.

All Acids used are quartz distilled, with the exception of HF which is distilled in a TeflonTM still. Water is 18 M Ω Milli-Q, and NH₄ is Aristar grade. Fe used for co-precipitation was cleaned by liquid - liquid extraction with isopropyl ether.

4.4.2 Mass spectrometry

Measurements were made using a Nu Instruments MC-ICP-MS (Belshaw et al., 1998). U was measured statically with ²³⁴U in an ion counter and ²³⁸U, ²³⁶U, and ²³⁵U in Faraday collectors (Table 2.6), utilising standard-sample bracketing with CRM-145 to correct for ion counter gain and abundance sensitivity (Section 2.5.2).

Measurement of Pa is covered in Section 2.5.5. Briefly, Pa was measured with

multiple ion counting channels, with ^{231}Pa in the central ion counting channel IC(-5) (equipped with an energy filter to improve abundance sensitivity from ^{232}Th and ^{235}U tailing if chemical separation was poor) and ^{233}Pa in the high mass ion counter IC(-3) (Table 2.6). Mass bias was assessed externally by bracketing samples with uranium standard CRM-145, during which, assessment of the gains of the ion counters was also made.

Interference from ^{232}ThH and abundance sensitivity from ^{232}Th was corrected by measuring the ^{232}Th in the Pa cut of each sample in F(-4) and bracketing every two samples with a Th standard with a known $^{232}\text{Th}/^{230}\text{Th}$, and monitoring the contribution to masses 233 and 231 (Sections 2.5.1 and 2.5.1). Although the ionisation efficiency of U and Pa are thought to be similar (Choi et al., 2001), there may be some difference, because their first ionisation enthalpies (597.6 and 568 kJmol^{-1}) are 5% different. The measurement of the Pa split is made within a week of separation to ensure that minimal decay of ^{233}Pa to ^{233}U had occurred.

Th was measured using a two step procedure (Table 2.6 and Section 2.5.3). Because samples were spiked to give a $^{229}\text{Th}/^{230}\text{Th} > 1$ the integration time for the step measuring ^{229}Th was reduced by half, thereby maximising collection time for ^{230}Th .

4.5 Results

4.5.1 Data and corrections

Uncorrected results of uranium isotopes and ^{232}Th are summarised in Tables 4.1 (surface sediments) and 4.2 (down core record of WIND 28K). Uncorrected ^{231}Pa and ^{230}Th data and finalised $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ are summarised in Tables 4.3 and 4.4 and in Figure 4.3. Data for which it is believed that incomplete spike sample equilibration has occurred are excluded from the analysis but are included in the

tables. Several corrections are applied to the raw ^{231}Pa and ^{230}Th concentrations to derive $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ values. Correction for ^{230}Th and ^{231}Pa associated with detrital and authigenic material are made using equations (4.1) and (4.2) (Henderson and Anderson, 2003). Calculation of the detrital (U/Th) is discussed in Section 4.5.2. The corrections made make the assumptions that: authigenic U is formed at the sediment-water interface at the time of deposition and has the U isotopic composition of seawater; and the detrital material is in secular equilibrium. Both $^{231}\text{Pa}_{\text{xs}}$ and $^{230}\text{Th}_{\text{xs}}$ are then corrected for decay since deposition with equations (4.3) and (4.4) to give the activities of ^{230}Th and ^{231}Pa that were derived from the water column at the time of deposition.

$$^{230}\text{Th}_{\text{xs}} = ^{230}\text{Th}_{\text{meas}} - \left\{ (\text{U/Th})_{\text{detrital}} \times ^{232}\text{Th}_{\text{meas}} \right\} - \left\{ \left[\begin{aligned} &^{238}\text{U}_{\text{meas}} - (\text{U/Th})_{\text{detrital}} ^{232}\text{Th}_{\text{meas}} \\ &\left[(1 - e^{-\lambda_{230}t}) + \frac{\lambda_{230}}{\lambda_{234} - \lambda_{230}} (e^{-\lambda_{230}t} - e^{-\lambda_{234}t}) \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{init}} - 1 \right) \right] \end{aligned} \right] \times \right\} \quad (4.1)$$

$$^{231}\text{Pa}_{\text{xs}} = ^{231}\text{Pa}_{\text{meas}} - \left\{ 0.046(\text{U/Th})_{\text{detrital}} \times ^{232}\text{Th}_{\text{meas}} \right\} - \left\{ \left[\begin{aligned} &0.046^{238}\text{U}_{\text{meas}} - 0.046(\text{U/Th})_{\text{detrital}} ^{232}\text{Th}_{\text{meas}} \\ &1 - e^{-\lambda_{231}t} \end{aligned} \right] \times \right\} \quad (4.2)$$

$$^{230}\text{Th}_{\text{xs}}^0 = ^{230}\text{Th}_{\text{xs}} e^{\lambda_{230}t} \quad (4.3)$$

$$^{231}\text{Pa}_{\text{xs}}^0 = ^{231}\text{Pa}_{\text{xs}} e^{\lambda_{231}t} \quad (4.4)$$

The age model (Figure 4.3, f) for core WIND 28K, used to make these corrections, is based on 6 AMS radiocarbon dates and the $\delta^{18}\text{O}$ of benthic foraminifer *C.wuellerstorfi* (Figure 4.3, b) (McCave et al., 2004).

4.5.2 Calculation of detrital (U/Th)

Knowledge of the ($^{238}\text{U}/^{232}\text{Th}$) ratio in the detrital component of sediment is important because it allows the amount of authigenic U to be calculated and hence corrections for ^{230}Th and ^{231}Pa , produced from detrital and authigenic U, to be made. Once the (U/Th) of detrital material is known, then assuming all the ^{232}Th in the sediment is terrestrially sourced, the amount of U in the detrital material can be calculated (Equation 4.5). U not accounted for in this way is defined as authigenic uranium (Equation 4.6).

$$U_{\text{detrital}} = (U/Th)_{\text{detrital}} {}^{232}\text{Th}_{\text{meas}} \quad (4.5)$$

and,

$$U_{\text{authigenic}} = U_{\text{total}} - U_{\text{detrital}} \quad (4.6)$$

Because authigenic U is thought to form near the sediment-water interface as bottom water diffuses into the sediment, or even within the water column (Anderson, 1982), it should have an initial uranium isotopic composition similar to the seawater from which it formed (i.e. $\delta^{234}\text{U}$ of +146). Detrital $\delta^{234}\text{U}$ should be much lower (≈ 0) due to the old age of detrital minerals with respect to the half life of ^{234}U . Because detrital particles in the ocean are the product of weathering, they may well have undergone some ^{234}U loss so they can potentially have $\delta^{234}\text{U}$ values < 0 . Samples with high $\delta^{234}\text{U}$ ($> +50$) are therefore assumed to contain significant authigenic U, while those with $\delta^{234}\text{U} < +50$ are assumed to be dominated by detrital U. It is noted that those samples at WIND 28K that have low $\delta^{234}\text{U}$ (i.e. $< +50$), also have (U/Th) of 0.45 ± 0.05 (2σ n = 23 Table 4.2). The consistency of (U/Th) in these samples also suggests that they have not experienced addition of authigenic U. The (U/Th) of the detrital component of the sediment at WIND 28 is therefore taken to be 0.45 ± 0.05 .

This method of determining the $(U/Th)_{\text{detrital}}$ is a significant improvement, on

the ocean basin approach described in Henderson and Anderson (2003) or the simple use of an average crustal value (Anderson, 1982), because it is more specific to an individual core and has a smaller uncertainty associated with it. This uncertainty becomes increasingly significant for the calculation of detritally supported ^{231}Pa and ^{230}Th in older samples. A similar method to determine $(\text{U}/\text{Th})_{\text{detrital}}$ is that of McManus et al. (2004), which uses the (U/Th) of a nearby core with no authigenic U. The method used here is however advantageous as it requires only one core and the $(\text{U}/\text{Th})_{\text{detrital}}$ is specific to that core, removing the uncertainty of local spatial variability. A limitation of this approach is that it requires the core being investigated to have significant portions with no authigenic U, from which the $(\text{U}/\text{Th})_{\text{detrital}}$ can be inferred.

4.5.3 Calculation of sedimentation proxies

Sediment mass accumulation rate, F_w , is calculated by inverting the $^{230}\text{Th}_{\text{xs}}$ concentration (Equation 4.7 (Bacon, 1984)), assuming a constant flux of ^{230}Th from the water column,

$$F_w = \frac{z(^{234}\text{U})\lambda_{230}}{^{230}\text{Th}_{\text{xs}}} \quad (4.7)$$

which assumes that the flux of ^{230}Th to the sediment is dependent only on depth, z in m, and the water column production of ^{230}Th from decay of U. (^{234}U) is the activity of ^{234}U in seawater in d.p.m.m $^{-3}$, λ_{230} is the decay constant of ^{230}Th in a $^{-1}$, and $^{230}\text{Th}_{\text{xs}}$ is the ^{230}Th in the sediment formed in the water column in d.p.m.g $^{-1}$, which gives the mass accumulation rate F_w in gm $^{-2}$ a $^{-1}$.

The sedimentation rate, F_a , inferred from the age model in cmka $^{-1}$ and the mass accumulation rate, F_w calculated from $^{230}\text{Th}_{\text{xs}}$ 0 (Equation 4.7, converting from gm $^{-2}$ a $^{-1}$ to gcm $^{-2}$ a $^{-1}$) are combined to give an estimate of sediment focusing on the

seafloor, Ψ (Equation(4.12)).

$$\Psi = \int_{z_2}^{z_1} ({}^{230}\text{Th}_{\text{xs}}^0 \rho dz) / (\beta_{230} t_2 - t_1) \quad (4.8)$$

From (Suman and Bacon, 1989), where ${}^{230}\text{Th}_{\text{xs}}^0 \rho$ is the decay corrected concentration of ^{230}Th in the sediment derived only from the water column times the density, ρ , of the sediment, and β_{230} is the production of ^{230}Th from the water column between two dated horizons t_1 and t_2 . From equation 4.7, because ${}^{230}\text{Th}_{\text{xs}}^0$ is the production rate of ^{230}Th in the water column divided by F_w , Ψ can be expressed:

$$\Psi = \int_{z_2}^{z_1} (\rho dz) / (F_w t_2 - t_1) \quad (4.9)$$

and as the depth between two dated horizons z_1 and z_2 , at times t_1 and t_2 yield the sedimentation rate, F_a :

$$F_a = \frac{z_2 - z_1}{t_2 - t_1} \quad (4.10)$$

integrating Equation 4.10 between z_1 and z_2 gives:

$$\Psi = \rho \frac{F_a}{F_w} \quad (4.11)$$

If we assume a sediment density of 1 gcm^{-3} ,

$$\Psi = \frac{F_a}{F_w} \quad (4.12)$$

In essence, where more ^{230}Th is accumulating in sediments than is produced in the water column above ($\Psi > 1$), then it must be added with additional sediment from elsewhere. $\Psi = 1$ represents a scenario with no sediment focusing and $\Psi < 1$ indicates winnowing of sediment from that location. As with the use of ${}^{230}\text{Th}_{\text{xs}}$ as a proxy for mass accumulation, this focusing proxy relies on the assumption that all

^{230}Th formed in the water column is removed to the seafloor with no advection of ^{230}Th .

Table 4.1

Sample	latitude		longitude E	water		authigenic							
	°S	°E	depth m	(238)	2se	(232)	2se	(U/Th)	2se	$\delta^{234}\text{U}$	sd	U ppm	2se
WIND 3B 0-2b	32.38.65	048.29.64	3731	0.44	0.71	0.42	0.01	1.04	1.69	-367.2	8.1	0.24	0.72
WIND 15B 0-2b	19.59.97	050.19.96	4629	1.47	0.01	2.85	0.08	0.52	0.01	50.8	8.1	0.14	0.28
WIND 28B 0-2b	10.09.33	051.46.22	4147	0.99	0.01	1.83	0.05	0.54	0.01	50.4	8.1	0.13	0.18
WIND 3B 0-2*	32.38.65	048.29.64	3731	0.240	0.001	0.58	0.02	0.42	0.02	-1002.6	5.8	-0.03	0.06
WIND 15B 0-2*	19.59.97	050.19.96	4629	1.55	0.01	3.95	0.12	0.39	0.01	-1000.1	5.8	-0.30	0.39
WIND 28B 0-2*	10.09.33	051.46.22	4147	1.00	0.01	2.57	0.07	0.39	0.01	68.0	5.8	-0.20	0.25
WIND35B 0-2*	16.25.33	058.03.94	3934	0.911	0.003	0.27	0.01	3.39	0.16	87.8	5.8	0.79	0.03
CD154 04-4PK	29.36.66	033.27.77	2533	0.48	0.01	0.75	0.02	0.63	0.02	25.8	8.1	0.12	0.07
CD154 05-5PK	29.55.26	033.47.53	1784	0.45	0.01	0.77	0.02	0.59	0.02	-7.3	8.1	0.09	0.08
CD154 16-15K	33.42.07	028.14.57	3166	1.35	0.01	1.89	0.05	0.71	0.02	-58.6	8.1	0.47	0.18
CD154 24-25K	36.57.73	021.32.91	3417	1.33	0.01	1.32	0.03	1.01	0.03	3.0	8.1	0.72	0.13
CD-154-07-7PK*	30.07.92	031.41.84	1017	1.69	0.02	2.55	0.07	0.66	0.02	-62.1	9.5	0.50	0.25
CD-154-13-10PK*	34.02.70	027.57.78	3569	1.07	0.02	1.69	0.04	0.63	0.02	-17.0	9.5	0.28	0.17
CD-154-23-24PK*	36.48.23	022.00.59	3173	1.52	0.02	1.81	0.05	0.84	0.02	-9.8	9.5	0.67	0.18
CD-154-25-19P*	37.24.54	020.03.24	3691	0.38	0.01	0.36	0.01	1.07	0.04	129.1	9.5	0.22	0.04

Table 4.1: Results for surface sediments from *RRS Charles Darwin* cruise 129 (WIND) and 154. Latitude and longitude are in degrees and decimal minutes. All measurements are reported as activities in d.p.m.g $^{-1}$ except $\delta^{234}\text{U}$ and authigenic U which are reported in ‰ variation from secular equilibrium and in ppm (weight). * These results were run in a batch of samples in which the ^{229}Th spike did not fully equilibrate with the samples.

Table 4.2

Sample	latitude		depth cm.b.s.f.	age		2se	(232)	2se	(U/Th)	2se	$\delta^{234}\text{U}$	authigenic		
	°S	°E		ka	(238)							sd	U ppm	2se
WIND 28K 3-4b	10.09.23	51.46.15	3	4	0.931	0.002	1.91	0.01	0.488	0.003	27.6	0.6	0.04	0.18
WIND 28K 3-4*			3	4	0.966	0.003	2.43	0.07	0.39	0.01	49.5	5.8	-0.18	0.24
WIND 28K 15-16			15	7	0.763	0.002	1.47	0.01	0.519	0.003	50.6	0.6	0.08	0.14
WIND 28K 32-33			32	11	0.601	0.002	1.12	0.01	0.536	0.004	51.5	0.6	0.08	0.11
WIND 28K 43-44			43	13	0.60	0.02	1.14	0.03	0.52	0.02	37.8	9.5	0.07	0.11
WIND 28K 43-44b			43	13	0.57	0.01	1.08	0.03	0.52	0.02	39.0	8.1	0.06	0.11
WIND 28K 51-52			51	15	0.612	0.002	1.27	0.01	0.479	0.003	30.7	0.6	0.02	0.12
WIND 28K 63-64b			63	18	0.663	0.003	1.52	0.01	0.437	0.003	23.2	0.6	-0.05	0.15
WIND 28K 63-64*			63	18	0.642	0.004	1.81	0.05	0.35	0.01	37.6	5.8	-0.20	0.18
WIND 28K 93-94			93	23	0.499	0.003	1.21	0.01	0.413	0.003	12.6	0.6	-0.06	0.12
WIND 28K 119-120			119	30	1.82	0.01	1.13	0.03	1.62	0.04	112.6	7.4	1.30	0.11
WIND 28K 119-120b			119	30	1.95	0.01	1.18	0.03	1.65	0.04	105.5	6.4	1.40	0.12
WIND 28K 157-158			157	37	1.00	0.01	1.50	0.01	0.67	0.01	60.6	0.6	0.30	0.15
WIND 28K 171-172b*			171	40	0.276	0.002	0.538	0.003	0.513	0.003	110.9	0.6	0.02	0.05
WIND 28K 171-172*			171	40	0.509	0.003	1.24	0.03	0.41	0.01	44.2	5.8	-0.07	0.12
WIND 28K 215-216			215	49	0.53	0.01	0.95	0.02	0.56	0.02	34.6	7.4	0.09	0.09
WIND 28K 271-272a			271	60	0.720	0.003	1.14	0.04	0.63	0.02	63.4	4.7	0.19	0.11
WIND 28K 271-272b			271	60	0.723	0.002	1.10	0.03	0.66	0.02	69.5	4.7	0.21	0.11
WIND 28K 287-288			287	64	0.72	0.01	1.53	0.04	0.47	0.01	26.9	7.4	0.01	0.15

Continued on next page...

Table 4.2 continued from previous page ...

Sample	latitude		depth	age	authigenic									
	°S	°E			cm.b.s.f.	ka	(238) 2se	(232) 2se	(U/Th) 2se	$\delta^{234}\text{U}$ sd	U ppm	2se		
WIND 28K 287-288b			287	64	0.73	0.02	1.54	0.04	0.47	0.02	-8.8	8.1	0.01	0.15
WIND 28K 303-304			303	68	0.813	0.002	1.79	0.07	0.46	0.02	-8.8	4.7	-0.02	0.18
WIND 28K 331-332			331	77	0.59	0.03	1.27	0.03	0.46	0.03	4.9	7.4	-0.01	0.13
WIND 28K 355-356a			355	85	0.757	0.002	1.63	0.05	0.46	0.01	-32.9	4.7	-0.01	0.16
WIND 28K 355-356b			355	85	0.74	0.02	1.71	0.04	0.43	0.02	1.7	9.5	-0.06	0.17
WIND 28K 367-368			367	90	0.66	0.01	1.48	0.04	0.44	0.01	-38.7	7.4	-0.03	0.15
WIND 28K 387-388			387	98	0.590	0.001	1.29	0.04	0.46	0.01	-30.9	4.7	-0.01	0.13
WIND 28K 411-412			411	107	0.63	0.01	1.46	0.04	0.44	0.01	3.4	7.4	-0.05	0.14
WIND 28K 431-432			431	112	0.702	0.002	1.75	0.05	0.40	0.01	-29.2	4.7	-0.11	0.17
WIND 28K 439-440			439	114	0.85	0.01	2.06	0.05	0.41	0.01	-27.6	8.1	-0.11	0.20
WIND 28K 455-456a			455	119	0.710	0.001	1.65	0.05	0.43	0.01	-29.7	4.7	-0.06	0.16
WIND 28K 445-456b			455	119	0.74	0.02	1.67	0.04	0.44	0.02	-41.6	9.5	-0.04	0.16
WIND 28K 471-472			471	124	0.66	0.01	1.59	0.04	0.41	0.01	-16.4	8.1	-0.09	0.16
WIND 28K 491-492			491	128	0.490	0.001	1.09	0.03	0.45	0.01	-30.6	4.7	-0.02	0.11
WIND 28K 510-511			510	132	0.593	0.005	1.58	0.01	0.374	0.004	49.8	0.6	-0.15	0.15
WIND 28K 528-529			528	137	1.38	0.01	1.24	0.03	1.11	0.03	149.4	8.1	0.80	0.12
WIND 28K 528-529b			528	137	1.34	0.02	1.21	0.03	1.11	0.03	136.1	6.4	0.78	0.12
WIND 28K 541-542			541	144	2.48	0.02	1.29	0.01	1.92	0.02	109.1	0.6	1.88	0.13

Table 4.2: U and Th results for down-core sediment samples from WIND 28K. For explanation see Table 4.1. * these results were run in a batch of samples in which the ^{229}Th spike did not fully equilibrate with the samples. cm.b.s.f is the depth in the core below the seafloor. The age of the samples is derived from $\delta^{18}\text{O}$ stratigraphy with 6 AMS radiocarbon dates, providing an age model from McCave et al. (2004) (Figure 4.3).

Table 4.3

Sample	latitude		longitude	water	depth m	$^{230}\text{Th}^0_{ex}$	2se	$(^{231}\text{Pa}^0_{ex}/^{230}\text{Th}^0_{ex})$				Fw	
	$^{\circ}\text{S}$	$^{\circ}\text{E}$						$^{231}\text{Pa}^0_{ex}$	2se	2se	t ka		$\text{g cm}^{-2}\text{kyr}^{-1}$
WIND 3B 0-2b	32.38.65	048.29.64	3731		15.5	0.4	0.52	0.01	0.034	0.001	0	0.71	0.02
WIND 15B 0-2b	19.59.97	050.19.96	4629		19.3	0.6	1.09	0.03	0.056	0.002	0	0.57	0.02
WIND 28B 0-2b	10.09.33	051.46.22	4147		20.9	0.6	1.12	0.02	0.054	0.002	0	0.52	0.01
WIND 3B 0-2*	32.38.65	048.29.64	3731		20.3	0.7	0.49	0.01	0.024	0.001	0	0.54	0.02
WIND 15B 0-2*	19.59.97	050.19.96	4629		26.1	0.9	1.08	0.08	0.041	0.004	0	0.42	0.02
WIND 28B 0-2*	10.09.33	051.46.22	4147		28.7	0.8	0.99	0.06	0.035	0.002	0	0.38	0.01
WIND 35B 0-2*	16.25.33	058.03.94	3934		17.4	0.5	0.41	0.02	0.024	0.001	0	0.63	0.02
CD154 04-4PK	29.36.66	033.27.77	2533		3.3	0.1	0.18	0.01	0.056	0.003	0	3.36	0.12
CD154 05-5PK	29.55.26	033.47.53	1784		1.6	0.1	0.15	0.01	0.096	0.007	0	6.82	0.38
CD154 16-15K	33.42.07	028.14.57	3166		3.9	0.2	0.24	0.01	0.062	0.004	0	2.82	0.16
CD154 24-25K [†]	36.57.73	021.32.91	3417		4.8	0.2	2.23	0.05	0.462	0.021	0	2.27	0.09
CD154 07-7PK*	30.07.92	031.41.84	1017		1.9	0.3	0.07	0.01	0.040	0.009	0	5.91	0.83
CD154 13-10PK*	34.02.70	027.57.78	3569		6.5	0.2	0.30	0.01	0.046	0.002	0	1.68	0.06

Continued on next page...

Table 4.3 continued from previous page...

Sample	latitude		longitude		water		$(^{231}\text{Pa}_{ex}^0 / ^{230}\text{Th}_{ex}^0)$		Fw	
	°S	°E	depth m	$^{230}\text{Th}_{ex}^0$	2se	$^{231}\text{Pa}_{ex}^0$	2se	t ka	$\text{gcm}^{-2}\text{kyr}^{-1}$	2se
CD154 23-24PK*	36.48.23	022.00.59	3173	4.2	0.2	0.23	0.01	0.055	0	2.62
CD154 25-19P*	37.24.54	020.03.24	3691	4.7	0.1	0.136	0.004	0.029	0	2.34

Table 4.3: ^{230}Th and ^{231}Pa results for surface sediment samples. Latitude and longitude are in degrees and decimal minutes and depth cm.b.s.f. is the depth in the core below the seafloor. $^{230}\text{Th}_{xs}^0$ and $^{231}\text{Pa}_{xs}^0$ are calculated from the concentrations of ^{230}Th , ^{231}Pa , ^{234}U , ^{238}U , and ^{232}Th in the sediment following equations 4.1 to 4.4. The mass accumulation rate, F_w , is given by equation 4.7. * these results were run in a batch of samples in which the ^{229}Th spike did not fully equilibrate with the samples. † for these results the ^{233}Pa spike did not fully equilibrate with the samples.

Table 4.4

Sample	latitude		longitude		depth		$(^{231}\text{Pa}_{ex}^0 / ^{230}\text{Th}_{ex}^0)$		Fw		Focusing	
	°S	°E	cm.b.s.f	$^{230}\text{Th}_{ex}^0$	2se	$^{231}\text{Pa}_{ex}^0$	2se	age ka	$\text{gcm}^{-2}\text{kyr}^{-1}$	2se	Fa cm/ka	Fa/Fw
WIND 28K 3-4b	10.09.23	51.46.15	3	20.8	0.3		0.043†	4.41	0.53	0.01	3.17	6.04
WIND 28K 3-4*			3			0.89	0.05	4.41			3.17	
WIND 28K 15-16			15	17.9	0.2			7.14	0.61	0.01	3.97	6.48
WIND 28K 32-33			32	12.4	0.2			10.60	0.88	0.01	4.76	5.41
WIND 28K 43-44			43	12.2	0.4	0.68	0.03	0.056	0.90	0.03	4.65	5.17

Continued on next page...

Table 4.4 continued from previous page ...

Sample	latitude		depth	$^{230}\text{Th}^0_{ex}$		$^{231}\text{Pa}^0_{ex}$		$(^{231}\text{Pa}^0_{ex}/^{230}\text{Th}^0_{ex})$		age		Fw		Focusing	
	°S	°E	cm.b.s.f	2se	2se	2se	2se	2se	2se	ka	ka	$\text{gcm}^{-2}\text{kyr}^{-1}$	2se	Fa cm/ka	Fa/Fw
WIND 28K 43-44b			43	11.9	0.4	0.66	0.01	0.055	0.002	12.93		0.92	0.03	4.65	5.04
WIND 28K 51-52			51	14.2	0.2					14.66		0.77	0.01	4.55	5.88
WIND 28K 63-64b			63	14.5	0.3			0.046 [†]	0.002	17.54		0.75	0.01	3.92	5.21
WIND 28K 63-64*			63			0.67	0.03			17.54				3.92	
WIND 28K 93-94			93	11.8	0.2					23.00		0.93	0.02	5.56	5.98
WIND 28K 119-120			119	12.9	0.4	0.72	0.03	0.056	0.003	29.90		0.85	0.03	3.60	4.23
WIND 28K 119-120b			119	13.8	0.5	0.79	0.02	0.057	0.002	29.90		0.79	0.03	3.60	4.55
WIND 28K 157-158			157	18.2	0.3					37.37		0.60	0.01	5.19	8.65
WIND 28K 171-172*			171	16.2	0.5	0.56	0.03	0.035	0.002	40.10		0.67	0.02	5.13	7.60
WIND 28K 215-216			215	11.7	0.4	0.62	0.02	0.053	0.003	48.65		0.93	0.03	5.13	5.49
WIND 28K 271-272a			271	12.5	0.6	0.67	0.03	0.053	0.003	59.53		0.88	0.04	5.19	5.92
WIND 28K 271-272b			271	12.6	0.5	0.71	0.03	0.056	0.003	59.53		0.87	0.03	5.19	6.00
WIND 28K 287-288			287	18.4	0.6	0.90	0.04	0.049	0.003	63.73		0.59	0.02	3.39	5.71
WIND 28K 287-288b			287	18.3	0.6	0.92	0.04	0.050	0.003	63.73		0.60	0.02	3.39	5.66
WIND 28K 303-304			303	20.1	1.0	1.05	0.06	0.052	0.004	68.41		0.54	0.03	3.42	6.28
WIND 28K 331-332			331	16.0	0.6	0.82	0.05	0.051	0.003	76.62		0.69	0.02	3.39	4.95
WIND 28K 355-356a			355	20.3	0.8	1.14	0.07	0.056	0.004	85.09		0.54	0.02	2.56	4.77
WIND 28K 355-356b*			355	22.6	0.8					85.09		0.48	0.02	2.56	5.30
WIND 28K 367-368			367	19.7	0.8	1.06	0.23	0.054	0.012	89.76		0.56	0.02	2.56	4.61
WIND 28K 387-388			387	17.2	0.7	1.03	0.07	0.060	0.005	98.23		0.64	0.03	1.62	2.54
WIND 28K 411-412			411	20.5	0.8	-0.05	0.27	-0.003	0.013	107.35		0.53	0.02	4.00	7.49
WIND 28K 431-432			431	20.9	1.0	1.16	0.12	0.055	0.006	112.05		0.52	0.02	4.00	7.65
WIND 28K 439-440			439	26.4	1.1	1.42	0.15	0.054	0.006	114.48		0.41	0.02	3.08	7.42

Continued on next page...

Table 4.4 continued from previous page . . .

Sample	latitude °S	longitude °E	depth cm.b.s.f	$^{230}\text{Th}_{ex}^0$	2se	$^{231}\text{Pa}_{ex}^0$	2se	$(^{231}\text{Pa}_{ex}^0 / ^{230}\text{Th}_{ex}^0)$		age ka	Fw $\text{gcm}^{-2}\text{kyr}^{-1}$	2se	Fa cm/ka	Focusing Fa/Fw
WIND 28K 455-456a			455	21.4	1.0	1.11	0.13	0.052	0.007	119.40	0.51	0.02	3.33	6.50
WIND 28K 455-456b [†]			455	24.0	1.0					119.40	0.46	0.02	3.33	7.32
WIND 28K 471-472			471	18.5	0.9	0.86	0.14	0.047	0.008	123.78	0.59	0.03	4.44	7.50
WIND 28K 491-492 [†]			491	11.3	0.6	1.52	0.13	0.134	0.014	128.18	0.97	0.05	4.44	4.59
WIND 28K 510-511			510	11.5	0.7					132.35	0.95	0.06	4.71	4.96
WIND 28K 528-529			528	11.6	0.7	0.38	0.15	0.033	0.013	137.30	0.94	0.06	2.00	2.12
WIND 28K 528-529b			528	10.8	0.7	0.44	0.15	0.040	0.014	137.30	1.01	0.07	2.00	1.97
WIND 28K 541-542			541	9.9	0.7					144.10	1.10	0.08	2.22	2.01

Table 4.4: ^{230}Th and ^{231}Pa results for down core sediment samples from WIND 28K. For explanation see Table 4.3. The age is derived from the age model of McCave et al. (2004), which also gives the accumulation rate, F_a , from which the sediment focusing is calculated using equation 4.12. * these results were run in a batch of samples in which the ^{229}Th spike did not fully equilibrate with the samples. [†] for these results the ^{233}Pa spike did not fully equilibrate with the samples. [‡] $(^{231}\text{Pa}_{xs}/^{230}\text{Th}_{xs})^0$ is calculated using values for $^{231}\text{Pa}_{xs}$ and $^{230}\text{Th}_{xs}$ taken from different sub-samples from the same depth in the core.

4.5.4 Description of results

The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ record shows no significant variation outside the analytical uncertainty over the past 140 ka (Figure 4.3 i). It is important to note, though, that the ratio is significantly lower than the production ratio of 0.093, typically around 0.05. The discordance of the two values of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ calculated from measurements of different sub samples of the same depth in the core (at 3 cm and 63 cm depth in the core, open squares in Figure 4.3 i), indicate that the sediment is quite heterogeneous with respect to ^{231}Pa and ^{230}Th but the ratio of the two in the sediment is relatively uniform.

Although the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ record shows no variation the sediment mass accumulation rate, calculated from $^{230}\text{Th}_{\text{xs}}^0$, shows significant variation correlated with benthic $\delta^{18}\text{O}$, although with a considerable lag. The mass accumulation rate (F_w) also generally correlates with $\%\text{CaCO}_3$ (although some of the larger changes in F_w do not have associated large changes in $\%\text{CaCO}_3$). Sediment focusing, Ψ , varies between 2 and 9 (Figure 4.3 g), indicating a net flux of sediment into the locality of WIND 28 by seafloor sediment redistribution. This is unsurprising because the core is in a contourite sediment drift. The variation in focusing does not appear to co-vary with either the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ or another potential flow speed proxy, sortable silt (Figure 4.3 j).

The (U/Th) ratio and hence also the authigenic U (Figure 4.3 c) is rather constant during the past 140 ka at a value close to 0.45 (i.e. zero authigenic U). The exception is the presence of 2 distinct peaks of authigenic U of ~ 1.5 ppm, at 30 and 144 ka, corresponding to peak glacial periods.

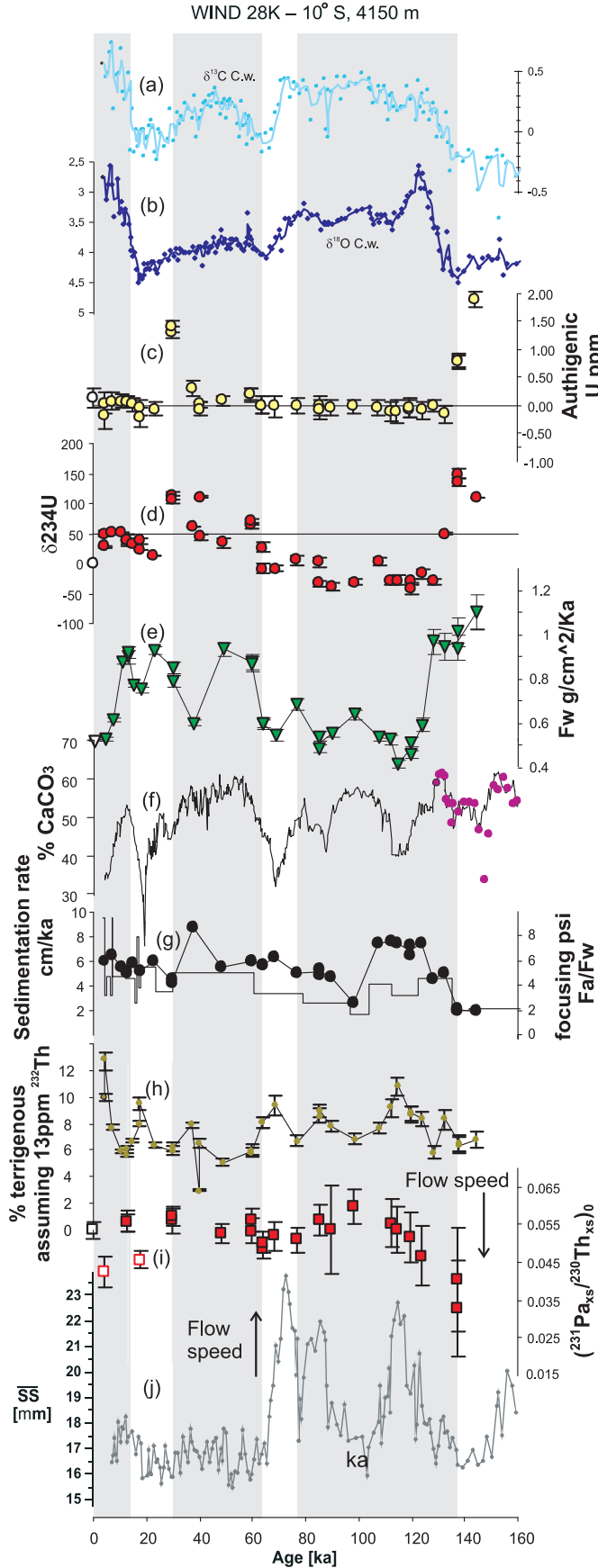


Figure 4.3: (a, and b) benthic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from McCave et al. (2004); (c) authigenic uranium; (d) $\delta^{234}\text{U}$ (e) Mass accumulation rate, F_w , calculated from measured ^{230}Th using Equation 4.7; (f) the % CaCO_3 in sediment estimated from the light reflectance, purple dots indicate values of sediment measured for CaCO_3 to calibrate the light reflectance (data from Torsten Keifer, pers corr); (g) the sedimentation rate from the age model of McCave et al. (2004) (black line) and sediment focusing derived from the sedimentation and mass accumulation rates (equation 4.12); (h) the % of the sediment derived from a terrigenous source, calculated from the mass accumulation rate of ^{232}Th assuming a terrigenous ^{232}Th concentration of 13 ppm; (i) the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$, open red squares representing $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ calculated from ^{231}Pa and ^{230}Th measured on different sub-samples from the same depth in the core; (j) the sortable silt record of this core from McCave et al. (2004). Open black symbols, for all plots, are values from the core top (0–2 cm) of WIND 28B – a box core – reflecting truly modern conditions.

4.6 Discussions

4.6.1 Consistency of AABW flow into the Indian Ocean

Bottom water leaving the Southern Ocean, such as the branch of Antarctic Bottom Water that fills the Indian Ocean through the Madagascar and Mascarene Basins, will have characteristically low ($^{231}\text{Pa}/^{230}\text{Th}$). This is due to the water passing through the opal belt on its way out of the Southern Ocean (as described in Chapter 3). Opal preferentially scavenges Pa relative to Th (Walter et al., 1997; Chase et al., 2002; Siddall et al., 2005), resulting in low water column ($^{231}\text{Pa}/^{230}\text{Th}$) in AABW, which gradually rises towards an equilibrium value as the water mass travels northwards (Chapter 3). The equilibrium value will be reached when the export of ^{231}Pa and ^{230}Th to sediments is at the production ratio (0.093). This increase of sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰ as the overlying AABW ages should allow its use as a proxy for the age of bottom water after it has left the Southern Ocean.

The ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰ of sediment at a point along the flow path of AABW as it travels northward will be dependent on 5 factors: the initial ($^{231}\text{Pa}/^{230}\text{Th}$) of water as it leaves the Southern Ocean; the flux and type of productivity between the opal belt and the point of interest; the total particle flux at the point of interest; the particle type at the point of interest; and the flow rate of AABW. The latter is important because it determines the length of time a particular water mass will have to approach equilibrium. If assumptions or constraints can be made about initial conditions and productivity, then the sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰ might be used to investigate the northward rate flow of AABW.

In Chapter 3 it was shown that the sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰ is set from the bottommost water mass (Thomas et al., 2006). The rate at which this bottom water will increase its ($^{231}\text{Pa}/^{230}\text{Th}$) towards the production ratio is determined by the production of ^{231}Pa and ^{230}Th within the bottom water and the rates of input

from the water above by sinking particles. This effect is explored in Section 4.6.6

The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ recorded in WIND 28K shows no significant variation, over the last 140 ka, from a value of approximately 0.055 (Figure 4.3 i). This value of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ – below the production ratio of 0.093 – means that the proxy is sensitive to any change in circulation or productivity along the path of water mass flow from the Southern Ocean. Thus, the most obvious inference from the constant value in the past is that, neither the deep water circulation nor the export productivity has changed in the Madagascar and Mascarene Basins during the last 140 ka.

It is feasible that two or more of the controls on $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ at WIND 28K are varying in such a way that the overall effect is to cancel each other out and thus produce a constant $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$. For instance, if reduced opal productivity in the Southern Ocean were coupled with increased AABW flow-speed into the Indian Ocean. In this case bottom water in the Southern Ocean would have less ^{231}Pa scavenged to sediments and hence would have a higher $(^{231}\text{Pa}/^{230}\text{Th})$ as it left the Southern Ocean, but as it would be moving more quickly it would reach WIND 28K in less time, and the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ exported to sediments will not rise as much towards the production ratio as would be the case if the water mass had more time. Thus it is possible that many combinations of productivity and flow can produce a constant $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$. However, the most likely scenario remains that of no change because a precise covariance between two components of the system is a more complex solution than that of no change. Also it is likely that any changes in circulation and productivity will have a phase shift due to the complex interrelationships within the ocean. For instance a change in productivity brought about by a change in upwelling will be a relatively in-phase relationship between circulation and productivity, while if a change in productivity is brought about by a change in the nutrient content of upwelled water due to large scale circulation changes then there

would be a considerable lag in the productivity change due to the long residence time of nutrients in the deep ocean.

The finding of this chapter that there is no change in deep circulation into the Indian Ocean on a glacial-interglacial timescale is in stark contrast to other observations in The Atlantic and Pacific Oceans. In the Atlantic it has been observed by McManus et al. (2004) and Gherardi et al. (2005) using the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy that meridional overturning circulation effectively shuts down during Heinrich events, although during non Heinrich glacial periods the strength of meridional overturning circulation is more similar to that in the Holocene. Using the Cd/Ca proxy for bottom-water nutrient content Boyle and Keigwin (1981) also found reductions in North Atlantic deep-water circulation during glacial periods. The deep-water inflow into the Pacific has also been observed to change on glacial-interglacial timescales, Hall et al. (2001) has shown using the $\overline{\text{SS}}$ proxy that flow rate is coherently correlated with benthic $\delta^{18}\text{O}$ over the past 1.2 Ma. The in-phase relationship indicates that faster flow speeds are associated with glacial periods.

The records of circulation from the North Atlantic and southwestern Pacific are anti-phased. During interglacials deep circulation in the Atlantic is strong and in the AABW flow into the Pacific is weak, while during glacials the reverse is true. The inflow of AABW into the Indian Ocean however remains unchanged throughout. A possible reconciliation of the discrepancy, that AABW flow varies into the Pacific but not into the Indian Ocean, is that the AABW that flows into the Indian Ocean is formed in the Weddell Sea, while that which flows into the Pacific is a combination of AABW from the Weddell Sea and the Adelie Shelf at 140°E (Figure 1.11). Thus the variation in the formation of deep water, involved in any interhemispheric climatic “seesaw” (Broecker, 1998), may involve changes in the formation of AABW around the coast of East Antarctica, at for instance the Adelie shelf, rather than in the Weddell Sea (Figure 1.11).

4.6.2 Authigenic U

For most of the last 140 ka the sedimentary (U/Th) ratio recorded in WIND 28K is constant, and there has been little authigenic U added. There are, however, two peaks in authigenic uranium at 30 and 140 ka. Authigenic U is formed in sediments which are experiencing reducing conditions due to a depletion of oxygen in the overlying water. Such conditions reduce the more soluble U^{6+} to the insoluble U^{4+} species in the sediment. This lowers the concentration of U in the pore water, establishing a concentration gradient which ‘pumps’ U from the overlying seawater into the sediment. Reduced oxygen in deep waters can be caused in two ways: firstly by high biological productivity in the overlying water column providing organic matter to the deep, so that the sediment becomes anoxic (Kumar et al., 1995; Anderson et al., 1998); secondly by deep water already being anoxic due to high productivity upstream, or lower “ocean-wide ventilation” (Mangini et al., 2001). Any changes to higher local productivity that could potentially cause sedimentary anoxia and authigenic U formation would be recorded as increased $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$. No such change in $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is observed in the 30 ka and 140 ka portions of WIND 28K, suggesting that authigenic U production is not controlled by local productivity but by changes in bottom water oxygenation. The required decrease in oxygenation might be caused by a low original O_2 in deep waters or by higher productivity upstream. Higher productivity upstream (i.e. in the Southern Ocean) would result in the $(^{231}\text{Pa}/^{230}\text{Th})$ of such water being altered. Depending on the particle type responsible for the extra productivity, the $(^{231}\text{Pa}/^{230}\text{Th})$ could be raised or lowered. Because the $(^{231}\text{Pa}/^{230}\text{Th})$ of AABW leaving the Southern Ocean has an influence on the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ recorded at WIND 28K, the lack of variation observed suggests that the productivity in the Southern Ocean has not changed significantly. Thus the decrease in oxygenation was likely due to low original O_2 in deep waters.

The Kumar et al. (1995) record of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ and authigenic U in the Atlantic sector of the Southern Ocean shows a similar trend in that there is higher authigenic U during glacial periods. The interpretation of this record however focuses on the productivity in the opal belt controlling the bottom water oxygenation rather than any preexisting low O_2 deep water. Mangini et al. (2001), from measurements in the Atlantic, suggest that Atlantic bottom water was depleted in oxygen during glacial periods thus supplying the Southern Ocean with low oxygen water which could lead to the conditions in the Southern Ocean and then in the Indian Ocean in which authigenic U can form. The data in this chapter supports a preexisting oxygen depletion in deep waters as a change in productivity in the Southern ocean should manifest as a change in the $(^{231}\text{Pa}/^{230}\text{Th})$ of water leaving the Southern Ocean which is not observed at WIND 28K.

It should be noted that the peaks in authigenic U that are observed in WIND 28K may have a greater amplitude and longer duration, particularly extending up the core to younger sediment. Loss of authigenic U may have occurred once oxic conditions returned and “burnt down” into existing sediment, oxidising organic matter and solubilising uranium (Mangini et al., 2001).

4.6.3 Detrital provenance

The $(\text{U}/\text{Th})_{\text{detrital}}$ presented here provides the first such value for the Indian Ocean. The value of 0.45 ± 0.05 is considerably lower than that used in previous studies in the Indian Ocean (Marcantonio et al., 2001; Pourmand et al., 2004) derived from the average crustal value of 0.8 ± 0.2 (Anderson et al., 1990; Taylor, 1964). The new value for the Indian Ocean lies within the estimate of Henderson and Anderson (2003) of 0.4 ± 0.1 for the Southern Ocean, south of the Antarctic Polar Front and is broadly similar to that of the Atlantic (0.6 ± 0.1) and the Pacific (0.7 ± 0.1). Although the Indian Ocean at WIND 28 appears to have $(\text{U}/\text{Th})_{\text{detrital}}$ similar to the Southern

Ocean, previous studies from north of the Polar Front in the Southern Ocean have indicated higher $(\text{U}/\text{Th})_{\text{detrital}}$. Walter et al. (1997) for instance, found large Latitudinal variations within the Southern Ocean with increasing values to the north. So it would therefore be unwise to associate the low $(\text{U}/\text{Th})_{\text{detrital}}$ observed at 10°S in the Indian Ocean with a Southern Ocean source. With only one measurement of $(\text{U}/\text{Th})_{\text{detrital}}$ in the Indian Ocean, the possibility of variations in the $(\text{U}/\text{Th})_{\text{detrital}}$ value within the basin remain likely.

The constant value of $(\text{U}/\text{Th})_{\text{detrital}}$ over the last 140 ka may be attributed to the source of the detrital material remaining the same. There are two plausible sources of the detrital material to WIND 28K: material from the eastern margin of Madagascar transported in the deep western boundary current; and aeolian dust. Although there are no constraints on the compositions of these components, the simplest explanation of the constant data is that the sources of detritus to the sediment, or the balance between the sources, have remained the same during the last 140 ka.

4.6.4 Mass accumulation rate: productivity vs. dissolution

If, as the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ record suggests, there has been no change in circulation or export productivity, then changes in sediment mass accumulation rate require an alternative explanation. Changes observed in the ^{230}Th -normalised mass accumulation rate (Figure 4.3 e) can only be attributed to variable particle flux to the seabed of a particle type that does not strongly scavenge ^{231}Pa or ^{230}Th or to variations in dissolution once on the sea floor because these mechanisms would not cause sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to change. Deposition of a particle type that does not fractionate ^{231}Pa and ^{230}Th is unlikely as, although there is considerable debate over the role of clays in scavenging ^{231}Pa and ^{230}Th – which may not have a role in ^{231}Pa and ^{230}Th fractionation (Chase et al., 2002; Siddall et al., 2005) –, the variation in the amount of ^{232}Th downcore (Figure 4.3 h) is not enough to suggest that the input

of detrital material has changed much over the past 140 ka. The role of particulate organic matter however is also poorly understood with respect to scavenging ^{231}Pa and ^{230}Th , and may have an effect on the rates of deposition without fractionating ^{231}Pa and ^{230}Th .

Dissolution of material once deposited to the seafloor can explain some of the variation in mass accumulation. The wt% calcite in the sediment (Figure (4.3, f)) shows variation covariant with mass accumulation, suggesting that some of the variable mass accumulation is due to dissolution of carbonate. Dissolution of carbonate, however, can't explain all of the variation in mass accumulation, particularly the large drop at 125 ka which is not associated with a drop in wt% calcite. This large shift remains unexplained, and is unlikely to be related to dissolution of another phase in the sediment such as opal or organic matter.

4.6.5 Comparison with the “sortable silt” flow-speed proxy

Sortable silt ($\overline{\text{SS}}$) is defined as the mean grain size of the 10-63 μm fraction of the terrigenous component of the sediment (McCave et al., 1995). Winnowing and selective deposition sort the sediment, such that higher flow speeds result in the deposition of sediment with a coarser $\overline{\text{SS}}$.

Three peaks in $\overline{\text{SS}}$ are observed in the last 140 ka portion of WIND 28K, at 75, 85, and 115 ka (Figure 4.3, j). These have been interpreted by McCave et al. (2004) to be caused by increases in flow speed as a result of a local geostrophic effect driven by bottom-water density changes. McCave et al. (2004) point out that two of these changes correspond to decreases of sea level (inferred from the sealevel curve of Siddall et al. (2003)) which might lead to an increased density contrast between surface and deep waters. The second peak in $\overline{\text{SS}}$ at 85 ka cannot be explained by this mechanism as sea level rises by 40-50 m during the peak of $\overline{\text{SS}}$. Other cores from the Madagascar–Mascarene Basin, WIND 5K (3680 m) and

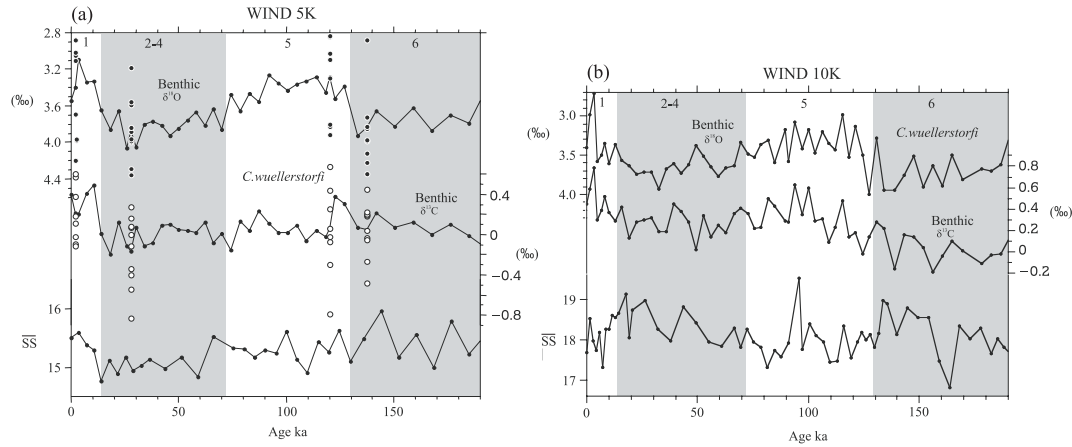


Figure 4.4: Benthic isotopic ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) and sortable silt mean size ($\overline{\text{SS}}$) data for core WIND 5K (a), and WIND 10K (b) plotted against age (from Figures 7 and 6 of McCave et al. (2004)). Single specimen stable isotope data from two peak glacial and two peak interglacial samples (solid dots, $\delta^{18}\text{O}$; open dots, $\delta^{13}\text{C}$) illustrate the attenuating effect of bioturbational mixing on the downcore record. WIND 5K and WIND 10K are at 3682 and 2848 m water depth.

WIND 10K (2870 m) (McCave et al., 2004), show no variation in $\overline{\text{SS}}$ (Figure 4.4). Thus the geostrophic effect would have to affect current speed only at depths below these cores (McCave et al., 2004), perhaps due to amplification by constriction of flow through the Amirante Passage near WIND 28K.

It has been shown (Thomas et al., 2006) that the sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is ‘set’ by the concentrations of ^{231}Pa and ^{230}Th in the bottom few hundreds of meters from the seabed. Thus the $\overline{\text{SS}}$ and $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxies should agree with each other, because the $\overline{\text{SS}}$ proxy is essentially a measure of the shear stress at the seabed. The two proxies should provide a record of the past flow rate of AABW. The two proxies, however, do not agree, because $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ does not show the same peaks in flow-speed as observed in $\overline{\text{SS}}$. The explanation for this discrepancy is that the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy is recording the amount of time it has taken the AABW to reach WIND 28K after leaving the opal belt and thus averages flow-rate over that distance, while $\overline{\text{SS}}$ records only the local conditions directly above WIND 28K. Because $\overline{\text{SS}}$ records the shear stress at the sediment water interface then any local

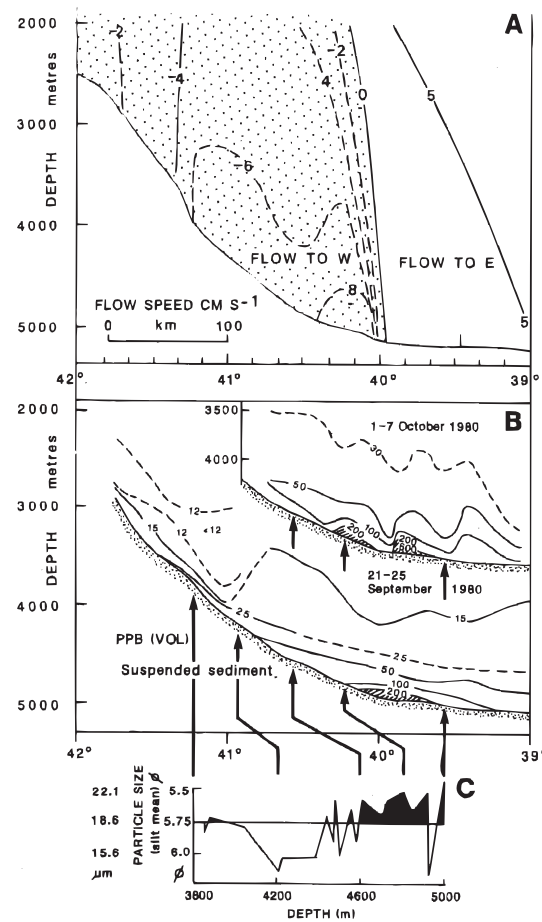


Figure 4.5: Measurements taken across a boundary current on the Nova Scotia Rise from McCave et al. (1995). (A) is the measured current speed, and (B) is the suspended sediment concentration in ppb by volume. (C) is the $\overline{SS}$ showing the high degree of variability across the flow of up to 8 μm .

variations in flow speed will be reflected in the $\overline{SS}$. This is observed across a current with $\overline{SS}$ varying on small scales by large amounts depending on the location within the current (Figure 4.5, McCave et al. (1995)). Therefore relatively small changes in the position of a current can have dramatic effects on the $\overline{SS}$ preserved in sediment at any one locality.

The $\overline{SS}$ proxy is also potentially vulnerable to changing inputs of detrital sediment down slope, rather than transport along the current path, in for instance turbidity flows. nearby down-slope transport of sediment could produce the large increases in $\overline{SS}$ seen in WIND 28K for instance. Such down-slope transport in turbidity currents

should be manifest in the character of the sediment but WIND 28K shows no evidence of such turbidity currents (McCave, pers comm). It is feasible, though, for down-slope sedimentation upstream to introduce sediment with a markedly different size distribution into the deep western boundary current where it could be transported to WIND 28K and alter the $\overline{\text{SS}}$. Such pulses of down-slope sedimentation could be induced by falling sea-level exposing the continental margin of Madagascar, supplying more material to the narrow shelf, which subsequently makes its way to the deep boundary current.

The possible alternative explanations of the large variations in $\overline{\text{SS}}$, coupled with the constancy of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ below the production ratio strongly suggest that the regional flow of AABW into the Indian Ocean has remained largely constant over the past 140 ka.

4.6.6 Modelling of water column ^{231}Pa and ^{230}Th

A 1D model of water column ^{231}Pa and ^{230}Th

To investigate the controls on sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in this regional setting a 1D water column model is used. The rate at which sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ returns to the production ratio after a change in boundary condition were investigated for a range of scenarios analogous to water flowing from the Southern Ocean into the southwest Indian Ocean. Two important changes occur during such transport:

1. Water initially enters the Southern Ocean with high $(^{231}\text{Pa}/^{230}\text{Th})$, before being subject to high rates of scavenging in the opal belt.
2. The resulting low $(^{231}\text{Pa}/^{230}\text{Th})$ water leaves the opal belt and moves northward into the Indian Ocean, where it is subject to low particle fluxes dominated by carbonate.

Variable	Symbol	Value	Units
^{231}Pa production from ^{235}U decay	β_{Pa}	2.45×10^{-3}	d.p.m. $\text{m}^{-3}\text{yr}^{-1}$
^{230}Th production from ^{234}U decay	β_{Th}	2.62×10^{-2}	d.p.m. $\text{m}^{-3}\text{yr}^{-1}$
export productivity	PR	0.1	$\text{gm}^{-2}\text{day}^{-1}$
particle sinking rate	S	500	myr^{-1}
partition coefficient of Pa on carbonate	$K_{\text{d,carb}}^{\text{Pa}}$	2.5×10^5	...
partition coefficient of Pa on opal	$K_{\text{d,opal}}^{\text{Pa}}$	1.67×10^6	...
partition coefficient of Th on carbonate	$K_{\text{d,carb}}^{\text{Th}}$	1.0×10^6	...
partition coefficient of Th on opal	$K_{\text{d,opal}}^{\text{Th}}$	5.5×10^5	...

Table 4.5: Parameters used in model of water column ^{231}Pa and ^{230}Th , and export to sediments. Values for K_{d}^i are based on those of (Siddall et al., 2005) with a scaling factor of 0.1 to allow realistic concentration profiles under the scavenging conditions of the model.

The model comprises a 1D water column divided into boxes of 500 m thickness. Each box can be assigned initial ^{231}Pa and ^{230}Th total activities, A_{t}^i , and the particle concentration is derived from the export production (PR) in the surface and the particle settling rate (S). During each time step the activities of ^{231}Pa and ^{230}Th in both the dissolved and particulate phase are calculated from K_{d}^i , where i is Pa or Th. K_{d}^i is defined as:

$$K_{\text{d}}^i = \frac{A_{\text{p}}^i}{A_{\text{d}}^i C_{\text{p}}} \quad (4.13)$$

where,

$$A_{\text{t}}^i = A_{\text{p}}^i + A_{\text{d}}^i \quad (4.14)$$

and A_{p}^i and A_{d}^i are the particulate and dissolved activities per unit of seawater, and C_{p} is the concentration of particle mass in seawater (Siddall et al., 2005). Once the particulate activity, A_{p}^i , has been established the export from the bottom of each box is calculated from the particle settling rate. Thus a new total concentration for each box can be calculated from the flux from the box above, the production from decay of U, and the flux out of the box on sinking particles. Decay of ^{231}Pa and ^{230}Th is insignificant. Sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is calculated from the ratio of ^{231}Pa to ^{230}Th on particles leaving the bottom box.

Application of the 1D model to the Indian Ocean

The model is initialised such that the starting water column profiles of ^{231}Pa and ^{230}Th are analogous to water being exported south from the Atlantic. This is achieved by starting the model with concentration profiles for ^{231}Pa and ^{230}Th of zero (Figure 4.6 b). The model is then run to equilibrium using K_d 's appropriate for carbonate particles (Table 4.5) and export productivity of $0.1 \text{ gm}^{-2}\text{yr}^{-1}\text{day}$. At equilibrium the export of ^{231}Pa and ^{230}Th on particles from the bottom box was equal to the production ratio of 0.093 (Figure 4.6 a & c).

The Southern Ocean scenario is then modelled. The concentration profiles produced from the initialisation are set as the initial conditions for water in the Southern Ocean (Figure 4.6 c). The model is run to equilibrium (Figure 4.6 a & d) with K_d 's appropriate for opal particles (Table 4.5) and an export productivity of $0.1 \text{ gm}^{-2}\text{day}^{-1}$. The opal K_d 's result in equilibrium profiles with significantly lower ^{231}Pa concentrations than for the carbonate dominated Atlantic (Figure 4.6 d).

The model run for the Southern Ocean conditions (Figure 4.6 a), reproduces the high $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ seen in Southern Ocean sediments (Yu et al., 1996; Kumar et al., 1993) due to the export of high concentrations of ^{231}Pa from the Atlantic to the Southern Ocean where it is scavenged to the seafloor on opal particles which favour sorption of Pa over Th. The ^{231}Pa concentration profile for water that has reached equilibrium in the Southern Ocean (Figure 4.6 d) is significantly lower than that in the Atlantic. This is in agreement with observations of deep water leaving the Southern Ocean and entering the Indian Ocean (Chapter 3, Thomas et al. (2006), and Chapter 5).

The scenario of water moving northward into the Indian Ocean is then modelled. The initial water column concentration profiles are set from the equilibrium state of the Southern Ocean scenario above (Figure 4.6 d). The model is then run to equilibrium (Figure 4.6 a, solid line), using K_d 's appropriate for carbonate particles

(Table 4.5) and export productivity of $0.1 \text{ gm}^{-2}\text{yr}^{-1}\text{day}$, where export to sediments is at the production ratio of 0.093. The equilibrium concentration profiles produced (Figure 4.6 e) are identical to those of the initialisation, which is reassuring because the scavenging conditions are identical and therefore the final equilibrium is independent of the starting conditions (Figure 4.6 c).

A second run of the model is performed for the Indian Ocean scenario with more realistic starting conditions. To mimic a layer of NADW over AABW the initial water column is split into two. The top layer from the surface to 2500 m is set from the first initialisation run, while the bottom layer from 2500 m to 4000 m is set from the equilibrium conditions of the Southern Ocean scenario (Figure 4.6 f). The model is then run to equilibrium under the same conditions as the first Indian Ocean scenario (Figure 4.6 a, dotted line). Once again the final equilibrium state reached is identical to the initialisation run due to the identical scavenging conditions.

Comparing the two Indian Ocean scenario runs, the rate of increase of the sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ (Figure 4.6 a, dotted line) is markedly increased by the presence of an overlying water mass with elevated ^{231}Pa , over that with initially low ^{231}Pa down the whole water column (Figure 4.6 a, solid line). This is an important finding as it shows that the $(^{231}\text{Pa}/^{230}\text{Th})$ of deep water, and hence the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ recorded in sediments is controlled by the composition of the whole water column over the duration of the flow since the $(^{231}\text{Pa}/^{230}\text{Th})$ ‘clock’ has been ‘reset’. A distinction should be made between this finding and that of Chapter 3, that sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is set from the bottom most water mass. At any one locality only the $(^{231}\text{Pa}/^{230}\text{Th})$ from the bottom most directly overlying water will be recorded in the sediments, but that water will in turn be effected by the water masses overlying it, and productivity, throughout its advection history.

The rate of increase of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to the measured value of ~ 0.055 in the Indian Ocean scenario run with the overlying ‘NADW’ suggests a transit time from

the Southern Ocean of 130 a (Figure 4.6 a). This is much longer than the estimate of 20-30 a from modern radiocarbon measurements (Broecker et al., 1984). This large discrepancy is due to the over simplistic initial conditions the model is given and the poor constraints on the scavenging conditions. The initial conditions for all of the scenarios investigated are taken from model runs which are allowed to reach equilibrium. This is clearly not the case in the natural system. In the Atlantic for example the water column does not reach equilibrium before it reaches the Southern Ocean this is evident in the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ of South Atlantic sediments which are below the production ratio (Yu et al., 1996). Because the water entering the Southern Ocean from the Atlantic has yet to reach equilibrium there, it therefore has a lower ^{231}Pa content than suggested in the simplistic model presented here and as such the model overestimates the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ of Southern Ocean sediments. Similarly for water entering the Indian Ocean if it does not spend enough time in the opal belt to reach equilibrium then less ^{231}Pa will be scavenged out resulting in the water leaving the Southern Ocean having higher $(^{231}\text{Pa}/^{230}\text{Th})$. In this respect the model underestimates the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ of sediments just north of the opal belt in the Indian Ocean.

The effect of varying the export productivity, PR, and hence the particle concentration is illustrated in Figure (4.7). Elevated particle concentrations resulting from increased export production causes the water column concentration profiles and hence the sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to reach equilibrium at a faster rate. While regions of the world's oceans do have markedly higher PR, such as the Southern Ocean, the PR for the model in this study is kept constant. The reasoning for this is, while the PR is a major control on the rate at which the model reaches equilibrium, and the effect of doubling the PR halves the concentration profiles, the model is only intended as a illustration and hence is kept as simple as possible.

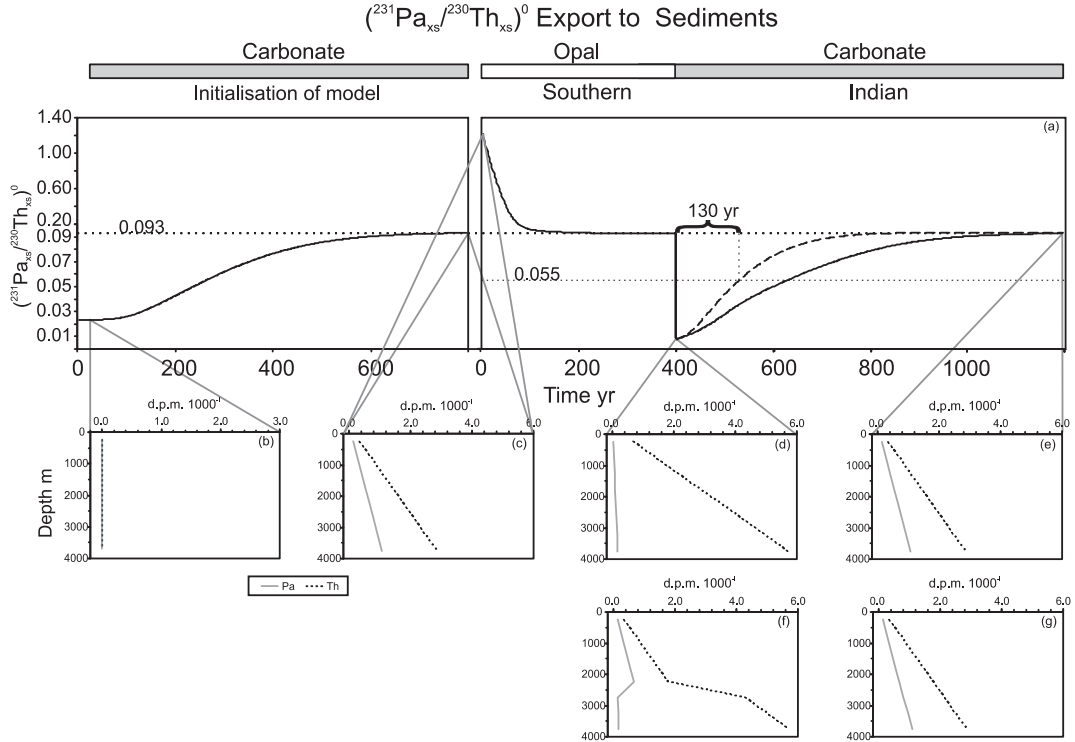


Figure 4.6: (a) The results of the model for the export to sediments over time for a hypothetical water mass during initialisation analogous to water advecting through the Atlantic and the model runs for the Southern Ocean scenario, and into the Indian Ocean scenario (solid line). The dashed line is the export to sediments if the initial water column profiles for the Indian Ocean scenario have been depleted in Pa in the lower portion of the water column only (f). Note the change in vertical scale above 0.093 in (a). The thick dotted line indicates the production ratio of 0.093. The thin dotted line indicates the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ measured at WIND 28K of ~ 0.055 . (b-e) water column profiles of ^{231}Pa (solid grey lines) and ^{230}Th (dotted black lines) at significant times during the models run (indicated by connecting grey lines). (f,g) initial and equilibrium water column profiles for water leaving the Southern Ocean and advecting through the Indian Ocean with an initial composition in the upper portion from the Atlantic equilibrium case (c) and the lower portion from the Southern Ocean equilibrium case (d). For parameters in used in the model see Table 4.5

The sensitivity of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ at WIND 28

Modelling of the export of ^{231}Pa and ^{230}Th to sediments has shown that the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ at WIND 28 is controlled by a variety of factors. As expected, the age of AABW (i.e. the rate of circulation) along with the productivity determines how close to the equilibrium value (0.093) the export to sediments can reach during transit from the Southern Ocean to WIND 28. Another control on how quickly the water mass can

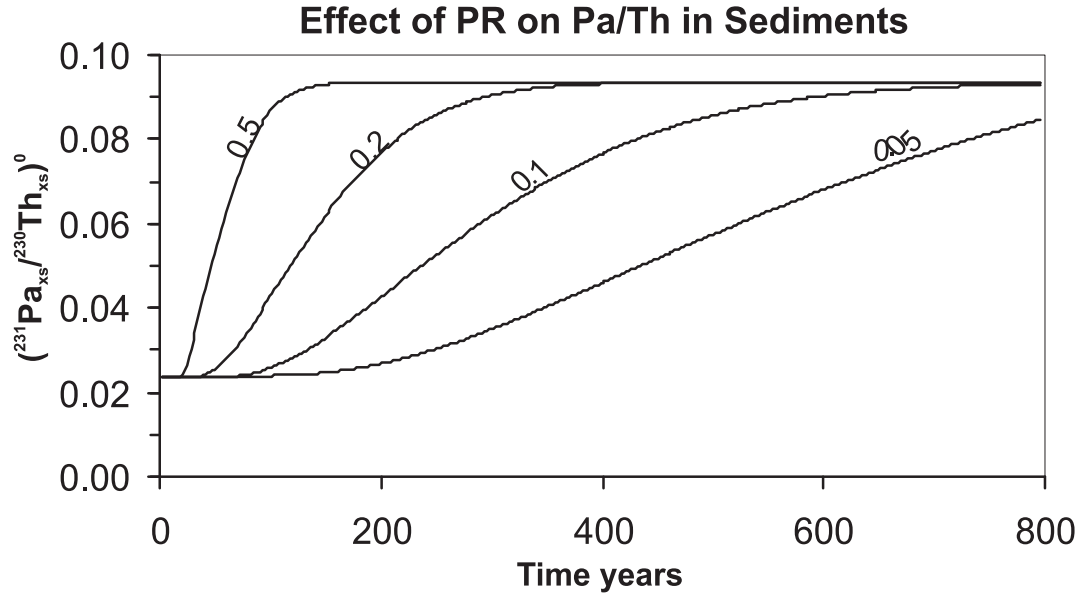


Figure 4.7: The effect of varying export productivity on the rate at which the model of $(^{231}\text{Pa}/^{230}\text{Th})_{\text{xs}}^0$ export to sediments reaches equilibrium. Shown are sensitivity tests for zero concentration profiles (Figure 4.6b), with the particle production rate, PR, set at 0.05, 0.1, 0.2, and 0.5 $\text{gm}^{-2}\text{day}^{-1}$. the initial period of no change in $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is a artifact of the model due to the slope of the initial concentration profiles being vertical so the first iterations of the model simply increase the concentration according to the production, β (Table 4.5) as there is initially no difference in the input to and output from each box on particles until the anomaly from the top box which has no input from above works its way down the water column.

reach equilibrium is the presence or absence of a ^{231}Pa rich overlying water mass (NADW). Thus indicating that the whole water column above AABW, over the course of its history, influences the $(^{231}\text{Pa}/^{230}\text{Th})$ of AABW at WIND 28. Because the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ measured at WIND 28 is below the production ratio then it can be assumed that the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy at WIND 28 is sensitive to changes in any of the above mentioned controls.

4.7 Summary

$(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ has been measured in a western Indian Ocean sediment core back to 140 ka. Extending the record further back in time would be problematic due to the large errors associated with the corrections for authigenic ^{231}Pa and ^{230}Th , and

the relatively short half life of ^{231}Pa (32,760 years).

Although it has been demonstrated to be sensitive to changes in circulation and export productivity, $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ does not change significantly over the past 140 ka, at core WIND 28K. This is most readily explained if both productivity, and advection from the Southern Ocean have remained approximately constant over this time in the southwest Indian Ocean. This is in marked contrast to the $\overline{\text{SS}}$ record in the same core which indicates periods of increased flow. These two observations can be reconciled because the $\overline{\text{SS}}$ record may be dominated by a local effects such as bathymetric focusing or changing sediment input. $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is effected by advection over a broader region and therefore is more representative on a basin-wide scale.

The $(\text{U}/\text{Th})_{\text{detrital}}$ has been determined to be 0.45 ± 0.5 , a significant improvement on the accuracy of pervious methods. Authigenic U has been shown to be negligible throughout the core, with the exception of two peaks at 30, and 144 ka. The production of authigenic U is attributed to oxygen depleted water covering the core location, most likely due to reduced oxygen in deep waters rather than increased productivity .

Chapter 5

A High Resolution ^{231}Pa and ^{230}Th Water Column Profile

5.1 Introduction

This chapter concerns the measurement of Pa and Th isotopes in a water column profile from the southwest Indian Ocean, close to the South African continental margin. The profile consists of 22 10 l samples and includes 4 filtered-unfiltered sample pairs. The conservative behaviour of uranium is demonstrated, as is the ability of ^{231}Pa to label distinct water masses. The presence of an expanded diluted nepheloid layer – as observed in ^{232}Th data – causes a change in the bulk particulate composition. The addition of carbonate poor material by resuspension into this layer alters the fractionation of ($^{231}\text{Pa}/^{230}\text{Th}$) between dissolved and particulate phases, and is therefore significant in controlling sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰.

5.2 Regional setting

Station CD 154-13, at 027°59.93'E 34°03.19'S, is located in the southwest Indian Ocean approximately 130 miles east of Port Elizabeth, at the bottom of the continental slope of the South African margin (Figure 5.1). The water depth as measured by echo sounder is approximately 3600 m.

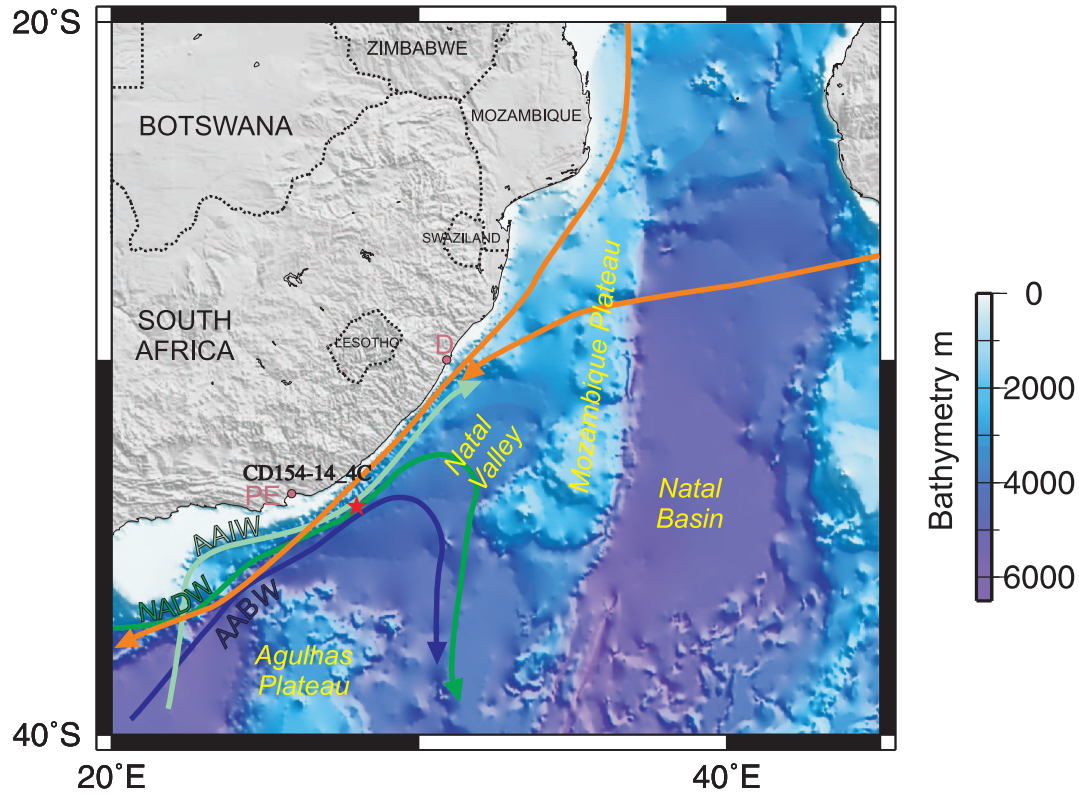


Figure 5.1: Locality of water column profile CD154-13 4C collected on *RRS Charles Darwin* cruise CD 154 (red star). Approximate flow paths of Antarctic Bottom Water (dark blue), north Atlantic Deep Water (green), and Antarctic Intermediate Water (light blue) are illustrated. Cities marked as D, Durban and PE, Port Elizabeth.

The surface water at this locality is the warm saline water of the Agulhas Current, a western boundary current driven by regional winds, in a similar fashion to the Gulf Stream in the North Atlantic (Section 1.2.1). The Agulhas Current is responsible for the transport of ~ 70 Sv ($1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$) of warm water, and most of the 0.66 PW of heat, south out of the Indian Ocean (Bryden and Beal, 2001). South of the tip of the African continent, the Coriolis force brings about the retroflexion of the Agulhas Current which brings most of the water back into the southern Indian Ocean. Some of the flow, however, breaks off as the current meanders, after leaving the South African coast, into cold core eddies (Boebel et al., 2003). These eddies are important because they are responsible for the return of heat to the Atlantic from the Indian Ocean and, as such, are a link in the global thermohaline conveyor

(Broecker, 1991).

Beneath the warm saline thermocline water of the Agulhas Current is Antarctic Intermediate Water (AAIW, Section 1.2.3), which is flowing northwards into the Indian Ocean (Figure 5.1). AAIW is characterised by low salinities (~ 34.5) and is found between ~ 750 and ~ 1750 m. Within the core of AAIW there is some interfingering mixing with a water mass with a high temperature and salinity (Figures 5.3 and 5.2), this is probably Red Sea Water (Gründlingh, 1985). Red Sea Water is formed in the Red Sea at a temperature of about 22°C and a salinity of about 39 and is similar to that formed in the Persian Gulf. These water masses overflow into the Indian Ocean where they sink to about 500 m in the northern Indian Ocean and form lenses of high-salinity high-temperature water. These lenses spread out and as they move south can sink due to baroclinic conditions to reach depths of 1000-1500 m in the southern Indian Ocean (Tomczak and Godfrey, 2002).

The dominant water mass at greater depth is derived from North Atlantic Deep Water (NADW, Section 1.2.3), also flowing northwards, and is characterised by a salinity maximum at 3000 m. This water arrives at this locality from the South Atlantic as a geostrophically constrained boundary current, hugging the base of the African continental rise. The bottommost water at station CD 154 13 shows the influence of Antarctic Bottom Water (AABW, Section 1.2.3). The temperature and salinity decrease with depth from approximately 3000 m to the seabed due to mixing with AABW. AABW and AAIW reaching this locality will have passed through the Southern Ocean since their formation close to the coast of Antarctica, and will have experienced high rates of scavenging onto siliceous particles in the opal belt (Figure 3.2). This contrasts with NADW which will have avoided such scavenging because it remains too far north as it passes around the tip of Africa.

5.3 Methods

5.3.1 Sampling strategy

Samples were collected on the *RRS Charles Darwin* Cruise 154 (principal investigators Ian Hall & Reiner Zahn), using a 24 Niskin bottle rosette, equipped with instruments to measure particle concentrations, chlorophyll concentration and oxygen concentration (Niel Brown MkII CTD. The CTD was also equipped with a Wetlab CStar nephelometer, a Seatech LS6000 light scattering sensor, a Chelsea Aqua 3 fluorometer and a SBE 43 dissolved oxygen sensor). The Wetlab CStar nephelometer measures particle concentration using the beam attenuation and transmission of light through the water, while the Seatech LS6000 measures the light backscattered from particles. Neither of the nephelometers were calibrated and only the LS6000 and the fluorometer produced consistent data, so only data from these two instruments were used for nephelometry.

As the CTD was lowered through the water column temperature and salinity were recorded to identify water masses, and the nephelometry used to identify the nepheloid layer near the seafloor. The CTD was lowered to within 5-10 m of the seafloor, using a pinger on the bottom of the rosette to gauge the distance to the bottom. Two Niskins were fired once this depth was reached and the CTD then raised immediately 20 m so as not to risk disturbing the sediment. Once raised clear of the seabed the pressures at which the remaining Niskins should be fired were decided. Pressures are chosen to best sample each water mass, and to provide enough water to perform filtered-unfiltered measurements within the nepheloid layer and above.

The depths from which samples were collected are shown in Table 5.1 and Figure 5.2 d. These depths were chosen to give high resolution in regions of interest, rather than to provide an equal spacing of measurements. The features of interest are: the

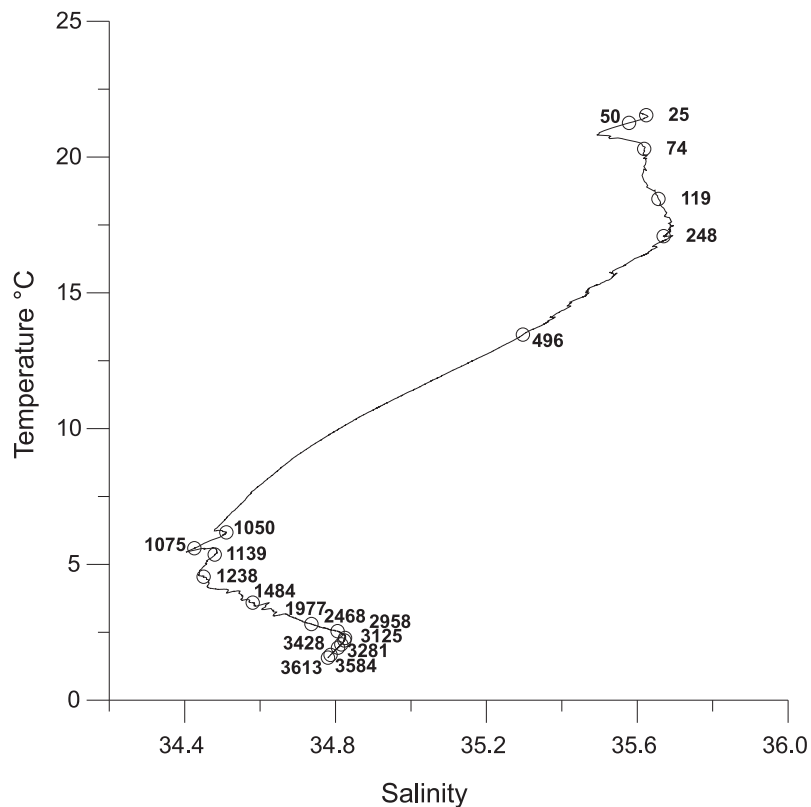


Figure 5.2: A temperature-salinity plot of CD 154-13C with the positions at which Niskins were fired. The numbers are depths calculated from shipboard temperature, salinity, and pressure data.

deepest water near the seafloor within the nepheloid layer; NADW above this; and a region at about 1100 m where AAIW is mixing with another water mass. There is also a concentration of samples near the surface as another investigator required shallow samples of the Agulhas Current.

5.3.2 Chemistry

The chemical treatment of samples is covered extensively in Section 2.3 and only summarised here: Once on deck, samples destined for unfiltered analysis were transferred to 10 l acid-cleaned polyethylene sample bottles, acidified to < pH 2 with nitric acid, and sealed. Samples for filtration were kept in the Niskins and transferred to the ships “wet lab”. In the wet lab the sample is inline filtered through a 142 mm

diameter $0.2\ \mu\text{m}$ cellulose nitrate filter, directly from the Niskin into an acid-cleaned sample bottle (Section 2.2.1), acidified and sealed.

After return to the laboratory in Oxford, the samples are weighed, and spiked with ^{229}Th , ^{233}Pa and ^{236}U . 50 mg of Fe is added as a carrier and the samples left to equilibrate for two days, shaking occasionally. The actinides are co-precipitated with Fe by neutralising the sample with NH_4 . The precipitated is washed with water before being dissolved ready for elemental separation by anion chromatography. Separation is by a three column pass through a 0.5 ml AG1 X8 anion column. The sample is loaded in 7.5N HNO_3 , Th eluted with 6N HCl , Pa with 6N $\text{HCl} + 0.05\text{N HF}$, and U with H_2O . Further details are provided in Section 2.3.6.

5.3.3 Mass spectrometry

The techniques used to measure U, Th and Pa are described in Section 2.5. Briefly, all measurements are made with a Nu Instruments MC-ICP-MS using a desolvating nebuliser to introduce the sample. U is measured in static mode with ^{234}U in an ion counter and all other isotopes in Faraday collectors. Standard-sample bracketing, with CRM-145, is utilised to correct for ion counter gain and mass bias. Th is measured in a dynamic mode, noise correcting the $^{230}\text{Th}/^{229}\text{Th}$ ratio with ^{235}U measured in both of the steps. The mass bias, ion counter gain, and abundance sensitivity are measured either side of a sample with appropriate U and Th standards. Pa measurement is made in static mode with multiple ion counting channels to measure the $^{231}\text{Pa}/^{233}\text{Pa}$ ratio, and as for thorium accounting for mass bias, ion counter gain, hydride formation, and abundance sensitivity with U and Th standards either side of the samples.

5.4 Results

Shipboard CTD data are shown in Figure 5.3. The particle concentration, estimated from light scattering, shows a near surface maximum associated with a peak in chlorophyll measured by fluorescence (Figure 5.3 a and b). There is also an increase in particle concentration near the seabed, measured in both the down and upcasts. The extent of these two regions of higher particle concentrations cannot be quantified with this measurement technique because concentrations appear to be below the detection limit. Oxygen concentration shows a marked depletion at depths of approximately 1500 m. As well as variability associated with variations in temperature and salinity within the core of AAIW, at 1050 and 1150 m (Figures 5.3 c and 5.2 d).

The measured U concentration shows significant variation with depth, from 3.12 to 3.24 ppm, that correlates perfectly with salinity (Figure 5.4) with an r^2 of 0.95. The isotopic composition of the water column does not vary significantly with depth and has a mean value $\delta^{234}\text{U}$ of 145.7 ± 4.5 .

The profiles of ^{230}Th and ^{231}Pa total concentration increase with depth from approximately 0.05 d.p.m./1000 l at the surface to 0.7 and 0.4 d.p.m./1000 l at 3600 m respectively (Figure 5.5 a, and Table 5.2). The ^{230}Th profile is roughly linear, while the ^{231}Pa profile shows more structure, notably around 1100 m associated with changes in the temperature and salinity (Figure 5.2), and below 3000 m. The filtered samples show the same general features as the unfiltered (total concentration) samples. The difference between the filtered and unfiltered concentration does, however, increase with depth: the proportion of the ^{230}Th (^{231}Pa) on the particulate phase rising from 8% (16%) to 23% (30%) respectively (Figure 5.5).

The ^{232}Th total concentration profile looks similar to that for ^{230}Th , increasing roughly linearly from 0.012 near the surface to 0.040 d.p.m./1000 l at 3600 m (Figure 5.5 b). The filtered samples, representing dissolved ^{232}Th , show no variation with depth remaining constant at approximately 0.011 d.p.m./1000 l. As with ^{230}Th and

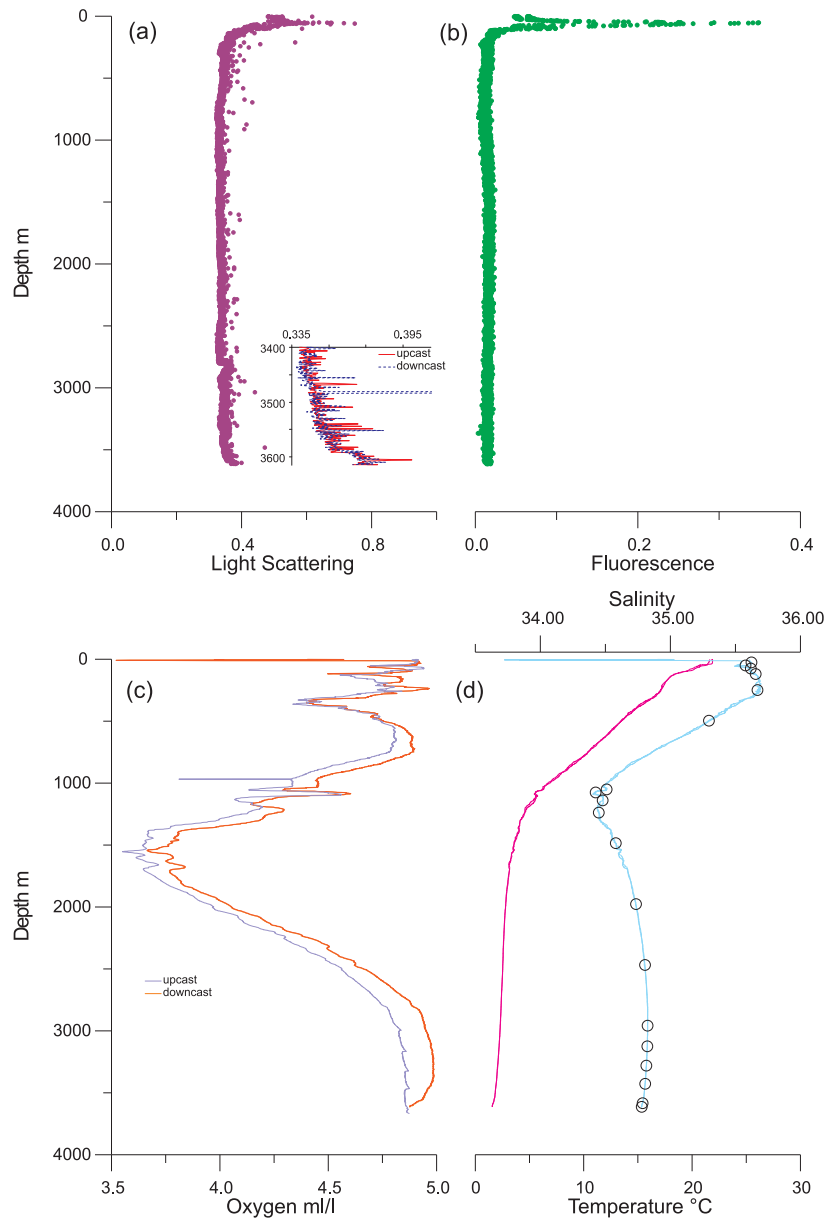


Figure 5.3: Shipboard CTD data: (a) Light scattering from the Seatech LS6000 nephelometer, the inset show the downcast (blue) and upcast (red), indicating that the signal at the bottom is real and not the result of sediment disturbance from the rosette. (b) The chlorophyll concentration in the water as measured with an Aqua 3 fluorometer, there are no units shown for either a, or b, because neither of the two instruments were calibrated so the values are purely qualitative. (c) Shows the O_2 concentration showing anomalies at 1100 m associated with T-S anomalies at the same depth and a large oxygen minimum at 1600 m associated with the top of NADW. both the down and up casts are shown There is a systematic offset between the two profiles, most likely due to instrument drift, but the two profiles do record the same general features on both small and large scales. (d) Temperature (pink) and salinity (blue) profiles with open circles showing the depths from which samples were taken.

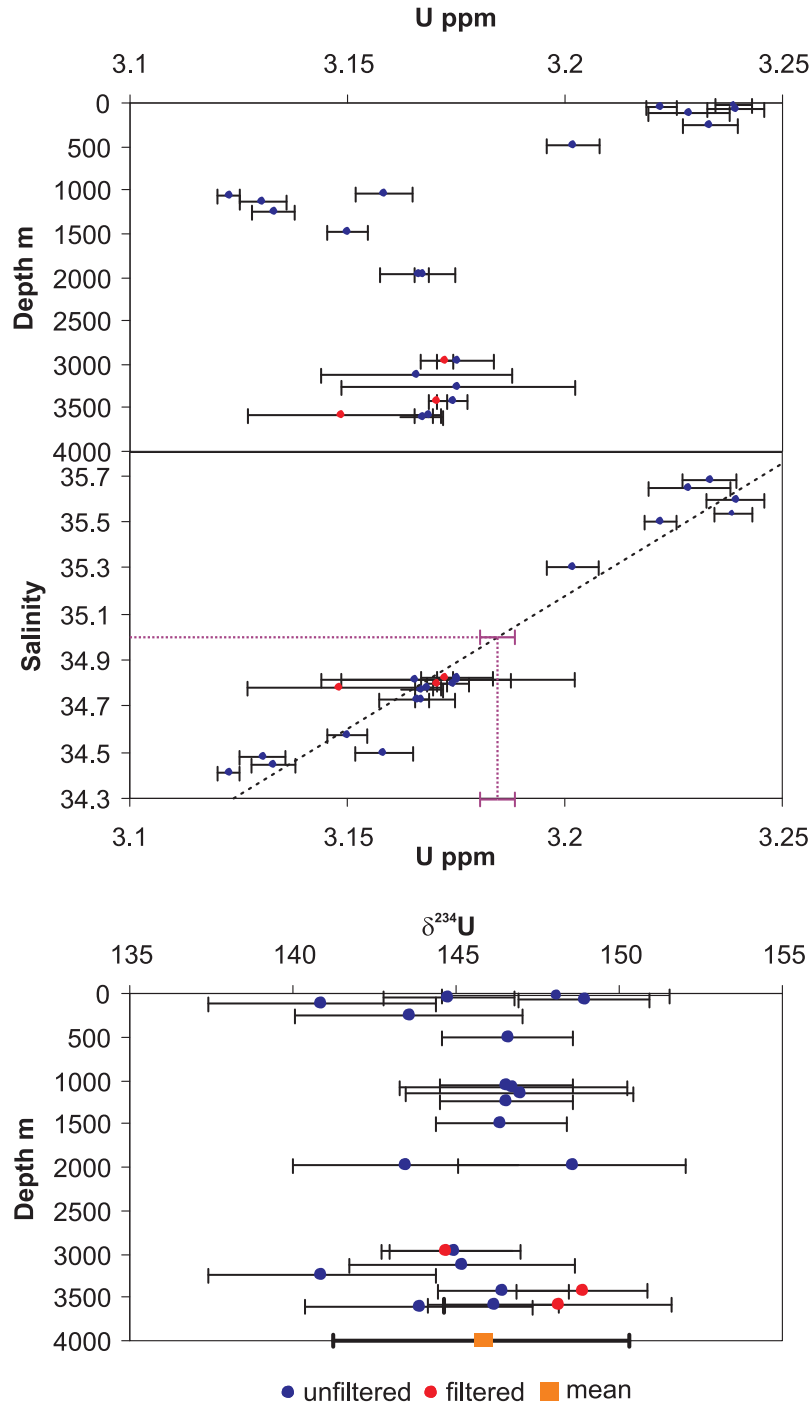


Figure 5.4: Uranium concentrations and isotopic compositions of samples from CD 154 13 4C. Shown in purple is the intercept, and uncertainty in the intercept, when salinity is normalised to 35. The isotopic composition is shown as the variation in parts per thousand from secular equilibrium of the $(^{234}\text{U}/^{238}\text{U})$ ratio, expressed in $\delta^{234}\text{U}$ notation. Errors are 2 s.d. based on internal variability of the $^{238}\text{U}/^{236}\text{U}$ ratio for U concentration, and the external repeatability of CRM-145 for $\delta^{234}\text{U}$.

Sample	Mass (kg)	^{238}U conc. (ppm)	error (2sd)	$\delta^{234}\text{U}$	error (2sd)	Pressure (db)	Depth (m)
CD154-13-4C #1	9.73	3.239	0.004	148.1	3.5	25	25
CD154-13-4C #2	9.73	3.222	0.004	144.8	2.0	50	50
CD154-13-4C #3	9.48	3.239	0.007	148.9	2.0	75	74
CD154-13-4C #4	10.42	3.229	0.009	140.9	3.5	120	119
CD154-13-4C #5	10.41	3.233	0.006	143.6	3.5	250	248
CD154-13-4C #6	10.29	3.202	0.006	146.6	2.0	500	496
CD154-13-4C #7	10.36	3.158	0.007	146.5	2.0	1060	1050
CD154-13-4C #8	10.20	3.123	0.003	146.8	3.5	1085	1075
CD154-13-4C #9	8.87	3.131	0.005	147.0	3.5	1150	1139
CD154-13-4C #10	10.41	3.133	0.005	146.6	2.0	1250	1238
CD154-13-4C #11	9.29	3.150	0.005	146.4	2.0	1500	1484
CD154-13-4C #12	7.25	3.166	0.009	148.6	3.5	2000	1977
CD154-13-4C #13F	9.38	3.167	0.005	143.5	3.5	2000	1977
CD154-13-4C #15F	9.79	3.173	0.006	144.7	2.0	3000	2958
CD154-13-4C #16	9.70	3.175	0.008	145.0	2.0	3000	2958
CD154-13-4C #17	9.56	3.166	0.022	145.2	3.5	3170	3125
CD154-13-4C #18	10.40	3.175	0.027	140.9	3.5	3330	3252
CD154-13-4C #20	10.37	3.174	0.004	146.4	2.0	3480	3428
CD154-13-4C #21F	9.80	3.171	0.007	148.9	2.0	3480	3428
CD154-13-4C #22	10.42	3.168	0.003	146.2	2.0	3640	3584
CD154-13-4C #23F	10.09	3.148	0.067	148.1	3.5	3670	3613
CD154-13-4C #24	9.81	3.167	0.005	143.9	3.5	3670	3613
				mean			
				145.8	4.5		
		ng					
-WATER BLANK #1		0.44		533.6	3.5		
-WATER BLANK #2		0.96		146.6	2.0		

Table 5.1: Results of analysis of Uranium in samples from CD 154 13 4C. F denotes a filtered sample. Pressure is measured directly by the CTD, while depth is derived, aboard the ship from a combination of temperature, salinity and pressure. The “WATER BLANK’s” are total procedural blanks processed alongside the samples. Niskin #19 misfired, and sample #14 was lost during chemistry.

^{231}Pa the proportion of ^{232}Th in the particulate phase increases with depth, in this case from 48% to 67%.

Total procedural blanks are 0.06, 0.01, and 0.06 d.p.m. for ^{230}Th , ^{232}Th , and ^{231}Pa respectively. The values used for the blanks are averages of all total procedural blanks measured up until, and including, the measurement of these samples. For low concentration surface samples the blank represents $\sim 10\%$ of the signal, and as such is a major source of uncertainty.

The ($^{231}\text{Pa}/^{230}\text{Th}$) ratio varies significantly down the water column (Figure 5.6 a). Near-surface water has high values, from 0.5 to 1.0, and large uncertainties due to the low concentrations. From 500 to 2000 m there is an increase in ($^{231}\text{Pa}/^{230}\text{Th}$) from 0.3 to 0.6. Between 1050 and 1150 m there is significant variation (dominated by changes

Sample	Depth (m)	Mass (kg)	²³⁰ Th		²³² Th		²³¹ Pa		⁽²³¹ Pa/ ²³⁰ Th)	
			(d.p.m./ 1000l)	(2σ)	(d.p.m./ 1000l)	(2σ)	(d.p.m./ 1000l)	(2σ)		(2σ)
CD154-13-4C #1	25	9.73	0.06	0.01	0.021	0.002	0.05	0.01	0.94	0.23
CD154-13-4C #2	50	9.73	0.05	0.01	0.016	0.001	0.03	0.01	0.64	0.19
CD154-13-4C #3	74	9.48	0.06	0.01	0.012	0.001	0.03	0.01	0.57	0.19
CD154-13-4C #4	119	10.42	0.07	0.01	0.013	0.001	0.06	0.01	0.81	0.16
CD154-13-4C #5	248	10.41	0.09	0.01	0.013	0.002	0.06	0.01	0.61	0.12
CD154-13-4C #6	496	10.29	0.18	0.01	0.014	0.001	0.06	0.01	0.33	0.04
CD154-13-4C #7	1050	10.36	0.34	0.02	0.014	0.001	0.13	0.01	0.37	0.03
CD154-13-4C #8	1075	10.20	0.32	0.02	0.013	0.001	0.16	0.02	0.51	0.07
CD154-13-4C #9	1139	8.87	0.37	0.01	0.020	0.002	0.20	0.01	0.53	0.04
CD154-13-4C #10	1238	10.41	0.38	0.01	0.014	0.001	0.15	0.01	0.40	0.03
CD154-13-4C #11	1484	9.29	0.42	0.01	0.016	0.001	0.20	0.01	0.48	0.03
CD154-13-4C #12	1977	7.25	0.43	0.02	0.022	0.002	0.30	0.02	0.70	0.06
CD154-13-4C #13F	1977	9.38	0.40	0.02	0.011	0.001	0.34	0.01	0.84	0.05
CD154-13-4C #15F	2958	9.79	0.52	0.01	0.011	0.001	0.22	0.01	0.42	0.02
CD154-13-4C #16	2958	9.70	0.56	0.01	0.027	0.001	0.26	0.01	0.46	0.02
CD154-13-4C #17	3125	9.56	0.66	0.02	0.029	0.001	0.41	0.02	0.63	0.03
CD154-13-4C #18	3252	10.40	0.62	0.02	0.028	0.001	0.33	0.02	0.52	0.03
CD154-13-4C # 20	3428	10.37	0.69	0.02	0.027	0.001	0.29	0.01	0.43	0.02
CD154-13-4C # 21F	3428	9.80	0.54	0.01	0.010	0.001	0.22	0.01	0.41	0.02
CD154-13-4C # 22	3584	10.42	0.65	0.02	0.032	0.001	0.25	0.01	0.39	0.02
CD154-13-4C #23F	3613	10.09	0.51	0.01	0.013	0.001	0.27	0.02	0.53	0.03
CD154-13-4C #24	3613	9.81	0.67	0.02	0.040	0.002	0.39	0.02	0.58	0.03

Table 5.2: Results of analysis of Th isotopes and Pa. concentrations are expressed as an activity per volume of seawater, d.p.m./1000l, assuming 1 fg/kg ²³⁰Th = 0.0456 d.p.m./1000l and 1 fg/kg ²³¹Pa = 0.105 d.p.m./1000l. Although a mass is measured by isotope dilution mass spectrometry, an activity is presented to be consistent with literature measurements made by alpha spectrometry. F, represents a filtered sample.

in the ²³¹Pa concentration) associated with the temperature and salinity anomalies at these depths. At greater depth, below 3000 m, the (²³¹Pa/²³⁰Th) decreases towards the seabed from 0.63 at 3125 m to 0.39 at 3584 m, while the measurement closest to the seabed is higher at 0.58.

Fractionation of (²³¹Pa/²³⁰Th) between the dissolved and particulate phases is defined by an F factor (Anderson et al. (1983a), Equation 1.37). Calculated values of F are very low typically between 0.5 and 1, and show no systematic variation with depth (Figure 5.6 b). The values for F (the fractionation of (²³¹Pa/²³⁰Th) between dissolved and particulate phases) calculated here (Table 5.3 and Figure 5.6) were derived from particulate (²³¹Pa/²³⁰Th) calculated from the residual of the filtered and unfiltered sample pairs, rather than from direct measurements of the filtered particles.

Samples	Depth (m)	Particulate				
		^{230}Th d.p.m./ 1000l	^{232}Th d.p.m./ 1000l	^{231}Pa d.p.m./ 1000l	$(^{231}\text{Pa}/^{230}\text{Th})$	F
CD154-13-4C #12+13F	1977	0.03 ± 0.03	0.010 ± 0.002	-0.04 ± 0.02	-1.4 ± -1.8	-0.6 ± -0.7
CD154-13-4C #15F+16	2958	0.05 ± 0.02	0.015 ± 0.002	0.04 ± 0.01	0.9 ± 0.5	0.5 ± 0.3
CD154-13-4C #20+21F	3428	0.15 ± 0.03	0.017 ± 0.002	0.07 ± 0.02	0.5 ± 0.1	0.9 ± 0.3
CD154-13-4C #23F+24	3613	0.15 ± 0.02	0.027 ± 0.002	0.11 ± 0.03	0.7 ± 0.2	0.7 ± 0.2

Table 5.3: Particulate concentrations of Th and Pa calculated from the difference in concentration of filtered and unfiltered pairs of samples from the same depth (Table 5.2). The measurement from CD 154 23 4C #13F is likely to be wrong: at the time of processing it was noted that there could have been some contamination, as visual inspection of the sample showed that some large particles had got into the sample. The fractionation factor, F, is calculated from the ratio of the dissolved and particulate ($^{231}\text{Pa}/^{230}\text{Th}$) ratios, and represents the preference of Th or Pa to sorb to particles. All uncertainties are 2σ .

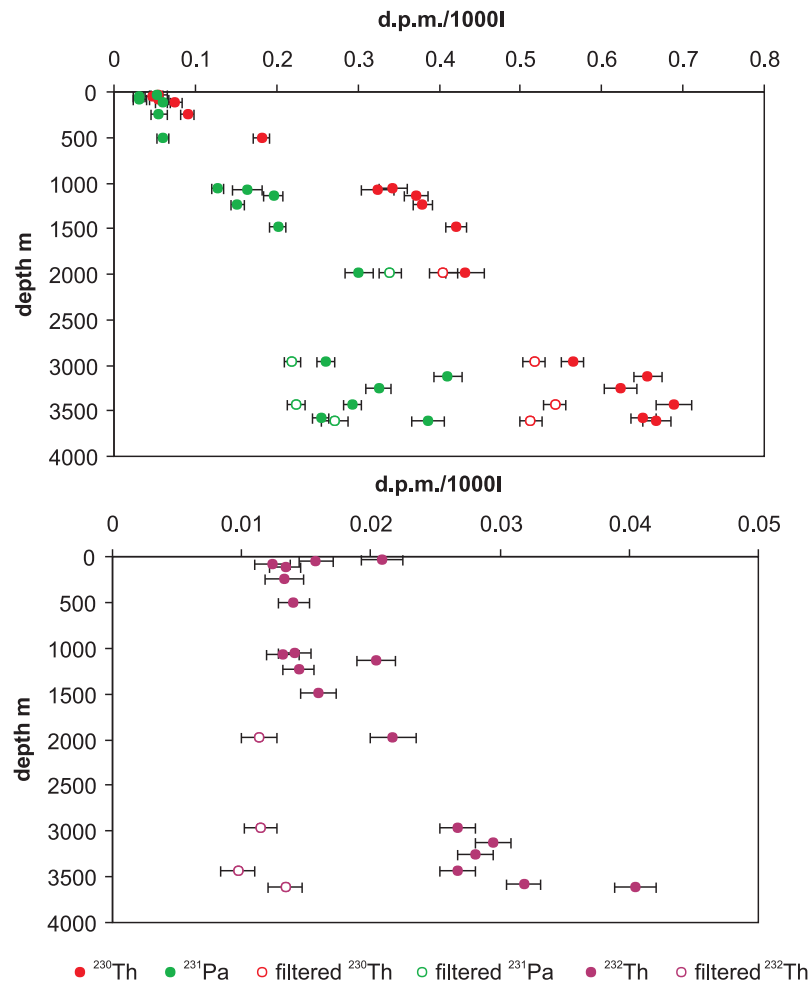


Figure 5.5: Concentration profiles of ^{231}Pa , ^{230}Th , and ^{232}Th at CD 154 13 4C. showing both filtered and unfiltered samples.

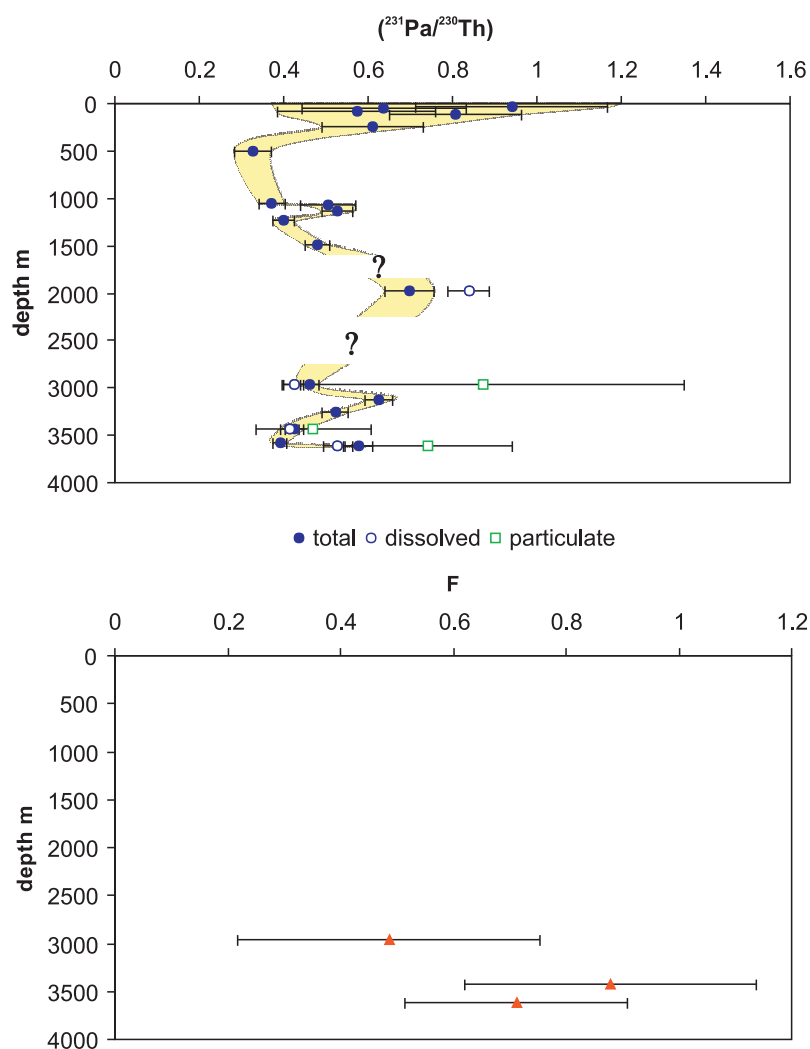


Figure 5.6: A $(^{231}\text{Pa}/^{230}\text{Th})$ profile at CD 154 13 4C, showing the unfiltered and filtered samples and the calculated particulate values. The yellow envelope is an interpretive extrapolation of the structure of the total, unfiltered, $(^{231}\text{Pa}/^{230}\text{Th})$ profile. Also shown are the calculated fractionation factors, F .

5.5 Discussion

5.5.1 Oceanic behaviour of uranium

The covariance of uranium concentration with salinity shows that uranium is behaving in a truly conservative manner. The best fit relationship between the two is (Figure 5.4):

$$\text{Salinity} = 11.5 \pm 0.6 \times [\text{U}] - 1.7 \pm 2.0 \quad (5.1)$$

The fact that the intercept is within error of zero adds confidence to the measurements accuracy and the assertion of conservative behaviour. The lack of significant variation of $\delta^{234}\text{U}$ (Figure 5.4) also confirms that ^{234}U is behaving in a conservative manner and suggests that no substantial exchange of uranium with sediments occurs.

The conservative nature of uranium is consistent with previous measurements of uranium in seawater (Chen et al., 1986; Robinson et al., 2004a). The normalised uranium concentration at a salinity of 35 is 3.184 ± 0.004 ppm (2σ). This is significantly lower than both the Chen et al. (1986) (3.21 ppm ± 0.03) and the Robinson et al. (2004a) (3.33 ppm) normalised concentrations (Figure 5.7). The reasonably large discrepancy with the Robinson et al. (2004a) study may have arisen from measurements of salinity in that study, where salinity was measured in the lab, some time after collection. A difference in spike calibration cannot account for the discrepancy as the same spike was used in this study and Robinson et al. (2004a). A systematic error in salinity meter calibration at that time could have occurred. In contrast, the salinity data presented here is from the CTD and was calibrated by shipboard bottle measurements of salinity on seawater standards and distilled water using an temperature controlled optical salinity meter. A comparison of the Equatorial Pacific subset of the Chen et al. (1986) data with the Indian Ocean data presented in this study (Figure 5.7) indicates that there may be some variation in U concentration between oceans. This difference may not, however, be real as no inter laboratory calibration

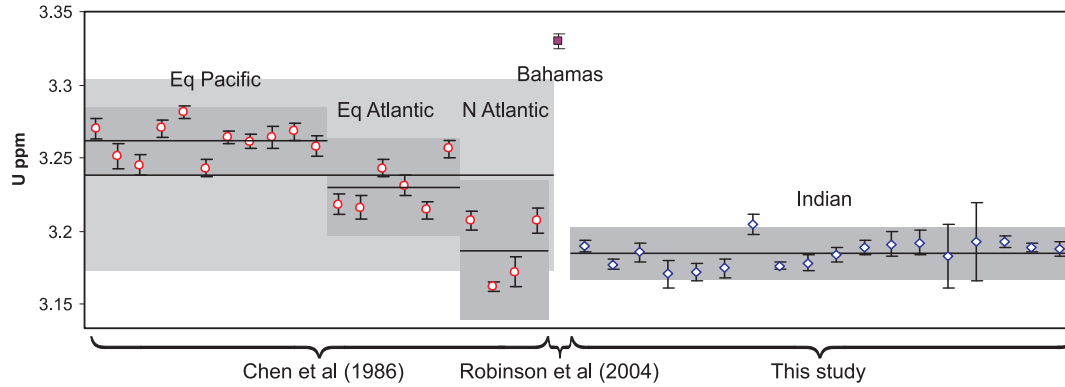


Figure 5.7: A comparison of ^{238}U concentration measurements normalised to a salinity of 35. The regions covered by Chen et al. (1986) are the Equatorial Pacific ($n = 11$), the North Atlantic ($n = 4$), and the Equatorial Atlantic ($n = 6$). All other uncertainties are 2σ of the salinity normalised concentration. The grey boxes represent 2 s.d. of each regional grouping of samples, the light grey box is the average and 2 s.d. of all of the Chen et al. (1986) data. The Robinson et al. (2004a) study is from the Bahamas Bank, and uncertainty is assessed from the average 2σ uncertainty in the U measurement, and is hence an underestimate of the uncertainty of the 14 samples measured in that study.

has been performed, and thus further investigation is required. Because there is no significant variation between water masses measured in the Indian Ocean, and these water masses originate from different oceans, any variation in U concentration is unlikely based on the measurements of this study alone.

Confirmation that uranium behaves conservatively in the ocean is useful for the ($^{231}\text{Pa}/^{230}\text{Th}$) proxy as it reinforces the notion of the constant production of ^{231}Pa and ^{230}Th . Constant oceanic $\delta^{234}\text{U}$ is also of importance to the U-Th dating of marine carbonates, whose initial $\delta^{234}\text{U}$ is generally assumed to be that of seawater (Bard et al., 1991; Gallup et al., 1994; Stirling et al., 1995).

5.5.2 Comparison of ^{231}Pa and ^{230}Th with existing data

Concentration profiles of ^{230}Th are similar to those of those from the western Indian Ocean (WIND), as reported in Chapter 3 (Figure 5.8, a). The upper water column

of CD154 13 4C matches well that of previous profiles, but at depth it shows a significant depletion of ^{230}Th relative to the WIND profiles and the Southern Ocean and global averages. The lower portion of the ^{230}Th profile is significantly lower in concentration than those of the WIND samples. The elevated ^{232}Th at depth suggest that this ^{230}Th depletion may be due to increased scavenging of ^{230}Th due to elevated particle concentration i.e. boundary scavenging. The ^{231}Pa profile is also similar to the WIND profiles in the upper water column, although a higher sampling resolution reveals structure to the profile at 1050-1150 m. The deeper ^{231}Pa samples are similar to those in the WIND study, any difference is hard to resolve due to the low sample density and large uncertainty of WIND measurements. Considerable improvement in the measurement uncertainty, relative to those of the WIND profiles, is largely due to improved yield through the co-precipitation step. That the ^{231}Pa profile is similar to the WIND profiles shows that the ^{231}Pa concentration does not change much as the water moves northwards into the Indian Ocean. Thus demonstrating the ability of ^{231}Pa to label water masses.

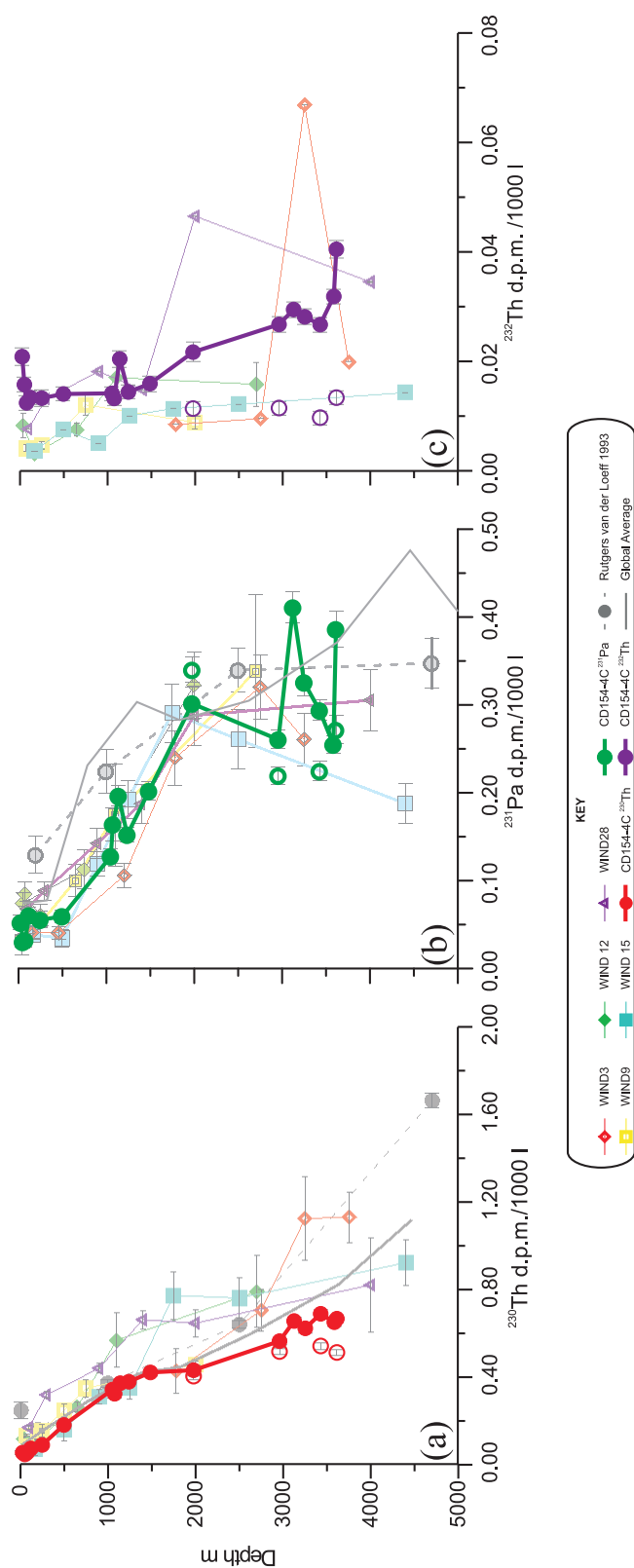


Figure 5.8: A comparison of data from the Madagascar and Mascarene Basins (WIND), measured in Chapter 3 (light colours), with those measured in this study (CD 154, darker symbols and Figure 5.5). Also shown are globally averaged profiles (Henderson and Anderson, 2003), and a profile from the Southern Ocean at 10.46°E 44.48°S (Rutgers van der Loeff and Berger, 1993). Open symbols denote filtered samples.

5.5.3 Deep particulate ^{232}Th

The ^{232}Th -total concentration profile is similar to that of ^{230}Th , showing an increase of concentration with depth. This increasing concentration can not, however, be due to reversible scavenging of ^{232}Th – as is the case for ^{230}Th – because the dissolved ^{232}Th measured in filtered samples shows no increase with depth. The increase of ^{232}Th -total concentration with depth therefore suggests the presence of a ‘nepheloid’ layer, which is much thicker than observed from light scattering (Figure 5.3). Absence of this expanded nepheloid layer in the light scattering data is probably due to the high detection limit of this measurement. The nepheloid layer must contain a particle phase that contains ^{232}Th , most likely terrestrial detrital material.

The interpretation of WIND data (Section 3.6.2), that a portion of ^{232}Th is reversibly scavenged is not supported by this new data because the dissolved ^{232}Th profile does not increase with depth. Rather, it is the particulate concentrations, reflected in the measurements of total ^{232}Th , that increase with depth. As mentioned above this might reflect a dilute expanded nepheloid layer. An alternative explanation, however, might involve a gradual change of particle type towards the seafloor. If the bulk particle composition changes such that the $K_{d,\text{Th}}$ increases, then reversible scavenging of ^{232}Th coupled with a higher affinity for particles will produce an increase in concentration on particles but not in the dissolved phase. This scenario is only possible if the increase in total concentration is exactly balanced by an increase in $K_{d,\text{Th}}$ to lead to constant dissolved concentrations. This increasing $K_{d,\text{Th}}$ hypothesis is supported by the coupling of the increase in % ^{232}Th on particles with that for ^{230}Th (Figure 5.9). The % ^{231}Pa on particles also increases with depth (Figure 5.9), so any change in the bulk particle composition must also produce an increase in $K_{d,\text{Pa}}$. A particle type that has high K_d s for both Th and Pa might be organic compounds (Guo and Gueguen, 2002). It is unlikely however, that the particulate fraction of organic material will increase at depth because organic

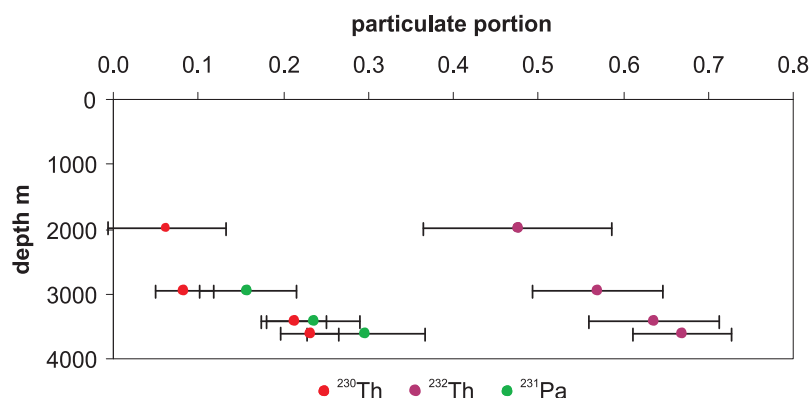


Figure 5.9: The proportion of ^{230}Th , ^{232}Th , and ^{231}Pa associated with particles, calculated from filtered and unfiltered pairs of samples. Errors are 2σ .

matter easily respire as particles sink. Overall, it therefore seems most likely that the increases of total ^{232}Th and % particulate ^{230}Th and ^{231}Pa are due to a dilute expanded nepheloid layer.

5.5.4 Interfingering of Red Sea Water

The temperature-salinity anomaly in the core of AAIW at ~ 1100 m (Figure 5.2 and 5.10), shows a mixing of a high salinity and high temperature water mass with AAIW. This mixing takes the form of two ‘fingers’ of high temperature and salinity water at ~ 1050 and ~ 1140 m. If the water mass mixing with AAIW is Red Sea Water (RSW) as suggested in Gründlingh (1985) (having a temperature of about 22°C and a salinity of about 39), then the interfingering seen at this locality represents a mixture of only 3% RSW with 97% AAIW. ^{231}Pa concentrations also show variability at this depth, although it is difficult to link this variability with water mass mixing. (Figure 5.10). Such linkage may be confounded by the downward transport of ^{231}Pa by reversible scavenging onto sinking particles. So it remains possible that ^{231}Pa variability in this depth interval reflects different water masses. As the temperature-salinity anomaly represents only a 3% mixing of RSW, it is however, unlikely that the associated high ^{231}Pa anomaly is representative of conservative mixing between AAIW and RSW

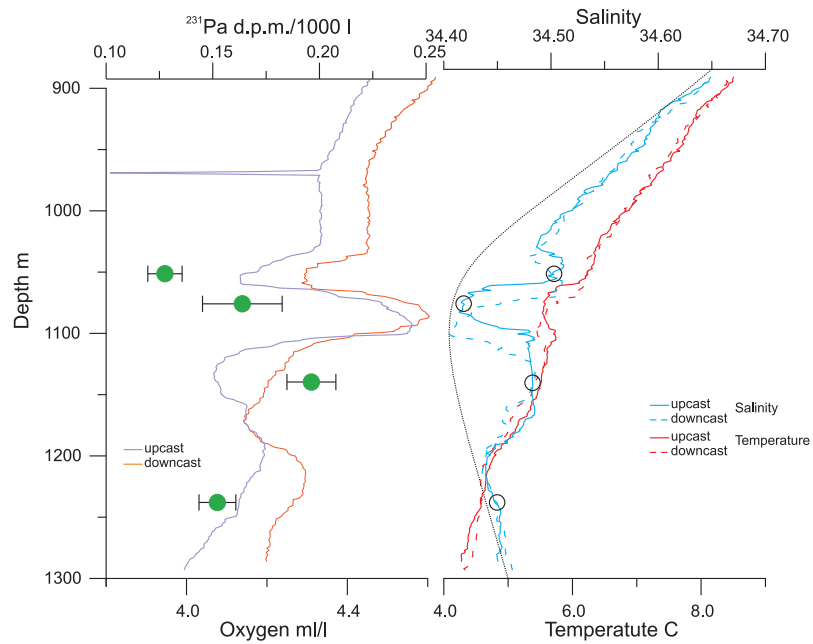


Figure 5.10: An expanded section of Figure 5.3 c and d showing the dissolved oxygen concentration and temperature-salinity anomalies associated with the interfingering of Red Sea Water (temperature 22°C, salinity 39) with AAIW. The black line is a hypothetical salinity profile if there were no intermixing of RSW. Also shown in green are the ^{231}Pa concentrations measured at these depths.

because this would require the ^{231}Pa concentration of pure RSW to be about 1.8 d.p.m./1000l, (outside the range of all observed seawater ^{231}Pa concentrations by a factor of 2 (Henderson and Anderson, 2003)). A more plausible explanation of the high ^{231}Pa , would be its acquisition by RSW during transit from the Red Sea to the sampling site. Although a particle scavenging regime that would supply a high ^{231}Pa concentration during the transit of RSW is not obvious, elevated ^{232}Th at 1139 m suggests that it may be the result of the addition of particles at this depth. A possible source of such particles may be interaction of RSW with the continental margin as it passed between Madagascar and Africa.

5.5.5 NADW and AABW mixing

The ^{231}Pa profile shows lots of structure apart from that associated with RSW mixing. Samples from 2958 m to the bottom of the profile (3613 m) represent water from the core of NADW mixing with AABW at greater depth. Generally, the deeper samples, associated with AABW, show a depletion in ^{231}Pa , and hence also ($^{231}\text{Pa}/^{230}\text{Th}$). This depletion is thought to be due to preferential scavenging of Pa onto opal particles as AABW passes under the high productivity opal belt as it leaves the Southern Ocean (as discussed in Chapter 3). The systematic decrease of ^{231}Pa and ($^{231}\text{Pa}/^{230}\text{Th}$) with depth (Figure 5.11) can therefore be attributed to a high ^{231}Pa water mass (NADW) flowing above a low ^{231}Pa water mass (AABW). High ^{231}Pa concentrations of the NADW will gradually work downward due to reversible scavenging onto sinking particles. This effect, combined with mixing, will give rise to the systematic change in ($^{231}\text{Pa}/^{230}\text{Th}$) between the water masses.

Notable excursions from this decreasing ^{231}Pa trend in deep to bottom water are the samples at the very bottom of the profile and at 3000 m. The bottom-most samples have higher ($^{231}\text{Pa}/^{230}\text{Th}$) than expected from the trend. This high ($^{231}\text{Pa}/^{230}\text{Th}$) close to the seabed could be due to the introduction of sediment from up-slope, which if directly under NADW would have a higher ($^{231}\text{Pa}/^{230}\text{Th}$). Re-suspension of such “NADW derived” high ($^{231}\text{Pa}/^{230}\text{Th}$) sediment would cause the Pa on those particles to exchange with the water – and to a lesser extent Th also – thus altering the ($^{231}\text{Pa}/^{230}\text{Th}$) of the water to higher values. The lower ^{231}Pa and ($^{231}\text{Pa}/^{230}\text{Th}$) at 3000 m is hard to explain. There is no data from immediately above so it is hard to ascertain how anomalous this data really is. There is a high in the nephelometry data just above this depth (Figure 5.3), but although consistent in both the down and up-casts the ^{232}Th shows no anomaly at 3000 m, it is therefore unclear whether a high particle load is playing a role in controlling the low ($^{231}\text{Pa}/^{230}\text{Th}$) at this depth.

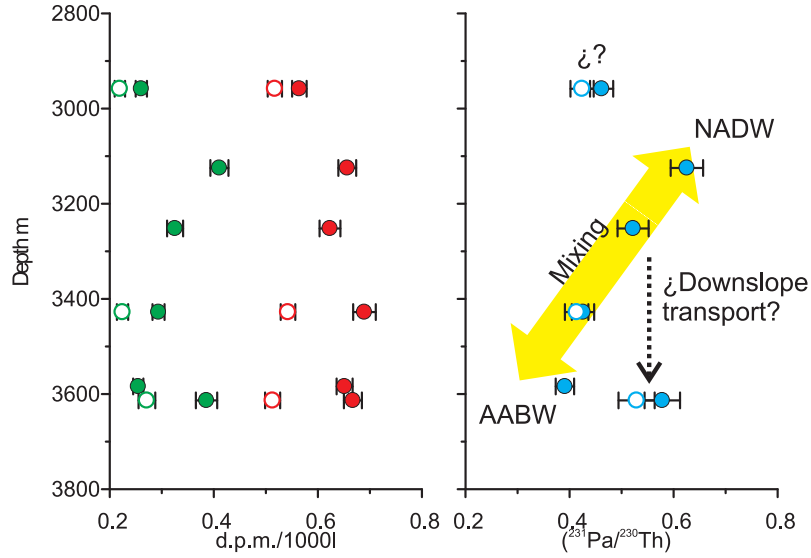


Figure 5.11: Expanded sections of Figures 5.5 and 5.6. ^{231}Pa and ^{230}Th total concentrations are shown in green and red circles respectively. The $(^{231}\text{Pa}/^{230}\text{Th})$ is shown in blue. open circles represent filtered water samples. Mixing between high $(^{231}\text{Pa}/^{230}\text{Th})$ and low $(^{231}\text{Pa}/^{230}\text{Th})$ is shown schematically in yellow.

5.5.6 Fractionation of Pa and Th isotopes by varying particle type

The fractionation of $(^{231}\text{Pa}/^{230}\text{Th})$ between the dissolved and particulate phase is defined as the ratio of $(^{230}\text{Th}/^{231}\text{Pa})$ on particles to that in the dissolved phase (Equation 1.37). The value of F indicates by how much ^{230}Th is preferentially scavenged onto particles over ^{231}Pa . An F greater than 1 indicates ^{230}Th is preferentially scavenged, and is linearly scaled so that for an F of 10 ^{230}Th is scavenged ten times more effectively than ^{231}Pa . Values of F less than 1 indicate ^{231}Pa is more effectively scavenged. The low F values measured in this profile (Table 5.3 and Figure 5.6) suggest, in the lower water column at least, that either there is little fractionation of $(^{231}\text{Pa}/^{230}\text{Th})$ between dissolved particulate phases, or there is a slight enrichment of ^{231}Pa on particles over ^{230}Th . This is an unexpected result because ^{230}Th is

expected to be scavenged more effectively than ^{231}Pa in most environments (Chase et al., 2002; Luo and Ku, 2004). Another view of the same data further illustrates that scavenging favours ^{231}Pa . The proportion of total nuclide on the particulate phase is higher for ^{231}Pa than for ^{230}Th (Figure 5.9), although it is possible that this is an artifact of the filtering process. If ^{231}Pa is scavenged onto the filter paper during filtration then this would bias the observed fractionation.

If the calculated values of F truly represent partitioning between dissolved and particulate then the particles at depth must be of a composition that either do not fractionate ^{231}Pa and ^{230}Th or slightly favour sorption of ^{231}Pa . Particles at depth are likely to contain opal and lithogenic material, because they are more resistant to dissolution, than organic matter and carbonate. The dissolution of carbonate, which favours sorption of ^{230}Th over ^{231}Pa (Luo and Ku, 1999; Chase et al., 2002), will result in a lowering of F for the particles that remain. Such carbonate dissolution will mostly occur at the seafloor. Although, at this locality the water depth is only 3615 m, and the calcite compensation depth is 4.5–5 km (Berger and Winterer, 1974). Resuspension of carbonate-poor material from the seafloor into a dilute expanded nepheloid layer, as observed in the ^{232}Th profile, may explain the observation that both ^{231}Pa and ^{230}Th are scavenged approximately equally at depth.

In the top 400 m of the water column the $(^{231}\text{Pa}/^{230}\text{Th})$ are higher than the water immediately below (Figure 5.6). The uncertainty in these ratios is large due to the low concentrations of ^{231}Pa and ^{230}Th in surface waters (Figure 5.5). Preferential export of Th out of the surface water can, however, explain this feature of the $(^{231}\text{Pa}/^{230}\text{Th})$ profile. The upper water column above the thermocline will experience a high degree of particle cycling, with biological activity in the photic zone – as observed by a chlorophyll maximum (Figure 5.3) – producing a high concentration of particles. These particles are likely to consist of predominantly carbonate and organic matter. These particles will sink and as they do so they will dissolve, so

most of the particles produced do not reach deeper water. The nutrients released by this dissolution returns to the surface via upwelling where more particles are formed. If this particle cycling is dominated by organic matter and carbonate rather than organic matter and opal then ^{230}Th will be preferentially removed from surface waters, resulting in a high ($^{231}\text{Pa}/^{230}\text{Th}$).

In summary, the fractionation of ($^{231}\text{Pa}/^{230}\text{Th}$) between particles and dissolved changes with depth due to the selective dissolution of particle phases and resuspension of dissolution-resistant particles. In the upper water column, scavenging on carbonate particles favours ^{230}Th , leaving surface waters with high ($^{231}\text{Pa}/^{230}\text{Th}$). At depth, once carbonate has dissolved, and the particles may be dominated by lithic and opal phases and the fractionation between ^{231}Pa and ^{230}Th is weak.

5.6 Summary

A high resolution water-column profile has been measured in the southwest Indian Ocean. It samples a variety of water masses from the Agulhas Current at the surface through AAIW and NADW, to a component of AABW at the base. Measurements of U show conservative behaviour, concentration only varying with salinity over a salinity range of 1.2. The isotopic composition of U is constant and is in agreement with previous measurements (eg Chen et al. (1986); Robinson et al. (2004a)), although the concentration of ^{238}U , normalised to a salinity of 35, of 3.18 ppm is lower than in Chen et al. (1986) (3.21 ppm) and Robinson et al. (2004a) (3.33 ppm). This discrepancy may be due to the large uncertainties of Chen et al. (1986) and the calibration of salinity measurements in Robinson et al. (2004a). Real spatial variation in the uranium concentration is unlikely due to the its long residence time.

An elevated concentration of ^{232}Th -bearing lithogenic particles is inferred from the ^{232}Th measurements in the lower half of the water column. Elevated total ^{232}Th

concentrations not associated with high dissolved ^{232}Th indicate the presence of an expanded nepheloid layer reaching 1700 m from the seabed.

The enhanced solubility of ^{231}Pa enables it to ‘trace’ water masses, although the ^{231}Pa concentration is not simply a function of the water masses source but is a product of the scavenging and advection history of the water mass. ^{231}Pa may be picking out RSW sourced from the northern Indian Ocean from AAIW sourced in the Southern Ocean. Water column ($^{231}\text{Pa}/^{230}\text{Th}$) reflects the differing histories of the different water masses: both AAIW and AABW have low ($^{231}\text{Pa}/^{230}\text{Th}$) indicative of scavenging of ^{231}Pa onto opal particles as they left the Southern Ocean; NADW has not experienced such preferential scavenging of ^{231}Pa in the opal belt and retains a high ($^{231}\text{Pa}/^{230}\text{Th}$); surface waters of the Agulhas Current have a high ($^{231}\text{Pa}/^{230}\text{Th}$) because of preferential removal of ^{231}Pa from surface water.

Fractionation of ($^{231}\text{Pa}/^{230}\text{Th}$) between dissolved and particulate phases is shown in the upper water column to favour sorption of ^{230}Th onto particles, resulting in an export of ^{230}Th from surface waters and a high ($^{231}\text{Pa}/^{230}\text{Th}$). Dissolution of carbonate as the particles sink, and resuspension of sediment from which carbonate has been dissolved while on the seafloor, introduces into the lower water column a mixture of particles. These are most likely opal and lithogenic, which either do not fractionate ^{231}Pa and ^{230}Th between dissolved and particulate phases or slightly favour sorption of ^{231}Pa onto particles. Thus sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰ will, in part, be dependent on the amount of resuspension of sediment, as this will effect the composition of particles suspended in the lower water column, if seafloor processes alter the bulk particulate composition. More resuspension will introduce more sediment from which carbonate has been removed into the water column. As the sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$)⁰ signal is representative of the last exchange of ^{231}Pa and ^{230}Th from seawater to the particles in the lower ~ 1000 m of the water column (Chapter 3), it will be the mixture of resuspended particles and those sinking from

above which will determine the bulk F and hence the fractionation from the bottom water ^{231}Pa and ^{230}Th to the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ preserved in sediments.

Chapter 6

Conclusions

6.1 U-series nuclides as an ocean circulation proxy

The use of ^{231}Pa and ^{230}Th as an ocean circulation proxy has dramatically expanded over recent years. The initial demonstration of the potential of sedimentary $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to record changes in basin-wide circulation came in 1996 (Yu et al., 1996). More recently, during the course of the research of this thesis, the first downcore record of circulation inferred from the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy has been published (McManus et al., 2004). This has been followed by another record from the North Atlantic similarly using $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ confirming that Atlantic meridional overturning circulation was weaker during glacial times and is shut down during Heinrich events (Gherardi et al., 2005). A study in the Arctic Ocean has also further demonstrated the potential of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ as a proxy for advection (Moran et al., 2005). The first realistic global models of ^{231}Pa and ^{230}Th in the ocean have been produced (Siddall et al., 2005). Comparing such modelled ^{231}Pa and ^{230}Th in the ocean with the increased amount of data now available for both surface sediments and seawater samples, enables the controls on the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ to be better understood. $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ is becoming more widely thought of as a flow-rate proxy of significant importance to paleoceanographers.

This thesis furthers the use of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ as a paleocirculation proxy

into the Indian Ocean, a previously understudied region. Measurements of water column profiles have shown that water masses can have distinct $(^{231}\text{Pa}/^{230}\text{Th})$ resulting from their advection and scavenging histories. It has been shown that the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ preserved in sediment at any one locality will be most representative of the $(^{231}\text{Pa}/^{230}\text{Th})$ in the bottommost water mass only. It is this constraint that allows the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy to be used to study the past flow of the bottommost water mass, AABW, into the Indian Ocean. Measurement of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ in a core spanning 140 ka has demonstrated that there has been no change in the flow of AABW into the Indian Ocean over the last glacial-interglacial cycle.

6.2 Future analytical developments

Improvements to the precision of measurements would be a valuable goal, particularly for ^{231}Pa . Because ^{231}Pa is the limiting isotope for the use of the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$, especially for older samples. At present the uncertainty in ^{231}Pa measurements is limited by the calibration of the spike, if sufficient ^{231}Pa is present in the sample such that the blank and counting statistics are negligible. Spike calibration in this study is of the order of 2%. Uncertainty in spike calibration via measurement – once ^{233}Pa has decayed to ^{233}U – against ^{236}U , is presently limited by the amount of ^{233}Pa available from each batch produced. The amount available for calibration is small (~ 100 fg) because as much spike as possible was used to measure samples rather than for calibration. In future studies utilising ^{231}Pa , a larger batch of ^{237}Np , or more convenient access to ^{232}Th irradiation, should be ensured so that more ^{233}Pa could be assigned to calibration, and hence reduce the counting statistics for the measured $^{233}\text{U}/^{236}\text{U}$, and allow more repeat calibrations to be made. Confirmation of ^{233}Pa spike calibration would also be possible using a secular equilibrium reference. A good candidate for such a reference material would be a speleothem tested with

the ^{238}U - ^{234}U - ^{230}Th series to be in secular equilibrium, because speleothems can have a high U content and are easily dissolved using similar protocols to those used in this thesis.

6.3 Extending the application of ^{231}Pa and ^{230}Th

6.3.1 Water column ^{231}Pa and ^{230}Th measurements

In this study ~ 10 l of seawater was required for a measurements of ^{231}Pa and ^{230}Th . If the required sample size can be reduced to 4-5 l then the measurements of seawater ^{231}Pa and ^{230}Th can become more widespread. Standard sample collection apparatus typically enables collection of up to 24 10 l samples from discrete depths. A requirement of 10 l of water is an inhibitor to the inclusion of ^{231}Pa and ^{230}Th measurements in most geochemical sampling strategies, where competition from the measurement of other trace elements (e.g. Fe, Mn, Al, Pb, Nd, and REEs) will reduce the amount of water available.

Presently measurements could be made on ~ 5 l of seawater (at least for deep water samples), and with improvements to the spike calibration and reduction to the blank, measurements on such small samples should yield results as precise as those in this thesis. Thus inclusion of ^{231}Pa and ^{230}Th measurements in more oceanographic cruises is possible alongside measurements of other geochemical tracers. If however the suspended particulate ^{231}Pa and ^{230}Th are to be measured, without further improvements in the uncertainty of measurements, larger 10 l samples will still be advantageous.

Greater global density of ^{231}Pa and ^{230}Th data, will not only provide better constraints for models of ^{231}Pa and ^{230}Th in the ocean (eg. Siddall et al. (2005)). Systematic sections of ^{231}Pa and ^{230}Th across ocean basins will help constrain the processes which control sedimentary ($^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}}$). More data covering a wide

range of particle scavenging regimes, both total flux and particle type, will enable field scale assessment of the particle type dependence on fractionation of ^{231}Pa and ^{230}Th , which remain controversial (Luo and Ku, 2004; Chase and Anderson, 2004; Li, 2005).

6.3.2 Testing the bipolar seesaw hypothesis

Temperature records derived from ice cores in Greenland and Antarctica show an anti phase relationship (Blunier et al., 1998) on a millennial time scale. In the North Atlantic these millennial scale rapid temperature vacillations are termed “Dansgaard-Oeschger” events, and are thought to be related to reorganisations of ocean circulation (Broecker, 1998). The oscillations comprise reversals of a transport of heat from the Southern Ocean to the North Atlantic which has been hypothesised to be driven by alternations in the intensity of deep water formation between the North Atlantic and the Southern Ocean (Seidov and Maslin, 2001; Stocker and Johnsen, 2003).

The $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})$ proxy has already been used to demonstrate variability of deep water formation in the North Atlantic associated with The Younger Dryas and Heinrich event I (McManus et al., 2004; Gherardi et al., 2005). Further high resolution studies of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})$ in the North Atlantic covering MIS 3 and MIS 4 would show whether Dansgaard-Oeschger events are associated with changes in NADW production. To test the seesaw hypothesis, that reduction of NADW formation will be compensated by increased AABW production, the past production of AABW must be assessed. Such an assessment has already been made in Chapter 4, showing no change in AABW production over the past 140 ka. The data in Chapter 4 is, however, low resolution and, as such, short-lived changes may have been missed though mixing of the sediment by bioturbation.

It is possible that the increased deep water production was AAIW rather than AABW which is expected in from a zonally averaged model of ocean circulation (Mar-

chal et al., 1999). Such changes in AAIW would be ‘invisible’ to the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})$ proxy at WIND 28K because AAIW is too high in the water column. Another possibility is that any increased AABW production does not affect the Indian Ocean, instead flowing into the Pacific and/or Atlantic basins. Any future attempt to use the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})$ proxy to constrain deep water formation in the Southern Ocean must use cores from north of the opal belt so as not to be biased by changes in particle type. Cores from beneath the opal belt would also be useful to constrain changes in the scavenging regimes as water moves from the Southern Ocean to the cores to the north, so that changes in circulation may be resolved from changes in particle type and flux. Furthermore by measuring a suite of cores covering depth from >4000 m to ~ 1500 m would allow changes in AABW and AAIW to be investigated.

6.3.3 Longer timescales and quantification

As well as investigating millennial scale variations in circulation, such as those associated with Heinrich events in the North Atlantic, the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy has been shown to be useful on orbital timescales. While the half-life of ^{231}Pa limits the use of $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ beyond the penultimate glacial, much could be gained by extending the McManus et al. (2004) and Gherardi et al. (2005) records back to cover a full glacial-interglacial cycle. Confirmation of the sortable silt record of AABW inflow into the Pacific (Hall et al., 2001), if only for the last 150 ka, is a worthwhile goal, both for better understanding of the two proxies and investigating whether the flow speed variations are regionally representative.

To fully understand past ocean circulation in any specific region, using the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ proxy, it is important to use a suite of cores at depths covering the whole water column because the $(^{231}\text{Pa}_{\text{xs}}/^{230}\text{Th}_{\text{xs}})^0$ preserved in sediments is representative of the bottommost water mass. To recover quantitative information about past flow it is also necessary to measure at least one core from downstream

along the flow path of the water to determine what the ‘initial’ ($^{231}\text{Pa}/^{230}\text{Th}$) of the bottom water was. Knowledge of the type and amount of particle productivity is also required to produce a quantitative estimate of flow. This information might be provided by a combination of sedimentology, mass accumulation rates, and independent productivity proxies such as biogenic barite or authigenic uranium.

Bibliography

- Adkins, J. F., Cheng, H., Boyle, E. A., Druffel, E. R. M., and Edwards, R. L. (1998). Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 14,400 years ago. *Science*, 280:725–728.
- Anderson, R. F. (1982). Concentration, vertical flux, and remineralisation of particulate uranium in seawater. *Geochimica Cosmochimica Acta*, 46:1293–1299.
- Anderson, R. F., Bacon, M., and Brewer, P. G. (1983a). Removal of ^{230}Th and ^{231}Pa from the open ocean. *Earth and Planetary Science Letters*, 62(1):7 – 23.
- Anderson, R. F., Bacon, M. P., and Brewer, P. G. (1983b). Removal of ^{230}Th and ^{231}Pa at ocean margins. *Earth and Planetary Science Letters*, 66:73–90.
- Anderson, R. F. and Fleer, A. P. (1982). Determination of natural actinides and plutonium in marine particulate material. *Analytical Chemistry*, 54(7):1142.
- Anderson, R. F., Fleisher, M. Q., and Leheray, A. P. (1989). Concentration, oxidation state and, particle flux of uranium in the Black Sea. *Geochim. Cosmochim. Acta*, 53:2215–2224.
- Anderson, R. F., Kumar, N., Mortlock, R. A., Froelich, P. N., Kubik, P., Ditttrich-Hannen, B., and Suter, M. (1998). Late-quaternary changes in productivity of the Southern Ocean. *Journal of Marine Systems*, 17(1-4):497–514. TY - JOUR.
- Anderson, R. F., Lao, Y., Broecker, W. S., Trumbore, S. E., Hofmann, H. J., and Wolfli, W. (1990). Boundary scavenging in the Pacific Ocean: a comparison of ^{10}Be and ^{231}Pa . *Earth and Planetary Science Letters*, 96:287–304.
- Argonne National Laboratory, E. (2005a). Human Health Fact Sheet: Natural radionuclides. Technical report.
- Argonne National Laboratory, E. (2005b). Human Health Fact Sheet: Transuranic radionuclides. Technical report.
- Bacon, M. P. (1984). Glacial to interglacial changes in carbonate and clay sedimentation in the Atlantic Ocean estimated from ^{230}Th measurements. *Isotope Geoscience*, 2(97-111).

- Bacon, M. P. and Anderson, R. F. (1982). Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. *Journal of Geophysical Research*, 87:2045–2056.
- Bacon, M. P., Cochran, J. K., Hirschberg, D., Hammar, T. R., and Fler, A. P. (1996). Export flux of carbon at the equator during the eqpac time-series cruises estimated from ^{234}Th measurements. *Deep Sea Research Part II: Topical Studies in Oceanography*, 43(4-6):1133–1153.
- Bacon, M. P., Huh, C.-A., Fler, A. P., and Deuser, W. G. (1985). Seasonality in the flux of natural radionuclides and plutonium in the deep Sargasso Sea. *Deep Sea Research*, 32:273–286.
- Bard, E., Fairbanks, R. G., Hamelin, B., Zindler, A., and Huang, C. T. (1991). Uranium-234 anomalies in corals older than 150,000 years. *Geochimica et Cosmochimica Acta*, 55:2385–2390.
- Bateman, H. (1910). Solution of a system of differential equations occurring in the theory of radioactive transformations. *Proceedings of the Cambridge Philosophical Society*, 15:423.
- Belshaw, N. S., Freedman, P. A., O’Nions, R. K., Frank, M., and Guo, Y. (1998). A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes. *International Journal of Mass Spectrometry*, 181(1-3):51–58.
- Berger, W. H. and Winterer, E. L. (1974). Plate stratigraphy and the fluctuating carbonate line. In Hsu, K. J. and Jenkyns, H. C., editors, *Pelagic sediments: on land and under the sea*, volume 1 of *Special publication of the international association of sedimentologists*, pages 11–48. Blackwell Scientific, Oxford.
- Bianchi, G., Hall, I. R., McCave, I. N., and Joseph, L. (1999). Measurement of the sortable silt current speed proxy using the sedigraph 5100 and coulter multisizer ii: precision and accuracy. *Sedimentology*, 46:1001–1014.
- Bigg, G. (2003). *The oceans and climate*. Cambridge University Press, 2nd edition.
- Blunier, T., Chappellaz, J., Schwander, J., Dallenbach, A., Stauffer, B., Stocker, T. F., Raynaud, D., Jouzel, J., Clausen, H. B., Hammer, C. U., and Johnsen, S. J. (1998). Asynchrony of Antarctic and Greenland climate change during the last glacial period. *Nature*, 394(6695):739–743.
- Bodu, R., Bouziges, H., Morin, N., and Pfiffelmann, J. (1972). Sur l’existence d’anomalies isotopiques rencontrées dans l’uranium du Gabon. *Compte Rendu de l’Académie des Sciences, Paris*, 275:1731.
- Boebel, O., Rossby, T., Lutjeharms, J., Zenk, W., and Barron, C. (2003). Path and variability of the Agulhas Return Current. *Deep-Sea Research II*, 50:35–56.

- Bourdon, B., Joron, J.-L., and Allegre, C. J. (1999). A method for ^{231}Pa analysis by thermal ionisation mass spectrometry in silicate rocks. *Chemical Geology*, 157:147–151.
- Bourdon, B., Turner, S., Henderson, G. M., and Lnuudstrom, C. C. (2003). Introduction to U-series geochemistry. In *Reviews in Mineralogy and Geochemistry "Uranium Series Geochemistry"*, volume 53, pages 1–21. MSA.
- Boyer, T. P., Stephens, C., Antonov, J. I., Conkright, M. E., Locarnini, R. A., O'Brien, T. D., and Garcia, H. E. (2002). Salinity. In Levitus, S., editor, *World Ocean Atlas 2001*, volume 2 of *NOAA Atlas NESDIS 50*, page 165 pp. U.S. Government Printing Office, Wash., D.C.
- Boyle, E. (1986). Paired Cd and $\delta^{13}\text{C}$ data from benthic foraminifera: implications for ocean circulation, phosphorus, and atmospheric CO_2 . *Geochim. Cosmochim. Acta*, 50:265–276.
- Boyle, E. A. and Keigwin, L. D. (1981). Deep circulation of the North Atlantic over the last 200,000 years: geochemical evidence. *Science*, 218(4574):784–787.
- Brix, H. and Gerdes, R. (2003). North atlantic deep water and antarctic bottom water: Their interaction and influence on the variability of the global ocean circulation. *Journal of Geophysical Research-Oceans*, 108(C2):3022.
- Broecker, W. S. (1991). The Great Ocean Conveyor. *Oceanography*, 4(2):79–89.
- Broecker, W. S. (1998). Paleoocean circulation during the last deglaciation; a bipolar seesaw? *Paleoceanography*, 13(2):119–121.
- Broecker, W. S., Mix, A., Andree, M., and Oeschger, H. (1984). Radiocarbon measurements on coexisting benthic and planktonic foraminifera shells: potential for reconstructing ocean ventilation times over the past 20000 years. *Nuclear Instruments and Methods in Physics Research*, B5:331–339.
- Broecker, W. S. and Peng, T.-H. (1992). Interhemispheric transport of carbon dioxide by ocean circulation. *Nature*, 356(6370):587.
- Bryden, H. L. and Beal, L. M. (2001). Role of the Agulhas Current in Indian Ocean circulation and associated heat and freshwater fluxes. *Deep Sea Res I*, 48(1821–1845).
- Bryden, H. L. and Imawaki, S. (2001). Ocean heat transport. In Siedler, G., Church, J., and Gould, J., editors, *Ocean Circulation and Climate*, volume 6.1, page 455474. Academic, London.
- Burnett, W. C. and Yeh, C. C. (1995). Separation of protactinium from geological materials via extraction chromatography. *Radioactivity & Radiochemistry*, 6(4):22–32.

- Carissimo, B. C., Oort, A. H., and Vonder Haar, T. H. (1985). Estimating the meridional energy transports in the atmosphere and ocean. *Journal of Physical Oceanography*, 15:82–91.
- Chase, Z. and Anderson, R. F. (2004). Comment on “On the importance of opal, carbonate, and lithogenic clays in scavenging and fractionating ^{230}Th , ^{231}Pa and ^{10}Be in the ocean” by S. Lou and T.-L. Ku. *Earth and Planetary Science Letters*, 220:213–222.
- Chase, Z., Anderson, R. F., Fleisher, M. Q., and Kubik, P. W. (2002). The influence of particle composition and particle flux on scavenging of Th, Pa and Be in the ocean. *Earth and Planetary Science Letters*, 204:215–229.
- Chase, Z., Anderson, R. F., Fleisher, M. Q., and Kubik, P. W. (2003). Scavenging of ^{230}Th , ^{231}Pa and ^{10}Be in the southern ocean (sw pacific sector): The importance of particle flux and advection. *Deep Sea Research II*, 50:739–768.
- Chen, J. H., Edwards, R. L., and Wasserburg, G. J. (1986). ^{238}U , ^{234}U and ^{232}Th in seawater. *Earth and Planetary Science Letters*, 80(241–251).
- Cheng, H., Edwards, R. L., Hoff, J., Gallup, C. D., Richards, D. A., and Asmerom, Y. (2000). The half lives of uranium-234 and thorium-230. *Chemical Geology*, 169:17–33.
- Choi, M., Francois, R., Sims, K., Bacon, M., Brown-Leger, S., Fler, A. P., Ball, L., Schneider, D., and Pichat, S. (2001). Rapid determination of ^{230}Th and ^{231}Pa in seawater by desolvated micro-nebulization inductively coupled magnetic sector mass spectrometry. *Marine Chemistry*, 76:99–112.
- Clarke, R. A. and Giscard, J. C. (1983). The formation of labrador sea-water.1. large-scale processes. *Journal of Physical Oceanography*, 13(10):1764–1778.
- Clegg, S. L., Bacon, M., and Whitfield, M. (1991). Application of a generalized scavenging model to thorium isotope and particle data at equatorial and high-latitude sites in the Pacific Ocean. *Journal of Geophysical Research, C, Oceans*, 96(11):20655–20670.
- Clegg, S. L. and Whitfield, M. (1990). A generalized model for the scavenging of trace metals in the open ocean - i. particle cycling. *Deep Sea Research*, 37(5):809–832.
- Clegg, S. L. and Whitfield, M. (1991). A generalized model for scavenging of trace metals in the open ocean - ii. Thorium scavenging. *Deep Sea Research*, 38(1):91–120.
- Cochran, J. K. (1992). The oceanic chemistry of the uranium and thorium-series nuclides. In Ivanovich, M. and Harmon, R., editors, *Uranium series disequilibrium-application to environmental problems: applications to earth, marine and environmental sciences*, 2nd edition, pages 334–395. Oxford University Press.

- Colling, A., Brown, E., Park, D., Phillips, J., Rothery, D., and Wright, J. (2001). *Ocean Circulation*. The Open University, Oceanography Series. Butterworth Heinemann.
- Conkright, M. E., Garcia, H. E., O'Brien, T. D., Locarnini, R. A., Boyer, T. P., Stephens, C., and Antonov, J. I. (2002). *Nutrients*, volume 4. Wash., D.C.
- Coriolis, G.-G. (1835). Sur les equations du mouvement relatif des systemes de corps. *J. de l'Ecole royale polytechnique*, 15:144–154.
- DeBievre, P. J. and Debus, G. H. (1965). Precision mass spectrometric isotope dilution analysis. *Nucl. Instrum. Meth.*, 32:224–8.
- Dezileau, L., Bareille, G., and Reyss, J. L. (2003). The $^{231}\text{Pa}/^{230}\text{Th}$ ratio as a proxy for past changes in opal fluxes in the Indian sector of the Southern Ocean. *Marine Chemistry*, 81(3-4):105–135.
- Donohue, K. A. and Toole, J. M. (2003). A near-synoptic survey of the southwest indian ocean. *Deep Sea Research*, Part II: Topical Studies in Oceanography. 50(12-13):1893–1931. Serial GeoRef, Copyright 2003, American Geological Institute. Reference includes data from CAPCAS, Elsevier Scientific Publishers, Amsterdam, Netherlands 0967-0645.
- Duplessy, J.-C., Shackleton, N., Matthews, R., Prell, W., Ruddiman, W., Caralp, M., and Hendy, C. (1984). ^{13}C record of benthic foraminifera in the last interglacial ocean: implications for the carbon cycle and the global deep water circulation. *Quaternary Research*, 21:225–243.
- Edwards, R. L., Chen, J. H., Ku, T. L., and Wasserburg, G. J. (1987). Precise timing of the last interglacial period from mass spectrometric determination of ^{230}Th in corals. *Science*, 236:1547–1553.
- Eikenberg, J., Bajo, S., Zumsteg, I., Ruethi, M., and Beer, H. (2001). Separation and measuerment techniques for the determination of ^{238}Th , ^{230}Th and ^{232}Th in various matricies. *Radiation Protction Dosimetry*, 97(2):127–131.
- Fanghanel, T. and Neck, V. (2002). Aquatic chemistry and solubility phenomena of actinide oxides/hydroxides. *Pure and Applied Chemistry*, 74(10):1895–1907.
- Francois, R., Altabet, M. A., Yu, E.-F., Sigman, D. M., Bacon, M. P., Frank, M., Bohrmann, G., Bareille, G., and Labeyrie, L. D. (1997). Contribution of Southern Ocean surface-water stratification to low atmospheric CO_2 concentrations during the last glacial period. *Nature*, 389:929–935.
- Friedlander, G. and Kennedy, J. W. (1995). *Nuclear and Radiochemistry*. John Wiley, New York.
- Gallup, C. D., Edwards, R. L., and Johnson, R. G. (1994). The timing of high sea levels over the past 200,000 years. *Science*, 263:796–800.

- Ganachaud, A. and Wunsch, C. (2000). Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data. *Nature (London)*, 408(6811):453–457.
- Gascard, J. C. and Clarke, R. A. (1983). The formation of labrador sea-water. 2. mesoscale and smaller-scale processes. *Journal of Physical Oceanography*, 13(10):1779–1797.
- Geibert, W. and Usbeck, R. (2004). Adsorption of thorium and protactinium onto different particle types: Experimental findings. *Geochimica et cosmochimica Acta*, 68(7):1489–1501.
- Gherardi, J. M., Labeyrie, L., McManus, J. F., Francois, R., Skinner, L. C., and Cortijo, E. (2005). Evidence from the Northeastern Atlantic basin for variability in the rate of the meridional overturning circulation through the last deglaciation. *Earth and Planetary Science Letters*, 240(3-4):710–723.
- Gillson, G. R., Douglas, D. J., Fulford, J. E., Halligan, K. W., and Tanner, S. D. (1988). Nonspectroscopic interelement interferences in inductively coupled mass-spectrometry. *Analytical Chemistry*, 60:1472.
- Girard, J. (2005). *Principles of Environmental Chemistry*. Jones and Bartlett.
- Goldstein, S. J., Lea, D. W., Chakraborty, S., Kashgarian, M., and Murrell, M. T. (2001). Uranium-series and radiocarbon geochronology of deep-sea corals; implications for Southern Ocean ventilation rates and the oceanic carbon cycle. *Earth and Planetary Science Letters*, 193(1-2):167–182.
- Goldstein, S. J., Murrell, M. T., and Williams, R. W. (1989). Half-life of ^{229}Th . *Physical Review C*, 40(6):2793–2795.
- Goldstein, S. J., Rodriguez, J. M., and Lujan, N. (1997). Measurement and application of uranium isotopes for human and environmental monitoring. *Health Physics*, 72(1):10–18.
- Gordon, A. L. (1982). Weddell Deep Water variability. *Journal of Marine Research*, 40:199–217.
- Gordon, A. L. (1985). Indian-Atlantic transfer of thermocline water at the Agulhas retroflexion. *Science*, 227:1030–1033.
- Gordon, A. L. (1986). *Southern Ocean Atlas*. A. A. Balkema, Rotterdam.
- Gründlingh, M. L. (1985). Occurrence of Red Sea Water in the southwestern Indian Ocean. *Journal of Physical Oceanography*, 15:207–212.
- Guo, L., Santschi, P. H., and Baskaran, M. (1997). Interactions of thorium isotopes with colloidal organic matter in oceanic environments. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 120(1-3):255–271.

- Guo, Laodong. Chen, M. and Gueguen, C. (2002). Control of Pa/Th ratio by particulate chemical composition in the ocean. *Geophys. Res. Lett.*, 29(20):1961.
- Hall, I. R., McCave, N. I., Shackleton, N. J., Weedon, G. P., and Harris, S. E. (2001). Intensified deep Pacific inflow and ventilation in pleistocene glacial times. *Nature*, 412:809–812.
- Henderson, G., Atkinson, C., and Thomas, A. L. (In Prep). $^{234}\text{U}/^{238}\text{U}$ variability in the Black Sea and eastern Mediterranean. *Earth Planet. Sci. Lett.*
- Henderson, G., Slowey, N., and Fleisher, M. Q. (2001). U-Th dating of carbonate platform and slope sediments. *Geochimica et Cosmochimica Acta*, 65(16):2757–2770.
- Henderson, G. M. (2002a). New oceanic proxies for paleoclimate. *Earth and Planetary Science Letters*, 203:1–13.
- Henderson, G. M. (2002b). Seawater ($^{234}\text{U}/^{238}\text{U}$) during the last 800 thousand years. *Earth and Planetary Science Letters*, 199(1-2):97–110.
- Henderson, G. M. and Anderson, R. F. (2003). The U-series toolbox for paleoceanography. In *Reviews in Mineralogy and Geochemistry "Uranium Series Geochemistry"*, volume 53, pages 493 – 531. MSA.
- Henderson, G. M., Heinze, C., Anderson, R. F., and Winguth, A. M. E. (1999). Global distribution of the ^{230}Th flux to the ocean sediments constrained by GCM modeling. *Deep Sea Research I*, 46:1861–1893.
- Heumann, K. G., Gallus, S. M., Radlinger, G., and Vogl, J. (1998). Precision and accuracy in isotope ratio measurements by plasma source mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 13:1001–1008.
- Holden, N. E. (1989). Total and spontaneous fission half-lives for uranium, plutonium, americium, and curium nuclides. *Pure & Applied Chemistry*, 61(8):1483–1504.
- Holden, N. E. (1990). Total half-lives of selected nuclides. *Pure & Applied Chemistry*, 62(5):941–958.
- Honeyman, B. D., Balistrieri, L. S., and Murray, J. W. (1998). Oceanic trace metal scavenging: the importance of particle concentration. *Deep Sea Research*, 35(2):227–246.
- Huh, C.-A. (1995). Th isotopes in the Santa Monica Basin: Temporal variation, long-term mass balance and rate constants. *Journal of Oceanography*, 15:363–373.
- Hunter, K. A., Hawke, D. J., and Lee, K. C. (1988). Equilibrium adsorption of thorium by metal oxides in marine electrolytes. *Geochim. Cosmochim. Acta*, 52(3):627–636.

- Jaffey, A. H., Flynn, K. F., Glendenin, L. E., Bentley, W. C., and Essing, A. M. (1971). Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U . *Physics Review C4*, page 1889.
- Keeling, C. D. and Heimann, M. (1986). Meridional eddy diffusion model of the transport of atmospheric carbon dioxide. 2. mean annual carbon cycle. *J. geophys. Res.*, 91:7782.
- Kigoshi, K. (1971). Alpha-recoil thorium-234: Dissolution into water and the uranium-234/uranium-238 disequilibrium in nature. *Science*, 173(3991):47–48.
- Klinkhammer, G. P. and Palmer, M. R. (1991). Uranium in the oceans - where it goes and why. *Geochimica Et Cosmochimica Acta*, 55(7):1799–1806.
- Ku, T. L. (1966). *Uranium series disequilibrium in deep sea sediments*. Ph.d, Columbia.
- Ku, T. L., Knauss, K., and Matthieu, G. (1977). Uranium in the open ocean: concentration and isotopic composition. *Deep Sea Res*, 11:1005–1018.
- Kumar, N., Anderson, R. F., Mortlock, R. A., Froelich, P. N., Kubik, P., Dittrich, H. B., and Suter, M. (1995). Increased biological productivity and export production in the glacial Southern Ocean. *Nature (London)*, 378(6558):675–680.
- Kumar, N., Gwiazda, R., Anderson, R. F., and Froelich, P. N. (1993). $^{231}\text{Pa}/^{230}\text{Th}$ ratios in sediments as a proxy for past changes in Southern Ocean productivity. *Nature (London)*, 362(6415):45–48.
- Langmuir, D. (1978). Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta*, 42:547–569.
- Layne, G. D. and Sims, K. W. (2000). Secondary ion mass spectrometry for the measurement of $^{232}\text{Th}/^{230}\text{Th}$ in volcanic rocks. *International Journal of Mass Spectrometry*, 203:187–198.
- Li, Y.-H. (2005). Controversy over the relationship between major components of sediment-trap materials and the bulk distribution coefficients of ^{230}Th , ^{231}Pa , and ^{10}Be . *Earth and Planetary Science Letters*, 233:1–7.
- Lide, D. R. (1998). *CRC Handbook of Chemistry and Physics*. Crc Pr I Llc, 79 edition.
- Lieber, W. and Leyerzapf, H. (1986). German silver: an historical perspective on silver mining in Germany. In Wilson, W. E., editor, *Silver*, volume 17 of *The Mineralogical Record*, pages 3–18.
- Ludwig, K. R., Simmons, K. R., Szabo, B. J., Winograd, I. J., Landwehr, J. M., Riggs, A. C., and Hoffman, R. J. (1992). Mass-spectrometric ^{230}Th - ^{234}U - ^{238}U dating of the Devils Hole calcite vein. *Science*, 258(5080):284–287.

- Lundstrom, C. C., Williams, Q., and Gill, J. B. (1998). Investigating solid mantle upwelling rates beneath mid-ocean ridges using U-series disequilibria, i: a global approach. *Earth and Planetary Science Letters*, 157:151–165.
- Luo, S. and Ku, T.-L. (1999). Oceanic $^{231}\text{Pa}/^{230}\text{Th}$ ratio influenced by particle composition and remineralization. *Earth and Planetary Science Letters*, 167:183–195.
- Luo, S. and Ku, T.-L. (2004). On the importance of opal, carbonate, and lithogenic clays in scavenging and fractionating ^{230}Th , ^{231}Pa and ^{10}Be in the ocean. *Earth and Planetary Science Letters*, 220(1-2):201–211. TY - JOUR.
- Lyle, M., Mitchell, N., Pisias, N. G., Mix, A. C., Martinez, J. I., and Paytan, A. (2005). Do geochemical estimates of sediment focusing pass the sediment test in the equatorial Pacific? *Paleoceanography*, 20(PA1005).
- Mangini, A., Jung, M., and Laukenmann, S. (2001). What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geology*, 177:63–78.
- Marcantonio, F., Anderson, R. F., Higgins, S., Fleisher, M. Q., Stute, M., and Schlosser, P. (2001). Abrupt intensification of the SW Indian Ocean monsoon during the last deglaciation; constraints from Th, Pa, and He isotopes. *Earth and Planetary Science Letters*, 184(2):505–514.
- Marchal, O., Francois, R., Stocker, T. F., and Joos, F. (2000). Ocean thermohaline circulation and sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ ratio. *Paleoceanography*, 15(6):625–641.
- Marchal, O., Stocker, T. F., and Joos, F. (1999). Physical and biogeochemical responses to freshwater-induced thermohaline variability in a zonally averaged ocean model. In Clark, P. U., Webb, R. S., and Keigwin, L. D., editors, *Mechanisms of global change at millennial time scales*, volume 112 of *Geophysical Monograph Series*, pages 263–284. American Geophysical Union, Washington DC.
- Marshall, J. and Schott, F. (1999). Open ocean deep convection: Observations model and theory. *Reviews of Geophysics*, 37(1-64).
- McCave, I. N., Kiefer, T., Thornalley, D. J. R., and Elderfield, H. (2004). Deep flow in the Madagascar-Mascarene Basin over the last 150 000 years. *Proceedings of the Royal Society*, 363:1–19.
- McCave, I. N., Manighetti, B., and Robinson, S. G. (1995). Sortable silt and fine sediment size/composition slicing; parameters for palaeocurrent speed and palaeoceanography. In *The biogeochemical ocean flux study*, volume 10; 3, pages 593–610. American Geophysical Union, Washington, DC, United States.
- McCave, I. N. and Tucholke, B. E. (1986). Deep current-controlled sedimentation in the western North Atlantic. In Vogt, P. R. and Tucholke, B. E., editors, *The geology of North America*, volume M, The western North Atlantic Region. Geological Society of America.

- McManus, J. F., Francois, R., Gherardi, J. M., Keigwin, L., and Brown-Leger, S. (2004). Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes. *Nature*, 428:834–837.
- McManus, J. F., Francois, R., Gherardi, J. M., and Nuwer, J. (2002). Variable rates of ocean circulation from sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ during the last ice age. In *Goldschmidt Conference Abstracts*, page A503.
- Michel, E., Labeyrie, L. D., Duplessy, J. C., Gorfti, N., Labracherie, M., and Turon, J. L. (1995). Could deep subantarctic convection feed the world deep basins during the last glacial maximum. *Paleoceanography*, 10(5):927–942.
- Moore, W. S. (1967). Amazon and Mississippi river concentration of uranium, thorium, and radium isotopes. *Earth and Planetary Science Letters*, 2:231–234.
- Moran, S. B., Charette, M. A., Hoff, J. A., Edwards, R. L., and Landing, W. M. (1997). Distribution of ^{230}Th in the Labrador Sea and its relation to ventilation. *Earth and Planetary Science Letters*, 150:151–160.
- Moran, S. B., Shen, C. C., Edwards, R. L., Edmonds, H. N., Scholten, J. C., Smith, J. N., and Ku, T. L. (2005). ^{231}Pa and ^{230}Th in surface sediments of the Arctic Ocean: Implications for $^{231}\text{Pa}/^{230}\text{Th}$ fractionation, boundary scavenging and advective export. *Earth and Planetary Science Letters*, 234(1-2):235–248.
- Moran, S. B., Shen, C. C., Weinstein, S. E., Hettinger, L. H., Hoff, J. H., Edmonds, H. N., and Edwards, R. L. (2001). Constraints on the deep water age and particle flux in the equatorial and South Atlantic Ocean based on seawater ^{231}Pa and ^{230}Th data. *Geophysical Research Letters*, 28(18):3437–2440.
- Morford, J. L. and Emerson, S. (1999). The geochemistry of redox sensitive trace metals in sediments. *Geochim. Cosmochim. Acta*, 63(11/12):1735–1750.
- Morgenstern, A., Apostolidis, C., and Mayer, K. (2002). Age determination of highly enriched uranium: separation and analysis of ^{231}Pa . *Analytical Chemistry*, 74(21):5513–5516.
- Mortlock, R., Fairbanks, R., Chiu, T., and Rubenstone, J. (2005). Th-230/U-234/U-238 and Pa-231/U-235 ages from a single fossil coral fragment by multi-collector magnetic-sector inductively coupled plasma mass spectrometry. *Geochimica et Cosmochimica Acta*, 69(3):649–657.
- Niven, S. E. H. and Moore, R. M. (1993). Thorium sorption in seawater suspensions of aluminium oxide particles. *Geochim. Cosmochim. Acta*, 57(10):2169–2179.
- Nour, S., Burnett, W. C., and Horwitz, E. P. (2002). ^{234}Th analysis of marine sediments via extraction chromatography and liquid scintillation counting. *Applied Radiation and Isotopes*, 57:235–241.

- Nozaki, Y. and Nakanishi, T. (1985). ^{231}Pa and ^{230}Th profiles in the open ocean water column. *Deep-Sea Res*, 32:1209–1220.
- Nozaki, Y., Yang, H. S., and Yamada, M. (1987). Scavenging of thorium in the ocean. *Journal of Geophysical Research*, 92(772-778).
- Osborne, N. S., Stimson, H. F., and C., G. D. (1937). Calorimetric determination of the thermodynamic properties of saturated water in both the liquid and gaseous states from 100 to 374 °C. *J. Res. Natl. Bur. Stand*, 18(389-447).
- Parish, T. R. (1988). Surface winds over the antarctic continent - a review. *Reviews of Geophysics and Space Physics*, 26:169–180.
- Pichat, S., Sims, K. W. W., Ball, L. A., and Francois, R. Sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) determination of ^{231}Pa , ^{230}Th , ^{232}Th and ^{238}U : methodology, optimisation, precautions, and corrections. In Press.
- Pickett, D. A., Murrell, M. T., and Williams, R. W. (1994). Determination of femtogram quantities of protactinium in samples by thermal ionization mass spectrometry. *Analytical Chemistry*, 66:1044–1049.
- Pillsbury, J. The Gulf Stream: general historical account of the Gulf Stream and its investigation up to the time of Franklin to those made by the U.S. coast survey. In *The Coast and Geodetic Survey Annual Report 1890*, chapter Appendix 10. US Coastguard.
- Pourmand, A., Marcantonio, F., and Schulz, H. (2004). Variations in productivity and aeolian fluxes in the northeastern Arabian Sea during the past 110 ka. *Earth and Planetary Science Letters*, 221:39–54.
- Quigley, M., Honeyman, B. D., and Santschi, P. (1996). Thorium sorption in the marine environment: equilibrium partitioning at the hematite/water interface, sorption/desorption kinetics and particle tracing. *Aquatic Geochemistry*, 1:277–301.
- Quigley, M., Santschi, P., Hung, C.-C., L., G., and Honeyman, B. D. (2002). Importance of polysaccharides for ^{234}Th complexation to marine organic matter. *Limnology and Oceanography*, 47(2):367–377.
- Ragueneau, O., Treguer, P., Leynaert, A., Anderson, R. F., Brezinski, M. A., DeMaster, D. J., Dugdale, R. C., Dymond, J., Fisher, G., Francois, R., Heinze, C., Maier-Reimer, E., Martin-Jezequel, V., Nelson, D. M., and Queguiner, B. (2000). A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. *Global and Planetary Change*, 26:317–365.
- Raven, J., Caldeira, K., Elderfield, H., Hoegh-Guldberg, O., Liss, P., Riebesell, U., Shepherd, J., Turley, C., and Watson, A. (2005). Ocean acidification due to increasing atmospheric carbon dioxide. Technical report, The Royal Society.

- Regelous, M., Turner, S. P., Elliott, T. R., Rostami, K., and Hawkesworth, C. J. (2004). Measurement of femtogram quantities of protactinium in silicate rock samples by multicollector inductively coupled plasma mass spectrometry. *Analytical Chemistry*, 76:3584–3589.
- Robert, J., Miranda, C. F., and Muxart, R. (1969). Mesure de la periode du protactinium-231 par microcalorimetrie. *Radiochimica Acta*, 11:104–108.
- Robinson, L., Belshaw, N., and Henderson, G. (2004a). U and Th concentrations and isotope ratios in modern carbonates and waters from the Bahamas. *Geochim. Cosmochim. Acta*, 68,(8):1777–1789.
- Robinson, L., Henderson, G., Hall, L., and Matthews, I. (2004b). Climatic control of riverine and seawater uranium-isotope ratios. *Science*, 305:851–854.
- Robinson, L. F. (2003). *Pleistocene climate chronology and ocean circulation in the Bahamas using U-series nuclides*. D.phil, Oxford University.
- Robinson, L. F., Henderson, G. M., and Slowey, N. C. (2002). U-Th dating of marine isotope stage 7 in Bahamas slope sediments. *Earth and Planetary Science Letters*, 196:175–187.
- Rosenthal, Y., Boyle, E. A., Labeyrie, L., and Oppo, D. (1995). Glacial enrichments of authigenic Cd and U in subantarctic sediments: A climatic control on the elements' oceanic budget? *Paleoceanography*, 10(3):395–414.
- Russell, W. A., Papantastassiou, D. A., and Tomborello, T. A. (1978). Ca isotope fractionation on the earth and other solar system materials. *Geochim. Cosmochim. Acta*, 42(8):1075–1090.
- Rutberg, R., Hemming, S., and Goldstein, S. (1998). Evidence for decreased NADW flux during glacial stages 2 and 4 from Nd isotopes in Southern Ocean sediments. *Mineralogical Magazine*, 62,(A):1304–5.
- Rutgers van der Loeff, M. M. and Berger, G. W. (1993). Scavenging of ^{230}Th and ^{231}Pa near the Antarctic Polar Front in the South Atlantic. *Deep-Sea Research*, Part I: Oceanographic Research Papers. 40(2):339–357.
- Rutherford, E. and Soddy, F. (1902). The radioactivity of thorium compounds. ii. the cause and nature of radioactivity. *Journal of the Chemical Society of London*, 81:837–860.
- Santschi, P., Murray, J. W., Baskaran, M., Benitez-Nelson, C. R., Guo, L., Hung, C.-C., Lamborg, C., Moran, S. B., Passow, U., and M., R.-B. (2005). Thorium speciation in seawater. *Marine Chemistry*, In Press.
- Sarmiento, J. L. and Toggweiler, R. (1984). A new model for the role of the oceans in determining atmospheric pCO_2 . *Nature*, 308:621.

- Scholten, J. C., Rutgers van der Loeff, M. M., and Michel, A. (1995). Distribution of ^{230}Th and ^{231}Pa in the water column in relation to the ventilation of the deep Arctic basins. *Deep Sea Research Part II: Topical Studies in Oceanography*, 42(6):1519–1531. TY - JOUR.
- Sclater, J. G., Jaupart, C., and Galson, D. (1980.). The heat flow through oceanic and continental crust and the heat loss of the earth. *Reviews of Geophysics and Space Physics*, 18(1):269–311.
- Seidov, D. and Maslin, M. (2001). Atlantic Ocean heat piracy and the bipolar climate see-saw during Heinrich and Dansgaard-Oeschger events. *Journal of Quaternary Science*, 16(4):321–328.
- Siddall, M., Rohling, E. J., Almogi-Labin, A., Hemleben, C., Meischner, D., Schmelzer, I., and Smeed, D. A. (2003). Sea-level fluctuations during the last glacial cycle. *Nature*, 423:853–858.
- Siddall, M., Stocker, T. F., Henderson, Gideon, M., Edwards, N. R., Muller, S. A., Joos, F., and Frank, M. (2005). $^{231}\text{Pa}/^{230}\text{Th}$ fractionation by ocean transport, biogenic particle flux and particle type. *Earth and Planetary Science Letters*, 237(1-2):135–155.
- Siegenthaler, U. and Wenk, T. (1984). Rapid atmospheric CO_2 variations and ocean circulation. *Nature*, 308:624.
- Sigman, D. M. and Boyle, E. A. (2000). Glacial/ interglacial variations in atmospheric carbon dioxide. *Nature (London)*, 407(6806):859–869.
- Sirinivasan, A., Top, Z., Schlosser, P., Hohmann, R., Iskandarani, M., Olson, D. B., Lupton, J. E., and Jenkins, W. J. (2004). Mantle ^3He distribution and deep circulation in the Indian Ocean. *Journal of Geophysical Research, C, Oceans*, 109:C06012.
- Sklodowska-Curie, M. (1903). *Recherches sur les Substances Radioactives*. Docteur `es sciences physiques, Faculté des Sciences de Paris.
- Stephens, G. L., Campbell, G. C., and Vonder Haar, T. H. (1981). Earth radiation budgets. *Journal of Geophysical Research*, 86:9737–9760.
- Stewart, R. H. (1997). *Introduction to Physical Oceanography*. < [http : //oceanworld.tamu.edu/resources/ocng_textbook/contents.html](http://oceanworld.tamu.edu/resources/ocng_textbook/contents.html) >.
- Stirling, C. H., Esat, T. M., Mcculloch, M. T., and Lambeck, K. (1995). High-precision U-series dating of corals from Western-Australia and implications for the timing and duration of the last interglacial. *Earth and Planetary Science Letters*, 135(1-4):115–130.
- Stirling, C. H., Halliday, A. N., and Porcell, D. (2005). In search of live Cm-247 in the early solar system. *Geochimica Et Cosmochimica Acta*, 69(4):1059–1071.

- Stocker, T. F. (1998). Climate change - The seesaw effect. *Science*, 282(5386):61–62.
- Stocker, T. F. and Johnsen, S. J. (2003). A minimum thermodynamic model for the bipolar seesaw. *Paleoceanography*, 18(4):1087.
- Stommel, H. (1958). The abyssal circulation. *Deep-Sea Research*, 5:80–82.
- Stossel, A., Kim, S.-J., and Drijfhout, S. (1998). The impact of Southern Ocean sea ice in a global ocean model. *Journal of Physical Oceanography*, 28(10):1999–2018.
- Suman, D. O. and Bacon, M. P. (1989). Variations in holocene sedimentation in the north american basin determined from ^{230}Th measurements,. *Deep Sea Research*, 36:869–878.
- Sverdrup, H. U., Johnson, M. W., and Fleming, R. H. (1942). *The oceans, their physics, chemistry, and general biology*. Prentice & Hall, New York.
- Swallow, J. C. and Pollard, R. T. (1988). Flow of bottom water through the madagascar basin. *Deep Sea Research*, 35:1437–1440.
- Taylor, S. R. (1964). Abundance of chemical elements in the continental crust: a new table. *Geochim. Cosmochim. Acta*, 28:1273–1286.
- Thomas, A. L., Henderson, G. M., and Robinson, L. F. (2006). The interpretation of a paleo-circulation proxy: $^{231}\text{Pa}/^{230}\text{Th}$ measurements in the south-western Indian Ocean. *Earth and Planetary Science Letters*, 241(3-4):493–504.
- Thompson, W. G. and Goldstein, S. (2005). Open-system coral ages reveal persistent suborbital sea-level cycles. *Science*, 308:401–404.
- Timm, B., Chandler, T., Burnett, W. C., and Schultz, M. (2002). Use of eichrom resins for bioassay Pa-231. Technical report, General Engineering Laboratories.
- Tomczak, M. and Godfrey, J. S. (2002). *Regional oceanography: An introduction*.
- Toole, J. M. and Warren, B. A. (1993). A hydrographic section across the subtropical South Indian Ocean. *Deep-Sea Research Part I-Oceanographic Research Papers*, 40(10):1973–2019. ME287 DEEP-SEA RES PT I-OCEANOGRAPHIC RES.
- Usman, K. and MacMahon, T. D. (2000). Determination of the half-life of ^{233}Pa . *Applied Radiation and Isotopes*, 52:585–589.
- Visbeck, M., Gordon, A., Smethie, B., Schlosser, P., Toole, J., Huber, B., and Krahnemann, G. (2001). The CORC/ARCHES observing system for Weddell Sea Deep and Bottom Water variability. *Exchanges*, 22.
- Vogler, S., Scholten, J., van, d. L. M. R., and Mangini, A. (1998). ^{230}Th in the eastern North Atlantic: the importance of water mass ventilation in the balance of ^{230}Th . *Earth and Planetary Science Letters*, 156(1-2):61–74.

- Walter, H. J., Rutgers van de Loeff, M. M., and Hoeltzen, H. (1997). Enhanced scavenging of ^{231}Pa relative to ^{230}Th in the South Atlantic south of the Polar Front: Implications for the use of the $^{231}\text{Pa}/^{230}\text{Th}$ as a paleoproductivity proxy. *Earth and Planetary Science Letters*, 149:85–100.
- Warren, B. A. (1981). Deep circulation of the world ocean. In Warren, B. A. and Wunch, C., editors, *Evolution of physical oceanography*, pages 6–42. MIT Press, Cambridge(Massachusetts).
- Wyrski, K. (1971). *Oceanographic atlas of the International Indian Ocean Expedition*. NSF Washington DC.
- Yu, E. F., Francois, R., and Bacon, M. P. (1996). Similar rates of modern and last-glacial ocean thermohaline circulation inferred from radiochemical data. *Nature*, 379:689–694.